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Hydrosilylation

A Comprehensive Review on Recent Advances

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Volume 1

Hydrosilylation: A Comprehensive Review on Recent Advances

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Editor

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Preface

Since the discovered of the catalyzed hydrosilylation of olefins by chloroplatinic acid in the mid 1950's, the original reaction and its numerous off-spring have shown a steady and continuous growth over the subsequent half-century. A number of excellent specialized reviews have appeared periodically since the original report, but the appearance of Professor Marciniec's "Comprehensive Handbook on Hydrosilylation" in 1992 was a landmark in the discipline. By that time the scope of the hydrosilylation reaction had been extended to include a wide range of additional unsaturated substrates. Its utiliarian scope had expanded far beyond its early specialized application to the technology of silicones, particularly into general organic synthesis and specialty materials chemistry. Hydrosilation mechanisms, subjects of lively debate for many years, were beginning to be firmly estabilised with the aid of improved experimental and theoretical tools. "Comprehensive Handbook on Hydrosilylation" provided the most thorough coverage of all aspects of the subject at the time of its publication and quickly became an obligatory volume for libraries and a highly respected resident of any synthetic chemist's bookshelf. One reviewer of the subject's assessment was that Marciniec's Handbook "is considered by many as the "Bible" on hydrosilylation".

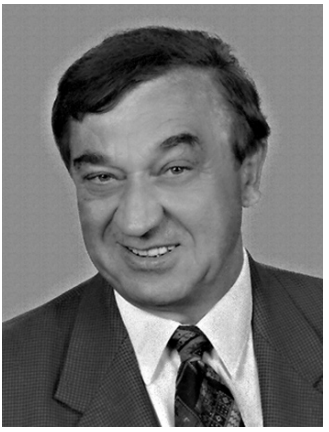
Time never stands still in the world of useful and interesting science, and this is certainly true of the world of hydrosilylation chemistry. Novel uses of hydrosilylation for the modification of materials appear almost daily. Functionalization of polymers and surfaces, stereo-, regio- and enantioselective synthesis of new and old molecules, construction of dendrimers and other novel molecular architectures, are but few of the many areas where this chemistry has had an important influence. Even in the area of mechanistic studies the subtle variations within the several "classical" reaction paths continue to be enriched by both experimental and theoretical approaches. Quite recently, a completely new and unprecedented mechanism for the hydrosilylation of 1-alkenes was reported (see:Glaser-Tilley mechanism in the present volume). All this is to say that it is time for a new, comprehensive overview of the subject. The present volume, "HYDROSILYLATION: A Comprehensive Review of Recent Advances" fulfills this need with the same systematic thoroughness that characterized "Comprehensive Handbook on Hydrosilylation". This extensively researched and well organized volume brings every aspect of the subject up to date.

I have no doubt it will quickly acquire a reputation as the "New Testament" companion to the earlier volume.

McGill University, Montreal, QC, Canada John F. Harrod
August, 2008

Biographical Note

Prof. Bogdan Marciniec



Photograph of Prof. Bogdan Marciniec reproduced with permission from KRZYSZTOF KOŁECKI. Copyright KRZYSZTOF KOŁECKI.

Professor Bogdan Marciniec, received M.Sc. (1963), Ph.D. (1970) and D.Sc. (1975) from the Adam Mickiewicz University, Poznan, Poland. Member of the Polish Academy of Sciences (1994). Head of the Department of Organometallic Chemistry (1987), President of the Adam Mickiewicz University (1988/1990), Director of Center of Excellence – Center of Silicon Chemistry (2000). He was a postdoctoral associate with Prof. R.C. Schowen, Kansas University (1970/1971).

His research activity is focused on the organosilicon chemistry and catalysis by organometallic compounds. Synthesis and catalytic reactions of the substituted silanes and (poly)siloxanes such as hydrosilylation of C=C and C≡C bonds, cross-metathesis and silylative coupling of olefins with vinylsilicon compounds, polycondensation, ADMET polymerisation and ring-closure metathesis of silicon containing dienes are of particular interest.

Activation of =C-H and ≡C-H bonds by M-Si, (silicometallics) as well as by M-B, M-Ge, M-Sn (general inorganometallics) and M-H complexes (where M = Ru, Rh, Ir, Cro, Fe) has been also his interest to lead towards new organometallic reagents for organic and asymmetric synthesis as well as precursors of new materials (including polymers) of special physico-chemical or optoelectronic properties. He is an author and co-author of 300 publications and 22 book chapters e.g. *Handbook of Metathesis* (Wiley-VCH, 2003), *Encyclopedia of Catalysis*, (J.Wiley & Sons, Inc. N.Y., 2003), *Applied Homogeneous Catalysis with Organometallic Compounds* (Wiley-VCH, 2002) as well as editor and co-author 12 books inter alia "*Comprehensive Handbook on Hydrosilylation*" (Pergamon Press, 1993), "*Progress in Organosilicon Chemistry*" (Gordon & Breach Publ., 1995). Professor Bogdan Marciniec was awarded of the Prime Ministry Award (2001) and J.Sniadecki Medal of the Polish Chemical Society (2003) for the outstanding achievements in chemistry. He is or was a member of Editorial Board of such journals as *Organometallics, Applied Organometallic Chemistry, Clean Products & Processes* and *Encyclopedia Britannica* (Polish Edition) as well as a member of Advisory Boards of International Symposia – International Symposium on Organosilicon Chemistry (since 1993), International Symposium on Olefin Metathesis and Polymerisation (1993), European Silicon Days (2000) and International Symposium on Homogeneous catalysis (2008). He was a Chairman of the X^{th} International Symposium on Organosilicon Chemistry – Poznan (1995), 16^{th} International Symposium on Olefin Metathesis – Poznan (2005) and will be the chairman of the 17^{th} International Symposium on Homogeneous Catalysis (2010).

Abbreviations

acac	acetylacetonate
ACCN	1,1′-azobis(cyclohexanecarbonitrile)
AIBN	azobisisobutyronitrile
t-Am	*tert*-Amyl
Ar-Bian	1,2-bis (arylimino)acenaphthene ligands
BINAP	2,2′-bis(diphenylphosphino)-1, 1′-binaphtyl
BMin	1-butyl-3-methylimidazolinum
Bn	benzyl
BOC	*tert*-butoxycarbonyl
bq	benzoquinone
cod	1,5-cyclooctadiene
coe	cyclooctene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
m-CPBA	*meta*-chloroperoxybenzoic acid
CPU	Central Processing Unit
Cy	cyclohexyl
dba	dibenzylideneacetone
DCE	1,2-dichloroethane
DCM	dichloromethane
dcpe	1,2-bis(dicyclohexylphosphino)ethane
DFT	Density Functional Theory
DIBAH	diisobutylaluminum hydride
dippe	1,2-bis(diisopropylphosphino)ethane
DMAP	4-dimethylaminopyridine
DMF	dimethylformamide
DMSO	dimethyl sulphoxide
DPE	diphenylethylene
dppm	bis(diphenylphosphino)methane
Dppp	1,3-bis(diphenylphosphino)propane
DVB	divinylbenzene
dvds	1,3-divinyltetramethyldisiloxane

EDTA	ethylenediaminetetraacetate
ee	enantiomeric excess
EXAFS	Extended X-ray Absorption Fine Structure
Fc	ferrocenyl
GPC	Gel Permeation Chromatography
hfac	hexafluoroacetylacetonate
HMG	3-hydroxy-3-methyl glutaric acid
Ind	indenyl
LIM	Liquid injection molding
LED	Light emitting diodes
Men	menthyl
Mes	mesityl
Mes*	2, 4, 6-tri-*tert*-butylphenyl
M_n	number average molecular weight
MOM	methoxymethyl
MTPA	α-methoxy-α-(trifluoromethyl)phenylacetic acid
M_w	weight average molecular weight
MW	microwave irradiation
nbd	norbornadiene
nbe	norbornene
NBS	*N*-bromosuccinimide
NHC	*N*-heterocyclic carbene
OTf	triflate ($-OSO_2CF_3$)
OTs	tosylate
PDI	Polydispersity Index
phen	phenanthroline
pic	2-pyridinecarboxylate
Piv	pivaloyl
PMBn	*p*-methoxybenzyl
PMHS	polymetylhydrosiloxane
Py	pyridyl
SDS	sodium dodecyl sulphate
TBAB	tetrabutylammonium bromide
TBAF	tetrabutylammonium fluoride
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
THP	tetrahydro-2H-pyran-2-yl
TIPS	triisopropylsilyl
TM	transition metal
TMDS	tetramethyldisiloxane
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl

TOF	turnover frequency
TON	turnover number
TPFPB	tetrakispentafluorophenyl borate
TPS	triphenylsilyl
TriMIM	tris(imidazolyl)

Contents

Introduction

The name hydrosilylation (or hydrosilation) refers to the reaction of addition of organic and inorganic silicon hydrides across multiple bonds, in particular carbon—carbon and carbon—heteroatom (i.e. carbon—oxygen and carbon—nitrogen) bonds as well as heteroatom—heteroatom (such as nitrogen—nitrogen and nitrogen—oxygen) bonds. The first example of hydrosilylation , i.e. the reaction occurring between trichlorosilane and 1-octene in the presence of acetyl peroxide was reported 60 years ago (1947) by Leo Sommer. However, a discovery of hexachloroplatinic acid in 1957 as a very efficient precursor of the Pt-catalyst by John L. Speier has become a strategic point for a wide and common application of this process as a fundamental and elegant method explored over the next 50 years for laboratory and industrial synthesis of organosilicon molecular and macromolecular compounds as well as other organic silyl derivatives, which can also be directly subjected to organic synthesis.

Although the reaction can occur by mediation of free-radicals generated in the reaction mixture, most catalysts used, predominantly transition-metal (TM) complexes (but also nucleophilic-electrophilic catalyst as well metal and supported metals) accomplish the process through a heterolytic mechanism.

Scientific literature provides a number of surveys of hydrosilylation reactions or particular aspects of these processes, including general reviews, chapters or books and articles reviewing special problems related to this process. The surveys that appeared before 1990 (44 references in total) have been listed in our previous book entitled “Comprehensive Handbook on Hydrosilylation”, published in 1992 [1].

That handbook consists of two basic parts. The first part of that book presents the types of catalysts used in the process (Chapter 2), the structures of organic (Chapter 3) and silicon hydride (Chapter 4) substrates, discussed from the point of view of the reaction mechanism and from that of the evaluation of the optimum conditions necessary for the synthesis of organosilicon compounds and organic derivatives of silicon. Two additional chapters focus on the hydrosilylation of unsaturated organosilicon compounds (Chapter 5) and application of these processes in synthesis of silane coupling agents, reduction of organic compounds and modification of polymers (Chapter 6). The second part of our handbook presenting the details of the reaction conditions, products and yields and/or selectivity was edited in the tabulated

form and for selected trisubstituted silanes the references were chosen from more than 2100 papers and patents published from 1965 to early 1990.

The aim of the present book is to supply a comprehensive review of the recent advances in all aspects of the hydrosilylation processes and their direct application covering the literature data that appeared over the last 18 years, i.e. 1990–2007.

This monograph includes also general reviews, chapters as well as individual review articles related to the hydrosilylation processes published in the last two decades, which are listed separately in the References under the heading [1–39]. The reader should note however, that these reviews attempting to provide a comprehensive coverage of literature were published usually some time ago.

Extensive reviews of literature in the field was provided by Ojima [2, 5] as well as by Lukevic's and Voronkov's group [3]. Concise accounts covering important aspects of the reaction have been published by Brook [7] and Reichl and Berry [6]. Our contribution to this field after [1] (1992) was concentrated on the hydrosilylation of carbon—carbon multiple bonds as an efficient method for obtaining organosilicon molecular and macromolecular products, approached from the point of view of catalysis, which is fundamental for the hydrosilylation reactions [4, 8, 9, 12, 14]. Individual aspects of the reaction initiated by free radicals were addressed by Chatgilialoglu et al. [10]. Trost and Ball provided a general overview of the alkyne hydrometallation including synthetic and mechanistic aspects of alkyne hydrosilylation [11]. A brief review covering the literature published since 1990 through mid 2005 on the significant advances from the viewpoint of homogeneous catalysis made by Roy appeared when we were completing this book [13].

Advances in asymmetric hydrosilylation of olefins, carbonyl derivatives and imines achieved in 1990s were reviewed by Nishiyama and Itoh [15]. Hayashi reviewed the catalytic and synthetic aspects of hydrosilylation of linear and cyclic olefins and dienes [16, 17]. Additionaly in a number of accounts Hayashi highlighted the progress in development of the family of chiral monodentate phosphine ligands (MOP) and their application in palladium catalysed asymmetric hydrosilylation of wide variety of olefins [18–20]. Accounts summarising the design of silicon-stereogenic silanes and their application in asymmetric catalysis including hydrosilylation were recently provided by Oestreich [21, 22].

Problems concerning the hydrosilylation processes in polymer chemistry and material science were discussed in most of the abovementioned reviews as well as others concentrating only on polymers [23, 24]. Some classes of functionalised silicones, on account of their practical importance, like fluorosiloxanes [25] liquid crystalline polysiloxanes [26] and silicone polyethers [27], were discussed separately.

Modifications of organic polymers with organosilicon compounds were reviewed by Grath and Tremont [28]. Synthesis and properties of silicon-containing dendrimers including hydrosilylation were the subjects of the review by Majoral and Caminade [29]. Functionalisation of silsesquioxanes via hydrosilylation [30,31] and production of new composite materials [32] were also presented.

Gonzalez and Nolan provided a general overview of the application of metal catalysed hydrosilylation (including the asymmetric hydrosilylation) of carbonyl

compounds covering the period (1999–2006) [33] followed by their very recent review of the reaction catalysed by copper, silver and gold complexes [34]. Development of copper catalysed 1,2- and 1,4-hydrosilylation was reviewed by Oestreich [35]. In a numer of reviews Nishiyama summarises the catalytic and synthetic aspects of asymmetric hydrosilylation of carbonyl and imine compounds [36, 37]. Advances in asymmetric hydrosilylation of carbonyl compounds and imines were reviewed by Carpentier and Riant who focused on the new catalytic systems and mechanistic aspects of the reaction as well as the new synthetic opportunities [38, 39].

In view of extensive development of research work concerning hydrosilylation of carbon—carbon multiple bonds on the one hand, as well as unsaturated carbon—oxygen and carbon—nitrogen bond, on the other, and application of catalytic hydrosilylation in asymmetric synthesis as well especially in polymer chemistry and materials science, this monograph was divided into three parts.

Part I presents all aspects of hydrosilylation of carbon—carbon multiple bonds. Various catalytic systems which are the basis of hydrosilylation of C=C bonds (Chapter 1) and C≡C bonds (Chapter 2) are discussed from two points of view: elucidation of the mechanisms of catalysis and finding the optimum conditions necessary for synthesis of organosilicon compounds. While in Chapter 1 more information is given on new catalysts leading to most effective synthetic routes of laboratory and industrial importance, regarding saturated organosilicon products, the hydrosilylation of alkynes (Chapter 2) is at the moment the most powerful and atom-economical approach for stereo- and regio-selective synthesis of alkenylsilanes. The latter are versatile building blocks in organic synthesis. The development of sequential processes including hydrosilylation of functionalised alkenes and alkynes as the initial step through the respective organosilicon intermediates has been further enhanced by several protocols for converting the silyl group into other functional groups. Thus in Chapter 3 advanced synthetic methodologies including hydrosilylation (one-pot processes) are summarised. Part I is completed by a review (Chapter 4) of asymmetric hydrosilylation of alkenes and alkadienes in the presence of chiral catalysts, which leads to synthesis of enantioenriched alkylsilanes and allylsilanes, respectively, or (if followed by oxidation) to the corresponding chiral alcohols.

The hydrosilylation processes, particularly of carbon—carbon multiple bonds, that have been in the last two decades extensively applied in the field of polymer chemistry and material science are described. Part II of the present book. The applications discussed in Chapter 5 employ the functionalisation of oligo- and polysiloxanes with Si—H bonds, which leads to reactive silicones, being the most attractive silicone materials for adhesives, binders, sealents, optical coating, dielectric coating and a lot of more applications. Catalytic cross-linking of polysiloxanes via the addition of polyfunctional silicon-containing hydride to poly(vinyl)siloxane leading to silicon rubber is also discussed in Chapter 5. The catalytic hydrosilylation of difunctional organosilicon monomers containing alkenyl (alkynyl) and/or Si—H bond leading to formation of saturated (unsaturated) organosilicon polymers bearing the Si—C (Si—C=) bonds is the subject of Chapter 6. While saturated polycarbosi-

lanes and related polymers are applied in heat resistant and moulding materials, silicon-containing σ-π conjugated polymers such as poly(silylene, vinylene)s or poly(arylene, silylene,vinylene)s can be of great importance as optoelectronic materials.

Functionalised (poly)silsesquioxanes and silicon-containing dendrimers synthesised via hydrosilylation procedures are described in Chapter 7. There is now a significant interest in both types of nanoscaled macromolecules with a particular architecture and their potential application as precursors of new materials and especially in the processing of composites.

Chapter 8 regards the application of hydrosilylation in the synthesis of hybrid organic-inorganic materials via functionalisation of unsaturated organic polymer by silicon compounds, and by multifunctionalised crosslinking reagents containing Si-H and vinyl groups as well as using functionalised silicon-containing dendrimers. Silsesquioxane-based nanocomposites materials are discussed in a separate Subchapter 8.3. Finally, the information on the surface modification of polymers as well as other materials, particularly silicon element via hydrosilylation to improve their hydrophilicity or hydrophobicity completes Chapter 8. All hydrosilylation processes utilised in the synthesis of polymers and (nano)materials occur predominantly in the presence of Pt-catalyst (usually Pt-Karstedt's catalyst or other platinum complexes or Pt/C catalyst).

Part III deals with the hydrosilylation of unsaturated carbon—heteroatom bond, mostly C=O and C=N (but also C≡N, N=N and N=O) bonds as a catalytic method for the reduction of C=O and C=N bonds - one of the most fundamental transformations in organic chemistry (Chapter 9). Both 1,2-hydrosilylation of carbonyl compounds or imines and 1,4-hydrosilylation of α,β-unsaturated systems were described. A separate section is devoted to the hydrosilylation of CO_2. Catalytic hydrosilylation of prochiral ketones and imines with substituted silanes and siloxanes which can provide (if followed by hydrolysis) convenient access to chiral alcohols and amines is discussed from the catalytic and synthetic point of view in Chapter 10. Contrary to the procedures used in the synthesis of hybrid inorganic-organic polymers and materials, the hydrosilylation of C=O and C=N bonds can proceed in the presence of other then Pt-complex catalysts as discussed in detail in Chapters 9 and 10.

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Part I
Hydrosilylation of Carbon—Carbon Multiple Bonds in Synthesis of Molecular Organosilicon Compounds

Chapter 1
Hydrosilylation of Alkenes and Their Derivatives

Abstract Hydrosilylation of C=C bonds as a most versatile synthetic route to formation of Si—C bond initiated by free-radicals has been well-known for 60 years, while that catalysed by platinum (starting from Speier catalyst) and other TM complexes – for 50 years. Chapter 1 presents a comprehensive survey of literature on hydrosilylation of alkenes and their derivatives by molecular compounds containing Si—H bond, published in the last two decades. Dehydrogenative silylation, related to the above process, is also discussed. New hydrosilylation catalysts, predominantly homogeneous and immobilised late and early TM-complexes have been developed but also nucleophilic-electrophilic catalysts, metals and supported metals as well as radical initiators have been cited. These catalysts offer many convenient synthetic routes to molecular organosilicon reagents characterised by increased efficiency i.e. the yield and selectivity as well as turnover rate. The choice of catalyst determines the mechanism of catalysis, whose rational development for individual catalytic systems is extensively discussed.

The catalytic addition of organic and inorganic silicon hydrides to alkenes, arylalkenes and cycloalkenes as well as their derivatives with functional groups leads to respective alkyl derivatives of silicon and occurs according to the anti-Markovnikov rule. However, under some conditions (e.g. in the presence of Pd catalysts) this product is accompanied by α-adduct, i.e. the one containing an internal silyl group. Moreover, dehydrogenative silylation of alkenes with hydrosilanes which proceeds particularly in the presence of iron- and cobalt-triad complexes as related to hydrosilylation (and very often its side reaction) is also discussed in this chapter.

Similarly to general reviews on hydrosilylation, this chapter is organised according to the types of the catalyst used since the mechanism of the catalytic processes strongly depends on the type of catalysis. While platinum and other late transition metal complexes catalyse the hydrosilylation of carbon—carbon bond involving the oxidative addition of silicon hydrides to metal, the hydrosilylation catalysed by early transition metal complexes leads to formation of Si—C *via* σ-bond metathesis, i.e. including no oxidative addition of Si—H.

In the next subchapters, transition metal complexes initiated by UV- and peroxide or immobilised on inorganic and/or polymeric supports as well as metals unsupported and supported on solids (usually silica) are discussed as catalysts of

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hydrosilylation of a variety of olefins. Contrary to previous period, in the last two decades only limited information has been reported on the hydrosilylation of C=C bond with the use of Lewis acids, bases and/or free radical initiation.

The synthetic aspects of the hydrosilylation of alkenes and their derivatives have been already comprehensively presented in detail in many reviews [1–14]. In this chapter, new catalysts and new mechanisms of catalysis have been discussed. In contrast, Chapters 2, 3, 4 present mainly the synthetic aspects of hydrosilylation of carbon—carbon multiple bonds in view of the new regio-, stereoselective as well as enantioselective routes revealed in the last two decades.

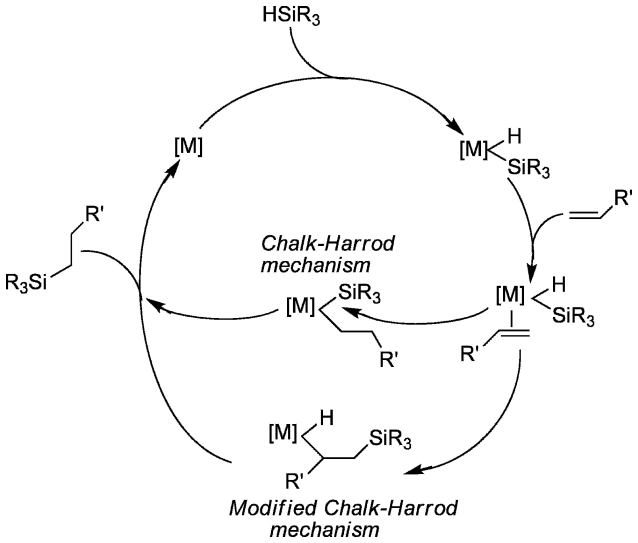
1.1 Late Transition Metal Complexes as Catalysts

1.1.1 Mechanism and Side Reactions of Transition Metal Complex Catalysed Hydrosilylation

Many reviews and publications concern the mechanism of catalysis of hydrosilylation by late transition metal complexes proposed in 1965 by Chalk and Harrod. This mechanism, originally derived from the studies of chloroplatinic acid as a precursor (Pt-catalyst), provided a qualitative rational generalisation of the role of catalyst for other transition metal complexes [15]. The mechanistic scheme presents the conventional oxidative addition – reductive elimination steps to explain the hydrosilylation. The oxidative addition of trisubstituted silanes $HSiR_3$ to a metal alkene complex (usually with d^8 and d^{10} configuration) is followed by migratory insertion of alkene into the M—H bond, and the resulting metal(silyl)(alkyl) complex undergoes reductive elimination by the Si—C bond formation and regeneration of metal alkene complex in excess of alkene. As a facile reductive elimination of silylalkane from [alkenyl-M]-SiR_3 species has not been well-established in stoichiometric reaction, a modified Chalk-Harrod mechanism has been proposed to explain the formation of unsaturated (vinylsilane) organosilicon product, which involves the alkene insertion into the metal—silyl bond followed by C—H reductive elimination (Scheme 1.1) [16].

Detailed theoretical study of $Pt(PH_3)_2$-catalysed hydrosilylation of ethylene has led to a conclusion that this process proceeds through the Chalk-Harrod mechanism [17–22]. The rate-determining step in this mechanism is the isomerisation of [Pt(silyl)(alkyl)] complex formed by ethylene insertion into the Pt—H bond, and the activation barrier of this step is 23 kcal/mol for R=Me, 25 kcal/mol for R=H, and 26 kcal/mol – for R=Cl. But in the modified Chalk-Harrod mechanism, the rate determining step can be ethylene insertion and isomerisation; the activation barrier in this modification is 44 kcal/mole for R=Me, 38 kcal/mol for R=H, and 60 kcal/mole for R=Cl.

The theoretical study shows that the transition states of Si—H oxidative addition to $Pt(PH_3)_2$ and C—H reductive elimination from $PtH(CH_3)(PH_3)$ are planar,

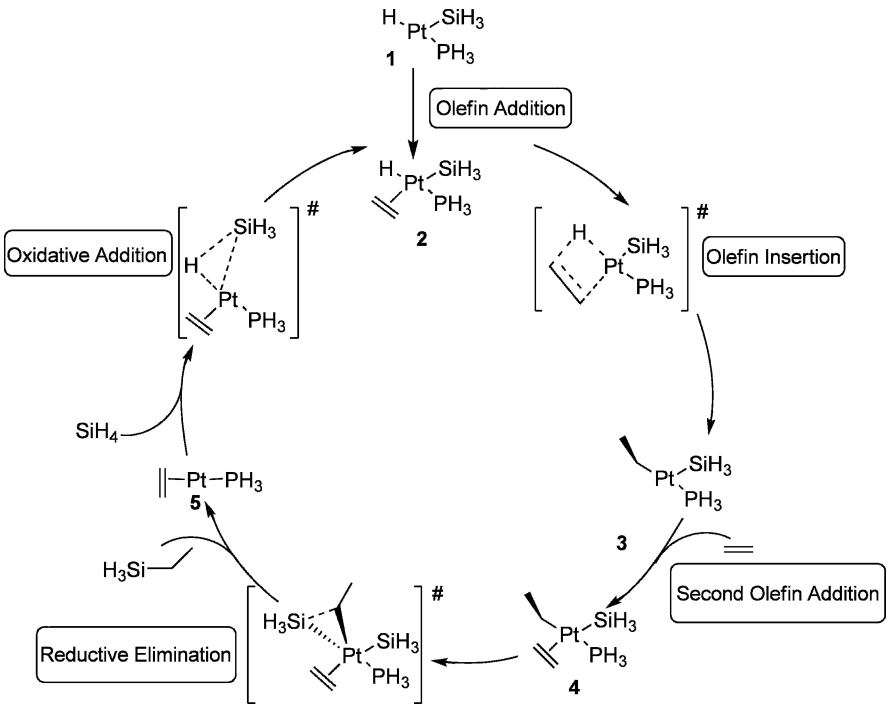


Scheme 1.1 Chalk-Harrod mechanism for hydrosilylation of olefins catalysed by late transition metal complexes

while the transition state of Si—C reductive elimination is non-planar against the expectation from the orbital interaction diagram [20]. Besides, the Si—C reductive elimination from Pt(II) complex is accelerated by coordination of ethylene instead of PH_3. The reason is that ethylene stabilises the trigonal bipyramidal transition state by a π-back donation.

Very recently nonlocal gradient-corrected DFT in conjugation with effective core potentials and valence basis set has been used by Tsipis et al. [23] to locate all of the stationary points in the catalytic cycle. Besides, a high level ab initio (CCSD(T)) method was employed in this work to compute the energies of all the stationary points. The mechanism of the reaction studied consists of the following four steps (see Scheme 1.2); (a) coordination of the ethene to the monomeric T-shaped $[Pt(H)(SiH_3)(PH_3)]$ species (i.e., containing only one phosphine molecule); (b) insertion of the olefin into the platinum-hydride bond; (c) reductive elimination of ethylsilane and (d) the oxidative addition process that regenerates the catalyst [23].

In this mode of catalysis, ethylene occupies a *trans* position to the SiH_3 ligand and adopts a coplanar orientation complex (**2**). In the next step, ethylene inserts into the Pt—H bond, through TSI_{2-3} to generate a coordinatively unsaturated 14e Pt—alkyl intermediate (**3**) with an activation barrier of 13.1 (15.2) kcal/mol. The subsequent step involves a coordination of another ethene molecules to generate coordinatively unsaturated 16e Pt(II) complex (**4**). The process is predicted to be also exothermic by -8.5 (-19.7) kcal/mol at the B3LYP (CCSD(T)) levels of theory. The next step involves the reductive elimination product $CH_3CH_2SiH_3$ and the catalytic species (**5**) through the transition state TS_{4-5} surmounting a relative low activation barrier of 16.5 (18.6) kcal/mol at the B3LYP (CCSD(T)) levels of theory.



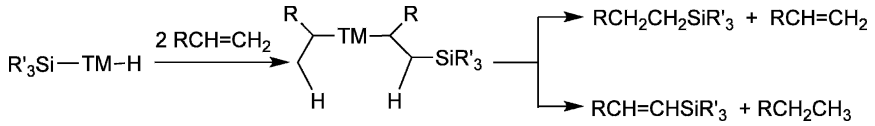
Scheme 1.2 Catalytic cycle of ethylene hydrosilylation by monosilane based on theoretical study [23]

Finally, the oxidative addition of H–SiH_3 to intermediate (**5**) regenerating catalytic species (**2**) corresponds to an exothermic process (-12.7 vs. -23.8 kcal/mol) at both levels of theory. In summary, these calculations predict that the rate-determining step for the hydrosilylation of ethene catalysed by [Pt(H)(SiH_3)(PH_3)] is the reductive elimination of the product [23], in contrast to the implications of the previous calculations [20, 22] as well as the hydrosilylation of ethyne, in which the hydride migration is the rate determining step [24].

Contrary to Pt complex catalysed reactions, the theoretical study of [RhCl(PH_3)$_3$] catalysed hydrosilylation of ethylene by the DFT, MP4 (SDQ) and CCSD(T) methods shows that the rate determining step in the Chalk-Harrod mechanism is the Si—C reductive elimination [25]. Moreover, the rate-determining step of the modified Chalk-Harrod mechanism is either ethylene insertion into the Rh—$SiMe_3$ bond (MP4(SDQ)/BSII level) or oxidative addition of H—$SiMe_3$ (DFT/BS-II level). In conclusion, it is worth emphasising that since the Si—C reductive elimination needs much greater activation energy than the oxidative addition of H—$SiMe_3$ and ethylene insertion into the Rh—$SiMe_3$ bond, the modified Chalk-Harrod mechanism is more favourable than the Chalk-Harrod mechanism in the Rh-catalysed hydrosilylation of ethylene [25].

The hydrosilylation of alkenes catalysed by TM complexes is often accompanied by side reactions such as isomerisation, oligomerisation, polymerisation and hydrogenation of alkenes as well as redistribution and dehydrogenation of silicon hydrides and reactions in which both substrates take part e.g. dehydrogenative silylation [12]. The latter reaction, which in certain conditions permits direct production of unsaturated silyl compounds, has been a subject of intense study over the last two decades.

TM complexes can catalyse both dehydrogenative silylation and hydrosilylation, competitively. The decisive step of the two alternative reactions is actually the competitive β-H transfer from the two ligands (σ-alkyl and σ-silylalkyl) of the complex formed during the reaction (as illustrated in Eq. 1.1).

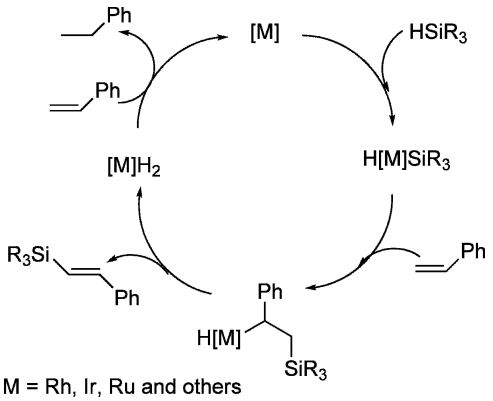


(1.1)

The migratory insertion of an alkene into the M—Si bond (silyl migration) is a key step in the dehydrogenative silylation catalysed by transition metal complexes since, as already mentioned, a theoretical study of the hydrosilylation of ethylene has the explained preference of rhodium over platinum complexes as catalysts in these reactions [23, 25].

In most cases, group R (Eq. 1.1) depicts an electronegative substituent in such olefins as e.g. styrene, substituted styrenes, trifluoropropene and vinyltrisubstituted silanes. Complexes of iron and cobalt triads have appeared extremely favourable catalysts of the dehydrogenative silylation but Ni, Pd and Pt complexes have recently also been reported as active catalysts of these olefins conversions [for reviews see [1, 4, 6, 12, 13].

A general scheme of the catalysis of the dehydrogenative silylation of styrene by TM complexes is given in (Scheme 1.3).



Scheme 1.3 Mechanism of catalysis of dehydrogenative silylation of styrene by TM complexes

Although a lot of data on such competitive reactions have been reported, the number of examples of selective dehydrogenative silylation remains limited. Over the past two decades, the research efforts have been focused on the search for new selective catalysts of dehydrogenative silylation ensuring efficient generation of vinylsilanes and other vinylsilicon compounds as well as on mechanistic implications of transition metal (TM) complexes as real intermediates of these complicated processes. Dehydrogenative silylation has become a useful method for synthesis of vinylsilanes although its drawback is a formation of a mixture of products. The formation of vinylsilane is promoted by a high alkene to silane ratio [12, 26, 27].

1.1.2 Platinum Complexes

Although a wide range of catalysts have been tested for hydrosilylation, most research and industrial syntheses have been carried out in the presence of platinum complexes whose initial precursor was preferably $H_2PtCl_6 \times 6H_20$. A solution of this catalyst in isopropyl alcohol (1–10%) is referred to as Speier's catalyst, the most widely used platinum catalyst [28]. In addition to isopropanol, other solvents (alcohols, ketones, aldehydes, ethers, esters, THF, hydrocarbons) have also been used for the preparation of active catalytic species from chloroplatinic acid. Since 1957, hundreds of catalysts based on chloroplatinic acid as a precursor and other d^8Pt(II) and d^{10}Pt(0) complexes have been reported [1, 5, 29]. Karstedt's catalyst obtained by treating hexachloroplatinic acid with vinylsiloxane was discovered in 1973 [30] but it has been extensively used in hydrosilylation reactions only in the late 1980th. Other Pt(II) and Pt(0) complexes have been used as catalysts for hydrosilylation, e.g. $PtCl_2L_2$ and $Pt_2Cl_4L_2$ (where L=alkene, nitrile, phosphine and alkyne, etc). In spite of high activity of H_2PtCl_6-solvent catalysts in many hydrosilylation processes, the presence of a co-catalyst is often necessary to enhance the catalytic activity and regioselectivity.

In the last 18 years many new platinum(0) and platinum(II) complexes have been synthesised and tested as efficient catalysts of the hydrosilylation of carbon—carbon multiple bonds [8, 9]. The catalytic aspects of the hydrosilylation in polymer chemistry are presented in a separate section. Here, we present only new catalysts and activators applied predominantly for synthesis of molecular organosilicon compounds.

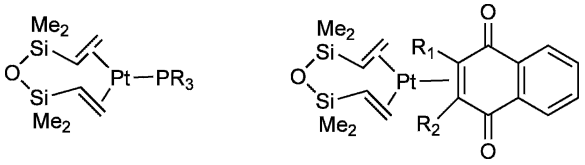
Of new Pt-catalysts reported since 1990 it is noteworthy to mention platinum complexes with new ligands and activators (such as alkadienes, norbornenes and cycloolefins [31–36]). Cyclodextrin complexes of platinum (as host–guest complexes) have been employed as hydrosilylation catalysts active at elevated temperatures after releasing the guest compound [37–39]. Other organic compounds have also been used as activators (ligands) of Pt complexes e.g. unsaturated secondary and tertiary alcohols and silylated unsaturated alcohols [40], alkadiynes and cyclooctadiene [41], vinyl-norbornene [42], quinones [43], methylnaphthoquinones or halogenated organic compounds [44]. Also peroxides being continuously present maintain high catalytic activity of Pt-complexes [45].

A possibility to transform the Speier's to Karstedt's hydrosilylation catalyst was reported by Lappert and Scott who explained the reaction pathway involving the

initial chloride-vinyl exchange followed by reductive elimination in which vinyl radicals and vinyl chloride may take part [46]. The same elementary paths were the basis of the explanation provided by Lewis et al. [47] of the conversion of Pt(IV) to Pt(0) species in the presence of vinyl-silicon-containing compounds. The effect of O_2 in hydrosilylation control, particularly as an agent protecting against deactivation of Pt-complexes, was described [48].

Many Pt(0) complexes being derivatives of the Karstedt's catalyst have been synthesised, and quite a few of them have proved selective and efficient for hydrosilylation of alkenes, e.g. complexes with various phosphines [49] and quinone [50] (see Fig. 1.1). Phosphine ligands protect against colloid formation.

Fig. 1.1



Marko in corporation with Rhodia described and developed a new class of *N*-heterocyclic carbene platinum(0) complexes which catalyse efficiently the hydrosilylation of alkenes [51–54] and alkynes [55]. Those organometallic ligands tolerate a wide range of functionalities and protecting groups producing low amounts of isomerised olefins and lead to undetectable formation of colloids [53] (Fig. 1.2).

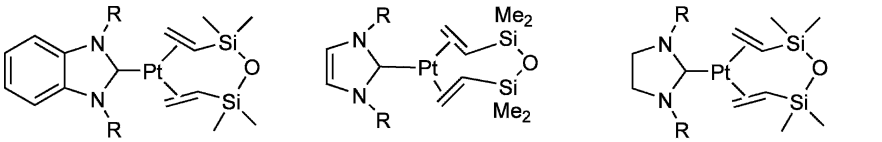
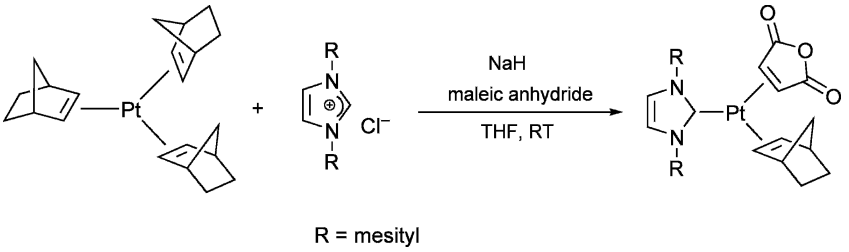


Fig. 1.2

A complex of platinum with fullerene $[(\eta^2 C_{60})Pt(PPh_3)_2]$ was reported as a catalyst for the hydrosilylation of 1-octene by triethoxysilane [56]. Chloroplatinic acid as a precursor was used for synthesis of new organosilicon derivatives via the hydrosilylation of vinylpyrrols [57] and also for synthesis of compounds containing silamethylene bonds [58] as well as in the hydrosilylation of fullerene [59], new cyclo-linear organosiloxanes [60] and disilacycloalkenes [61].

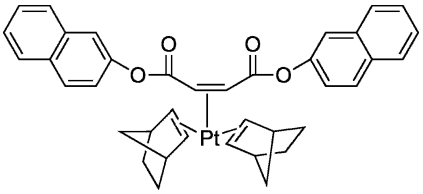
In situ generated platinum (*N*-heterocyclic carbene) catalysts appeared highly active and selective in the hydrosilylation of styrene by triethylsilane with no dehydrogenative silylation products detected [62].



(1.2)

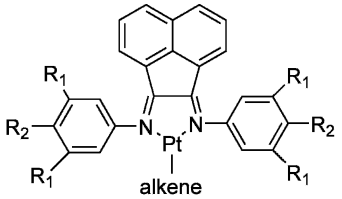
Catalyst starting from Pt(η^2-norbornene) with maleate and fumarate ligands were also effective in the hydrosilylation of styrene, but the most attractive appeared the Pt-complex with diphenyl fumarate ligand (99% yield in 4 h) [63] (Fig. 1.3).

Fig. 1.3



Other platinum(0) and (II) complexes with imines [64] and diimines [65] chelating ligands have also been described, e.g. [Pt(Ar-bian)(η^2-alkene)] [65] (Fig. 1.4).

Fig. 1.4



alkene: maleic anhydride, tetracyanoethene, dimethyl fumarate

The platinum complexes with chelating carbene ligands are also potentially interesting compounds for homogeneous hydrosilylation [66] (Fig. 1.5).

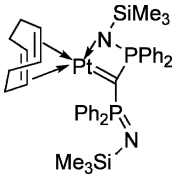
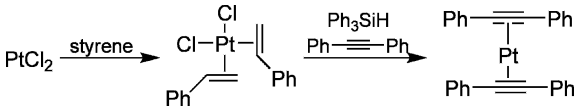


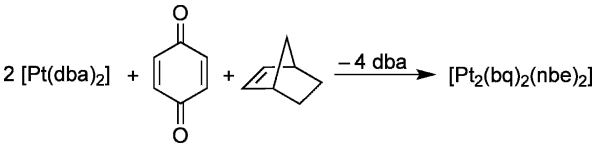
Fig. 1.5

Instead of the olefins and carbene ligands diphenylacetylene can be used to stabilise platinum at the zero oxidation state [67].



(1.3)

In 2003 Yamamoto described dimeric platinum(0) complex with norbornene and p-benzoquinone which was synthesised by substitution of dibenzylideneacetone ligands (dba) in [Pt(dba)$_2$] [68].



(1.4)

New cationic platinum(II) complexes as alkene (and alkyne) hydrosilylation catalysts were recently reported; particularly interesting were those containing phenanthroline [69, 70] and P,N- functionalised indene [71] as bidentate ligands (Fig. 1.6).

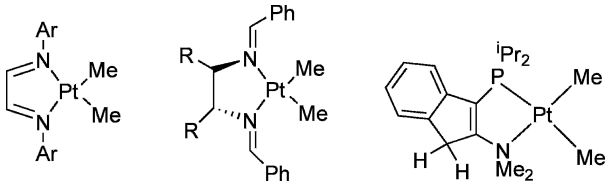
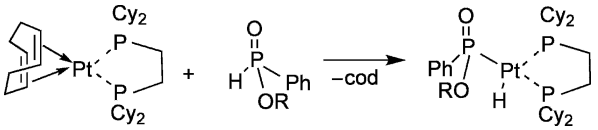


Fig. 1.6

The complexes containing new type of organophosphorus ligands – phosphiranes have been also noted as hydrosilylation catalysts. The phosphirane significantly enhances the catalytic activity of platinum when compared to PPh_3 under identical conditions [72, 73]. For examples see (Fig. 1.7).

Tanaka et al., reported the synthesis of platinum(II) complex containing (RO)PhP(O) and hydrido ligands via addition of (RO)PhP(O)H to [Pt(dcpe)(cod)] [74].



(1.5)

Also, a variety of platinum(II) complexes containing silyl [75], bisalkyl or alkyl—silyl [76] and alkynyl [77–82] ligands have been tested as hydrosilylation catalysts, e.g. (Fig. 1.8).

Very recently a new platinum based catalyst, namely platinum oxide was found to be a versatile and powerful hydrosilylation catalyst of functionalised alkenes

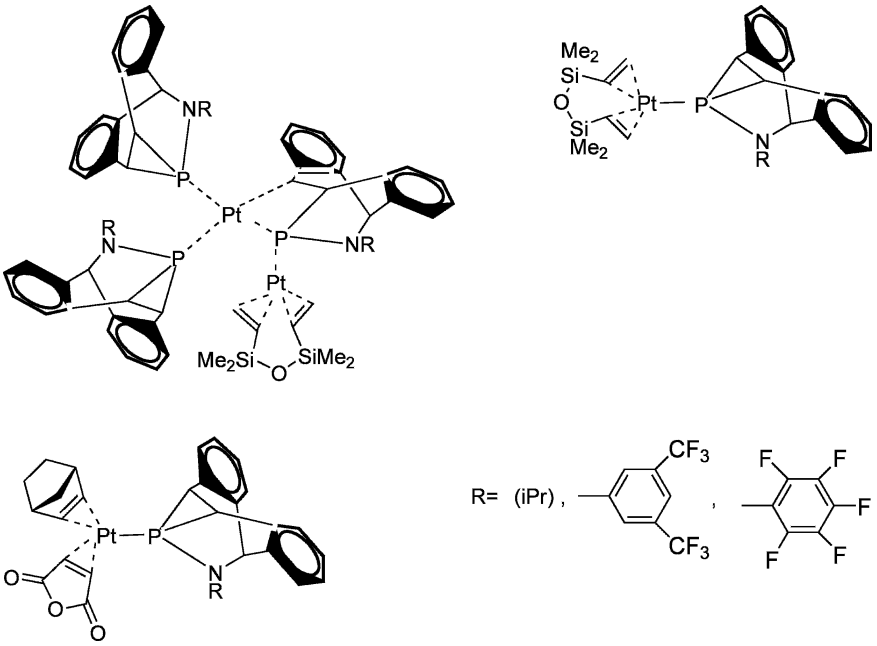


Fig. 1.7

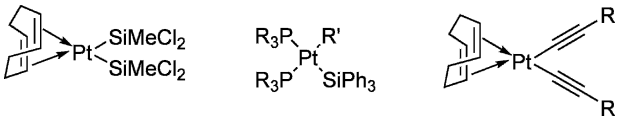
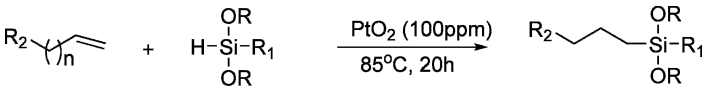


Fig. 1.8

especially for substrates containing chelating bisamino group. The catalyst can be conveniently removed by simple filtration [83].



R_1 = alkyl, aryl
R_2 = NH_2, NHR, CN, COOR, COOH, COR, OR, epoxide (1.6)

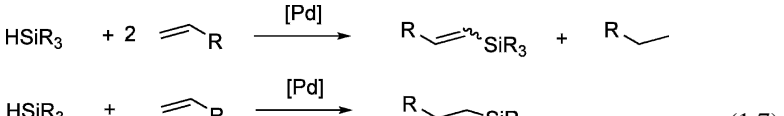
This new catalyst can be also used also in hydrosilylation of allylamine by heptamethylhydrocyclotetrasiloxane [84].

1.1.3 Palladium and Nickel Complexes

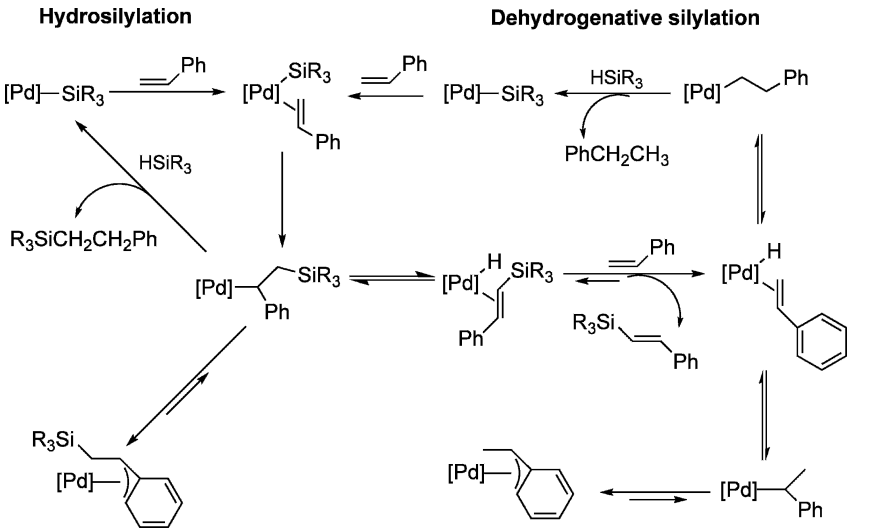
Palladium complexes are not generally regarded as good hydrosilylation catalysts because of the ease of their reduction to the metal by silicon hydride. However,

many reports have suggested that some phosphine Pd(0) and Pd(II) complexes (e.g. $[Pd(PR_3)_4]$, $[PdX_2(PR_3)_2]$, $[Pd(chelate)(PPh_3)_2]$, $[Pd(RCN)_2 + PPh_3]$), are effective in the hydrosilylation of alkenes, alkadienes, cycloalkadienes, and especially conjugated dienes, similarly to nickel complexes. Coordination of the metal with suitable ligands, mostly tertiary phosphines, prevents the palladium complexes from being reduced to metal [2,5,8]. After completion of the reaction, the catalyst can be regenerated by a further addition of triphenylphosphine. These reactions generally occur in solvents such as benzene, toluene, hexane, ethers or $CHCl_3$ but proceed also in their absence. The hydrosilylation of 1-alkenes in the presence of $Pd(PPh_3)_4$ leads to a regioselective formation of products bearing terminal silyl groups [85]. The activity of the catalyst increases with increasing electron-withdrawing character of the substituents at the phosphorus atom, i.e. in line with the subsequent decrease in the σ-basicity of the ligands [86].

Independent mechanistic study by Brookhardt [87] and Hayashi [88] on the catalysis by cationic Pd(II) $[(phen)Pd(CH_3)(L)]^+ BAr'_4$ where phen=1,10-phenatroline and L=Et_2O, $Me_3SiC{\equiv}CSiMe_3$; Ar′=3,5-$(CF_3)_2C_6H_3$ [87] and π-allyl Pd(II) [{Pd $Cl(\eta^3\text{-}C_3H_5)_2$}] [88] complexes in the hydrosilylation (the first one also in the dehydrogenative silylation) of olefins has shown that the reaction occurs via migratory insertion of the olefin into Pd—Si bond. Cationic Pd(II) complexes are highly electrophilic and therefore the hydrosilylation is accompanied by the dehydrogenative silylation, whereas in the Pd(0)-catalysed hydrosilylation the dehydrogenative silylation step is not observed [87] (see Scheme 1.4).

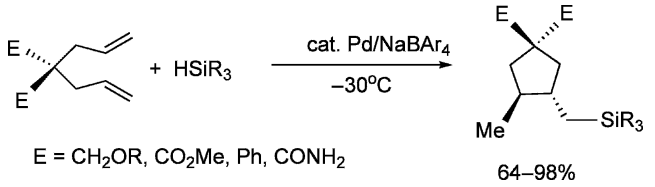


(1.7)



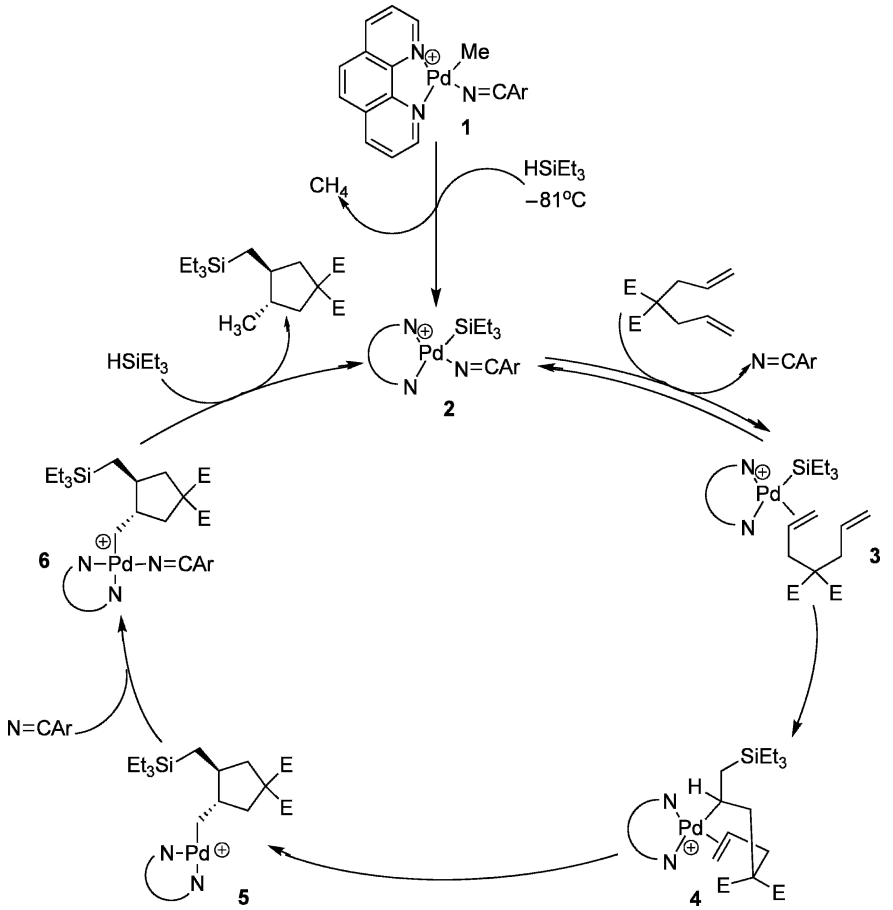
Scheme 1.4 Hydrosilylation vs. dehydrogenative silylation of styrene catalysed by Pd complex

R.A. Widenhoefer developed a mechanistic study on cyclisation / hydrosilylation of various functionalised dienes catalysed by cationic palladium phenanthroline or oxazoline complex [89–94].



(1.8)

Kinetic, deuterium-labelling, and low-temperature NMR studies permitted establishing a mechanism for the palladium-catalysed cyclisation hydrosilylation of dimethyldiallylmalonate with triethylsilane [92, 93] (see Scheme 1.5).

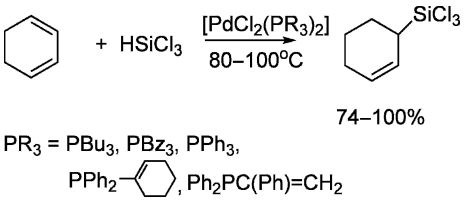


Scheme 1.5 Mechanism of cyclisation/hydrosilylation of dimethyldiallylmalonate

Silylation of precatalyst **1** with triethylsilane leads to formation of the observed palladium silyl complex **2**. Displacement of the nitrile ligand of **2** with one of the double bonds of the substrate would lead to (olefin)Pd—Si intermediate **3**. The next insertion of the coordinated olefin into the Pd—Si bond followed by rapid irreversible complexation of pendant olefin would give complex **4**. The subsequent insertion of the pendant olefin into the Pd—C bond of **4** leads to palladium cyclopentylmethyl complex **5** whose formation is followed by a rapid exothermic ligand capture with NCAr to get **6**. Associative silylation of **6** with triethylsilane releases carbocycle – product and regenerates palladium-silyl complex **2**.

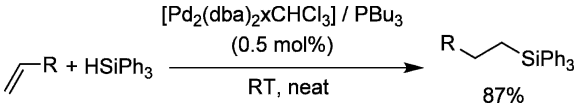
In contrast to unsubstituted 1-alkenes, the hydrosilylation of their derivatives with electron-acceptor substituents, e.g. acrylonitrile, styrene or vinyltrichlorosilane, in the presence of phosphine complexes of palladium, leads to a selective formation of α-adducts [1, 5].

The catalytic activity of Pd(II) phosphine complexes in the hydrosilylation of isoprene, 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene is strongly effected by the nature of the phosphorous containing ligand [95].



(1.9)

Following the report on efficient [Pd]-PCy_3 complex catalysed hydrosilylation of alkynes with trihydrosilanes was subsequently extended for $Pd_2(dba)_2CHCl_3 \times PCy_3$ complex catalysed hydrosilylation by triorganosilanes with excellent regiocontrol at room temperature and tolerating of variety of functionalisations [96].



(1.10)

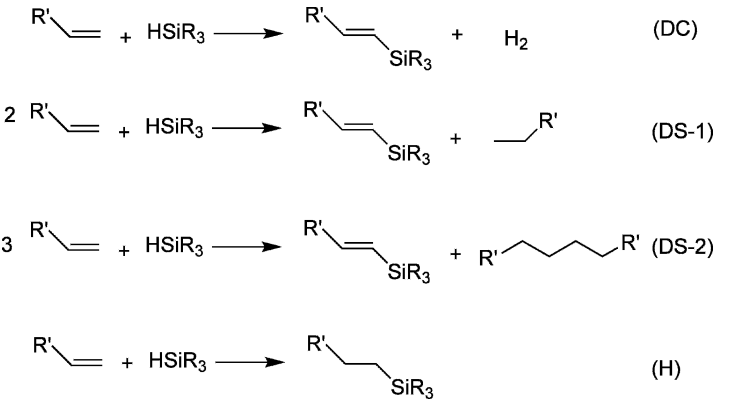
A comprehensive study on homoleptic dinuclear Pd(0) compounds gives significant results especially for the operation of naked Pd(0) and L—Pd(0) complexes in homogeneous catalysis [97]. It seems quite possible that these complexes, e.g., Pd-analogue of Karstedt's catalyst (i.e. with tetramethyldivinyldisiloxane ligand), would replaced the Karstedt's catalyst in the hydrosilylation processes.

Numerous complexes of nickel(II) and nickel(0) catalyse the addition of the Si—H bond to olefins. Among such catalysts are nickel-phosphine complexes, e.g., $[Ni(PR_3)_2X_2]$ (where X=Cl, I, NO_3; R=alkyl and aryl), $[Ni(PPh_3)_4]$ and $[Ni(CO)_2(PPh_3)_2]$ as well bidentate complexes of $[NiCl_2$-(chelate)], $[Ni(acac)_2L]$ (L=phosphine), and $[Ni(cod)_2(PR_3)_2]$. A characteristic feature of the nickel-phosphine-catalysed olefin hydrosilylation is the occurrence of side reactions such

as H/Cl redistribution at silicon and the formation of substantial amounts of internal adducts in addition to the terminal ones [1, 2, 4, 98, 99].

Phosphine complexes of nickel are used as catalysts in the hydrosilylation of olefins with functional groups, e.g. vinyl acetate, acrylonitrile and methylacrylate, as well as in the hydrosilylation of acetylene derivatives.

Nickel complexes such as $Ni(acac)_2$, $Ni(cod)_2$ and nickel's equivalent of Karstedt's catalyst [$\{Ni(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}_2\{\mu\text{-}(\eta\text{-}CH_2{=}CHSiMe_2)_2O\}$] appeared to be very efficient precursors of the catalysts for the dehydrogenative silylation of vinylsilanes, styrene and other olefins [100–106]. The reaction proceeds via three steps yielding the unsaturated product and respective products i.e., of direct dehydrogenation (DC), olefin hydrogenation (DS-1) as well as the hydrogenative dimerisation (DS-2) according to the following equations [105].



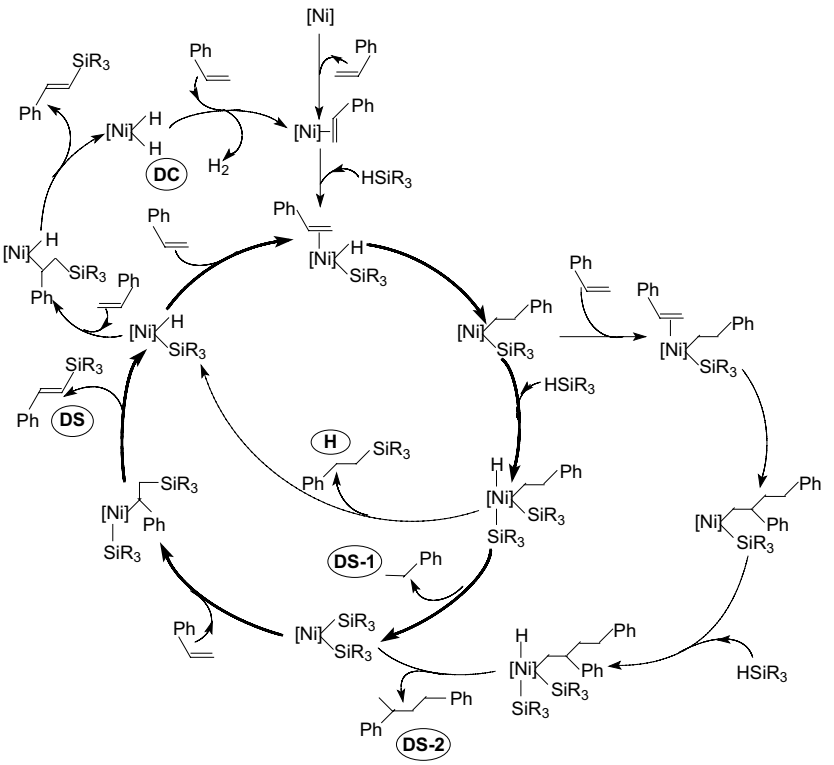
(1.11)

In particular, the nickel equivalent of Karstedt's catalyst was found to be attractive for the dehydrogenative silylation [105] as well as under special conditions of the hydrosilylation [106] of vinyl derivatives.

Synthesis of bis(triethoxy(silyl)-divinyltetramethyldisiloxane) nickel complex and particularly the first documented insertion of olefin (styrene) into the Ni—Si bond of this complex as well as all catalytic data have led to a scheme of catalysis of this reaction. (Scheme 1.6) which shows that all the reactions mentioned above (DC, DS-1, DS-2 and H) occur as a consequence of the insertion of styrene (olefin) into the Ni—Si, Ni—H and Ni—C bonds [105].

Ni(0)-phosphine complexes were applied for hydrosilylation of alkenes [107] and butadienes [108]. Cationic nickel complexes such as $[(Ind)Ni(PPh_3)]^+$ [109] $[Ni(\pi\text{-allyl})PR_2(CH_2CH{=}CH_2)]^+$ [110] were reported as novel effective catalysts of regioselective hydrosilylation of styrene by $PhSiH_3$.

As to the Ni cationic initiators, the authors propose that Ni—H intermediate is generated via the transfer of H- from the silane to the coordinately unsaturated and highly electrophilic species such as $[IndNi(PPh_3)]^+$ leaving a $[PhSiH_2]^+$ which might be trapped by free PPh_3 furnishing $[Ph_3PSiH_2Ph]^+$. However, it was not possible to detect (by NMR) the formation of Ni—H bond although free phosphine



Scheme 1.6 Mechanism of hydrosilylation and dehydrogentive silylation of styrene catalysed by Ni equivalent of Karstedt's catalyst

was detected at the early stages of the catalytic cycle [109, 111]. As far as the $[Ni(\pi\text{-allyl})(PR_2CH_2=CH=CH_2)]^+$ complex is concerned, the initial activation process of the precatalyst with $PhSiH_3$ although does not involve phosphine dissociation, yields the catalytically active species. However, since Si—H bond activation takes place, the participation of Ni—Si and Ni—H species is also assumed [110].

Neutral R-indenyl $Ni(PPh_3)_3Cl$ can also catalyse the hydrosilylation of styrene in the absence of cationic initiation, but the steric bulk of indenyl substituents induces the dissociation of PPh_3 ligand and may facilitate the hydrosilylation by $PhSiH_3$ [111].

1.1.4 Cobalt Triad Complexes

Rhodium complexes have been used for 40 years as highly effective catalysts of hydrosilylation. Two types of rhodium complexes are usually employed: $[RhX(R_3P)_3]$ (where X=Cl, R=Ph, Wilkinson's catalyst) and $[RhX(CO)(R_3P)_2]$. In addition, dinuclear rhodium complexes containing π-acceptor ligands not involving phosphines

have been used, i.e. $[Rh_2X_2Y_4]$ (where X=Cl, R, $OSiMe_3$; Y=C_2H_4, C_8H_{14} and other olefins, CO, cod, $P(OR)_3$ and recently Cp and Cp*).

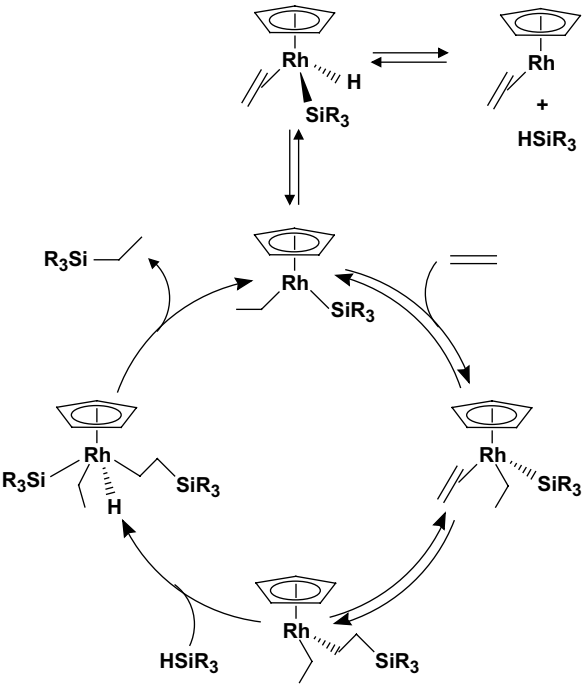
There are many other Rh(I) and Rh(III) complexes catalysing the hydrosilylation reaction, e.g. $[RhH(PPh_3)_4]$, $[RhCl_3(PPh_3)_3]$ and $RhCl_3 \times 3\ H_2O$ [1,2,4–6,98,112]. In the last two decades the $[(cod)RhCl]_2$-L system has been found to be highly selective in the hydrosilylation of alkenes where L=PPh_3 [113,114], $^tBu_2PCH_2P^tBu_2$ [115]. Phosphine and phosphinocarbonyl complexes of rhodium effectively catalyse the hydrosilylation of 1-alkenes and dienes, styrene and olefins with functional groups.

One of the most confusing problems in the catalysis of the hydrosilylation by rhodium complexes is the influence of molecular oxygen as a co-catalyst. Such a phenomenon is general, and also occurs in the presence of other transition metal complexes, particularly those with CO and phosphine ligands, e.g. of platinum and ruthenium. The concerted mechanism of hydrosilylation processes catalysed by the Wilkinson's catalyst involves predissociation of phosphine from the complex. In this respect, molecular oxygen functions as a promoter since the dissociation of phosphine occurs more readily from $[RhCl(O_2)(PPh_3)_3]$, than from the original precursor. Apparently, the formation of the highly active, coordinatively unsaturated species, $RhCl(PPh_3)_2$, via preliminary oxygenation of phosphine to phosphine oxide, is the key to co-catalysis in metal phosphine complexes [1]. In the last two decades, Wilkinson complex and related phosphine complexes of rhodium(I) were used in numerous reactions for synthetic purposes, e.g. in the hydrosilylation of styrene and vinylcyclopropene to yield ring opening products [116] as well as in the hydrosilylation of vinylamines [117]. The $[(dippe)Rh]_2(\mu\text{-}H)_2]$ complex (where dippe=1,2-bis(diisopropylphosphino)ethane) appeared to be active in the hydrosilylation of olefins by diphenylsilane [118]. Rhodium complexes were found to be extremely favourable catalysts for dehydrogenative silylation of alkenes [119–121] and divinyldiorganosilanes [122].

Rhodium complexes are very often applied for mechanistic discussion, particularly to follow two competitive pathways – an insertion of olefin into M—Si vs. M—H bonds. Duckett and Perutz used $[CpRh(C_2H_4)(SiEt_3)H]$ as a precursor, finally proposing an alternative mechanism based on a "two-silicon cycle" as illustrated in Scheme 1.7 [123]. This mechanism includes the initial formation of $[CpRh(C_2H_5)SiEt_3]$, followed by ethylene insertion (silyl migration) step but the integrity of the original ethene ligand is proved to be retained. The oxidative addition of Et_3SiH would generate Rh(V) intermediate containing two silyl groups. Such Rh(V) intermediates (i.e. $[\eta^5\text{-}C_5Me_5Rh(H)_2(SiEt_3)_2]$) were earlier proposed by Maitlis group [1] (Scheme 1.7).

Numerous examples of the olefin insertion into M—Si bonds, which have been demonstrated for Fe, Co as well as Ru and Rh complexes, support the evidence for generality of this reaction [6,7].

Cationic rhodium complexes have recently appeared regio- and stereoselective catalysts for dehydrogenative silylation of alkenes. $[Rh(coe)]^+ClO_4^-$ and $[\{(C_4H_6)_2Rh\}^+ClO_4{}^-]$ proved to be effective in the hydrosilylation of alkenes [124].



Scheme 1.7 Two-silicon cycle mechanism of hydrosilylation by rhodium(III) complex

A comprehensive study by Ojima et al. of the catalysis of hydrosilylation by carbonyl clusters resulted in the application of $[Rh_4(CO)_{12}]$, $[Co_2Rh_2(CO)_{12}]$ and $[Co_3Rh(CO)_{12}]$ in the hydrosilylation of isoprene [125] by trisubstituted and disubstituted silanes. Similarly to platinum ones, also rhodium-carbene complexes have been tested recently in the hydrosilylation of alkenes and alkynes. Especially, rhodium complexes with *N*-heterocyclic carbenes [NHCs] have attracted considerable attention. Their performance is comparable with that of phosphine complexes.

The following exemplary ligands were used:1,3-imidazoylidene [126]; chelate bis imidazolinum-carbene [127] phosphine-functionalised NHC [128]; alkylammonium-imidazolium chloride salts [129]; NHC pincer complexes [130] (Fig. 1.9), pyridine-functionalised *N*-heterocyclic carbenes (also with iridium) [131] bis(dichloroimidazoylidene) (also with iridium) [132].

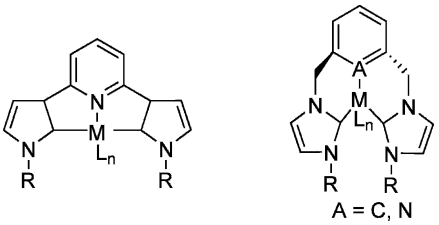


Fig. 1.9

A family of neutral cationic and zwitterionic Rh(I) and Ir(I) complexes with P,N- P,O-, P(S),O- and P(S),N- substituted indene ligands have been tested in the hydrosilylation and the dehydrogenative silylation of styrene (Fig. 1.10) [133–135, 151, 152].

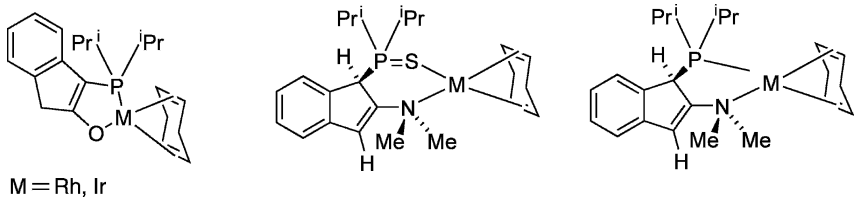
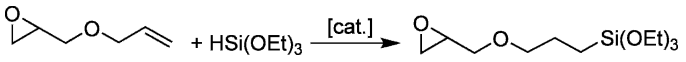


Fig. 1.10

Molecular compounds incorporating TM—O—Si groups are of great interest, particularly as models of metal complexes immobilised on silica and silicate surfaces known to catalyse a variety of organic transformations [136–138]. However, according to a general idea presented by Wolczanski [139], alkoxide and siloxide ligands are alternative to cyclopentadienyl complexes of TM. Therefore, the properties of siloxide as ancillary ligands in the system TM—O—SiR_3 can be effectively utilised in molecular catalysis (for recent review see [140, 141]).

Siloxide complexes of rhodium and iridium appeared to be much more effective then the respective chloro-complexes in hydrosilylation of a variety of olefins such as 1-hexene [142], vinylsilanes [143] and allyl alkyl ethers [144–146]. [Rh(cod)(μ-$OSiMe_3)_2$] as well as [Rh(cod)$(PCy_3)_3(OSiMe_3)$] in particular, are very active and selective catalysts for the hydrosilylation of glycidyl ether by triethoxysilane yielding commercially available silane coupling agent according to the following equation [146]:

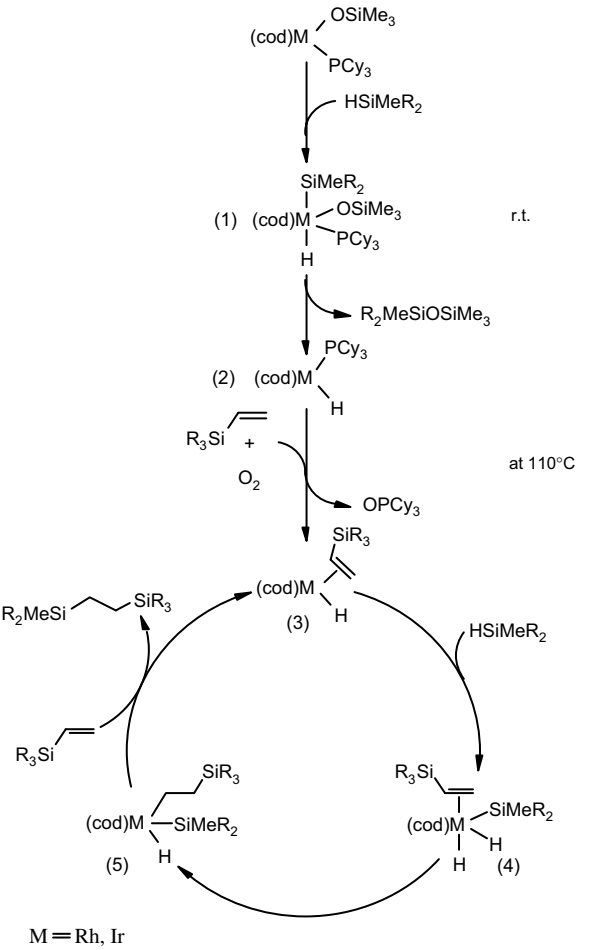


(1.12)

The catalysis of hydrosilylation either by dimeric or by monomeric rhodium and iridium siloxide complexes occurs via preliminary oxidative addition of hydrosilane followed by elimination of disiloxane (detected by GC-MS) to generate square planar 16e complex containing M—H and π-bonded olefins (for catalysis by monomeric Rh and Ir complexes of vinylsilane hydrosilylation – see Scheme 1.8).

The latter complex initiates the real catalytic cycle for hydrosilylation of olefins. Efficient oxygenation of tertiary phosphine observed in air vs. dissociation of phosphine in oxygen-free conditions, particularly observed at elevated temperature (60°C), (a formation of OPR_3' vs. PR_3' is detected by ^{31}P NMR) is the crucial stage for generation of [M(cod)H(alkene)] intermediate [140, 141, 146].

[Rh(cod)$(OSiMe_3)$] as well as monomeric iridium-siloxide complexes appeared also very efficient catalysts in comparison to Karstedt's catalyst on modification and crosslinking of silicones via hydrosilylation (see Chapter 5).



Scheme 1.8 Mechanism of vinylsilane hydrosilylation by transition metal siloxide complexes, M=Rh, Ir

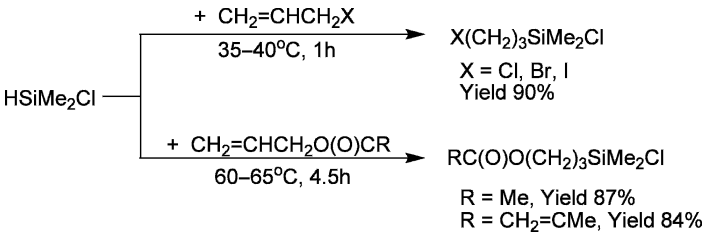
The rhodium dimeric siloxide complexes $[\{Rh(\mu\text{-}OSiMe_3)(cod)\}_2]$ in imidazoyl ionic ligands (especially [TriMIM]$MeSO_4$]) appeared to be very active catalytic systems in the hydrosilylation of alkenes, allyl glycidyl ether and allyl polyether with hydrotrisiloxane [147].

Iridium complexes Ir(I), Ir(III) and Ir(V) stabilised by oxygen-donor ligands such as $[IrH_2(triso)(SiMePh_2)_2]$, [Ir(triso)$(coe)_2$] (coe = cyclooctene) and [Ir(triso) $(C_2H_4)_2$] menthanide, were triso = tris(diphenyloxophosphoranyl), are excelent catalysts for hydrosilylation of 1-alkynes [148] and 1-alkenes [149]. A family of cationic catalysts like $[Ir(cod)(PCy_3)Py^+[PF_6]^-$ (Crabtree catalyst) [150] and zwitterionic Ir(I) complexes [151,152] have been tested in the hydrosilylation of styrene and make an effective class of the hydrosilylation catalysts to yield predominantly β-adduct accompanied by α-adduct and traces of unsaturated products. A detailed

mechanism of the hydrosilylation of ethylene was worked out using heterodinuclear complex $[Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2]$ [150].

The complexes of the composition $[\{Ir(\mu\text{-}X)(diene)\}_2]$, where X=halogen, OH, OMe, e.g. [IrCl(CO)(cod)] appeared to be very effective catalysts for hydrosilylation of allyl chloride by trialkoxy- and alkylalkoxy- silanes [153]. Other iridium complexes have been subsequently reported as catalysts for synthesis of silane coupling agents via hydrosilylation of olefins with alkoxysubstituted and other hydrosilanes [154, 155].

The $[\{Ir(\mu\text{-}X)(cod)\}_2]$, complexes (where X=Cl, Br, I) appeared to be effective catalysts for synthesis of halopropyldimethylchlorosilane and silylpropylesters from dimethylchlorosilane and respective allyl derivatives via hydrosilylation proceeding according to the following equation [155–157]:

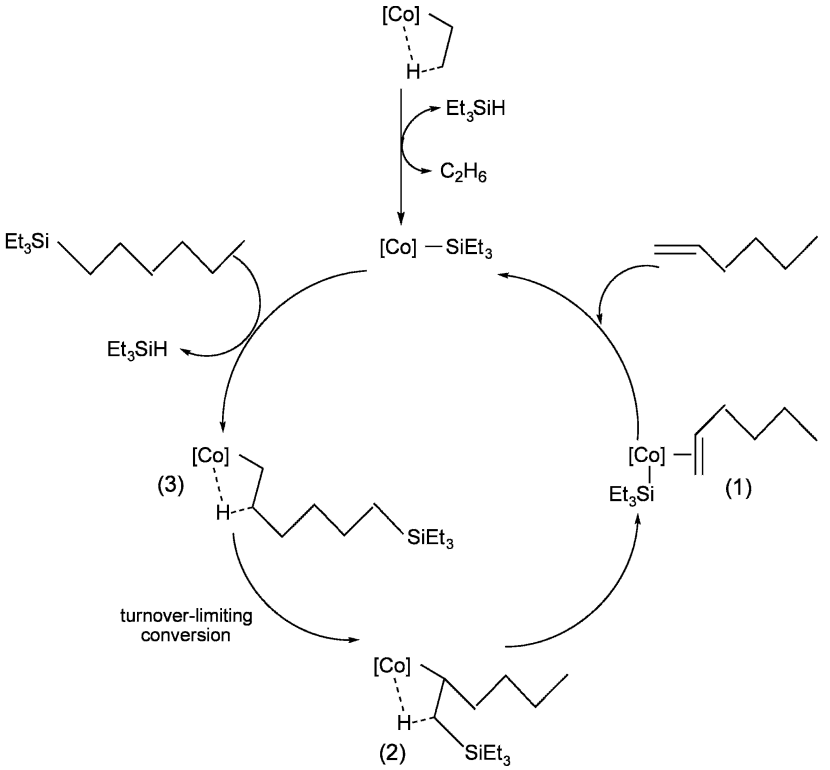


(1.13)

Transition metal carbonyls such as $Co_2(CO)_8$ and $CoH(CO)_4$, formed in the reaction of R_3SiH with dimer (but also $Fe(CO)_5$ and $M_3(CO)_{12}$ (M= Fe, Ru, Os)) have been found to be active catalysts for the hydrosilylation of olefins, dienes, unsaturated nitriles and esters. In the $Co_2(CO)_8$ catalysed hydrosilylation of allyl acetate with $HSiEt_2Me$ the insertion of olefin into Co—Si rather then into Co—H was postulated [158]. Hydrosilylation of phenylthioacetylenes in the presence of this catalyst is extremely regioselective [159]. Cobalt(I) complexes, e.g. $[CoH(X)_2L_3]$ (X=H, N), seem to be prospective candidates for investigation of the effectiveness of alkene hydrosilylation by trialkoxysilanes as well as the dehydrogenative silylation [160].

Direct evidence for the silyl migration mechanism operative in a catalytic hydrosilylation pathway was presented by Brookhart and Grant [161] using the electrophilic Co(III) cationic complex. The pathway shown in Scheme 1.9 involves insertion of hexene into the [Co]-Si bond where $[Co]=[Cp^*Co[P(OMe)_3]CH_2CH_2\text{-}\mu\text{-}H]^+[BAr_4]^-$; $(Ar=3,5\text{-}(CF_3)_2C_6H_3)$. A comprehensive mechanistic study has supplied a proof for formation of a secondary alkyl cobalt complex with agostic (μ-H) bonding (2) and its unexpected isomerisation to the primary alkyl(silyl) Co complex with (μ-H) bonding (3). The latter is a turnover-limiting step of the whole process. The final step yielding the Si—C compound can occur either via oxidative addition of silane at a cationic Co(III) centre to yield cationic Co(V) intermediate (as in the case of Duckett and Perutz [123] mechanisms) or alternatively via the σ-bond metathesis.

A few reports on the $Co_2(CO)_8$ catalysed hydrosilylation of allyl esters of monosaccharides [162] and α-sugar allenes [163] have been focused on synthesis of the corresponding alkylsilanes and vinylsilanes

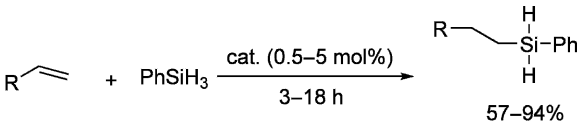


Scheme 1.9 Mechanism of catalysis of 1-alkene hydrosilylation by Co(III) cationic complex

1.1.5 Iron Triad Complexes

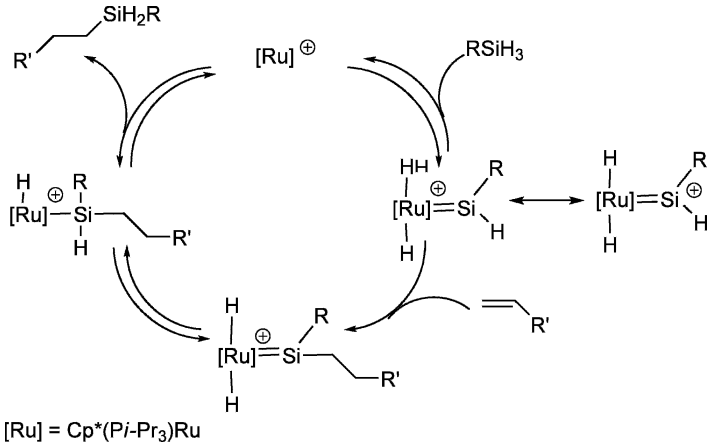
Most Fe and Ru (and also Os) complexes including carbonyls used in the hydrosilylation of olefins give either hydrosilylation products accompanied by unsaturated vinylsilyl derivatives as products of dehydrogenative silylation or exclusively the latters [1, 8, 9, 12].

In the recent years, all new mechanistic implications on the late transition metal catalysed hydrosilylation of olefins reported involve ruthenium complexes as model transition metal centres of molecular catalysis [164–168]. Until now the most catalysts feature electron-rich transition metals such as platinum and rhodium, which typically operate by the Chalk-Harrod and/or modified Chalk-Harrod mechanisms [9]. In all commonly accepted proposals a bond formation occurs via coordination of both silane and olefin to the transition metal. Very recently Tilley et al., proposed a new mechanism (called the Glaser-Tilley mechanism), which involves activation of two (sp^2)Si—H bonds of the silane substrate, direct addition of (sp^2)Si—H to alkene and finally the 1,2-H-migration and reductive elimination step (Scheme 1.10) [164, 169].



R = Ph, H, n-Bu

cat. = $[Cp(^{i}Pr_3P)(H)_2Ru{=}Si(H)Ph \times Et_2O][B(C_6F_5)_4]$ (1.14)



Scheme 1.10 Glaser-Tilley mechanism for ruthenium-complex catalysed hydrosilylation of 1-alkenes by primary silanes

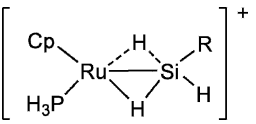
The catalytic hydrosilylation by cationic ruthenium silylene complexes was investigated by Beddie and Hall [165, 166] as well as Bohme [167] using the density functional theory (DFT) method. The authors provided theoretical evidence for importance of the new mechanism. The highest energy transition state in the Glaser – Tilley hydrosilylation mechanism is more then 8 kcal/mol lower in energy than the highest energy transition states in the Chalk-Harrod and modified Chalk-Harrod mechanism. Unfortunately, this mechanism accounts for the alkene hydrosilylation only by primary silanes, i.e., $RSiH_3$, required for formation of a hydrogen substituted silylene ligands. Therefore, it cannot be applied to hydrosilylation leading to industrially important organosilicon products.

Very recently the first evidence for the key-step in the proposed Glaser-Tilley mechanisms has been presented [169]. The authors have demonstrated that reactive coordinations unsaturated intermediate are capable of extruding silylene fragments from Ph_2SiH_2 and $PhSiH_3$ in a stoichiometric fashion by way of double geminal Si—H bond activation leading to ruthenium-silylene complex [169].

The crucial point of this mechanism is a direct insertion of the alkene into the Si—H bond of a ruthenium-silylene complex (without preliminary coordination of alkene to the ruthenium centre).

A subsequent DFT study has confirmed the new mechanism of olefin hydrosilylation [167] but found that catalytically active complex has a nonclassical η^3-bonded silane ligand i.e., Ru—Si bond is bridged by two hydrogen atoms (Fig. 1.11).

Fig. 1.11



$Ru_3(CO)_{12}$ appears to be a very active catalyst for the dehydrogenative silylation predominantly of trialkyl- and phenyldialkylsilanes (but also triethoxysilane) to styrene and its p-substituted derivatives, vinylnaphthalene, trifluoropropene and pentafluorostyrene leading exclusively to the corresponding vinylsilanes. $Ru_3(CO)_{12}$ has been reported to be effective catalyst for hydrosilylation of 1-octene [170] (50–75°C) and – especially important – for production of silane coupling agents. In hydrosilylation of allyl chloride (80°C) [171] by trialkoxysilane. $[Ru(CO)_3(PPh_3)_2]$ appeared to be an effective catalyst for the hydrosilylation of allylamine [172].

The complex $[RuHCl(CO)(i\text{-}Pr_3)_2]$ was found to be a very active and highly selective catalyst for the addition of triethylsilane [173]. $[RuHCl(CO)(PPh_3)_3]$ was used in non-selective reaction of 1-(trimethylsilyl)-1-buten-3-yne with triorganosilanes [174, 175]. On the other hand, $[RuH_2(H_2)_2(PCy_3)_2]$ is a highly effective precursor for the selective dehydrogenative silylation of ethylene to vinyl-silane [176].

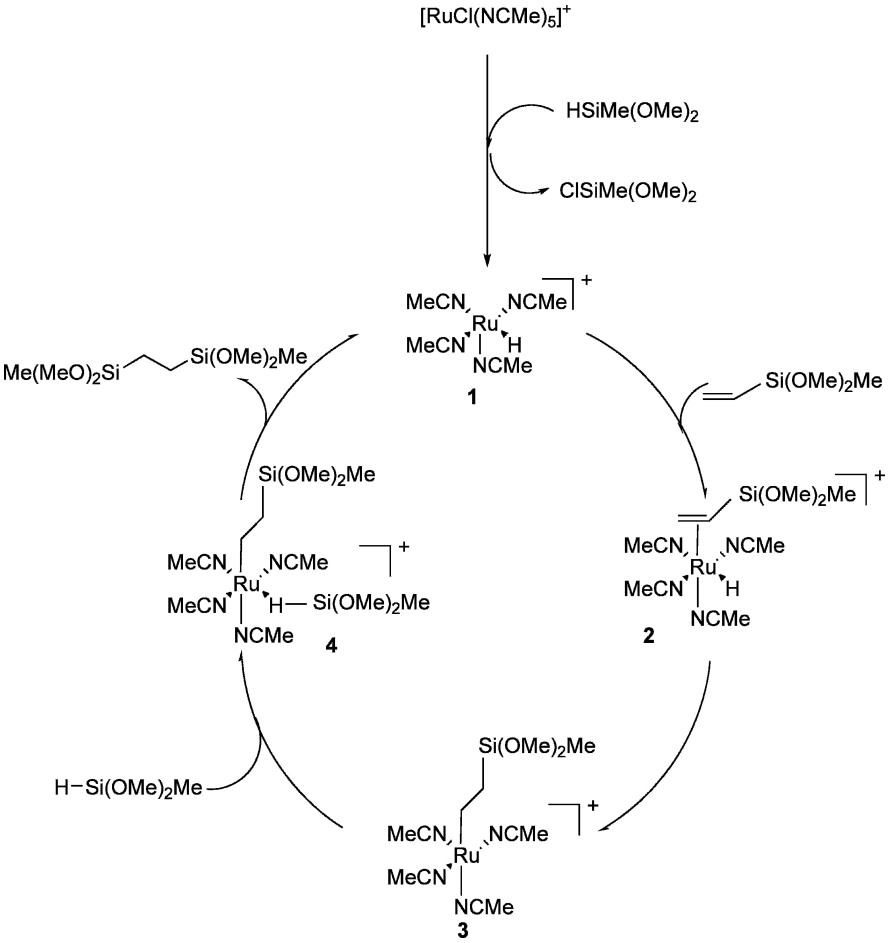
The σ-bond metathesis which is well established for early transition metal catalysts [9] was very recently proposed by Weis et al. [168] on the basis of the computational results of the hydrosilylation of methylvinyldimethoxysilane with methyldimethoxysilane (catalysed also by cationic $[RuCl(NCMe)_5]^+$ as a precursor).

The induction period of the catalysis involves the replacement of an acetonitrile ligand by silicon hydride followed by σ-bonding metathesis reaction which cause the exchange H-atom of silicon hydride for the Cl-atom of Ru-complex to form $[RuH(NCMe)_4]^+$ (see (**1**) on Scheme 1.11) with elimination of chlorosilane. (**1**) initiates the catalytic cycle where the transformations (**1**) → (**2**) → (**3**) → (**4**) are facile.

The formation of ruthenium hydride catalyst (**4**) → (**1**) that generates the product is a rate- determining step of the whole process (see Scheme 1.11).

$$HSiMe(OMe)_2 + CH_2{=}CHSiMe(OMe)_2 \xrightarrow{[RuCl(NCMe)_5]^+} (MeO)_2MeSiCH_2CH_2SiMe(OMe)_2 \quad (1.15)$$

The B3LYP calculated activation enthalpy (Δt=13.1 kcal/mol) for the process catalysed by the precursor is consistent with the experimentally observed activity of $[RuH_2(H_2)(PCy_3)_2]$ and the respective ethylene complex catalysed efficiently three processes of ethylene with $HSiMe_2SiMe_2H$ (and with $HSiMe_2(CH_2)_nSiMe_2H$), i.e.



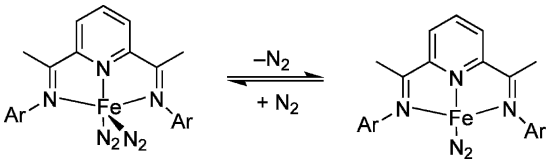
Scheme 1.11 Mechanism of catalysis of vinylsilane hydrosilylation by $RuCl[NCMe]_5^+$ complex

hydrosilylation, dehydrogenative silylation and cyclisation [177]. $RuCl_2[PC_6H_4\text{-}\gamma\text{-}(CF_3)_3]_3$ very efficiently catalyses the hydrosilylation of olefins in carbon dioxide [178] which can be applicable to the synthesis of fluorous silane coupling agents.

Iron pentacarbonyl was the first reported metal carbonyl catalyst for hydrosilylation and, although this reaction occurs under ambient conditions (temperature below 100°C), it takes a somewhat unexpected course. In the presence of this catalyst, the hydrosilylation of ethylene and its derivatives is accompanied by the dehydrogenative silylation [1]. In excess of alkene, vinyltrisubstituted silanes are produced almost exclusively.

Iron carbonyl complexes such as $Fe(CO)_5$ at high temperature hydrosilylate simple olefins with significant dehydrogenative hydrosilylation as a side reaction [see [1,8,9]]. Using $Fe_3(CO)_{12}$ as the catalyst, the reaction of styrenes with triethylsilane gave exclusively *E*-β-(triethylsilyl)styrene in 66–89% [179] as a product of

the dehydrogenative silylation. On the other hand, recent study of the catalytic activity of high spin d^8 square pyramidal iron(0) bis(dinitrogen)complex [(pdi)Fe$(N_2)_2$] (where pdi=tridentate pyridinediimine ligands of the general formula [(2,6-ArN=C(Me))$_2C_5H_3N$], Ar = aryl groups) has shown that iron complexes in an appropriate coordination geometry and spin state may be a reasonable alternative to Pt, Rh, Ru complexes also in the hydrosilylation of carbon-carbon multiple bonds. In solution this complex loses 1 equiv. of N_2 to afford the mono(dinitrogen)adduct according to the following equation [180, 181]:

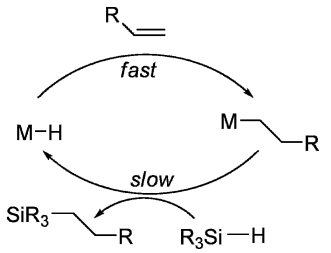


(1.16)

The mechanism of the hydrosilylation by $PhSiH_3$ and $PhRSiH_2$ is proposed to involve an intermediate iron-olefin complex which undergoes oxidative addition to the $L_3Fe(O)$ fragments by the Chalk-Harrod or modified Chalk-Harrod insertion and reductive elimination pathways. In both cases the anti-Markovnikov (saturated) product was formed exclusively and the hydrosilylation with $PhSiH_3$ proceeded much faster then the corresponding reaction with Ph_2SiH_2 [180].

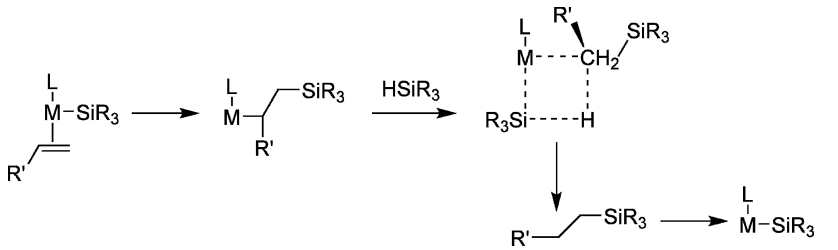
1.2 Early Transition Metal, Lanthanide and Actinide Complexes as Catalysts

Although the vast majority of hydrosilylation catalysts are late transition metal complexes, the results of the last 15 years have revealed that early – transition metal complexes are active precursors of the olefin and acetylene hydrosilylation. Catalysis by d^0 transition metal complexes such as organolanthanide or organoyttrium ones is explained by a generally accepted mechanism involving rapid olefin (acetylene) insertion into the M—H bond followed by a low Si—C bond formation via σ-bond metathesis of the resulting metal-alkyl with silane [182] (see Scheme 1.12).



Scheme 1.12 Mechanism of alkene hydrosilylation by d^0 TM complexes

However, also in zirconium catalysed hydrosilylation a pathway including formation of alkylsilane via the insertion of the alkene into M—Si bond followed by σ-bond metathesis is proposed [183] (Eq. 1.17).



(1.17)

The Cp_2MCl_2/nBuLi (where M=Ti, Zr, Hf) catalysed reactions of $PhMeSiH_2$ occurring in the presence of cyclic and acyclic olefins include hydrosilylation of olefins isomerisation/hydrosilylation of internal olefins, as well as dehydrocoupling of the silane and dehydrogenative silylation of olefins [184].

In the 1990s, some metallocene complexes of either group 3 and 4 were reported to catalyse hydrosilylation reactions of unsaturated hydrocarbons [184–192]. Among them were $[Cp^*_2YCH_3—THF]$ [170], $[Cp^*_2LnCH(SiMe_3)_2]$ (where L_n=Sm, Yb) [186], $[\{Cp^*NdH\}_2]$, $[Cp_2NdCH(SiMe_3)_2]$ [187], $[Cp_2Zr(H)SiHPh_2]$ [191].

Zirconium metallocene (Cp_2Zr) catalysed hydrosilylation has been a good model since 1991 for experimental and theoretical study of the mechanism of catalysis by early transition metals. All relevant reports suggest that Cp_2Zr catalysed hydrosilylation of olefins proceeds through a new mechanism including the coupling reaction between Cp_2Zr(alkene) and silane instead of either the alkene insertion into Zr—H bond or alkene insertion into Zr—SiR_3 bond [183, 184, 193, 194].

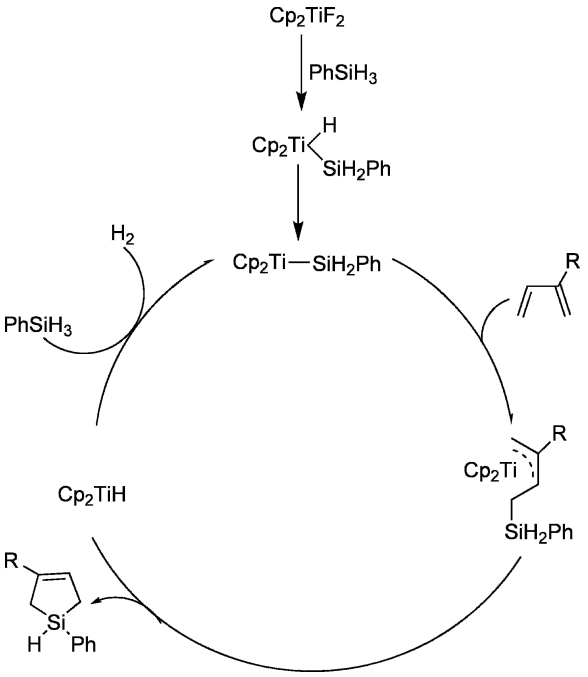
As already mentioned, Sakaki et al. have investigated theoretically the late transition complex hydrosilylation of ethylene and have explained why the platinum catalysed and the rhodium catalysed hydrosilylations take place through the Chalk-Harrod and modified Chalk-Harrod mechanism, respectively [3, 4, 6, 7, 11].

A comprehensive theoretical study by the same authors with the DFT and MP_2-MP_4 (SDQ) of the Cp_2Zr catalysed hydrosilylation of ethylene by monosilane allowed them to propose a very complicated reaction mechanism which involves a new type of Si—H σ-bond activation reaction between Cp_2Zr (alkene) and silane as a key interaction in the coupling reaction earlier suggested by the experimenters [195]. The product release process occurs via ethylene-assisted C—H reductive elimination. The reason for the difference between the late transition metal (Pt, Rh) catalysed hydrosilylation and the Cp_2Zr ones is that the occupied d orbital of the Cp_2Zr catalyst has much higher energy than those of the respective late transition metals (Pt(0) and Rh(I)) complexes.

As a continuation of their experimental study, Takahashi et al. reported [193] a unique method of controlling the two addition models in the zirconone-catalysed hydrosilylation of terminal styrene derivatives. The system Cp_2ZrCl_2 (+ 3 equiv. % BuLi) promotes hydrosilylation of styrene according to the Markovnikov rule, while the regioselectivity is reverse, when Cp_2Zr/BuLi=1/2 [196].

Ab initio electronic calculations were used to investigate a reaction pathway for the hydrosilylation catalysed by divalent titanium modelled by TiH_2 and $TiCl_2$. All levels of the theory predict a barrierless reaction path against the barrier of 78 kcal/mol for the uncatalysed reaction [197, 198].

Also a novel route of the hydrosilylation of dienes catalysed by Cp_2TiF_2 complex as a precursor has been reported recently [199]. The reaction proceeds with an unprecedented regio- and diastereo selectivity to give *E*-allylsilanes in good to excellent yields. The activation of the precatalyst in the excess of $PhSiH_3$ and in the absence of diene promotes the dehydrogenative double silylation of dienes to yield silacyclopentene according to the following scheme (Scheme 1.13):



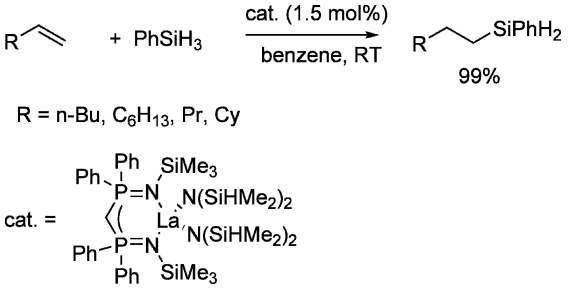
Scheme 1.13 Mechanism of dehydrogenative double silylation of dienes catalysed by Cp_2TiF_2

Titanocene based complexes were also used in the hydrosilylation of a variety of alkenes [200]. Recently, the first rhenium complex, $[ReBr(CO)_3]$ as a catalyst of styrene hydrosilylation was reported to proceed with high regioselectivity to afford anti-Markovnikov adducts in good to high yields [201]. Organolanthanide and group 3-organometallic catalysts provide a new alternative to traditional late TM-based catalysts for selective hydrosilylation of alkenes and alkynes (for recent reviews see [202]). Mechanistically, the transformation is characteristic of early TM-catalysed reaction, i.e. the process also involves the olefin (acetylene) insertion into the M—H bond and σ-bond metathesis bond formation. The earliest reported examples of group 3 or organolanthanide – catalysed hydrosilylation emphasised reaction with simple alkenes (1-octene, styrene) provided modest to good yields of the desired terminal (internal) products [203]. Later development in catalysis

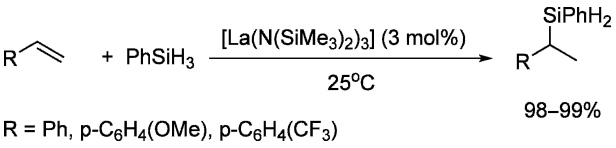
particularly of yttrium, lanthanum and samarium organometallics provided a major breakthrough in terms of efficiency and selectively in the synthesis of organosilanes [204, 205].

Recent (after 2000) study in this field has been focused on the influence of the ligand structure on the activity and regioselectivity [206–211] and on extending the topic over functionalised and internal olefins as well as dienes [211–213].

Below see a few examples of recent lanthanum catalysts used in the hydrosilylation of olefins.



(1.18)



(1.19)

Finally, it is worth mentioning that the most research on catalysis by organolanthanide is unfortunately limited to hydrosilylation by primary silanes $RSiH_3$.

New reports on application of organoactinides in catalysis also mention catalytic hydrosilylation of alkynes [214] and alkenes (for a recent review see [215]). For alkenes the hydrosilylation reaction promoted by organoactinides is much slower (by about one order of magnitude) than that promoted by the respective organolanthanides of the types Cp^*_2LnR (Ln=Sm, La, Li) or $Me_2Si(C_5Me_4)_2SmR$(R=alkyl). The difference is found for linear terminal alkenes, which lanthanides catalyse hydrosilylation to form both isomers while actinides yield exclusively 1,2-adduct [8,9]. Thus organoactinides can be complementary catalysts to organolanthanides and other TM-complexes. It is worth adding that the application of organoactinides is also mostly limited to hydrosilylation by $RSiH_3$.

1.3 Photo- and Peroxide-Initiated Catalysis by Metal Complexes

Photogenerated catalysts obtained by the light-induced generation of a ground-state catalyst from a catalytically inactive precursor, have become a topic of current interest in catalysis by transition-metal complexes. Such methods have also been applied in hydrosilylation.

The first photocatalyst discovered was $Cr(CO)_6$, which is active in the 1,4-hydrosilylation of 1,3-dienes to yield allylsilanes using a method of synthetic utility [2]. Recently, more details have been reported on this reaction to proceed smoothly at ambient temperature to give *cis*-1,4- addition products exclusively [216]. Low-valent metal complexes containing non-carbonyl ligands also exhibit d–d transitions in the near-UV, and give rise to similar photodissociative behaviour. The effect of phosphine and phosphite was also examined [217]. When reaction catalysed by Pt and Rh complexes, e.g. by Wilkinson's catalyst containing phosphine ligands, is performed in air, a secondary photooxidation of free ligand to phosphine oxide occurs readily in a manner characteristic of thermal reaction [4, 5, 218].

UV radiation can lead to generation of high concentrations of coordinatively unsaturated centres by ligand dissociation and free ligand modification to prevent back-reactions. Photochemically induced hydrosilylation by platinum compounds, e.g. chloroplatinic acid, was reported to increase the yield (above 90%) of cycloalkylsilane compounds and enable the process to occur at ambient temperature [218]. Irradiation of platinum bis(β-diketonates), e.g. $Pt(acac)_2$ [219] Pt(hfac) [220] and $Pt(PPh_3)_2Cl_2$ catalyst [221], in the presence of hydrosilanes and olefins results in olefin hydrosilylation. Also photolysis of η^5-cyclopentadienyl trimethyl platinum(IV) complexes [222–224] and Pt-triazenido complex [PhN=N—$N(C_6H_{13})_4$-Pt] [225] in the presence of a hydrosilane leads to formation of an active hydrosilylation catalyst currently believed to be a platinum colloid or cluster. Dioxygen or oxygen containing photolysis products of the solvent can act as stabilisers of the Pt-colloid or other Pt-intermediates.

In most of the above mentioned photocatalysed reactions, no hydrosilylation products have been formed under controlled conditions either in the absence of UV radiation or in the absence of a catalyst. This proves that an active catalyst is photogenerated from the initial metal complex.

Molecular oxygen has become a commonly used co-catalyst for inactive or weakly active transition metal complexes. In addition, other oxidizing agents, mainly peroxides, have been used in particular as active rhodium complexes. The high catalytic activity of platinum catalyst in the hydrosilylation of the C=C bond, e.g. the addition of $MeHSiCl_2$ to allyl chloride, can be maintained by the addition of benzoyl or *tert*-butyl peroxides [1]. The Wilkinson complex, $[RhCl(PPh_3)_3]$, becomes moderately active at room temperature during the hydrosilylation of 1-octene with triethylsilane, when various organic peroxides are used as co-catalysts in the molar ratio peroxide/Rh=8:1. Chromium triad carbonyls $M(CO)_6$, where M=Cr, Mo, W, have been tested to examine the effect of various organic peroxides on the hydrosilylation of 2,3-dimethyl-1,3-butadiene by triethyl-, triethoxy- and methyldiethoxysilanes [1]. The results have shown that provided the correct choice of the organic peroxide is made, it is possible to enhance the activity of these hexacarbonyls.

The oxidation products are known to posses much weaker coordinating ligands than those initially formed. The evidence for organic oxidant promotion of RhCl(cod)phosphine catalysed hydrosilylation of 1-hexene was also demonstrated [226].

1.4 Immobilised Metal Complexes as Catalysts

Over the past few decades major research effort has been devoted to development of a new generation of heterogenised TM complex catalysts which would combine the advantages of heterogeneous catalyst (easy catalyst recovery) with high activity and selectivity of homogeneous complexes. Transition metal complexes can be immobilised either on the appropriate (mostly cross-linked) polymer such as polystyrene-divinylbenzene and polyvinyl chloride, or inorganic supports such as silica, Al_2O_3, glass and molecular sieves. Polymer and inorganic support bound metal complexes have been synthesised by the introduction of functional groups which act as ligands (e.g. phosphines, amines, SH, CN, acac, etc) followed by anchoring the TM precursor onto each heterogenised ligands [227].

This process is illustrated in Fig. 1.12.

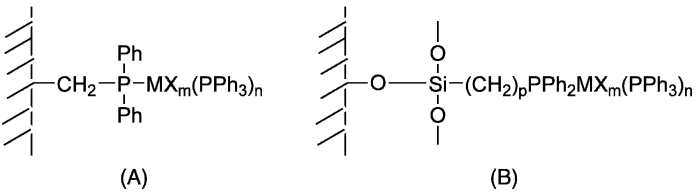


Fig. 1.12

The application of polymer-supported catalysts has now been extended to the synthesis of complexes between transition metal derivatives and structurally ordered macromolecular ligands to give catalytic systems exhibiting high activity and stereoselectivity.

Effective polystyrene and polymethacrylate resin-supported Pt catalysts have been reported [228–231]. Very good recyclability more that 90% of conversion after 10 runs at room temperature in the hydrosilylation of 1-octene by methylodichlorosilane was observed [231] (Fig. 1.13).

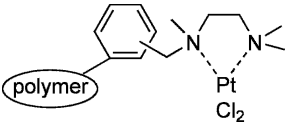
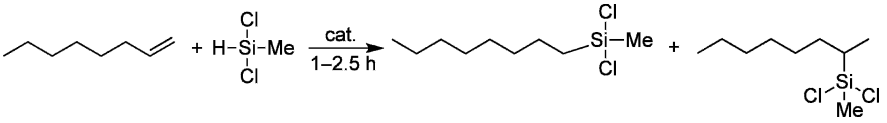


Fig. 1.13

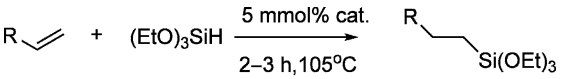


(1.20)

Good activity, selectivity and stability of polystyrene-resin-supported Pt-catalyst as well as excellent recyclability relative to Speier's catalyst in the room temperature solventless hydrosilylation of 1-octene using trichlorosilane have been reported [229].

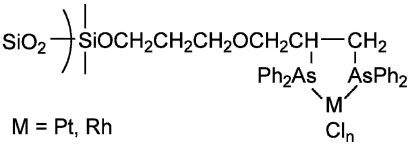
Less effective are Pt—Rh – containing polymer derived from polystyrene-polybutadiene-block copolymers in the hydrosilylation of styrene and 1-hexene [232]. Polyamides have been recently synthesised as very suitable polymers for heterogenisation which do not need any further functionalisation and exhibit much higher thermal stability than conventional polystyrene supports [230, 233, 234].

Immobilisation of platinum complexes onto silica using pyridine phosphine or arsine complex has also been reported [235, 236], eg. Fig. 1.14.



73–93% (1.21)

Fig. 1.14



Vinyl-functionalised polysiloxanes grafted onto silica were also efficiently used for immobilizing Pt and Rh complexes as catalysts for olefin hydrosilylation [237–240], (Fig. 1.15), e.g. synthesis of methyl-(γ-chloropropyl)dichlorosilane [240].

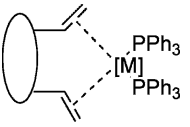
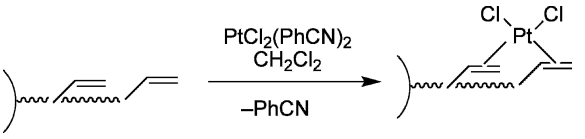


Fig. 1.15 [M] = Pt, [Rh]Cl



(1.22)

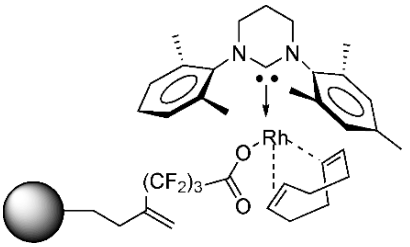
Applicability of all the above TM complexes immobilised via phosphine and amine is limited due to leaching of the metal observed when they are reused in multiple catalytic cycles [239].

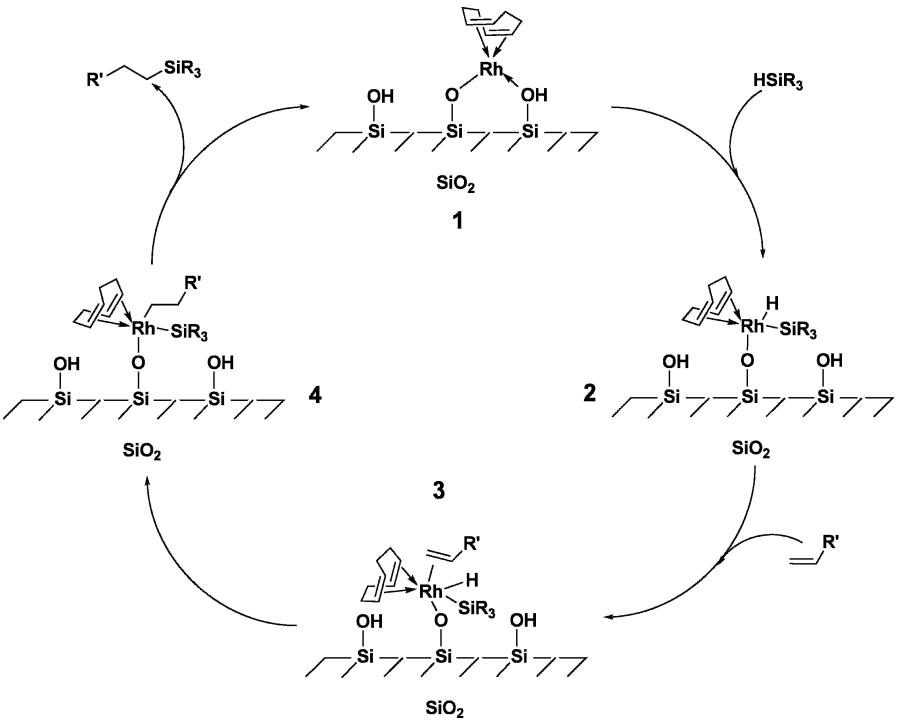
Gold supported on CeO_2 and well-defined phosphine—free organogold(III) complexes have been revealed as selective catalysts for hydrosilylation of carbon—carbon and carbon—oxygen bonds. Au/CeO_2 is able to efficiently catalyse these reactions owing to the presence of stabilised Au(III) on the surface. All those catalysts can be recycled without the loss of activity and regioselectivity [241].

Polysilanes have also been used as macroligands. These polymers are able to bind Pt complexes in the hydrosilylation of olefins [242]. A new method of the Pt-catalyst immobilisation onto polymers (termed polymer incarcerated method) has been recently developed by Kobayashi et al. [243]. The method is based on microencapsulation and cross-linked. This platinum catalyst shows high activity in hydrosilylation of alkenes and alkynes and fifth reuse of the catalyst has been attained without loss of activity.

Polystyrene-DVB – supported *N*-heterocyclic carbene – derivatives Rh(I) complex was recently reported to be efficient catalyst for the hydrosilylation of olefins as well as ketones, aldehydes and acetylenes [244] (Fig. 1.16).

Fig. 1.16





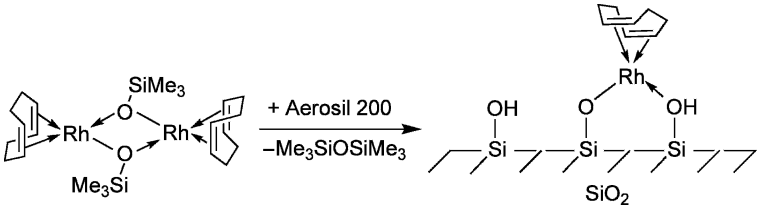
Scheme 1.14 Mechanism of heterogeneous catalysis of hydrosilylation by surface rhodium(diene) siloxide compolex

Other heterogenised Pt catalysts linked to inorganic or organic supports via various functional groups have been very extensively studied for the hydrosilylation of 1-alkenes, styrene, allyl derivatives and 1,3-dienes [245–248].

The sol-gel method was applied for the preparation of heterogenised complexes based on the polycondensation of suitable trialkoxysilyl-substituted organosulphides, -phosphines and -amines bound as ligands to a given complex (Pt, Rh, Ir, Ru). Their advantages are non-swelling properties and resistance to organic solvents and reagents, high temperature stability as well as a possibility of use in aqueous and organic media. Schubert et al. synthesised the catalysts of this type by polycondensation of $[Rh(CO)Cl\{PPh_2CH_2CH_2Si(OEt)_3\}_2]$ with tetraethoxysilane, which shows a catalytic activity in the hydrosilylation of 1-hexene similar to that of a homogeneous analogue attached to the surface of silica [249].

Pt(0) – based catalyst supported on silica containing ethylene oxide units have been recently reported to show high activity and air stability in hydrosilylation of olefins. The generation of the catalyst is based on the hydrolysis and polycondensation of α,ω-bis(triethoxysilylpropyl)di(ethylene oxide) in the presence of K_2PtCl_4 as the platinum source [250].

We reported very recently the synthesis and characterisation of the well-defined rhodium-siloxide complex immobilised on silica for the first time obtained by direct reaction of molecular rhodium siloxide precursor with Areosil [251].



(1.23)

The complex characterised by ^{13}C, CP, MAS NMR spectra and elementary analysis appeared to be a highly effective catalyst for hydrosilylation of 1-alkenes, vinylsiloxane [251, 252] and other olefins [252–255].

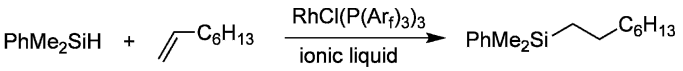
The solid-state NMR results have shown the presence of surface siloxide complex $\equiv SiORh(H)SiMe_2Ph$ **2** identified as a product of the oxidative addition of dimethylphenylsilane to the initial complex **1**. The absence of the disiloxane elimination in this system (recorded by GC-MS) is an additional evidence for formation of such a key intermediate in the heterogeneous system. Therefore, the catalytic cycle of the hydrosilylation by **1** has to be different from that of the homogeneous one and should involve a catalytic pathway protecting the surface-siloxide intermediates against leaching during whole cycle. Apparently, the reaction proceeds via the well-known Chalk-Harrod mechanism (see Scheme 1.14) initiated by stable immobilised [$\equiv$SiORh(I)(diene)] complex **1**. The process of the oxidative addition of silicon hydride to (**1**→**2**) was proved by NMR study. The subsequent coordination of alkene to the surface-siloxide (**2**→**3**) rhodium complex is followed by its insertion into Rh—H bond (**3**→**4**) with final elimination of the hydrosilylation prod-

uct and regeneration of stable surface rhodium-siloxide species **1**. The interaction of the surface silanol groups in **1** seems to be responsible for the high stability of such a single-site rhodium catalyst, which can be recycled at least 10–20 times without a decrease in the high yield and selectivity [251].

The characterisation of **2** by solid state NMR spectroscopy as well as elemental analysis (only 28% decrease of rhodium contents in the samples after 20 cycles in the hydrosilylation) are convincing evidence of high efficiency of surface rhodium siloxide complexes in the hydrosilylation of carbon—carbon multiple bonds as well as presumably in other reactions catalysed by late transition metal siloxides synthesised via direct reaction of molecular late transition metal siloxide precursors with silica.

The preparation of air- and water-stable imidazolium-based ionic liquids as solvents for TM catalysis have received growing attention for the last 15 years [256, 257]. In addition, these ionic liquids show limited miscibility with most of the common organic solvents offering potential for efficient catalyst recovery by facile phase separation. Therefore, ionic –liquids have been recently recognised as potential media for the immobilisation of catalysts with considerable success in a wide range laboratory and even industrial scale reactions [257, 258].

However, reports on biphasic hydrosilylation are scarce. One of them is the Wilkinson complex catalysed hydrosilylation of 1-octene in fluorous room temperature ionic liquid [259].



$Ar_f = C_6H_4(SiMe_2CH_2CH_2C_6F_{13})$-*p*

ionic liquid = $[BMIn][B(Ar_f)_4]$ (1.24)

The catalyst can be recycled by biphasic separation with an average retention of catalytic activity of 94% [259]. Similar results have been recently reported using N-alkylpyridinum or N. N-dialkylimidazolium salts as supports of the Wilkinson catalyst in the 1-alkene hydrosilylation by triethoxysilane. The catalytic system $(PPh_3)RhCl$ / ionic liquid (molten salts) can be recycled at least 10 times without noticeable decrease in the activity and selectivity [260].

The hydrosilylation of 1-heptene, allyl glycidyl ether and allylpolyether by heptamethyl(hydrosiloxane) and respective polysiloxanes (see Chapter 6) catalysed by rhodium siloxide complex in imidazolium ionic liquids (especially [TriMIM] $MeSO_4$) gives heptylglycidoxyfunctional (poly)siloxanes and silicone polyethers with high yield and selectivity. The catalytic system can be easily separated and successfully reused up to five times [261].

Weyershausen group from Degussa have used a variety of platinum precatalysts such as K_2PtCl_4 and $[Pt(PPh_3)_4]$ dissolved in the ionic liquid $[C_4py][BF_4]$ and $[C_4$-3-pic$]BF_4$ in modification of polysiloxanes via the biphasic hydrosilylation of 1-hexadecene [262] and as well as terminal polyether olefins (see also Chapter 6) [263–265].

Generally, the catalytic activity of all types of the immobilised complexes is comparable to that of their homogeneous analogues, although an increase in selectivity and/or activity of heterogeneous catalysts has been noted.

1.5 Metal and Supported Metal Catalysts

Another group of catalysts active in the addition of the Si—H bond to unsaturated compounds are metals supported on inorganic materials or carbon. Initially, only a platinum catalyst supported on carbon, silicates and silica appeared to be effective in the reactions of trichlorosilane with ethylene, acetylene, butadiene, allyl chloride and vinylidene fluoride. However, it was soon established that other metals could also be used to catalyse hydrosilylation reactions, viz. Rh, Ru, Pd, Ni, and Ir. These metals are usually supported on active carbon, γ-Al_2O_3, SiO_2 or $CaCO_3$. Platinum supported on carbon (usually in 5%wt concentration) is the most common and most efficient metal catalyst for polyaddition and hydrosilylation of carbon—carbon multiple bonds [1] (for recent review see [266]).

A production of 3-glycidoxypropyltrialkoxysilane on Pt/C was reported by Degussa-Huls to show high efficiency (conversion up to 100% and selectivity over 90% [267]). 5% Pt/C was also used in the hydrosilylation of unsaturated fatty acid esters with triethoxysilane and dimethylchlorosilane [268]. We have also studied the commercially important process of the hydrosilylation of allyl chloride by trichlorosilane in the presence of Pt/C catalyst to determine the rate constants and activation energy. On the basis of the kinetic equation we have concluded that the process proceeds according to the Chalk-Harrod type mechanism [269, 270].

Bimetallic (Pt—Cu or Pt—Ru) supported on active carbon of high surface area (1100–1300 m^2) have been recommended as novel effective catalysts in the hydrosilylation of allyl chloride, alkenes and trifluoropropene [271].

However, not only microporous active carbon of high surface area, but also mesoporous carbon black of lower surface area (216 m^2/g) can serve as an excellent support for Pt-Cu catalyst in hydrosilylation of alkenes with polyhydrosiloxanes to produce silicone waxes with a long chain (>C8) [261] as well as in the addition of trichlorosilane to allyl chloride and 1-octene [270]. Platinum catalyst (0.5%) supported on porous Al_2O_3 appeared very attractive in the industrially important hydrosilylation of cyclopentene and cyclohexene [272].

Mesitylene solvated heterogeneous Pt catalysts, obtained by treatment of carbon, graphite or γ-Al_2O_3 with mesitylene solvated platinum atoms are good catalysts for selective hydrosilylation of isoprene, and other allyl derivatives [273, 274].

Metals, which are usually colloids and formed in situ by the reduction of metal salts (mainly nickel, but also Pt, Pd and others) provide catalysts activity similar to that of the supported metals.

Early concepts regarding the extremely efficient catalysis of hydrosilylation by chloroplatinic acid involved the reduction of the complex to colloidal platinum, which was believed to be the real catalyst (for review see [275]. The reports by

Lewis et al. [276–280] have shown that the processes leading to colloid formation can account for the high activity of a hydrosilylation catalyst based on the complexes of Pt(0) with olefins and dienes such as divinyltetramethyldisiloxane (Karstedt's catalyst) and cyclooctadiene. The reactivity order of platinum group metal colloids prepared according to the equation [281]:

$$Me_2(OEt)SiH(excess) + MCl_x + D_4^{Vi} \longrightarrow H_2 + Si\ products + M\ colloid \qquad (1.25)$$

where M=Pt, Rh, Ru, Ir, Os, Pd; D_4^{Vi} (D_4^{Vi} = [Me(vinyl)SiO]$_4$) serves (except for Pt) as a colloid stabiliser, is as follows: Pt > Rh > Ru—Ir > Os, Pd [276, 277]. The proposed mechanism of the hydrosilylation involves the formation of the metal colloid – R_3SiH intermediate followed by a nucleophilic attack of the olefin. The function of O_2 is predominantly to prevent irreversible colloid agglomeration (colloids have reduced activity).

However, extensive studies, particularly by Lewis and Stein and co-workers (from General Electric), have revealed an essential difference between the morphologies of the Pt colloid formed under particular conditions in the hydrosilylation of various olefins by Et_3SiH in the presence of the Karstedt's pre-catalyst [281]. Relations of the reaction kinetics and the product distribution to the catalyst structure in solution (NMR, EXAFS) and the formation of metal colloids led to a clear conclusion that the catalytic hydrosilylation under such conditions is a molecular process proceeding via metal clusters and that formation of colloids is associated with deactivation of the system according to the following equation [281]:

$$(M) \underset{olefin}{\overset{\equiv SiH}{\rightleftharpoons}} (cluster) \overset{\equiv SiH}{\rightleftharpoons} colloid \longrightarrow bulk\ metal \qquad (1.26)$$

A recent more precise formulation of this conclusion is that regardless of the stoichiometric ratio of hydrosilane to olefin, the catalyst is a monomeric platinum compound with silicon and carbon in the first coordination sphere. The platinum end product, however, is a function of the stoichiometry of the reactants. At an excess olefin concentration, the platinum end product contains only platinum-carbon bonds, whereas at a high hydrosilane concentration, the platinum end product is multinuclear and also contains Pt—Si bonds [282].

Colloidal silica particles modified with triethoxysilane in the absence of excess water distribute into a thick (13 nm) mobile hydridosilsesquioxane layer on the surface. This layer reacts with Pt(0) complexes to form a catalyst active after at least three times recycling. Just the mobile silsesquioxane layer prevents aggregation of platinum into active colloidal species [283] and the hydrosilylation can be performed heterogeneously.

The formation of metal colloid from molecular complexes in the induction period has some disadvantages which are avoided by a direct use of prefabricated colloids. The size of such colloids can be strictly controlled, a condition not possible for metal complexes and the hydrosilylation can be performed heterogeneously.

However, the third advantage of the prefabricated colloids is the ability to enhance the catalytic properties of a known metal by preparing it in the form of a bimetallic species. Schmid et al. synthesised bimetallic colloids (basically alloys) consisting of a ligand-stabilised Pt shell on Au or Pd cores supported by alumina [269, 270]. They examined the influence of the electronegativity of the colloid core metals on the activity and selectivity of the Pt surface in hydrosilylation reactions. Only the combination of Pt with Pd (which is more electropositive than Pt) in the form of bimetallic layered colloid, improves markedly the activity of the test hydrosilylation reactions of heptamethyltrisiloxane with 1-octene [284]. Hydrosilylation of methyl undecenylate catalysed by the initial $Pt(cod)_2$ precursor of platinum colloid may also occur in a two-phase system [285]. The very specific co-activator for Pt/C catalyst appeared to be peroxide, whose continuous presence is a factor maintaining the high catalytic activity during the reaction [45].

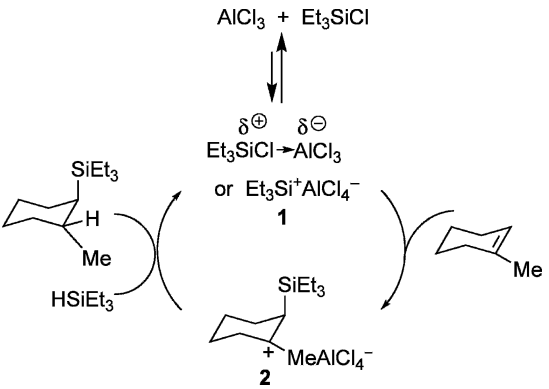
1.6 Nucleophilic – Electrophilic Catalysis

Most substitution reactions involving the Si—H bond occur via the ionic mechanism either involving the attack of a nucleophile on the silicon atom or the electrophilic interaction with hydridic hydrogens. The possibility of such a heterolytic cleavage of the Si—H bond systems follows from the fact that silicon is more electropositive than carbon and that the d-orbitals of silicon are capable of participating in bond formation. However, strong electronegative substituents at silicon, e.g. chlorine, can lead to a decrease in the electron density at the central atom, and may reverse the polarisation of the Si—H bond $Cl_3Si^{\delta-}$-$H^{\delta+}$, particularly in the absence of any nucleophilic reagent. Different properties of the Si—H bond, depending on the substituents at silicon, may account for the two different mechanistic pathways for nucleophilic (basic) catalysis by organic bases (nucleophiles), for the addition of hydrosilanes to C=C and C≡C bonds. Nucleophilic hydrosilylation is the predominant mechanism during the addition of trichlorosilane, less dominant for addition of dichloro(methyl, phenyl, hydro)silane to vinyl derivatives, e.g. acrylonitrile, styrene and vinyltrichlorosilane and of even lower significance for allyl derivatives and other organic compounds with C=C and C≡C bonds [1, 9].

From the mechanistic viewpoint it is interesting to note numerous reported examples of base (nucleophile) catalysed addition, simultaneously promoted by electrophilic metal ions. A typical example of nucleophilic-electrophilic catalysis is provided by the addition of hydrochlorosilanes to alkenes, which occurs in the presence of Cu(II) and/or Cu(I) salts, and tertiary amines [1], e.g. Cu_2O-tetramethylethylenediamine system [286] catalyses exclusively β-hydrosilylation of acrylates. In the aspect of nucleophilic-electrophilic interactions, it is possible to discuss other metal salts (mainly $ZnCl_2$, but also $SnCl_2$, $PdCl_2$, $NiCl_2$, $InCl_3$ and $GaCl_3$, $AlCl_3$, $M^+[AlR_4]^-$ + MCl; where M=Li, Na, K) and non-metal compounds $BF_3 \times Et_2O$ as electrophilic (Lewis acid) catalysts, which are chiefly effective without any additional bases in the hydrosilylation of carbon—oxygen and carbon—nitrogen

bonds, but also in C=C and C≡C bonds [286]. Silanes having electron-donating substituents such as alkyl groups are more suitable for Lewis acid-catalysed hydrosilylation.

Jung reported the first example of the regio- and stereoselective addition of trialkylsilanes to cyclic and linear alkenes catalysed by Lewis acids under mild conditions [287] (Scheme 1.15). The reaction gave the corresponding trialkylsilylalkanes in fair to good yields. Cycloalkenes having an alkyl group at the double-bonded carbon showed better reactivity than monosubstituted compounds. The catalytic activity of Lewis acids decreases in the following order: $AlBr_3 > AlCl_3 > HFCl_4 > EtAlCl_2 > ZrCl_4 > TiCl_4$. A possible mechanism for the $AlCl_3$ catalysed hydrosilylation based on the $AlCl_3$-catalysed allylsilylation reactions presented earlier was proposed in [287]. The key intermediate (**1**) is trialkylsilylenium ion [$Et_3Si^+AlCl_4^-$] or polarised donor-acceptor complex ($Et_3Si^{\delta+}$–Cl → $AlCl_3^-$) formed from $AlCl_3$ and Et_3SiCl at the beginning stage of the reaction (see Scheme 1.15). The formation of a more stable tertiary carbocation in the intermediate (**2**) would be responsible for the regioselectivity in the products formed.

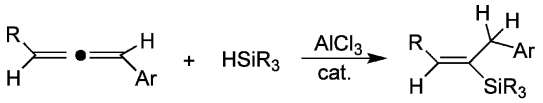


Scheme 1.15 Mechanism of $AlCl_3$ catalysed hydrosilylation of cycloalkenes

The stereochemistry of the hydrosilylation of exemplary olefin (methylcyclohexene) could be explained by the approach of silicon hydride to the intermediate (**2**) from the other side of the triethylsilyl group, which is a less hindered approach.

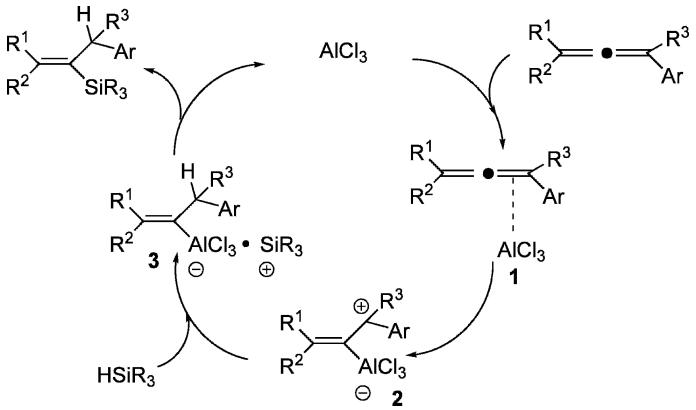
Moreover, the highly regioselective hydrosilylation of 1-alkyl, 1-aryl, 1,1-dialkyl substituted cyclopropanes with chlorodimethylsilane catalysed by $AlCl_3$ has been recently reported [288].

The hydrosilylation of aromatic allenes is also efficiently catalysed by $AlCl_3$ to give the corresponding vinylsilanes regio- and stereo-selectively in high yield (60–96%).



R = H, Me; Ar = C_6H_5, p-Me-C_6H_4, p-F-C_6H_4 (1.27)

The mechanism of this process assumes coordination of $AlCl_3$ to the double bond of allene to produce the zwiteterionic intermediate (**2**) through π-complex (**1**). Hydride transfer from $HSiR_3$ to (**2**) can give the ate-complex (**3**) which undergoes facile trans-metallation to afford the vinylsilane and $AlCl_3$ [289] (Scheme 1.16).



Scheme 1.16 Mechanism of $AlCl_3$catalysed hydrosilylation of aromatic allenes

While aromatic groups such as p—CH_3—C_6H_4 and p—F—C_6H_4 stabilise significantly the benzyl cation p—CF_3—C_6H_4 destabilises this carbocation to the strong electron- withdrawing effect of CF_3 group. Accordingly, in the latter case the reaction does not proceed at all [289].

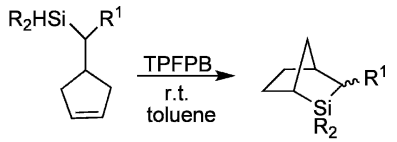
Contrary to the above examples, a quite new class of catalysts based on early main group metals (Ca, Sr and K) was recently reported to promote general conversion of conjugated double bond [290]. The catalytic reaction is initiated by the formation of a highly reactive metal hydride which either adds to an alkene or to silane. The regiochemistry for the hydrosilylation of 1,1-diphenylethylene (DPE) catalysed by calcium complex can be completely controlled by the polarity of the solvent. The preliminary report [290] can be a valuable starting point for other applications.

Amine borane and phosphine borane complexes were successfully used as effective catalysts for hydrosilylation of organic compounds with internal unsaturated bond [291], which cannot be selectively hydrosilylated in the presence of Pt-catalysts.

A quite unusual catalytic hydrosilylation was suggested by Lambert and Zhao [292]. Their finding that trityl cation efficiently catalyses the hydrosilylation of

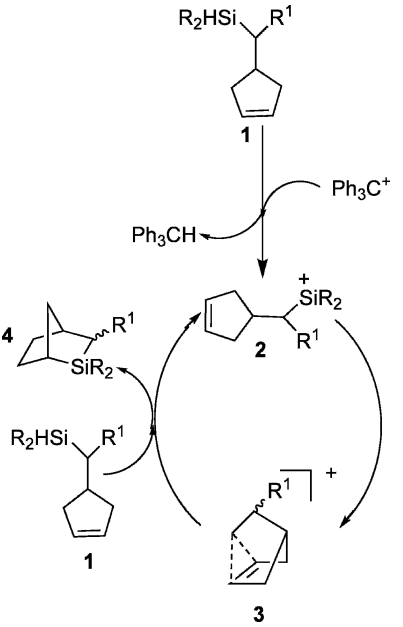
1,1-diphenylethene by triethylsilane suggests the incorporation of silylium ion and β-silyl substituted carbocation in catalysis of the reaction.

Similarly, tetrakispentafluorophenyl borate (TPFPB) appeared to be an attractive pre-catalyst for intramolecular hydrosilylation of cyclopentenemethylsilanes to produce 2-silanobornanes under mild conditions in high isolated yields (85–94%) [293].



R = H, Me, Ph; R^1 = neo-C_5H_{11} (1.28)

The key intermediates in this process are silanorboryl cations (Scheme 1.17). In the first step, the catalytic active species was formed by a hydride transfer reaction from silane (**1**) to trityl cation. The silylenium ions (**2**) undergo fast intramolecular reaction to the more stable silanorbornyl cations (**3**). In access of silane (**1**) a second hydride transfer takes place which results in the final formation of silanorbornane (**4**) and regeneration of silyl ions (**2**). The catalytic metal-free (and radical free) intramolecular hydrosilylation appeared to be more efficient than the traditional hydrosilylation reaction using TM complex (and radical initiators as well).



Scheme 1.17 Mechanism of TPFPB catalysed intramolecular hydrosilylation of cyclopentenemethylsilanes

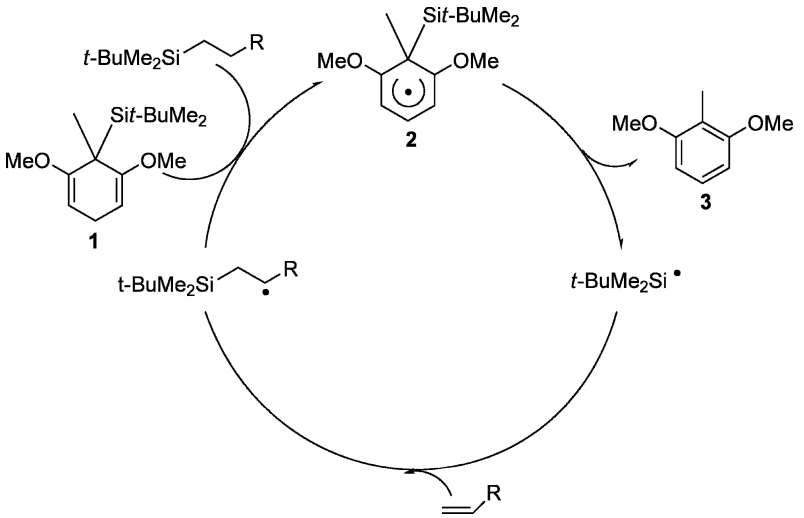
1.7 Free-Radical Initiated Hydrosilylation

In early reports it was suggested that addition of hydrosilanes to multiple bonds could proceed as free-radical chain process because of a relatively low energy of the Si—H bond in comparison to that of the C—H bond. For this reason many synthetic and mechanistic studies have been devoted to the hydrosilylation of carbon—carbon (C—C, C≡C) bonds initiated by free radicals generated in the reaction mixture [1, 2, 5]. Free-radical addition of hydrosilanes resembles the addition of hydrogen bromide to alkenes and always occurs according to the anti-Markovnikov rule [1].

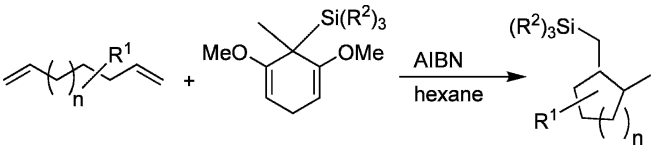
In general, radical hydrosilylation of alkenes cannot be conducted using trialkylsilanes. This is due to a rather strong Si—H bond in trialkylsilanes. However, the hydrosilylation of carbon—carbon multiple bonds with modified silanes such as tris(trimethylsilyl)silane have been successfully used in radical hydrosilylation [10].

Studer et al. presented the results on the radical hydrosilylation using silylated cyclohexadienes as radical initiators [294]. The bisvinylic methylene group acts as the hydrogen donor in these reaction. H-transfer leads to a cyclohexadienyl radical (**2**) which subsequently rearranges to provide *tert*-butyldimethylsilyl radical and arene (**3**) (see Scheme 1.18) [295].

Silyl radical addition to the alkene leads to a β-silylalkyl radical, which upon reduction with **1** affords the hydrosilylated alkene and the chain carrying radical **2**. Hydrosilylation of various olefins such as allyl acetate 4-phenyl-1-butene, cyclohexene and β-pinene have been obtained in the good yield 54–70% [296]. But the most successful was the application of this initiator in intramolecular radical hydrosilylation of alkadienes to synthesise silylated cycloalkanes according to the following equation [295, 296].



Scheme 1.18 Mechanism of radical hydrosilylation of alkenes initited by silylated cyclohexadienes



(1.29)

The hydrosilylation products, if appropriately substituted at silicon can be readily oxidised to the corresponding alcohols using the well-know Tamao-Fleming oxidation protocol (see also Section 1.4).

The reversible addition of tris(trimethylsilyl)silyl [$(TMS)_3Si$] radical to the C=C bonds is due to the ability of this radical to isomerise alkenes. The hydrosilylation of monosubstituted and gem-disubstituted olefins are efficient processes and have been shown to proceed with high regioselectivity in the case of both electron-rich and electron-poor olefins [297].

It is quite interesting that besides the light-induced generation of a ground state catalyst from a catalytically inactive TM-complex (see Section 1.5) organometallics such as $[Cp^*Pt(CH_3)_3]$ ($Cp^* = \eta^5$-$C_5H_4CH_3$) appeared at highly efficient photoinitiators of radical hydrosilylation [298].

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Chapter 2
Hydrosilylation of Alkynes and Their Derivatives

Abstract The design and development of highly efficient and selective methods for the synthesis of alkenylsilanes, based on alkyne hydrosilylation, have been the subjects of extensive study, because of their versatile application in organic synthesis and material science. This chapter describes recent progress in the development of new alkyne hydrosilylation protocols as well as related processes employing hydrosilanes and alkyne derivatives leading to acyclic and cyclic alkenylsilanes, taking into consideration their regio- and stereoselective modes. Synthetic and mechanistic aspects of transition metal- and Lewis acid-catalysed as well as radical-initiated hydrosilylation of both terminal and internal alkynes and their functionalised derivatives proceeding *via* inter- or intramolecular fashion are discussed.

Of the available methods for preparation of alkenylsilanes, the class of compounds that has attracted considerable attention in recent years as versatile building blocks in organic synthesis, the hydrosilylation of alkynes is the most direct, powerful and atom-economical approach [1]. Unsaturated hydrosilylation products are particularly attractive scaffolds for further transformations including oxidation (Tamao-Fleming protocol), electrophilic substitution, palladium catalysed cross-coupling (Hiyama coupling), rhodium-catalysed nucleophilic addition etc. Moreover, the ease of handling, low cost, minimal toxicity and compatibility with a range of organic transformations have greatly stimulated their synthetic advancements. However, the synthetic utility of the alkenylsilanes remains dependent on the possibility of preparing them with high levels of regio- and stereocontrol.

This chapter is focused on the synthetic aspects of both terminal and internal alkyne hydrosilylation as well as related processes employing hydrosilanes and alkyne derivatives, taking into consideration the processes occurring in regio- and stereoselective manners.

As the synthetic utility of the hydrosilylation processes in modern organic synthesis is the topic of a separate chapter 3, this particular chapter is limited to some recent advances in hydrosilylation methodologies leading to stereo-and regiodefined alkenylsilane derivatives, but without presentation of their further transformations. For the same reason, the recent progress in the intramolecular alkyne hydrosilylation, which is currently widely used as a key step in the sequential synthesis

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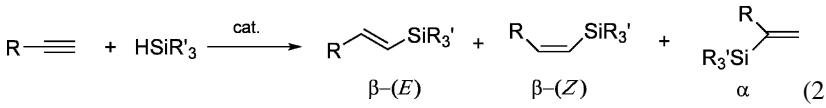
of natural products, is only briefly mentioned here and discussed in details in the chapter 3 concerning applications of the hydrosilylation in organic synthesis.

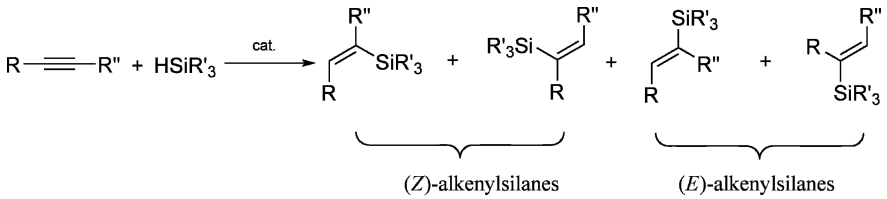
2.1 Regio- and Stereoselective Hydrosilylation of Alkynes Catalysed by Late Transition Metal Complexes

Although the radical [2–5] and Lewis acid [6–9] induced procedures have been recently reported, the transition metal catalysed reactions continues to play a dominant role in terminal and internal alkyne hydrosilylation. However, their widespread use has been partially hampered because of difficulties in accessing regio- and stereodefined isomers as a result of the possibility of forming a mixture of three (for terminal alkynes) isomeric alkenylsilanes: β-(*E*), β-(*Z*) and α (Eq. 2.1).



(2.1)

The hydrosilylation of internal alkynes offers a greater synthetic challenge than that of terminal alkynes because of the potential for a broader product distribution. Nonselective hydrosilylation of internal alkynes would potentially give four isomeric addition products (disubstituted alkenylsilanes) (Eq. 2.2).



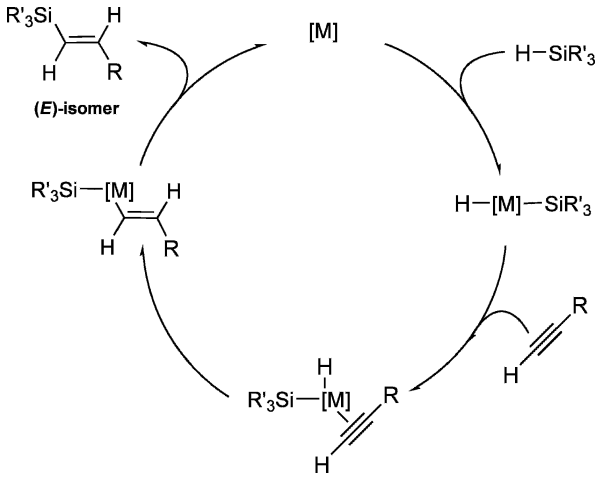
(2.2)

As far as the terminal alkyne derivatives are concerned, both β-(*E*)- and β-(*Z*)-alkenylsilanes ((*E*)- and (*Z*)-1-silyl-1-alkenes) are obtained *via* the addition of hydrosilane across the carbon—carbon triple bond, where the silicon atom attaches to the terminal carbon. The addition of a hydrosilane to the same face of triple bond (*cis*-addition (*syn*-addition) process) results in the formation of the (*E*)-product, while the *trans*-addition (*anti*-addition) provides the respective (*Z*)-alkenylsilane derivative. The reversed addition of a hydrosilane to the terminal alkyne gives a geminal alkenylsilane α (2-silyl-1-alkene) as an internal adduct. Although β-(*E*)-alkenylsilanes, the thermodynamic products, are usually formed as a major isomer in most of the transition metal catalysed reactions developed, in the last decade significant progress has been made to enable the selective synthesis of each of the regioisomers.

The regio- and stereochemical outcome of this process depends on several factors including the catalytic system (the metal and ligands), the substituents on both

alkyne and hydrosilane employed, the reaction parameters such as solvent, temperature, catalyst loading or even on the sequence of addition of the reagents. Considering the potential utility of stereodefined alkenylsilanes in synthetic organic chemistry, efficient catalytic systems for the highly selective formation of each of these isomers are strongly desirable.

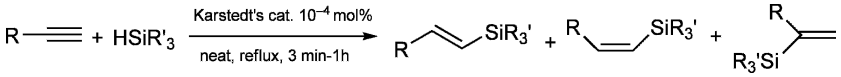
Hydrosilylation of terminal alkynes in the presence of platinum complexes provides usually exclusive *cis*-addition to produce the α- and β-(*E*)-alkenylsilanes, with the latter one being predominant. The classical Chalk-Harrod mechanism based on the oxidative addition, migratory insertion, and reductive elimination has been successfully applied to explain such a reaction mode (Scheme 2.1) [10].



Scheme 2.1 Chalk-Harrod mechanism of alkyne hydrosilylation

The conventional platinum catalyst such as Speier's catalyst [H_2PtCl_6] and Karstedt's catalyst [$Pt_2(dvds)_3$]which have the advantage of high turnover numbers (often > 10,000) are usually quite nonselective in hydrosilylation of alkynes by various hydrosilanes [11,12]. Classical investigation carried out by Lewis et al. gives the example product distribution in alkyne hydrosilylation in the presence of Karstedt's catalyst (Table 2.1) [12].

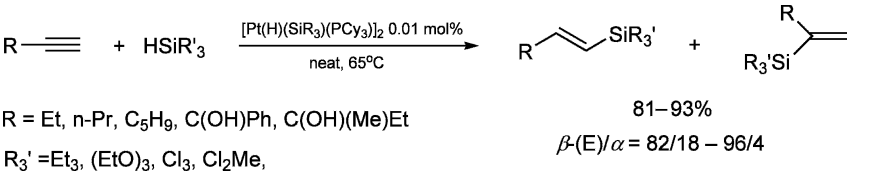
Table 2.1 Alkyne hydrosilylation in the presence of Karstedt's catalyst



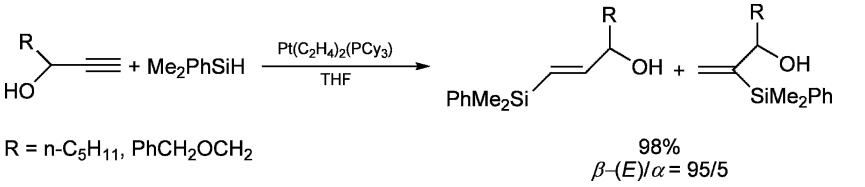
Alkyne	Silane R'$_3$SiH	β-(*E*)/β-(*Z*)/α
$CH_3(CH_2)_2C{\equiv}CH$	Et_3SiH	89/0/11
	$PhMe_2SiH$	70/5/25
	$(EtO)_3SiH$	56/6/38
$PhC{\equiv}CH$	Et_3SiH	81/1/18
	$(EtO)_3SiH$	70/0/30
	Ph_3SiH	78/15/7
t-$BuC{\equiv}CH$	Ph_3SiH	100/0/0

The H_2PtCl_6-catalysed hydrosilylation of terminal alkynes by phenylmethylsilanes and $CpFe(CO)_2SiPh_2H$ performed in the presence of carbon monoxide has reduced the usually high levels of *cis*-addition products to favour the formation of α-alkenylsilanes [13].

In contrast, the platinum phosphine complexes, especially those containing bulky trialkyl phosphines, show improved regioselectivity. The use of $[Pt(C_2H_4)_2(PCy_3)]$ and their silyl derivatives e.g. $[\{Pt(H)(SiR_3)(PCy_3)\}_2]$, provides a useful approach to (*E*)-alkenylsilanes [14,15] (Eq. 2.3 and 2.4). It is worth noting, that these catalytic systems allow the use of alkoxy- or chloro-substituted silanes [13] and functionalised alkynes such as substituted propargyl alcohols [15] (Eq. 2.4), which is of importance with regard to their further transformations.

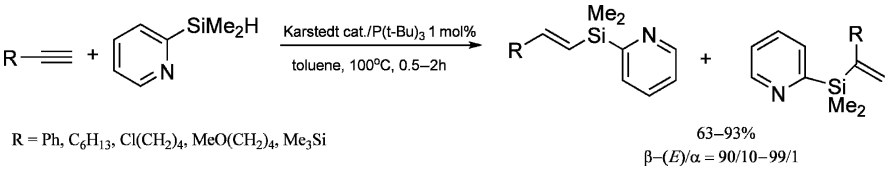


(2.3)



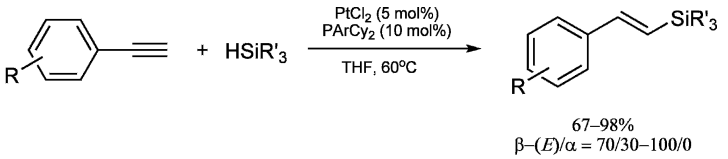
(2.4)

Recent reports describe the use of Pt(dvds)-P(*t*-Bu)$_3$ catalytic system for achieving higher β-(*E*)-selectivities for a variety of terminal alkynes employing alkoxysilanes [16]. An elegant application of the [Pt(dvds)/P(*t*-Bu)$_3$] catalyst, allowing nearly total control in the synthesis of (*E*)-alkenylsilanes, is the sequential hydrosilylation-Hiyama coupling reaction recently reported by Denmark et al. [17]. Similar results have been achieved by Itami et al., for the hydrosilylation of terminal alkynes by dimethyl(2-pyridyl)silane [18] (Eq. 2.5).

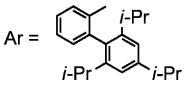


(2.5)

Highly regioselective hydrosilylation of functionalised terminal arylalkynes by alkyl- or alkoxysilanes has been recently achieved using $PtCl_2$ associated with the air-stable bulky aryldicyclohexylphosphine. Regardless of the electronic nature and position of the substituents on the aromatic ring, a single β-(*E*)-styrylsilane was obtained with excellent yield [19] (Eq. 2.6).

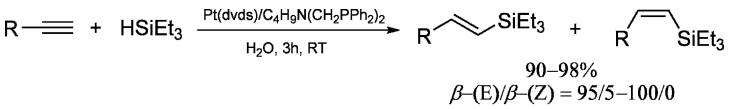


R = H, 4-MeO, 4-Me, 4-MeO_2C, 4-CN, 4-Br, 2-Me, 2-MeO_2C
R'_3 = Et_3, $(OEt)_3$, $Me_2(OEt)$,



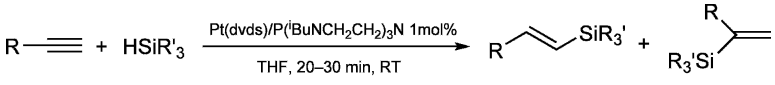
(2.6)

A method for stereoselective hydrosilylation of alkynes by triethylsilane in water was reported by Li and co-workers [20]. The use of [Pt(dvds)] complex and bis(diphenylphosphinomethylene)butylamine ($C_4H_9N(CH_2PPh_2)_2$) as a catalytic system led to a nearly quantitative yield and a 100% (*E*)-stereoselectivity, at room temperature in aqueous media. For all compounds, except trimethylsilylacetylene, the (*E*)-products were obtained exclusively or selectively. Selected results are presented in (Eq. 2.7).



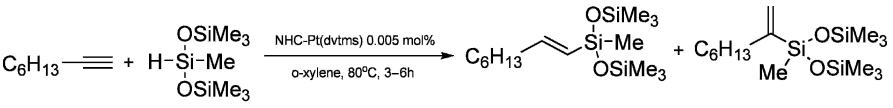
R = C_5H_{11}, Bu, CH_2Ph, CH_2OH, $C_6H_{11}(OH)$, $(CH_2)_2OH$, $CH_2{=}CHCH_2OCH_2$ (2.7)

More recently, platinum-divinyltetramethyldisiloxane complex containing bulky phosphatrane ligands has been employed in the hydrosilylation of alkynes [21] (Eq. 2.8). Although excellent selectivities and broad functional group tolerance have been observed, high catalyst loading is required in this process. Moreover, only silanes of limited utility in terms of their further transformation have been reported to be used.



R = Bu, Ph, CH_2OH, CH(Me)OH, $(CH_2)_2OH$, CH_2NH_2
R' = Et, Ph (2.8)

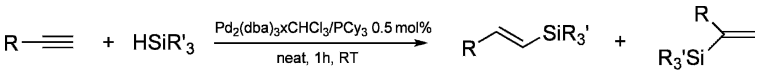
The hydrosilylation of 1-octyne and phenylacetylene by a series of hydrosilanes and hydrosiloxanes catalysed by *N*-heterocyclic carbene (NHC) platinum(0) complexes has been also recently investigated [22], however, the selectivity and efficiency of this process strongly depends on the structure of the NHC ligand applied. An example is given in (Eq. 2.9).



β–(E)/α = 10.1–10.6

(2.9)

Photoactivated hydrosilylation of alkynes catalysed by [Pt(acac)$_2$] has been also reported to give (*E*)-alkenylsilanes as predominant products [23]. A well-known cross-coupling palladium catalyst [$Pd_2(dba)_3xCHCl_3$] in combination with tricyclohexylphosphine has been also found as a good catalyst for regioselective hydrosilylation of functionalised alkynes to yield substituted (*E*)-alkenylsilanes [24] (Eq. 2.10). The regioselectivity of this process is similar or even higher than that obtained in the conventional Pt(0)-catalysed hydrosilylation.



R = *t*-Bu, $(CH_2)_4C(O)OEt$, $(CH_2)_6C(O)OEt$, $CH_2=CH(CH_2)_8$
R_3' = Ph_3, Ph_2Me

36–95%
β–(E)/α = 94/6–99/1

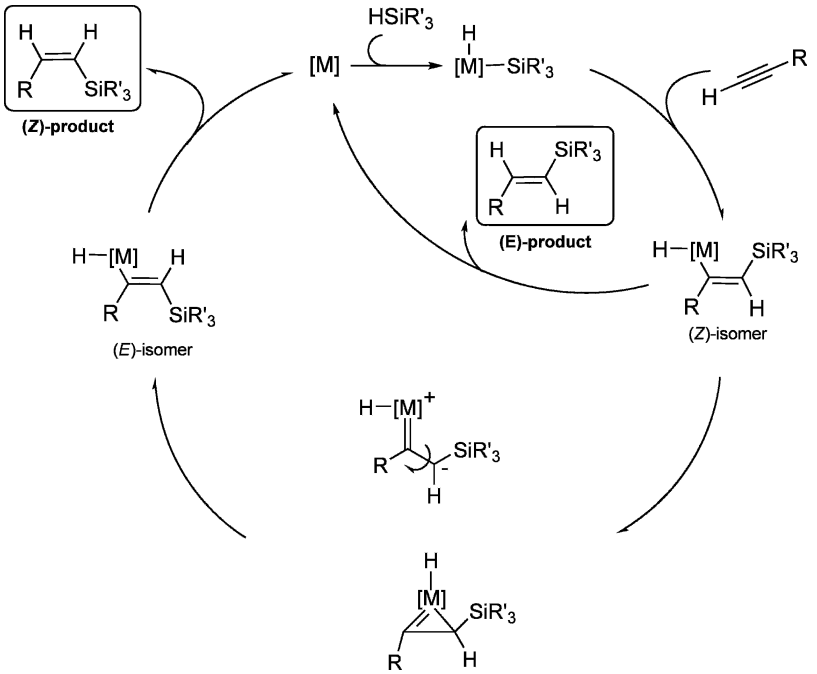
(2.10)

Palladium(0) complexes obtained in situ from [$\{\eta^3$-$C_3H_5PdCl\}_2$] and phosphites $P(OAr)_3$ catalyse the hydrosilylation of 1-alkynes with $HSiCl_3$ at room temperature to yield 1,3-dienylsilanes of the general formula RCH=CH-C(R)=CH$SiCl_3$ as predominant products [25].

While the β-(*E*)-alkenylsilanes are obtained with the highest selectivity using Pt-based complexes, the selective formation of the stereoisomeric β-(*Z*)-products is generally achieved using the Rh, Ir and Ru-based catalysts. The hydrosilylation of terminal alkynes catalysed by rhodium complexes proceeds predominantly in unusual *trans*(*anti*-)-fashion giving thermodynamically unfavourable (*Z*)-alkenylsilanes as the major product.

These observations do not cleanly fit with the Chalk-Harrod mechanism. To explain the predominant appearance of unusual *trans*-addition products (*Z*-alkenylsilanes), Crabtree [26] and Ojima [27] proposed a mechanism based on silylmetallation in the migratory insertion step followed by *E*/*Z* isomerisation (Scheme 2.2). The most significant feature of this mechanism is the exclusive insertion of alkyne into the M—Si bond, forming a (*Z*)-silylvinylene complex. Because of the steric repulsion between the silyl group and the substituted metal atom, the (*Z*)-silylvinylene intermediate isomerises to thermodynamically favourable (*E*)-silylvinylene complex through either zwitterionic carbene species [27] (proposed for Rh-catalysed processes) or metallacyclopropene intermediate [26] (postulated for Ir-catalysed reactions). Since the reductive elimination is the rate–determining step, (*Z*)-alkenylsilanes are formed as the kinetic products.

The Crabtree-Ojima mechanistic proposal fits well with the available data. The electron-rich silanes (e.g. trialkyl-substituted hydrosilanes) and relatively unhindered terminal alkynes produce (*Z*)-alkenylsilanes as the major products, while



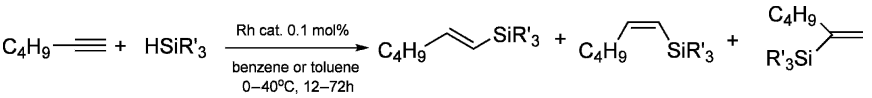
Scheme 2.2 The Crabtree-Ojima mechanism for *Z*-selective alkyne hydrosilylation

silanes bearing electron-withdrawing groups (e.g. alkoxy- or chloro-substituted) generally provide good selectivity for the *cis*-addition process to give (*E*)-alkenylsilanes [26–28]. The bulkiness of the alkyne substituents has also a strong influence on the *Z/E* selectivity. When alkynes with bulky cycloalkyl or tertiary alkyl groups are used, the reaction yields (*E*)-alkenylsilanes selectively. Moreover, the use of cationic rhodium complexes exhibits high (*E*)-selectivity [29–33], whereas the neutral rhodium complex-catalysed hydrosilylation usually provides (*Z*)-alkenylsilanes.

Efforts to tune the reactivity of the rhodium catalysts by altering the structure, solvent, and other factors (e.g. the order of addition of the reagents) have been pursued. Rigorous stereocontrol to yield either (*E*)- or (*Z*)-alkenylsilanes (suppressing the formation of an internal adduct (α-isomer) in both cases) has been achieved independently by Takeuchi [29–33], and Ojima [27, 28]. Some results illustrating the effects of substituents in 1-hexyne hydrosilylation in the presence of neutral rhodium complexes and Rh-Co clusters are presented in Table 2.2.

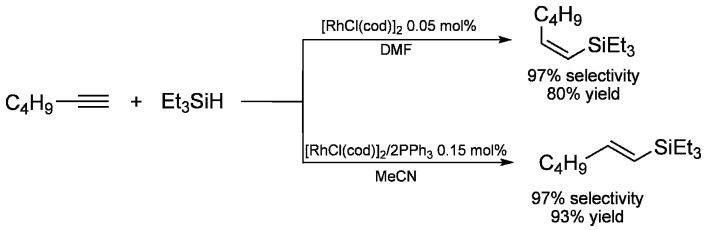
Well-defined layer-segregated polynuclear ruthenium-platinum cluster $[Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)]$ [34] and alkyne bridged mixed-metal clusters of the general formula $[MPt_2(CO)_5(PPh_3)_2(PhC_2Ph)]$ (M=Ru, Os, Fe) [35] have been also found as effective catalysts for the hydrosilylation of diarylacetylenes by triethylsilane to selectively yield (*E*)-1,2-diarylvinyltriethylsilane.

Table 2.2 Hydosilylation of 1-hexyne in the presence of neutral Rh and Rh-Co complexes



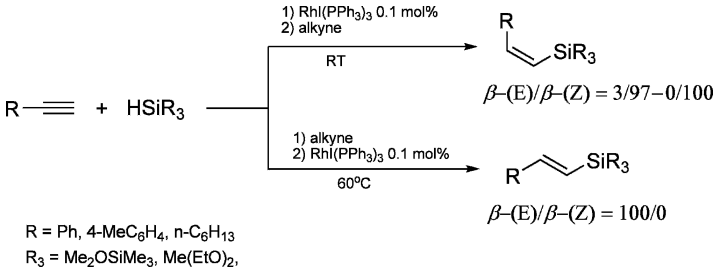
Catalyst	Silane R'_3SiH	Yield (GC) (%)	β-(*E*)/β-(*Z*)/α
$RhCl(PPh_3)_3$	Et_3SiH	100	3/94/3
$RhCo_3(CO)_{12}$	Et_3SiH	100	2/96/2
$Rh_2Co_2(CO)_{12}$	Et_3SiH	100	2.5/95/2.5
$Rh_4(CO)_{12}$	Et_3SiH	100	5/90/5
$Rh_4(CO)_{12}$	$PhMe_2SiH$	100	27/60/13
$Rh_4(CO)_{12}$	$(MeO)_3SiH$	98	95/0/5
$Rh_4(CO)_{12}$	Me_2ClSiH	76	80/0/20
$Rh_4(CO)_{12}$	$MeCl_2SiH$	70	65/0/35

Neutral rhodium complexes such as $[\{RhCl(cod)\}_2]$, $[RhH(CO)(PPh_3)_3]$ or $[RhH(PPh_3)_4]$ also give (*Z*)-alkenylsilanes as predominant products when the reactions are conducted in aromatic solvents [30]. However, it was shown that hydrosilylation stereoselectivity of the Rh-catalysed reactions can be efficiently controlled by a proper combination of the solvent and the ligand. For example, the hydrosilylation of 1-hexyne by Et_3SiH catalysed by $[\{RhCl(cod)\}_2]$ in DMF led to (*Z*)-1-silyl-1-hexene, whereas the catalytic system containing $[\{RhCl(cod)\}_2]$ and 2 equivalents of PPh_3 in acetonitrile afforded (*E*)-1-silyl-1-hexene with 97% selectivity [29] (Eq. 2.11).



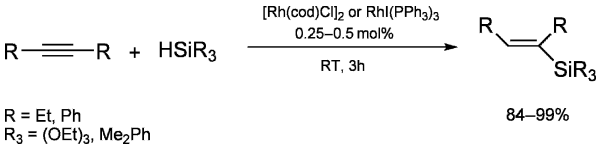
(2.11)

Wilkinson's catalyst $[RhCl(PPh_3)_3]$ was also demonstrated to yield the (*E*)-product in polar solvents (e.g. MeCN, *n*-PrCN), with the (*Z*)-isomer predominating in non-polar media (e.g. benzene, CH_2Cl_2) [30]. Mori at el. found that the use of $[RhI(PPh_3)_3]$ as a catalyst for the hydrosilylation of terminal alkynes furnishes (*E*)- and (*Z*)-alkenylsilanes in stereochemically divergent manners by switching the order of addition of the reagents and the reaction conditions [36, 37] (Eq. 2.12). When an alkyne is added to a reaction mixture consisting of hydrosilane and a catalyst at room temperature, after 2h (*Z*)-alkenylsilane can be obtained with excellent stereoselectivity (up to 99%). On the other hand, reaction of the mixture of silane, alkyne and the catalyst at 60^{o}C led to the (*E*)-product with almost quantitative yield (99%) and perfect stereoselectivity (>99%)



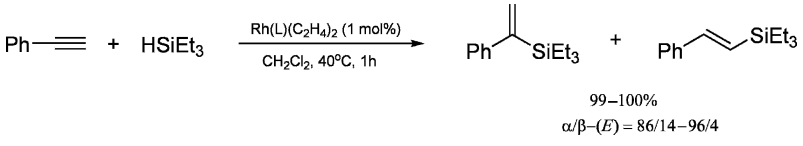
(2.12)

As the (*E*)- and (*Z*)-alkenylsilanes obtained possess heteroatom substituents at the silicon atom, they can be subjected to stereospecific cross-coupling reactions to give π-conjugated organic products [38]. As an extension to this work, the authors reported also stereoselective rhodium-catalysed hydrosilylation of internal alkynes. The hydrosilylation of both symmetrical and unsymmetrical internal alkynes was found to proceed at room temperature with rhodium complexes: $[\{Rh(cod)Cl\}_2]$ or $[RhI(PPh_3)_3]$ as catalysts to afford (*E*)-1,2-disubstituted alkenylsilanes [38] (Eq. 2.13).



(2.13)

Rhodium(I) alkene complexes of the general formula: $[Rh(L)(C_2H_4)_2]$, (L=acac, hfa) catalyse hydrosilylation of phenylacetylene with trialkylsilanes to unexpectedly produce geminal alkenylsilanes as predominant products [39] (Eq. 2.14)

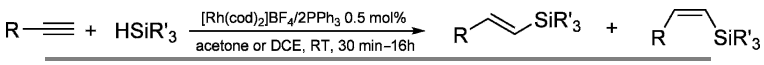


(2.14)

Rhodium cationic complexes in combination with phosphine, such as $[\{Rh(cod)_2\}BF_4/PPh_3]$, or $[\{Rh(cod)_2\}PF_6/PPh_3]$, are very good and selective catalysts for hydrosilylation of terminal alkynes, independently of the structure and bulkiness of the latter, to provide simple and stereoselective access to the β-(*E*)-alkenylsilanes [29–33]. The effectiveness of the cationic rhodium complex catalysis was demonstrated for the synthesis of simple (*E*)-1-silyl-1-alkenes [29,30] as well as (*E*)-γ-silyl-allylic alcohols [31, 32] or silylated (*E*)-propenyl amines and their sulphonamide derivatives [33], which are useful building blocks in organic synthesis (Table 2.3).

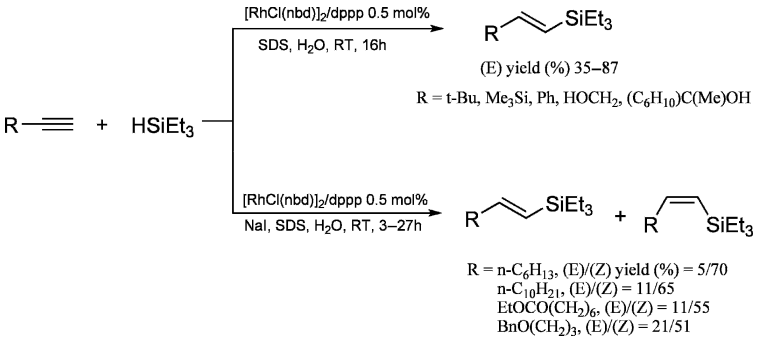
More recently, rhodium-catalysed hydrosilylation of terminal alkynes in aqueous media has been reported. A combination of $[\{RhCl(nbd)\}_2]$ and bis(diphenylphosphino)propane (dppp) in the presence of sodium dodecyl sulphate (SDS) in

Table 2.3 [{Rh(cod)$_2$}BF$_4$/PPh$_3$] catalysed hydrosilylation of terminal alkynes



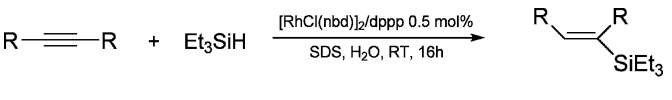
Alkyne	Silane R$_3$SiH	Isolated yield (%) of (*E*)-alkenylsilane	*β*-(*E*)/*β*-(*Z*)
n-Bu	Et_3SiH	90	99/1
C_6H_{13}	Et_3SiH	90	97/3
OH	Et_3SiH	82	100/0
Ph, OH	Et_3SiH	94	100/0
OH	Et_3SiH	92	100/0
NHMs	Ph_2MeSiH	82	100/0
N, Ms, Me	$EtMe_2SiH$	91	100/0

water, which generates rhodium cationic species, effects (*E*)-selective hydrosilylation of terminal alkynes with good yields [40]. However, the selectivity of this process can be easily switched from *E* to *Z* in the presence of sodium iodide (Eq. 2.15)



(2.15)

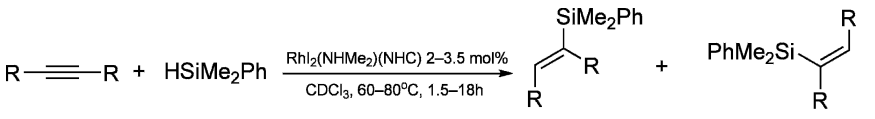
Application of the [RhCl(nbd)]$_2$/dppp/SDS catalytic system to the hydrosilylation of internal alkynes led to substituted (*E*)-alkenylsilanes with perfect regio- and stereoselectivity [40] (Eq. 2.16).



R = Et, Ph 53–66% (2.16)

Symmetrical internal alkynes can be also effectively hydrosilylated in the presence of rhodium pincer complexes containing *N*-heterocyclic carbene ligands,

however, the stereoselectivity of this process is lower than that reported for the other rhodium catalysts [41] (Eq. 2.17).

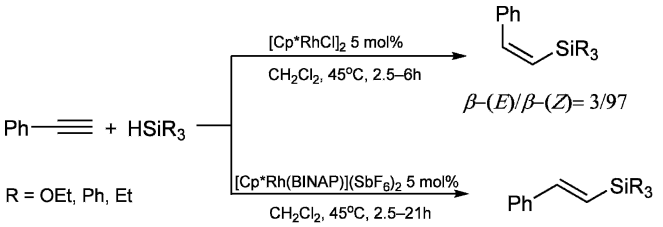


	E/Z
R = Ph	89/11
R = Et	85/15
R = n-Pr	79/21

(2.17)

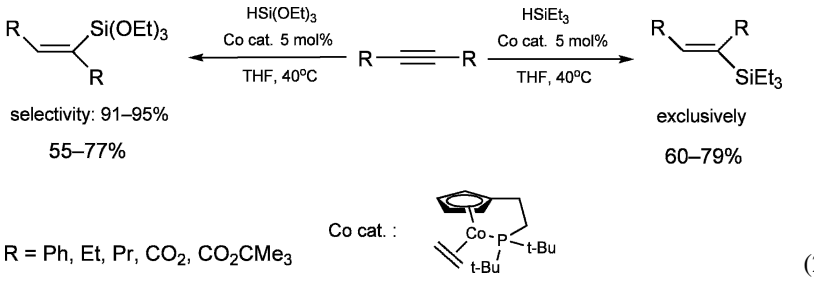
Very recently the catalytic activity of rhodium(I) complexes containing amino-alkyl functionalised *N*-heterocyclic carbene ligands in the hydrosilylation of terminal alkynes with dimethylphenylsilane has been investigated. As a result, excellent (*Z*)-selectivity was found in the reaction of 1-hexyne, whereas the hydrosilylation of triethylsilylacetylene afforded predominantly the β-(*E*)- and α-isomers [42]. On the other hand, rhodium(I) complexes containing *N*-heterocyclic carbene ligands were found as highly efficient catalysts in the hydrosilylation of terminal alkynes to give (*E*)-alkenylsilanes in chemoselective fashion [43].

Interesting results of the stereodivergent hydrosilylation using rhodium complexes have been presented by Faller and Alliessi [44]. The authors have shown, that dicationic rhodium complex [{Cp*Rh(BINAP)}$(SbF_6)_2$] (where BINAP is 2,2'-bis(diphenylphosphino)-1,1'-binaphtyl) and the neutral rhodium dimer [{Cp*RhCl}$_2$] give opposite selectivities in the hydrosilylation of phenylacetylene using both trialkyl- and trialkoxy-substituted silanes (Eq. 2.18)



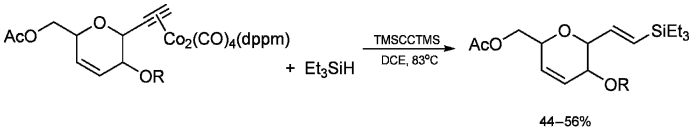
β–(*E*)/β–(*Z*)/α = 81/0/19 – 99/1/0 (2.18)

Highly selective, stereodivergent hydrosilylation of internal alkynes catalysed by cyclopentadienyl cobalt(I) complex with a hemilabile phosphane ligand has been reported [45]. While the reaction of internal alkynes exclusively affords *cis*-addition products with triethylsilane, the reaction with triethoxysilane shows predominant *trans*-stereoselectivity (Eq. 2.19).

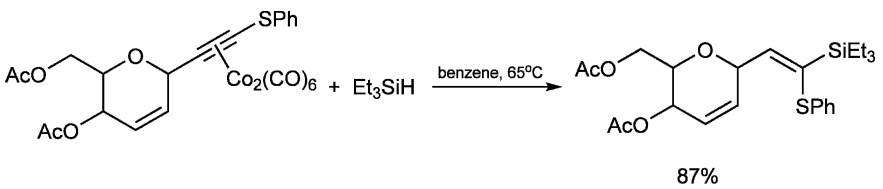


(2.19)

The regioselective hydrosilylation of terminal and internal alkynes *via* acetylenedicobalt complexes: [acetylene-$Co_2(CO)_6$] and [acetylene-$Co_2(CO)_4$(dppm)] to produce functionalised (*E*)-alkenylsilanes has also been reported [46–48]. The extremely high regioselectivity has been noted with ethynyl and phenylthoacetylene group containing sugar derivatives (Eq. 2.20 and 2.21).

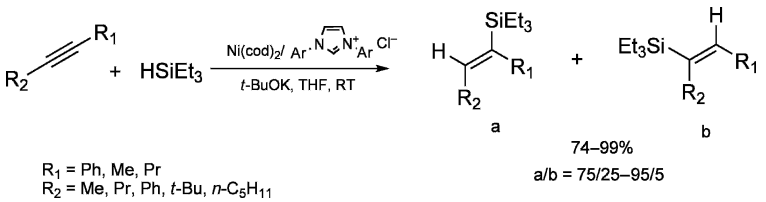


(2.20)



(2.21)

An efficient method for both internal and terminal alkyne hydrosilylation involving Ni(0) complexes of *N*-heterocyclic carbenes has been developed, however, the regioselectivity of this process depends on the structure of alkyne and carbene ligand [49]. Selected examples are presented in Eq. 2.22.

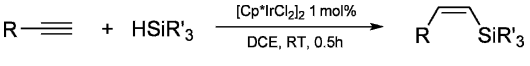


(2.22)

The use of Ni(0) complexes as catalysts for the hydrosilylation of phenylacetylene with triphenylsilane and internal alkynes and diynes with Ph_2SiH_2, $PhMe_2SiH$ and Et_3SiH has also been reported [50, 51].

High selectivity for β-(*Z*)-alkenylsilanes has also been reported with iridium complexes. Several catalytic systems including iridium-hydride [26], oxo-phos-

phoranyl [52], *N*-heterocyclic carbene [53–56], cyclooctadiene [57] and dimeric cyclopentadienyl [58] complexes have been successfully employed to afford selectively the β-(*Z*)-alkenylsilanes in high yields. However, in some cases, a mixture of isomers was formed after prolonged standing, due to subsequent iridium-catalysed (Z)→(*E*) isomerisation [58]. Hydrosilylation of terminal alkynes in the presence of $[\{Cp^*IrCl_2\}_2]$ is outlined in Eq. 2.23.

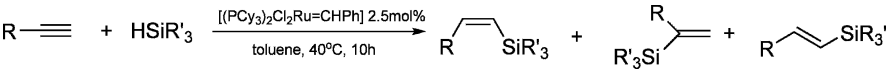


R = Ph, Cy, n-Bu
R_3' =Et_3, Ph_3

exclusively (Z)
89–94% (2.23)

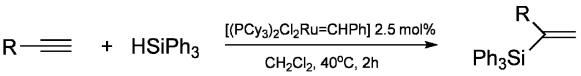
Ruthenium-based catalysts also allow stereoselective access to β-(*Z*)-alkenylsilanes. Under certain conditions, Grubbs' 1st generation catalyst gives (*Z*)-products, although the stereo- and regioselectivity of the hydrosilylation is highly dependent on the alkyne, silane, solvent and substrate concentration [59, 60]. Moreover, in some cases, depending on the alkyne structure, either β-(*Z*)-alkenylsilane or isomeric α-alkenylsilane can be selectively formed. Some examples are presented in Table 2.4.

Table 2.4 Terminal alkyne hydrosilylation in the presence of Grubbs catalyst



Alkyne	Silane R'$_3$SiH	Isolated yield of the alkenylsilane mixture (%)	β-(*Z*)/α/β-(*E*)
$C_8H_{17}C{\equiv}CH$	Et_3SiH	86	91/9/0
$PhC{\equiv}CH$	Et_3SiH	74	95/5/0
	$PhMe_2SiH$	81	95/0/5
$BnOCH_2C{\equiv}CH$	$PhMe_2SiH$	62	0/93/7
	$(EtO)_3SiH$	90	0/97/3
$BnO(CH_2)_2C{\equiv}CH$	$(EtO)_3SiH$	90	5/92/3
$HOCH_2C{\equiv}CH$	$PhMe_2SiH$	59	0/100/0
$BuC{\equiv}CH$	Et_3SiH	–	96/4/0

The hydrosilylation of alkynes without directing groups catalysed by Grubbs' 1st generation catalyst affords selectively α-vinylsilanes under the conditions established by Cossy and co-workers [61] (Eq. 2.24).



R = $PhCH_2$, $AcO(CH_2)_4$, $PhCH{=}CHC(O)O(CH_2)_2$

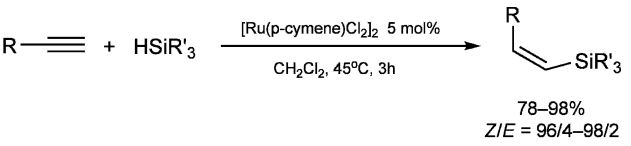
88–92%
α/β = 97/3–100/0 (2.24)

The (*Z*)- and (*E*)- isomers of alkenylsilanes can be independently synthesised from the same substrates, by the choice of ruthenium catalyst. For complexes

with phosphine ligands, the basicity of phosphine plays a dominant role in the stereoselectivity and overall product distribution. Ozawa et al. reported that the treatment of an alkyne with hydrosilane-containing aromatic substituents in methylene chloride in the presence of the ruthenium-hydride catalyst [$RuHCl(CO)(PPh_3)_3$] brings about the formation of respective (*E*)-alkenylsilane in over 99% selectivities. On the other hand, the same starting material can be effectively converted into isomeric (*Z*)-alkenylsilane with 91–99% selectivities using ruthenium-silyl complex [62, 63]. Extension of these convenient protocols to 1,4-diethynylbenzene led to obtain stereoselectively isomeric 1,4-bis(β-silylethenyl)benzenes – useful precursors for poly(phenylenevinylene)s [64]. Such phosphine-substituent effects were also demonstrated by Oro and co-workers [65–67]. It is worth noting that whereas [$RuHCl(CO)(P\textit{i}\text{-}Pr_3)_2$] has been found to provide Z-selectivity, the corresponding osmium(II) hydride complex yields *Z*-adduct or *E*-adduct depending on a stoichiometric or excess amount of the silane used [68].

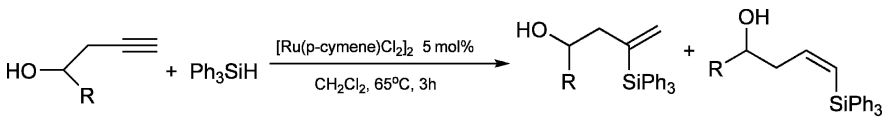
On the other hand, the [$RuCl_2(PPh_3)_3$]-catalysed hydrosilylation of a series of *p*-substituted phenylacetylenes with $HSiMeCl_2$ led to formation of the corresponding β-(*Z*)-silylstyrenes, indicating that the ruthenium-catalysed hydrosilylation activity and selectivity can be promoted by electron-withdrawing substituents at both silicon atom and phenyl ring [69].

[{Ru(*p*-cymene)Cl_2}$_2$] has been recently demonstrated as an active catalyst for the efficient hydrosilylation of a wide range of functionalised alkynes [70]. Besides the high yields, the selectivities for (*Z*)-alkenylsilanes obtained are some of the best yet reported (Eq. 2.25).



R' = Et, Ph
R = Bu, Ph, $(CH_2)_3Cl$, $CH_2CH(Me)OBn$, CH_2OBn, $(CH_2)_2C(O)OBn$, 4-MeC_6H_4 (2.25)

Interestingly, when alkynes having a hydroxyl group at the β-position to the triple bond were employed as a substrate in the presence of ruthenium-arene complex [{Ru(*p*-cymene)Cl_2}$_2$], regioisomeric α-alkenylsilanes were generated with excellent selectivity (Eq. 2.26) [70]



R = H, Me

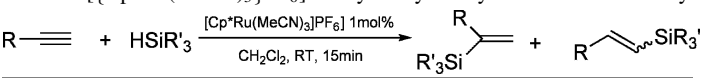
47–59%
α/β–(*Z*) = 98/2

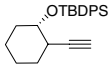
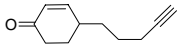
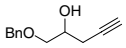
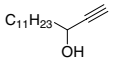
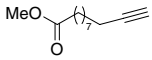
(2.26)

Similar hydroxyl-directed terminal alkyne hydrosilylation catalysed by Grubbs' 1st generation catalyst resulting in a highly selective formation of the α-isomer was reported by Maifeld et al [60]. In addition, carbonyl groups have been also shown to direct hydrosilylation to provide internal alkenylsilanes, presumably due to coordination effect [71].

While several methods for preparation of both β-(E) and β-(Z)-alkenylsilanes are known, until recently there has been no general method for the preparation of 1,1-disubstituted α-vinylsilanes. As shown above, the formation of α-alkenylsilanes is accomplished by incorporating functionality in the substrate, which can coordinate to the metal complex and deliver the silicon and hydrogen substituents to the alkyne in an intramolecular fashion [60, 70]. Recently, Trost et al. developed a mild and flexible protocol for hydrosilylation of terminal alkynes in the presence of cationic cyclopentadienyl ruthenium(II) complex [{Cp*Ru(MeCN)$_3$}PF$_6$] to give α-alkenylsilanes in good to excellent yields, which remains the only general method for accessing geminal alkenylsilanes *via* hydrosilylation [72,73]. The reaction is tolerant to a wide range of functional groups, including halogens, unprotected alcohols, esters, amines etc. Selected examples are collected in Table 2.5.

Table 2.5 [{Cp*Ru(MeCN)$_3$}PF$_6$]-catalysed hydrosilylation of terminal alkynes

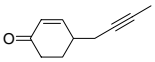
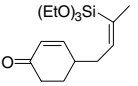
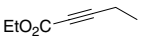
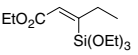
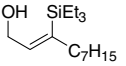
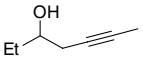
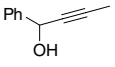
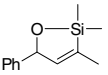
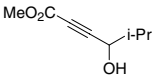
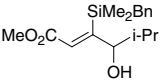
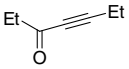
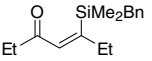


Alkyne	Silane R'$_3$SiH	Isolated yield (%) of α-alkenylsilane	α/β
3-MeOC$_6$H$_4$C≡CH	Me(EtO)$_2$SiH	86	9/1
2-BrC$_6$H$_4$(CH$_2$)$_2$C≡CH	(EtO)$_3$SiH	92	13/1
	(EtO)$_3$SiH	87	20/1
	(EtO)$_3$SiH	77	13/1
	BnMe$_2$SiH	91	14/1
	(EtO)$_3$SiH	58	13/1
	BnMe$_2$SiH	99	20/1

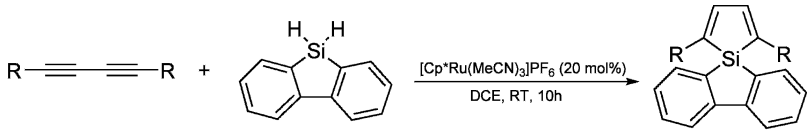
Trost and Ball have also demonstrated that hydrosilylation of the wide range of internal alkynes, including propargylic alcohols and α,β-alkynyl carbonyl compounds, in the presence of [{Cp*Ru(MeCN)$_3$}PF$_6$] allows regioselective formation of trisubstituted (*Z*)-alkenylsilanes, as a result of *trans*-addition of hydrosilane to alkyne [73–76]. Hydrosilylation of 2-alkynes results in the formation of (*Z*)-alkenes with the silyl substituent occupying the less sterically-demanding position, whereas, for the other internal alkynes, silyl group substitutes the more sterically-demanding position in the (*Z*)-alkene. For propargylic alcohols and their homologues as well as

for alkynyl carbonyl compounds, in the hydrosilylation process the silyl group selectively occupies the distal position to the hydroxyl functionality of the (*Z*)-alkene, however, the hydrosilylation of unprotected propargylic alcohols by alkoxysilanes under the conditions applied led to formation of cyclic alkenylsilanes. Selected examples of [{Cp*Ru(MeCN)$_3$}PF$_6$]-catalysed hydrosilylation of functionalised internal alkynes are given in Table 2.6.

Table 2.6 [{Cp*Ru(MeCN)$_3$}PF$_6$]-catalysed hydrosilylation of internal alkynes

Alkyne	Silane R'$_3$SiH	Product	Yield (%)	α/β
	$(EtO)_3SiH$		86	5/1
	$(EtO)_3SiH$		99	5/1
	Et_3SiH		99	13/1
	$(EtO)_3SiH$		71	5/1
	$(EtO)Me_2SiH$		73	5/1
	$BnMe_2SiH$		86	7/1
	$BnMe_2SiH$		98	20/1

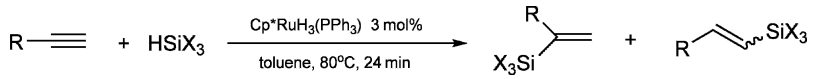
Ruthenium cationic complex [{Cp*Ru(MeCN)$_3$}PF$_6$] has been also successfully applied in the double *trans*-hydrosilylation of 1,4-diaryl-1,3-butadiynes by 9-silafluorene to afford 2,5-diarylsiloles [77] (Eq. 2.27).



R = Ph, 2-naphtyl, 4-MeC_6H_4, 4-MeOC_6H_4, 4-FC_6H_4, 3-BrC_6H_4, 3$^-$(pin)BC_6H_4, 3-thienyl, Cy, CH_2=CHC_6H_4, 4-F_3C-C_6H_4, 4-Me_3Si-C_6H_4

(2.27)

Another ruthenium-cyclopentadienyl complex [Cp*RuH_3(PPh_3)] has been also shown to catalyse hydrosilylation of 1-alkynes by chloro-substituted silanes to afford preferentially internal adducts (2-silyl-1-alkenes) in good yields [78] (Eq. 2.28).



yield = 65–89%

α/β–(E+Z) = 99/1–69/31

X = Cl_3, $MeCl_2$, Me_2Cl

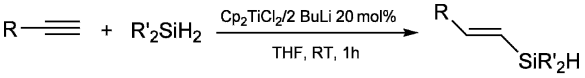
R = n-C_5H_{11}, n-C_6H_{13}, AcO$(CH_2)_3$, AcO$(CH_2)_2$, Ph, *t*-Bu, $PhOCH_2$

(2.28)

2.2 Regio- and Stereoselective Hydrosilylation of Alkynes Catalysed by Early Transition Metal Complexes

Early transition metal catalysts (except Group 4 tetrachlorides which are commonly used in Lewis acid-catalysed *trans*-hydrosilylation of alkynes), despite their wide application in carbon–heteroatom double bond hydrosilylation, have been little used in alkyne hydrosilylation.

Takahashi et al. reported hydrosilylation of a number of terminal (Eq. 2.29) and both symmetrical and unsymmetrical internal alkynes (Eq. 2.30) using the titanocene catalyst, formed in situ from titanocene dichloride and 2 equivalents of *n*-butyllithium, which led to (*E*)-alkenylsilanes with excellent regio- and stereoselectivity in good yields [79]. However, very high catalyst loading (20 mol%) is required in this process.

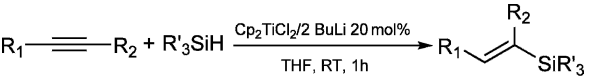


R' = Ph, Me

R = Bu, n-C_6H_{13}, n-C_5H_{11}, n-C_8H_{17}

58–67%

(2.29)



R'3 = Ph_2H, MePhH, PhH_2

R_1 = Et, n-Pr, $SiMe_3$

R_2 = Et, n-Pr, Me

44–70%

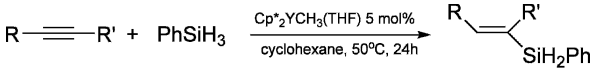
(2.30)

It is worth noting, that other Group 4 metallocenes do not catalyse the reactions under the analogous conditions, although zirconium and hafnium complexes have been known to catalyse the hydrosilylation of olefins.

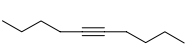
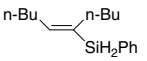
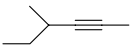
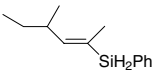
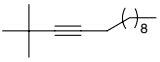
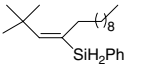
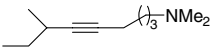
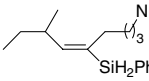
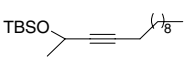
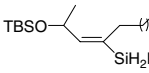
Organometallic yttrium complexes such as [$Cp^*_2Y(CH_3)(THF)$] and [$Cp^*_2YCH(SiMe_3)_2$] have been found to be excellent catalysts for regioselective hydrosilylation of functionalised symmetrical and unsymmetrical internal alkynes with $PhSiH_3$ [80–83]. The reaction with symmetrically substituted alkynes results in a single (*E*)-stereoisomer as the product of *cis*-addition, whereas the hydrosilylation of unsymmetrical alkynes bearing substituents at the α-position to triple bond produce one regioisomer containing the silyl group at the less hindered carbon of the alkyne (Table 2.7). Although only silanes of limited utility in terms of the further transformation of the resulting trisubstituted alkenylsilanes can be applied in this

system, the reaction tolerates various functional groups e. g halides, amines or protected alcohols. Unfortunately, terminal alkynes cannot be subjected to lanthanide catalysis because of the acidity of alkyne.

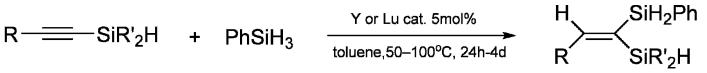
Table 2.7 Yttrium – catalysed hydrosilylation of internal alkynes



100% selectivity

Alkyne	Product	Isolated yield (%)
		83
		74
		28
		73
		89

The organolanthanide: [{$Cp^{TMS}{}_2LuMe$}$_2$] and Group 3 metallocene [$Cp_2{}^*YMe$ (THF)] and [{$Cp_2{}^*YMe$}$_2$]-catalysed hydrosilylation of alkynylsilanes has been found to provide (*Z*)-1,1-bis(silyl)alkenes in a regioselective manner [84] (Eq. 2.32).



R' = i-Pr, Me
R = i-C_5H_{11}, Cy, Ph, $Ph(CH_2)_2$, $Cl(CH_2)_3$, $TBSO(CH_2)_3$

yield: 58–82%
selectivity Z/E = 10/1–100/0 (2.31)

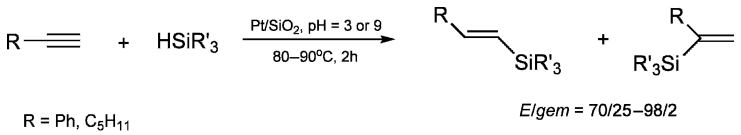
Effective use of actinide catalysts for the hydrosilylation of terminal alkynes by $PhSiH_3$ has been demonstrated by Eisen and co-workers [85–88]. Although, the organoactinide complexes of the type [$Cp^*{}_2AnMe_2$] (An=U, Th) have been found to be efficient hydrosilylation catalysts, the chemoselectivity and regioselectivity of the reaction depend strongly on the nature of the catalyst, the silane and alkyne substituents, the stoichiometry of the substrates, the polarity of the solvent and the reaction temperature.

2.3 Hydrosilylation of Alkynes on Heterogeneous Catalysts

Although many heterogeneous catalysts show high activity in alkyne hydrosilylation, the selectivity of these reactions is usually much lower than those carried out

over homogeneous catalysts. However, recently a few reports on the successful and selective alkyne hydrosilylation in the presence of transition-metal heterogeneous catalyst have appeared. Excellent yields and β-selectivity can be obtained using platinum on carbon or platinum on silica gel, providing significant cost advantages over homogeneous platinum catalysts.

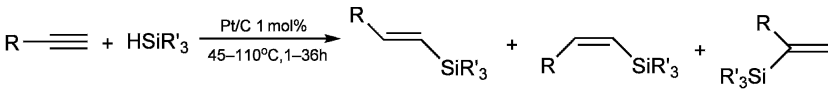
Heterogeneous catalysts Pt/SiO_2 obtained by the sol-gel process at different pHs have been used in the hydrosilylation of phenylacetylene and 1-heptyne using various silanes to yield (*E*)-alkenylsilanes as major products [89] (Eq. 2.32). Unfortunately, other platinum catalyst obtained via this method such as Pt/MgO or $Pt/Mg(OH)_2$ (nevertheless their high catalytic activity) showed much lower selectivity to yield a mixture of isomeric (*E*)- and *gem*-alkenylsilanes [90, 91]



R = Ph, C_5H_{11}
R'3 = Me_2Ph, Ph_3, Ph_2Me

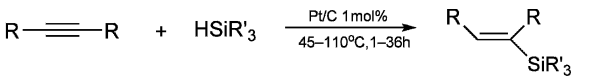
E/*gem* = 70/25–98/2 (2.32)

Boudjouk and co-workers reported efficient hydrosilylation of both terminal and internal alkynes using platinum on carbon [92]. While the hydrosilylation of symmetrical internal alkynes by platinum on carbon gave only one isomer – β-(*E*)-alkenylsilane, the selectivity of the terminal alkyne hydrosilylation depended on the particular silane used, however, in all cases β-(*E*)-alkenylsilane was formed as a predominant product (Eq. 2.33 and 2.34).



R = Ph, Bu, $SiMe_3$
R'3 = Cl_3, $MeCl_2$, $PhCl_2$, $(EtO)_3$, Ph_2Me, Et_3

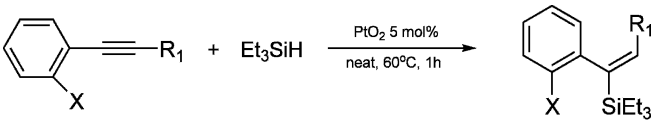
71–97%
(*E*)-Selectivity 74–100% (2.33)



R = Ph, Et
R'3 = Cl_3, $MeCl_2$, $(EtO)_3$, Ph_2Me, Et_3

63–95%
Selectivity 91–100% (2.34)

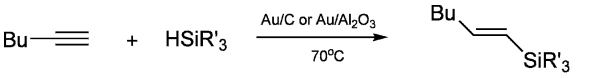
More recently, PtO_2 has been reported to be a selective catalyst for the hydrosilylation of *ortho*-substituted internal arylalkynes by triethylsilane [93, 94] (Eq. 2.35). *Ortho*-directing effect of the substituents, regardless of their electronic nature, led to high regioselectivity in this process giving single isomeric α-aryl-substituted alkenylsilanes (Eq. 2.35).



R = Ph, C_5H_{11}
X = NO_2, CHO, CN, CO_2Et, OAc, iPr

68–92% (2.35)

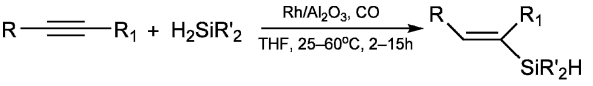
Supported gold nanoparticles, prepared by deposition of acetone solvated Au atoms on the supports such as carbon and γ-Al_2O_3, have been found valuable catalysts for the regioselective hydrosilylation of 1-hexyne with different silanes to give (*E*)-hexenylsilanes with selectivities even higher than those obtained for the Pt/C catalyst [95] (Eq. 2.36).



E/*gem* = 92/8–99/1

R'$_3$ = $MeCl_2$, $(EtO)_3$, Ph_2Me, Et_3 (2.36)

Hydrosilylation of 1-alkynes and 4-octyne with $PhMeSiH_2$ and Ph_2SiH_2 catalysed by rhodium species generated in situ from rhodium on alumina in the presence of carbon monoxide gave exclusively (*E*)-alkenylsilanes with high yield under mild conditions [96] (Eq. 2.37).



R = Ph, C_5H_{11}, $SiPh_3$, CH_2SiMe_3, Pr
R_1 = H, Pr
R'$_2$ = MePh, Ph_2, $C_8H_{17}Me$

75–97% (2.37)

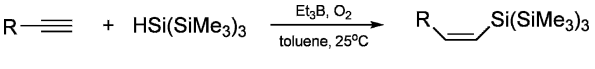
Hydrosilylation of phenylacetylene with triethoxysilane catalysed by polyamide-supported Rh(I) and Pt(II) complexes has also been investigated [97].

2.4 Hydrosilylation of Alkynes in the Presence of Radical Initiators and Lewis Acids

Although the most studied and utilised alkyne hydrosilylation processes are those catalysed by transition metal complexes, the alkyne hydrosilylation under free-radical conditions has been recently re-examined.

Chatgilialoglu and co-workers reported that tris(trimethylsilyl)silane reacts with terminal and internal alkynes in the presence of AIBN=azoisobutyronitrile or BEt_3/O_2 under mild conditions to give substituted vinylsilanes with high stereoselectivity [3, 4]. Although, the *Z*/*E* selectivity in AIBN-initiated reactions is dependent on the reaction conditions as well as the steric and electronic nature of the

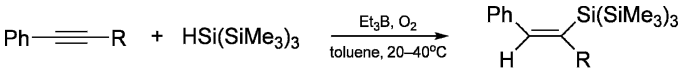
substituents of alkyne, the reaction of terminal alkynes in the presence of BEt_3/O_2 at lower temperatures favours the formation of the (*Z*)-vinylsilanes, according to the (Eq. 2.38).



R = *n*-Bu, *n*-C_6H_{13}, $EtCO_2$

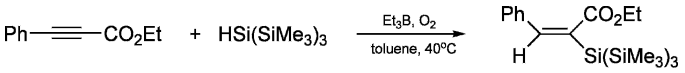
83–88%
Z/E = 95/5–99/1 (2.38)

High selectivity for the (*Z*)-trisubstituted vinylsilanes was also observed for radical hydrosilylation of substituted phenylacetylenes with formyl and nitrile groups, while ethyl phenylpropiolate gave the (*E*)-isomer exclusively [4] (Eq. 2.39 and 2.40).



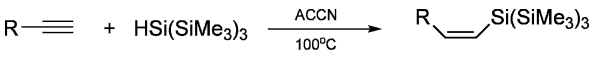
R = CHO, CN

55–62%
Z/E = 87/13–89/11 (2.39)



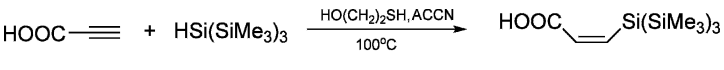
58%
E/Z = 99/1 (2.40)

$(Me_3Si)_3SiH$ was also recently used in the (*Z*)-selective alkyne hydrosilylation performed in water [98]. The system comprising the reagents and 1,1'-azobis(cyclohexanecarbonitrile) – ACCN, worked well for both hydrophilic and hydrophobic substrates as presented below (Eq. 2.41 and 2.42).



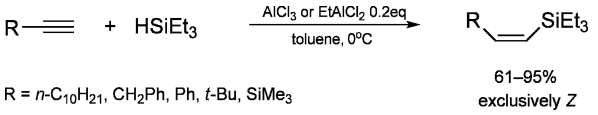
R = Ph, C_6H_{11}

90–93%
Z/E = 74/26–99/1 (2.41)



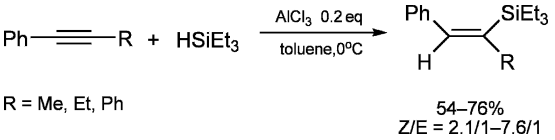
95% (2.42)

Strong Lewis acids have been demonstrated to catalyse both terminal and internal alkyne hydrosilylation. Aluminum chloride and $EtAlCl_2$ were found to be very active catalysts for the terminal alkyne hydrosilylation by triethylsilane producing the corresponding (*Z*)-vinylsilane with high regio- and stereoselectivieties as a result of *trans*-addition [6, 7]. It is worth noting that the other classical Lewis acid catalysts such as $HfCl_4$ or $ZrCl_4$ gave low yields or only traces of products under similar conditions (Eq. 2.43).



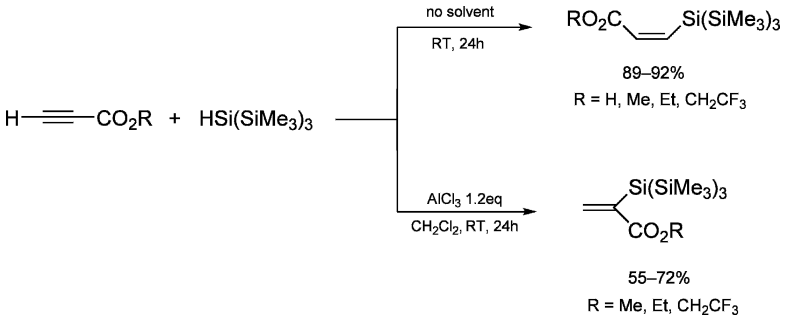
(2.43)

Under analogous reaction conditions, hydrosilylation of internal alkynes proceeded smoothly to produce trisubstituted (*Z*)-vinylsilanes in good yields as predominant products [6, 7] (Eq. 2.44).



(2.44)

Hydrosilylation of propiolate esters by $HSi(SiMe_3)_3$ without Lewis acid and solvent gave exclusively β-silicon-substituted (*Z*)-alkenes, whereas the reaction in the presence of Lewis acid such as $AlCl_3$ or $EtAlCl_2$ conducted in dichloromethane led to selective formation of α-silyl-substituted alkenes [9] (Eq. 2.45).

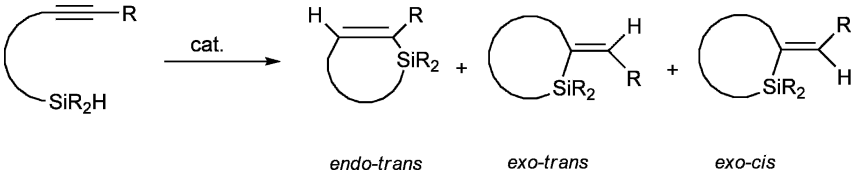


(2.45)

2.5 Intramolecular Hydrosilylation of Alkynes

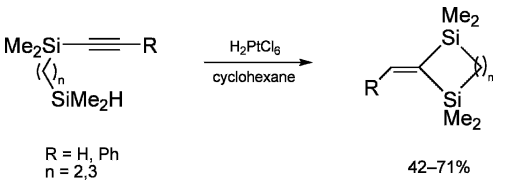
Intramolecular hydrosilylation of functionalised alkynes has gained increasing attention since it enables the synthesis of stereodefined silacyclic compounds, which can serve as diverse platforms for further transformations [99].

Intramolecular hydrosilylation of alkynes provides three different types of unsaturated silacyclic compounds depending on the mode of the cyclisation and addition of Si—H bond (Eq. 2.46).



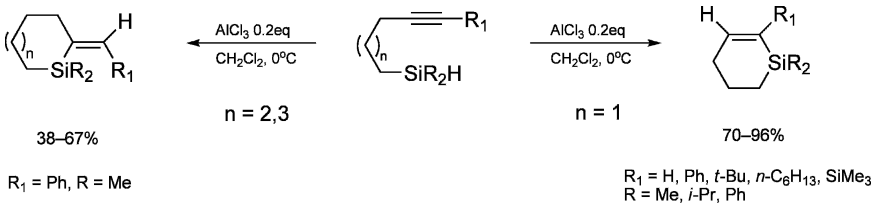
(2.46)

The intramolecular hydrosilylation of disilylalkynes of the general formula $HMe_2Si(CH_2)_nSiMe_2C{\equiv}CR$, where R=H, Ph and n=2–3, catalysed by H_2PtCl_6 proceeds *via exo*-dig manner to give *exo*-cyclic disilylalkenes exclusively, except for the reaction of 1-(ethynyldimethylsilyl)-3-(dimethylsilyl)propane, in which a minor amount of *endo*-cyclic product is formed [100] (Eq. 2.47).



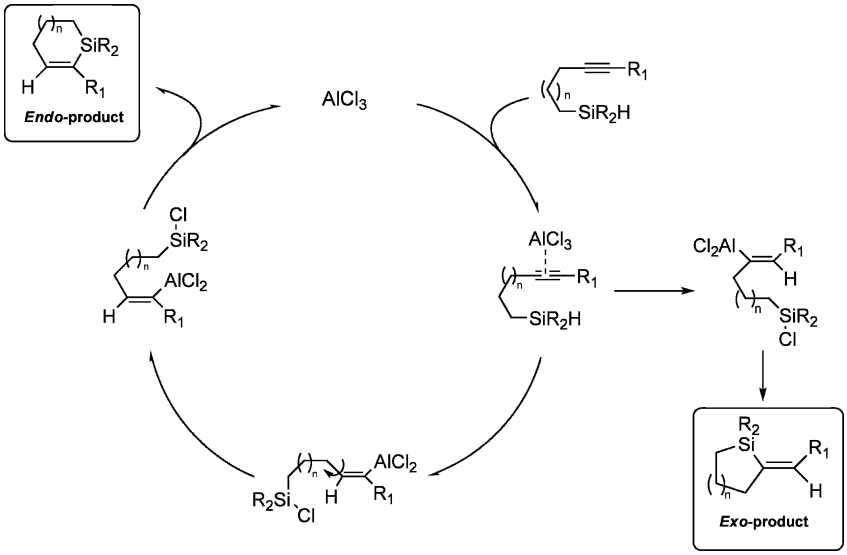
(2.47)

More recently, Yamamoto et al. reported that the Lewis acid-catalysed intramolecular *trans*-hydrosilylation of unactivated alkynylsilanes proceeds either in the *endo*- or *exo*-mode, depending on the substrate structure to form *endo*- or *exo-trans* silacyclic products [8] (Eq. 2.48).



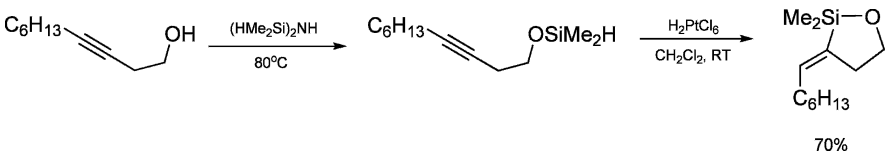
(2.48)

The mechanism of Lewis acid-catalysed intramolecular *trans*-hydrosilylation of alkynes was proposed by Yamamoto and co-workers [8] (Scheme 2.3).



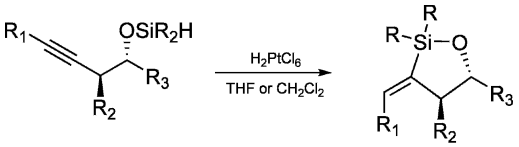
Scheme 2.3 The mechanism of Lewis acid-catalysed hydrosilylation of alkynes

Regio- and stereoselective intramolecular hydrosilylation of silylated homopropargyl alcohols and their homologues is an extremely useful tool in modern organic synthesis. Pioneering studies published by Tamao et al. established that platinum-catalysed hydrosilylation of silylated homopropargyl alcohols allows selective *exo*-dig cyclisation to form five-membered cyclic silyl ethers of defined (*E*)-configuration, useful for a variety of subsequent transformations [101] (Eq. 2.49).



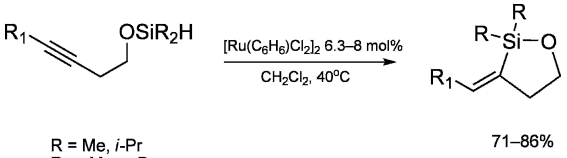
(2.49)

More recently, Marshall and Denmark independently pursued intramolecular hydrosilylation of silylated homopropargyl alcohols in the context of generating stereodefined organosilicon platforms for the subsequent oxidation [102] or cross-coupling reactions [103]. (Eq. 2.50).



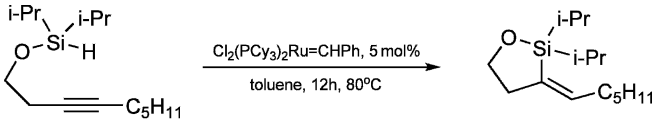
(2.50)

A complimentary strategy to access the opposite geometrical isomers of alkylideneoxasilacyclopentanes through intramolecular *anti*-hydrosilylation has been successfully developed by the use of ruthenium-arene complex: $[\{Ru(C_6H_6)Cl_2\}_2]$ as a catalyst [104] (Eq. 2.51). However, in the presence of methyl substituents at the silicon atom, the resulting (*Z*)-alkylideneoxasilacyclopentane underwent rapid oligomerisation.



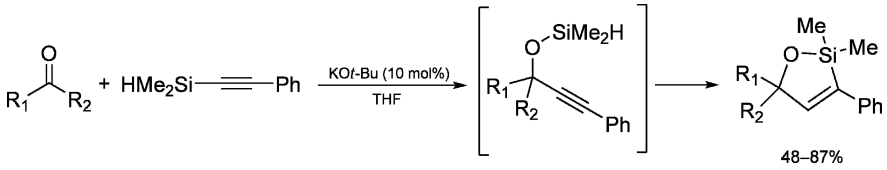
(2.51)

Grubbs' catalyst: $[Cl_2(PCy_3)_2Ru{=}CHPh]$ has been also shown to act as an intramolecular *trans*-hydrosilylation catalyst of internal alkynes to give *exo-(Z)* product [60] (Eq. 2.52).



(2.52)

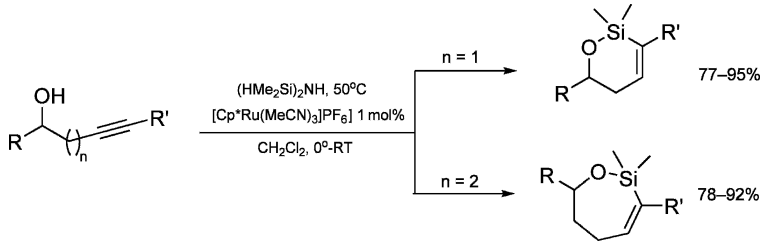
Oxasilacyclopentenes containing *endo*-cyclic bonds can be formed *via* unusual base-promoted tandem reaction sequence from carbonyl compounds and alkynylsilanes through intramolecular *trans*-hydrosilylation of alkynyl hydrosilyl ether intermediates [105] (Eq. 2.53).



R_1, R_2 = H, Ph, 2-furyl, Me, alkenyl

(2.53)

Recently Trost et al. reported an unprecedented *endo*-dig *trans*-hydrosilylation in the presence of ruthenium catalyst [106]. The cationic ruthenium complex: $[\{Cp^*Ru(MeCN)_3\}PF_6]$ induces intramolecular hydrosilylation of homopropargylic and bishomopropargylic alcohols producing cyclic compounds of unique stereochemistry under very mild conditions [106] (Eq. 2.54). It is worth noting that this new hydrosilylation strategy is useful since it enables the synthesis of important organosilicon precursors that are not otherwise readily available (Table 2.8).

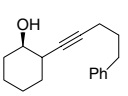
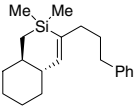
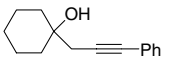
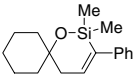
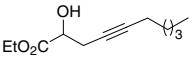
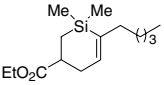
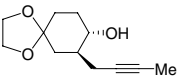
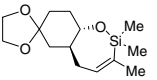
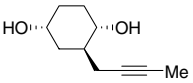
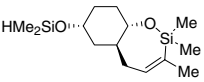


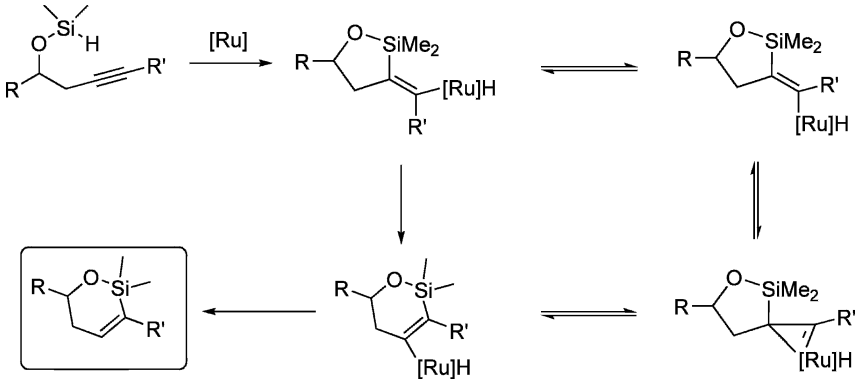
(2.54)

The results of this intramolecular *endo*-dig hydrosilylation have forced a re-examination of the mechanistic pathways providing *trans*-hydrosilylation reactions, based on the concerted oxidative addition and alkyne insertion into a stable ruthenacyclopropene intermediate (rearrangement mechanism) [107] (Scheme 2.4).

An alternative explanation of this selectivity on the basis of the accepted Ojima-Crabtree mechanism has been recently proposed [108].

Table 2.8 $\{Cp^*Ru(MeCN)_3\}PF_6]$ – catalysed intramolecular hydrosilylation of functional alkynes

Alkyne	Product	Isolated yield (%)
		85
		95
		77
		78
		85



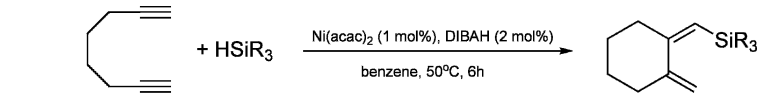
Scheme 2.4 The intramolecular *endo*-dig hydrosilylation mechanism

2.6 Transition Metal-Catalysed Cyclisation/Hydrosilylation of Diynes and Enynes

The cyclisation/hydrosilylation (also known as silylcarbocyclisation or hydrosilylative carbocyclisation) of diynes and enynes employing hydrosilanes as the stoichiometric reductant is a synthetically useful transformation leading to formation of both a C—C bond (carbocyclisation) and C—Si bond (hydrosilylation) [99, 109]. Cyclisation /hydrosilylation processes are also of particular interest because of ready

availability of the silanes and the reactivity of the silylated carbocycles formed in these transformations e.g. in the synthesis of polycyclic molecules.

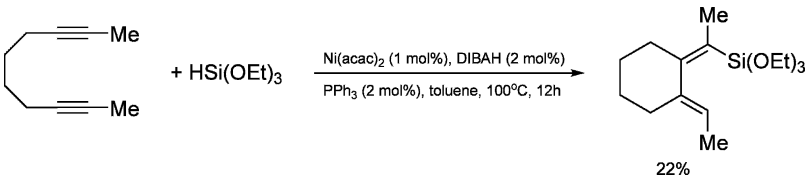
Pioneering work in this area was reported by Tamao et al. who disclosed Ni(0)-catalysed cyclisation/hydrosilylation of both terminal and internal 1,7-diynes providing access to 1,2-dialkylidenecyclohexanes containing (*Z*)-vinylsilane moiety [110] (Eq. 2.55).



52–70%
Z/E = 96/4–100/0

SiR_3 = $Si(OEt)_3$, $SiMe(OEt)_2$, $SiMe_2(O\text{-}iPr)$, $SiMe_2Et$, $SiMe_2(NEt_2)$ (2.55)

Although internal 1,7-diynes were less reactive in this process, and reacted only in the presence of triphenylphosphine as accelerating additive, the reaction was stereoselective and exocyclic silyl diene with (*Z*)-vinylsilyl group was formed [110] (Eq. 2.56).

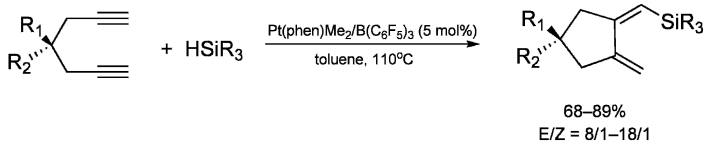


22%

(2.56)

Although Ni(0) complexes catalysed the cyclisation/hydrosilylation of 1,7-diynes, these complexes do not cyclize 1,6-diynes. Matsuda and co-workers reported, that rhodium phosphine complex $[RhCl(PPh_3)_3]$ catalysed the cyclisation/hydrosilylation of 1,6-diynes to form predominantly (*E*)-1,2-dialkylidenecyclopentanes, but this protocol suffered from limited substrate scope and low yield [111, 112]. Similarly, rhodium carbonyl complexes such as $[Rh(acac)(CO)_2]$ $[Rh_4(CO)_{12}]$ or $[Rh_2Co_2(CO)_{12}]$ catalysed the cyclisation/hydrosilylation of simple and heteroatom-containing 1,6-diynes but led to formation of primarily bissilylated mono-alkylidene-cyclopentanes and silylbicyclisation products [113].

Widenhoefer and et al., solved these difficulties by using transition metal cationic complexes as catalysts [114]. The cationic platinum complexes generated in situ from the mixture of platinum phenantroline complex $[(phen)PtMe_2]$ and the Lewis acid $B(C_6F_5)_3$ catalysed the cyclisation/hydrosilylation of functionalised terminal 1,6-diynes to form silylated 1,2-dialkylidenecyclopentanes in good yield and with high *Z*-selectivity [114] (Eq. 2.57). Platinum-catalysed diyne cyclisation/hydrosilylation tolerated a range of functional groups including esters, sulphones, acetals, amides and hindered ketones.

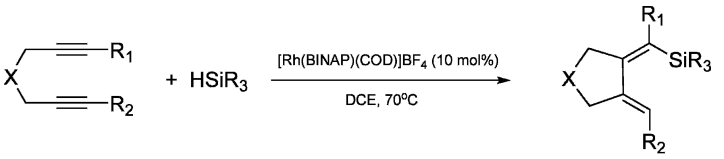


68–89%
E/Z = 8/1–18/1

R_1 = CO_2Me, CH_2OPv, CH_2OBn, CH_2OTBMS,
R_2 = CO_2Me, CH_2OPv, CH_2OBn, CH_2OTBMS, Ph, SO_2Me, $CONMe_2$
SiR_3 = $SiEt_3$, Si(*n*-Bu)$_3$, $SiMe_2Bn$, $SiMe_2$(*t*-Bu) (2.57)

Similar results on the cyclisation/hydrosilylation of diyne derivatives were achieved using the equimolar mixture of platinum dimethyldiimine complex [$PtMe_2$(PhN=C(Me)C(Me)=NPh)] and $B(C_6F_5)_3$ [115].

The cationic rhodium complex [{Rh(BINAP)(cod)}BF_4], where BINAP is (*R,S*)-2,2'-bis(diphenylphosphino)binaphthyl, catalysed the cyclisation/hydrosilylation of a number of functionalised internal 1,6-diynes including dialkynyl ethers and amines to form silylated 1,2-dialkylidenecyclopentanes in moderate to high yield with high diastereoselectivity [116] (Eq. 2.58).

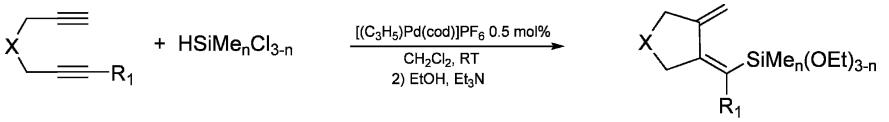


40–73%

X = $C(CO_2Me)_2$, $C(CH_2OR)_2$, O, NTs
R_1,R_2 = Me, Et, C_5H_{11}
SiR_3 = $SiEt_3$, $SiMe_2Et$, $SiMePh_2$ (2.58)

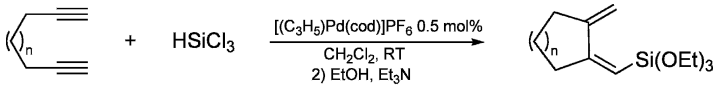
It is worth noting that the reaction of 1,7-diyne containing four ester groups in the presence of either platinum or rhodium catalyst led to 1,2-dialkylidenecyclohexane derivative in 29% and 74% yield, respectively, and *E/Z* ratio ranging from 25/1 to 26/1 [115, 116].

Yamamoto and et al., reported that palladium cationic complex [{(η^3-C_3H_5)Pd(cod)}PF_6] is also a very effective catalyst for cyclisation/hydrosilylation of functionalised α,ω-diynes with trichlorosilane at room temperature to afford (*Z*)-1-methylene-2-silylmethylenecycloalkane derivatives with 5-, 6- and 7-membered ring in good yields [117] (Eq. 2.59 and 2.60).



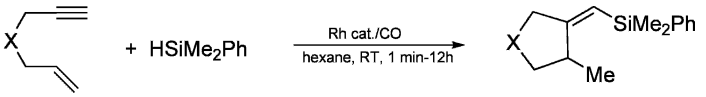
X = $C(CO_2Me)_2$, O, NTs
R_1 = H, Me

33–56%
Z/*E* = 92/8–100/0 (2.59)



n = 2,3 20–68% (2.60)

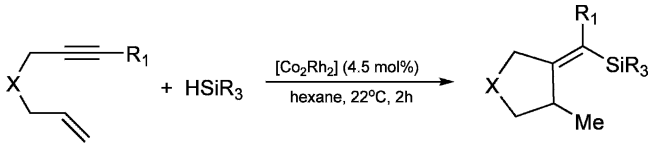
The silylcarbocyclisation of enynes has been recently intensively studied. Ojima and co-workers have developed a highly efficient silylcarbocyclisation of functionalised 1,6-enynes with hydrosilanes under very mild conditions with a broad range of substrates [118, 119]. The silylcarbocyclisation of 4,4-functionalised-1,6-enynes or allyl propargyl amines and allyl propargyl ether with $PhMe_2SiH$ catalysed by rhodium carbonyl complexes ($[Rh(acac)(CO)_2]$ $[Rh_4(CO)_{12}]$ or $[Rh_2Co_2(CO)_{12}]$) proceeded at ambient temperature and CO atmosphere to give corresponding 3-*exo*-silylmethylenecyclopentanes, pyrrolidines or tetrahydrofuran, respectively, with high yields (Eq. 2.61).



52–95%

X = $C(CO_2Et)_2$, $C(CH_2OMe)_2$, $C(CH_2OH)_2$ $C(CH_2OAc)_2$, O, NTs, NBn, NC_3H_5, NCH(Me)Ph (2.61)

Recently immobilised cobalt/rhodium bimetallic nanoparticles derived from $[Co_2Rh_2(CO)_{12}]$ were successfully applied to the silylcarbocyclisation of 1,6-enynes with hydrosilanes under the atmosphere of CO to give 2-methyl-1-silylmethylene-2-cyclopentanes as sole products with high yields [120] (Eq. 2.62). It is worth noting, that the Rh/Co nanoparticles can be reused without the loss of activity even for five times.

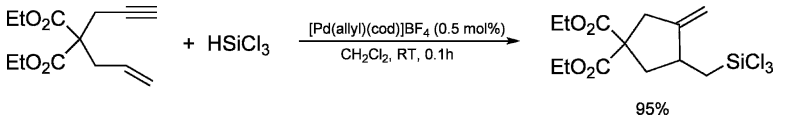


83–97%

X = $C(CO_2Me)_2$, $C(CO_2Et)_2$, $C(CH_2OH)_2$, O, NTs
R_1 = H, Me, Et, Ph, Bu
SiR_3 = $SiEt_3$, $SiMe_2Ph$ (2.62)

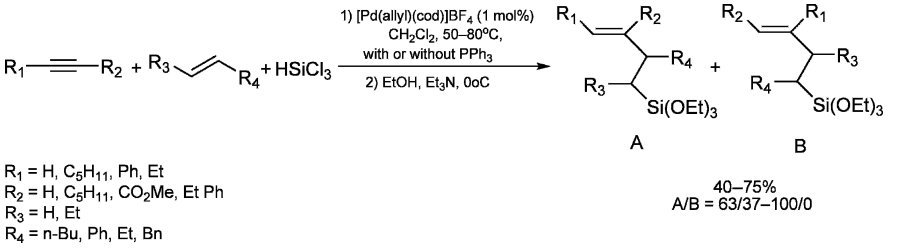
The use of rhodium *N*-heterocyclic carbene complexes in cyclisation/hydrosilylation of functionalised 1,6-enynes and their nitrogen or oxygen-containing derivatives has been reported [121]. Notably, asymmetric variants of rhodium-catalysed enyne silylcarbocyclisation have appeared recently [122, 123].

Palladium complex-catalysed 1,6-enyne silylcarbocyclisation protocol employing trichlorosilane under very mild conditions has been disclosed by Yamamoto and et al., [124] (Eq. 2.63).



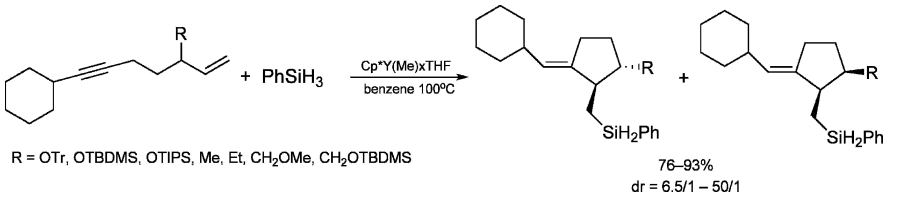
(2.63)

The interesting intermolecular version of this reaction led to couple alkynes with alkenes under hydrosilylation conditions [125] (Eq. 2.64).



(2.64)

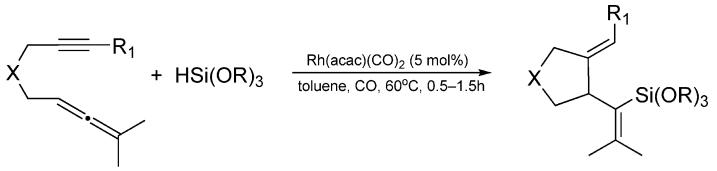
Organolanthanide complexes have been successfully used as catalysts for the cyclisation/hydrosilylation of enynes [126,127]. Yttrocene derivative [Cp*Y(CH_3)x THF] has been shown to be an effective precatalyst for the selective silylcarbocyclisation of 1,6- and 1,7-enynes. Selected examples of the 1,6-enyne transformation are presented in Eq. 2.65.



(2.65)

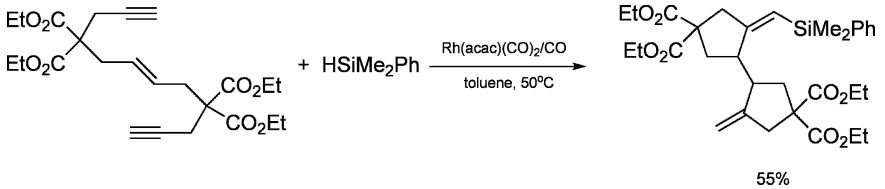
The use of lutetium catalyst [Cp*Lu(CH_3)xTHF] allowed the preparation of various nitrogen-containing ring systems in good yields and high diastereoselectivities [127]

[Rh(acac)$(CO)_2$]-catalysed hydrosilylative carbocyclisation of various allenynes was studied by Shibata and co-workers [128]. The cyclisation/hydrosilylation of functionalised allenynes with trialkoxysilanes proceeded under an atmosphere of carbon monoxide regio- and chemoselectively to give hydrosilylated cyclopentane, pyrrolidine or tetrahydrofuran derivatives (Eq. 2.66).

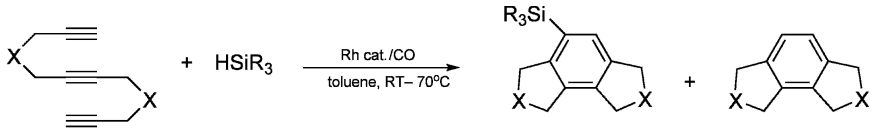


(2.66)

The cyclisation/hydrosilylation process has been further extended to cascade silylcarbocyclisation, which provide powerful method for the construction of polycyclic systems. The cascade silylcarbocyclisation reactions were successfully applied by Ojima and et al., for enediynes and triynes [129, 130]. Typical results for the synthesis of bicyclic or tricyclic systems are presented in Eq. 2.67 and 2.68.



(2.67)



X = $C(CO_2Et)_2$, NTs, NBn, O, $C(CH_2OR)_2$
R_3 = Me_2Ph. $MePh_2$, Ph_3, t-$BuMe_2$, $(EtO)_3$, $(EtO)_2Me$

(2.68)

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Chapter 3
Hydrosilylation of Carbon—Carbon Multiple Bonds in Organic Synthesis

Abstract Growing interest in the development of sequential processes, including regio- and stereoselective hydrosilylation of functionalised alkenes and alkynes as the key step, stems from the ability to assemble stereodefined complex molecules from simple starting materials through organosilicon intermediates in a convergent and flexible manner. This chapter describes some recent advances in the sequential synthetic strategies including both transition-metal catalysed intra- and intermolecular hydrosilylation of C=C and C≡C bonds followed by desilylative oxidation, cross-coupling, proto- and halodesilylation, cycloaddition, nucleophilic addition and other transformations, leading to stereodefined organic derivatives which are widely applied as fine chemicals, synthetic building blocks or are key intermediates in total synthesis of natural products.

Organosilicon reagents play a pivotal role in organic synthesis. Much of the impetus for the growing relevance of organosilicon compounds arises from the successful stereospecific oxidation (Tamao-Fleming protocol) or cross-coupling (Hiyama coupling) strategies developed for these useful organometallic reagents in the last three decades. On the other hand, organosilicon chemistry has matured substantially over the course of the past decade and new methods have been developed for the regio- and stereoselective introduction of the silyl groups into unsaturated molecules. The value of these organosilicon products has been further enhanced by several new protocols for converting the silyl groups into other functional groups using electrophilic substitution, reduction (protodesilylation), nucleophilic addition and many other processes [1].

As hydrosilylation is the most direct and flexible method for introduction of the silyl groups into unsaturated molecules, and the resulting products are particularly useful intermediates that can participate in a host of synthetically valuable organic reactions, there has been extraordinary progress in the development of stereoselective methods of their synthesis and further transformations without the need of their isolation (one-pot processes).

Growing interest in the development of sequential processes, including hydrosilylation as the initial step, stems from the ability to assemble complex molecules

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from simple starting materials (functionalised alkenes and alkynes) through organosilicon intermediates in a convergent and atom-economical manner.

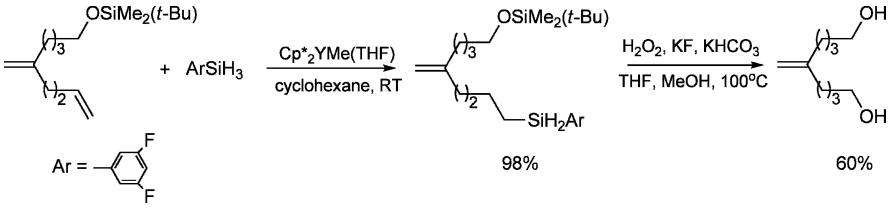
Despite a growing interest in the application of the both inter- and intramolecular hydrosilylation processes in the organic synthesis and an increasing number of papers devoted to these problems, literature does not offer a comprehensive review of the recent achievements in the field. However, selected aspects of the applications of the hydrosilylation of alkenes and alkynes have been discussed in the excellent review papers on the alkyne hydrometallation [2], stereochemical control in organic synthesis using organosilicon compounds [3], intramolecular hydrosilylation [4] silicon tethered reactions [5, 6] and oxidation of the carbon—silicon bond [7].

As the synthetic utility of the carbon—heteroatom double bond hydrosilylation processes is the topic of a separate chapter, the content of this particular chapter is limited to some recent advances in the sequential synthetic strategies including hydrosilylation of C=C and C≡C bonds, leading to stereodefined organic derivatives which are widely applied as fine chemicals, synthetic building blocks or are key intermediates in total synthesis of natural products.

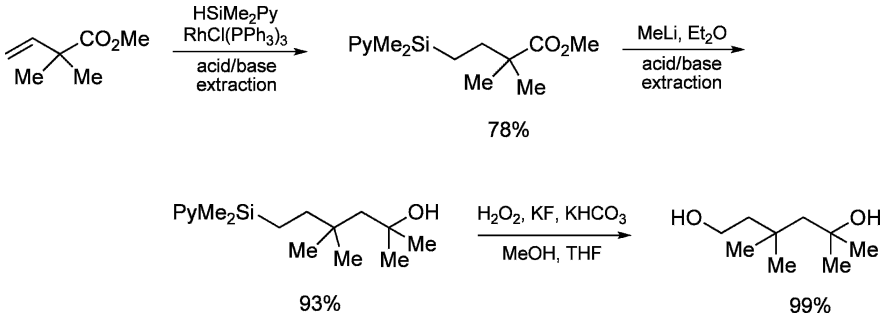
3.1 Hydrosilylation – Oxidation Strategy

Since its discovery, the oxidation of silanes to alcohols (Tamao-Fleming oxidation) has played an important role in organic chemistry [8, 9]. In recent years the strategic use of the hydrosilylation/oxidation sequence has been well recognised as a powerful method for the stereoselective synthesis of various structurally diverse alcohols, ketones or hydroxyketones from simple and readily available starting materials [6].

In the pioneering report, Tamao and co-workers developed a new methodology for the one-pot *anti*-Markovnikov hydration of terminal olefins to primary alcohols, by a sequence of platinum-catalysed alkene hydrosilylation with $HSiMe(OEt)_2$ and the oxidation of the resulting alkylsilanes [8]. Although the applicability of the intermolecular version of this process is limited, a few examples on the successful use of the sequential alkene hydrosilylation – oxidative desilylation strategy in the synthesis of terminal alcohols have recently appeared [10, 11]. In both cases presented, stable silanes with untypical substituents at silicon atoms have been applied (Eq. 3.1 and 3.2).



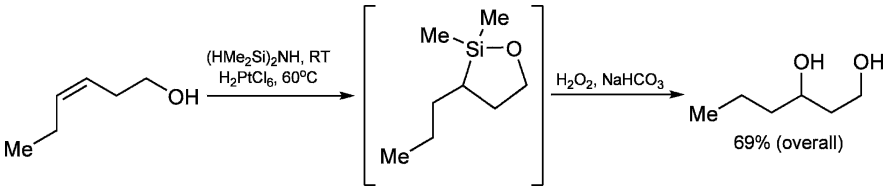
(3.1)



(3.2)

On the other hand, the intramolecular alkene hydrosilylation of allyl and homoallyl alcohols and subsequent oxidative cleavage of the cyclic organosilicon intermediates has been found to be widely applicable to the regio- and stereo-controlled synthesis of a wide variety of 1,3-diols [12, 13]. Alcohol silylation is typically performed through mild heating of the substrate in neat tetramethyldisilazane. As three steps of this transformation i.e. alcohol silylation, hydrosilylation and C—Si bond oxidation are mutually compatible, the reaction sequence can be carried out as a one-pot process, which is of great importance to organic synthesis.

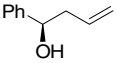
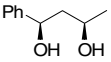
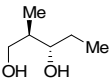
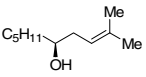
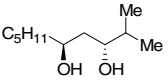
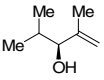
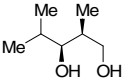
The unique feature of this methodology is that the stereochemistry of this process can be controlled during the addition of the Si—H bond to the olefin and the oxidative cleavage of the resulting carbon—silicon bond, which has been shown to proceed with retention of the configuration at the carbon atom and allows the formation of stereodefined diols. Preliminary studies have established that platinum catalyst allows clean 5-*exo*-hydrosilylation of silylated internal homoallyl alcohol [12, 13] (Eq. 3.3).



(3.3)

The regioselectivity of this process was examined with various types of allyl and homoallyl alcohols in the presence of H_2PtCl_6 or Karstedt's catalyst. In the case of internal olefins the *exo*-ring closure occurred exclusively for both allyl and homoallyl alcohols to give 1,2- or 1,3-diol as a final product, respectively. With the terminal alkenes, an *endo*-process took place highly selectively for allylic alcohols to form α,ω-diols, while *exo*-ring closure predominated in the case of homoallyl alcohols [12]. It should be noted that intramolecular hydrosilylation gives comple-

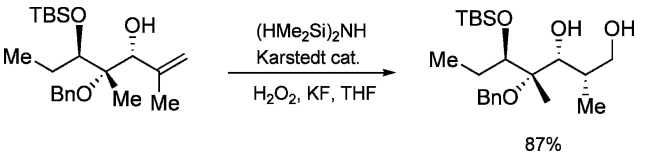
Table 3.1 Synthesis of 1,3-diols from homoallyl alcohols

Alcohol	Product	Selectivity	Isolated yield (%)
		100/1	73
		100/1	52
		5.7/1	71
		6.1/1	67
		5.3/1	72
		24/1	66

mentary regioselectivity to the intermolecular hydroboration of the same allylic or homoallylic alcohol substrates.

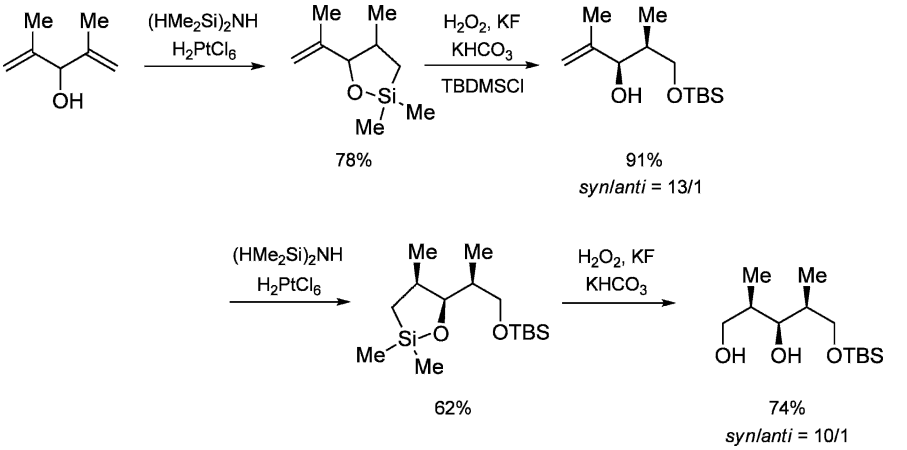
The power of the one-pot intramolecular hydrosilylation/oxidation was demonstrated by the regioselective hydroxylation of substituted allylic and homoallylic alcohols to give a number of 1,3-diol skeletons [14]. The afore-mentioned process displayed varying degrees of stereocontrol as indicated in Table 3.1. Cyclic homoallyl alcohols led to *cis*-1,3-diols exclusively. *Syn*-selectivity was achieved with terminal olefins, whereas *anti*-selectivity predominated for trisubstituted alkenes.

Intramolecular hydrosilylation of more complex allylic alcohol followed by Tamao-Fleming oxidation to yield 1,3-diol as a single diastereoisomer has been recently used as a key step in total synthesis of (*9S*)-*dihydroerythronolide A* [15] (Eq. 3.4).



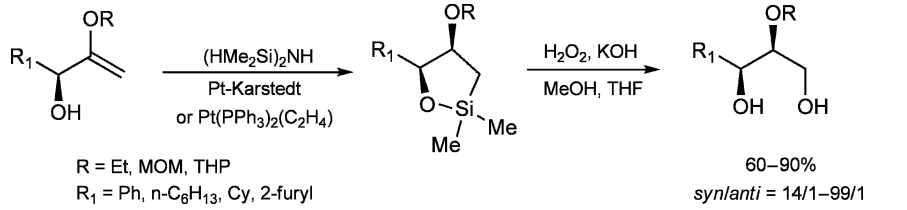
(3.4)

Bis-allylic alcohols undergo intramolecular hydrosilylation in the presence of H_2PtCl_6 to give, after subsequent oxidation, monoprotected triols with high *syn*-selectivity [14] (Eq. 3.5).



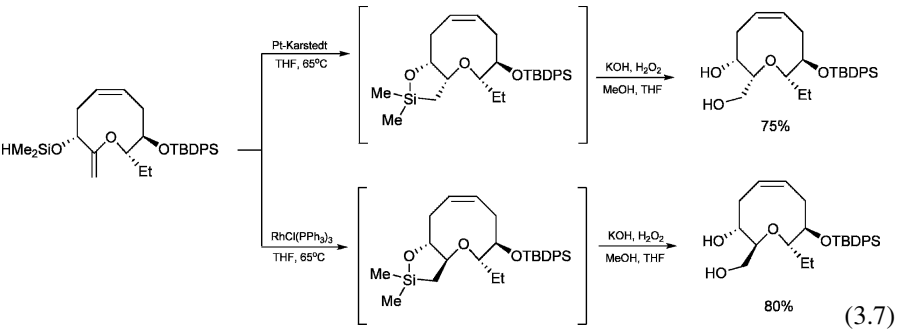
(3.5)

Related methodology has been used for the highly *syn*-selective synthesis of polyhydroxylated compounds by platinum-catalysed intramolecular hydrosilylation/ oxidation of α-hydroxy enol ethers [16] (Eq. 3.6). As an application of this process, the stereoselective synthesis of enantiopure pentitols, *D*-arabinitol and xylitol as their pentaacetates have been achieved in four steps from enantiopure glyceraldehyde ketals [16].



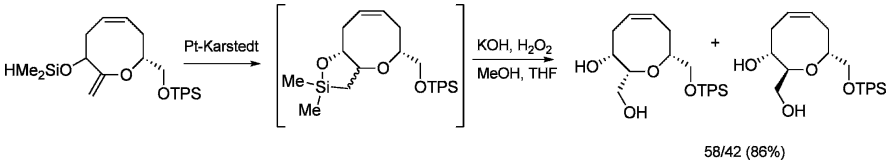
(3.6)

Hydrosilylation of α-hydroxy enol ethers has been studied in the context of the total synthesis of nine-membered medium ring ether natural product (+)-*obtusenyne* (Eq. 3.7). It was shown that the stereochemistry of the Si-H addition can be controlled by the choice of catalyst [17–19].



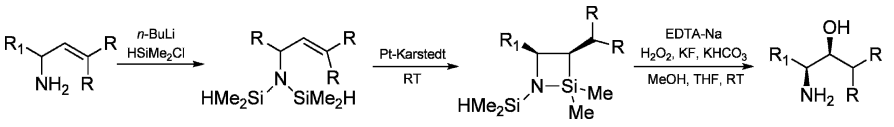
(3.7)

Similar methodology involving intramolecular enol ether hydrosilylation and subsequent oxidation was successfully applied by Holmes et al., in the total synthesis of eight-membered ring ether natural product (+)-*laurencin* [20] (Eq. 3.8).



(3.8)

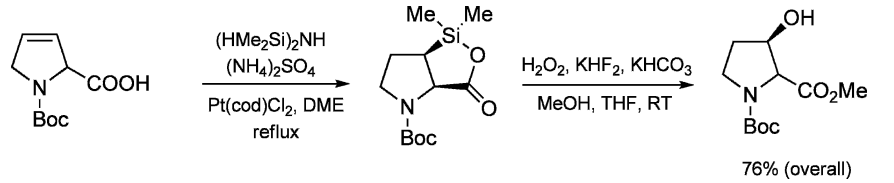
Platinum-catalysed intramolecular hydrosilylation of protected allylamines gives products of the opposite regiochemistry compared to the corresponding allyl alcohols. Bis(dimethylsilyl)allylamines in the presence of Pt-Karstedt's catalyst produce 1-aza-2-silacyclobutane derivatives *via* 4-*exo*-cyclisation as single isomers, which then can be transformed into 2-aminoalcohols by oxidation with hydrogen peroxide in the presence of potassium fluoride and potassium bicarbonate [21, 22] (Eq. 3.9). Remarkable influence on the regioselectivity is observed when the reaction is performed in the presence of rhodium catalysts. Using $[RhCl(PPh_3)_3]$ or $[\{RhCl(C_2H_4)_2\}_2]$ as a catalyst, the intramolecular hydrosilylation of *N,N*-protected allylamines proceeds *via* 5-*endo*-hydrosilylation to give 1-aza-2-silacyclopentanes (Table 3.2).



(3.9)

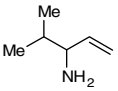
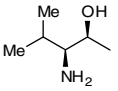
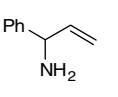
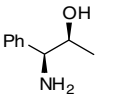
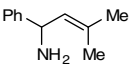
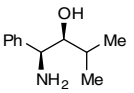
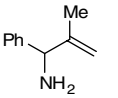
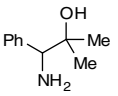
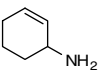
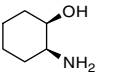
Detailed deuterium-labelling studies of the intramolecular hydrosilylation of silylated allyl alcohols and allyl amines have shown that 5-*endo* cyclisation proceeds *via* a Chalk-Harrod mechanism, while 4-*exo*-cyclisation process includes a Seitz-Wrighton type silylmetallation pathway [22].

An interesting extension of the intramolecular hydrosilylation/oxidation protocol by using a carboxylic acid as the directing group in β,γ-unsaturated acids has been reported. This approach is illustrated in the stereoselective synthesis of (*2S,3R*)-3-hydroxy-*N*-BOC-proline methyl ester [23] (Eq. 3.10).

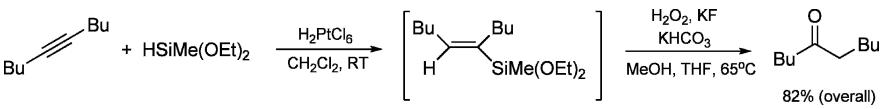


(3.10)

Table 3.2 Synthesis of aminoalcohols from allylamines

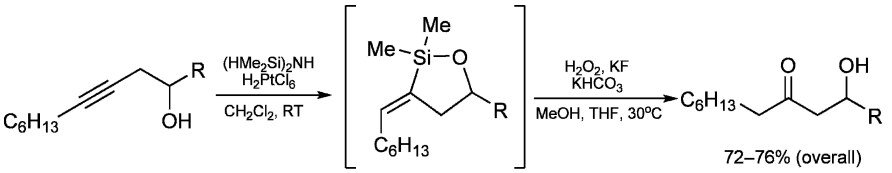
Allylamine	Aminoalcohol	Selectivity syn/anti	Isolated yield (overall) (%)
		77/23	53
		80/20	77
		99/1	76
		–	57
		99/1	72

The one pot conversion of internal alkynes to ketones through stereoselective platinum-catalysed intermolecular hydrosilylation and oxidation [8] has been reported by Tamao et al. (Eq. 3.11).



(3.11)

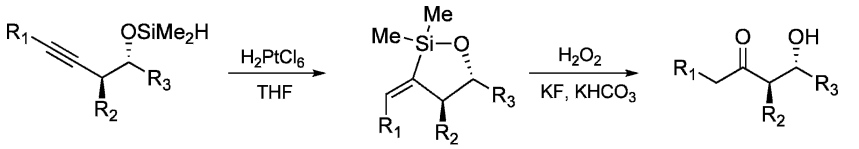
Further studies performed by Tamao et al. established that *exo*-cyclic silyl ethers obtained by platinum-catalysed intramolecular hydrosilylation of silylated homopropargyl alcohols underwent selective oxidative cleavage to yield β-hydroxyketones [24] (Eq. 3.12).



R = H, CH_2Cl

(3.12)

More recent applications of the platinum-catalysed intramolecular *cis*-hydrosilylation of homopropargylic alcohols have expanded the utility of this reaction. Marshall et al. have demonstrated that the intramolecular hydrosilylation – oxidation of homopropargylic alcohols (easily obtained from streoselective aldehyde propargylation) serves as an efficient and versatile method for the stereocontrolled synthesis of substituted β-hydroxyketones, providing access to stereodefined, highly substituted polyketide fragments [25] (Eq. 3.13).

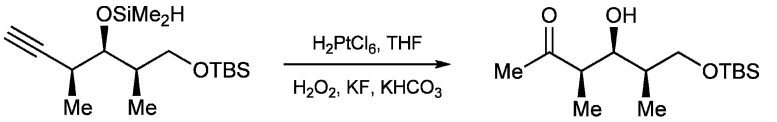


75–92% 74–85%

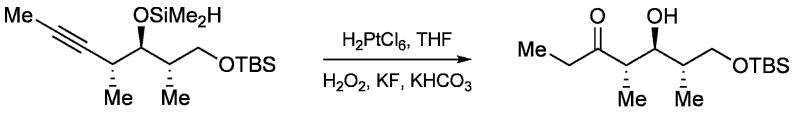
R_1, R_2 = H, Me
R_3 = Ph, Cy

(3.13)

Importantly, the methodology reported by Marshall et al., provides also an efficient route to enantioenriched β-hydroxyketones from readily available (reaction of allenylmetals with aldehydes) hindered silylated homporopargyl alcohols of any desired stereochemical configuration [25]. Two selected examples are presented in Eq. 3.14 and 3.15:

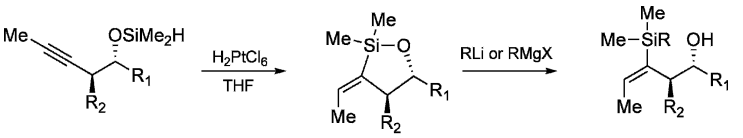


70% (3.14)



72% (3.15)

The two-step protocol including intramolecular hydrosilylation and subsequent treatment of the resulting silacycles with organolithium or Grignard reagents affords the synthetically useful γ-hydroxyvinylsilanes [25] (Eq. 3.16).



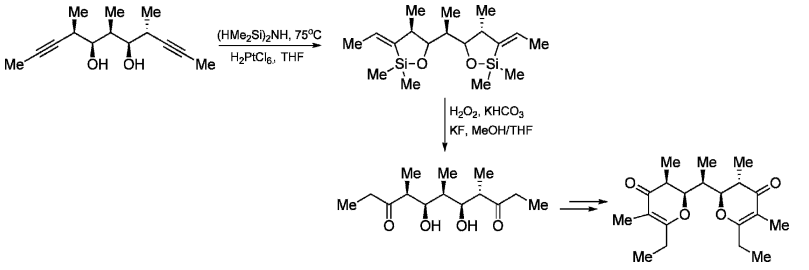
R_1 = Cy, Ph
R_2 = H, Me
R = Me, Ph, Bn

68–95%

(3.16)

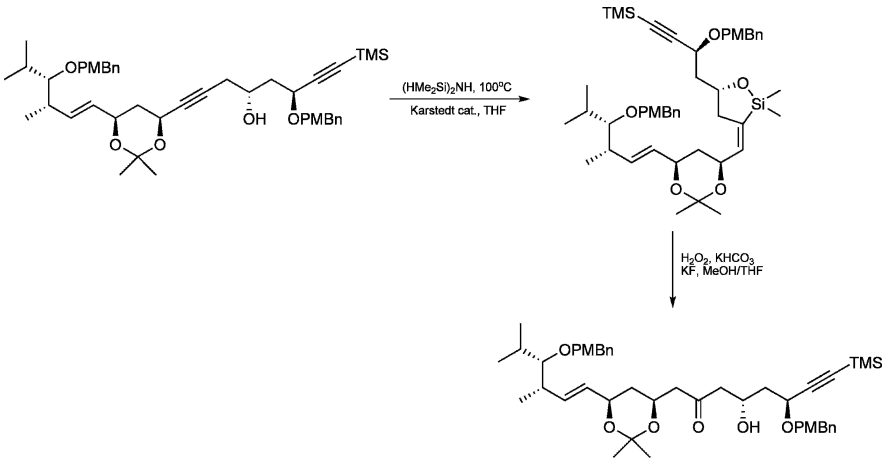
The synthetic methodology exploiting the high synthetic potential of stereodefined oxasilacycloalkenes as masked hydroxyketones has been widely applied to the total syntheses of various natural products.

Marshal et al. reported the utility of double intramolecular hydrosilylation/Tamao-Fleming oxidation in the total synthesis of (-)-*membrenone C* – cyclic chemical defence substance isolated from marine mollusc [26] (Eq. 3.17).



(3.17)

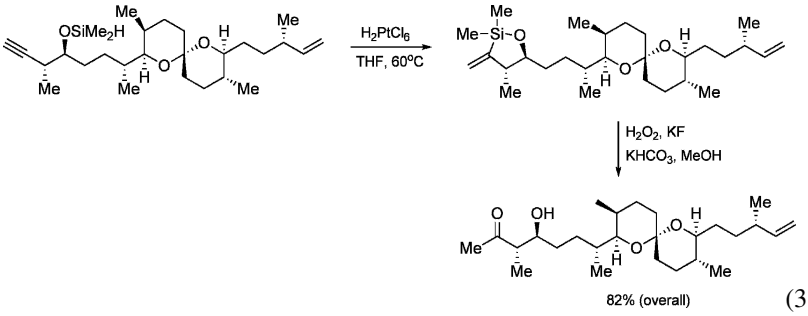
Hydroxyl-directed intramolecular hydrosilylation – oxidation strategy was successfully used in the stereoselective conversion of the hydroxyalkyne fragment to the β-hydroxy ketone segment as the key step in the total synthesis of the polyene-macrolide RK-397 [27] (Eq. 3.18).



43%

(3.18)

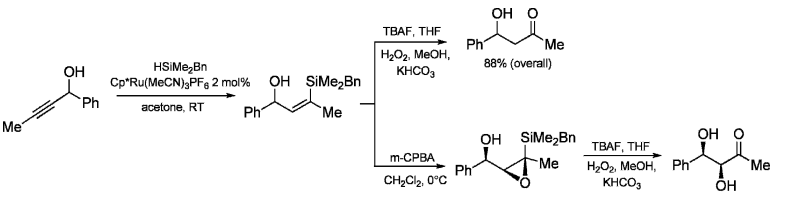
The intramolecular hydrosilylation – Tamao oxidation methodology to form β-hydroxyketone fragment from the homopropargyl group-containing complex substrate was applied for the synthesis of C1-C21 subunit of protein phosphatase inhibitor *Tautomycin* [28] (Eq. 3.19).



(3.19)

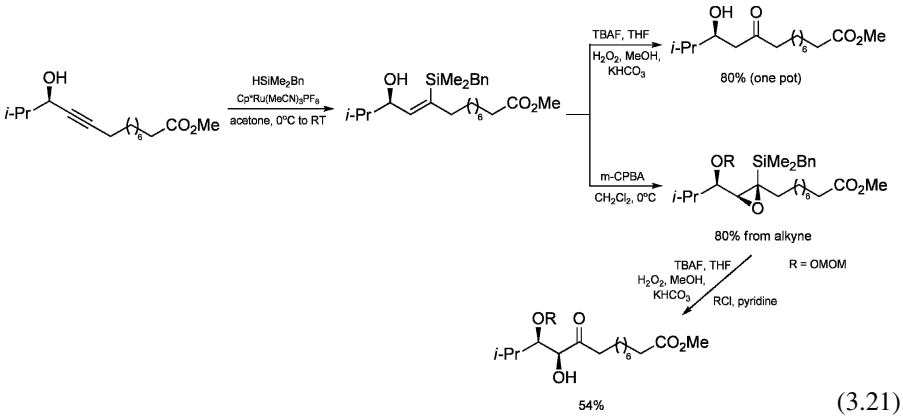
The breakthrough in the investigation on the use of the sequential hydrosilylation/oxidation process in organic synthesis was the derivation of the universal reaction of hydrosilylation of functionalised alkynes in the presence of cationic ruthenium complex: $[\{Cp^*Ru(MeCN)_3\}PF_6]$ published by Trost and co-workers [29–31]. Thanks to the compatibility of this complex with a series of the sequential desilylation reactions such as protodesilylation, desilylative oxidation or cross-coupling, this useful and universal process can be applied as a direct method of alkyne functionalisation without the necessity of isolation of organosilicon intermediates.

Using the sequential ruthenium catalysed hydrosilylation – oxidative desilylation process, propargylic alcohols and their homologues were shown to serve as precursors for ketone or α-hydroxy ketone functionality [31–33]. The one-pot hydrosilylation/oxidation of propargyl alcohols gave the corresponding β-hydroxy ketones, provided that a regioselective introduction of a carbonyl group at the alkyne β-carbon to the alcohol can be performed [32,33] (Eq. 3.20). Additional complexity at the α-carbon can be introduced through the epoxidation of the (*Z*)-alkenylsilane intermediate prior to the oxidation. Diastereoselective epoxidation of the (*Z*)-alkenylsilanes followed by the treatment with TBAF and Tamao oxidation provides the *syn*-diols with excellent selectivity [32,33] (Eq. 3.20 and 3.21). It is worth noting that the above-mentioned intramolecular hydrosilylation of homopropargyl alcohols has also been used to obtain β-hydroxy ketones, however, in that case alkenylsilane intermediate does not allow functionalisation at the α-carbon [25].



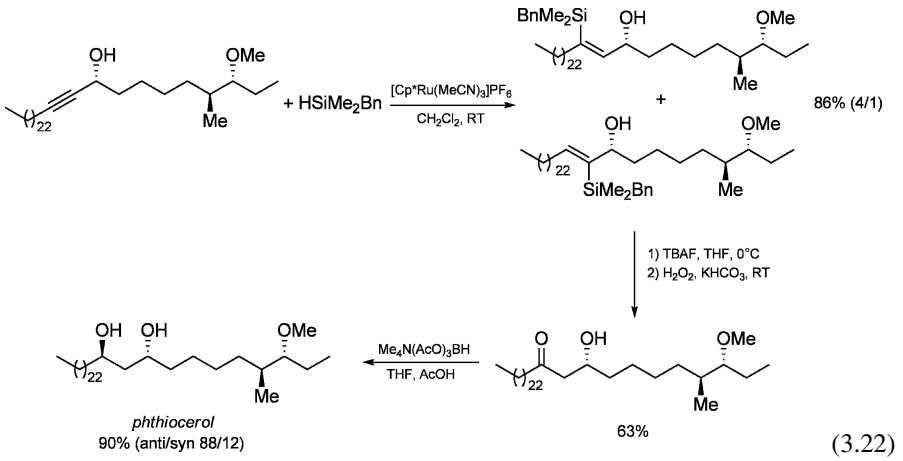
(3.20)

The one-pot hydrosilylation/oxidation sequence fits well also with more complex and functionalised molecules being an the equivalent of stereoselective aldol process [33] (Eq. 3.21).



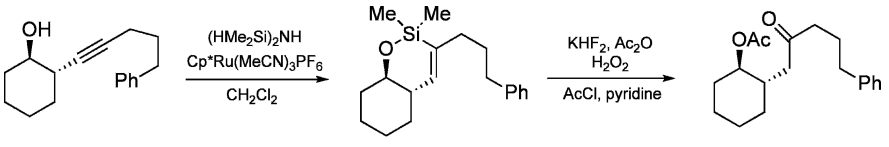
(3.21)

The utility of ruthenium-catalysed hydrosilylation/desilylative oxidation of functionalised propargylic alcohols was demonstrated in asymmetric total synthesis of *phthiocerol* – mycobacterial cell wall lipid component [34] (Eq. 3.22).



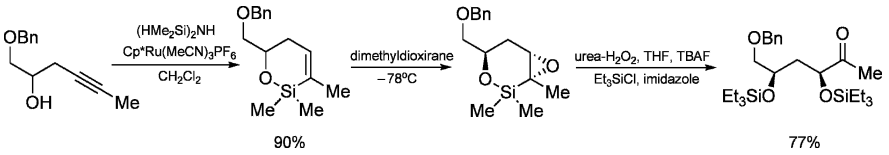
(3.22)

Homopropargyl alcohols can be surrogates for γ-hydroxy ketones (homoaldol products) [30,33]. The approach hinges on the intermediacy of cyclic alkenylsilanes formed through stereoselective *endo-dig* intramolecular hydrosilylation catalysed by [{Cp*Ru(MeCN)$_3$}PF$_6$] and their subsequent oxidation. An example of such a process, in which an alkyne serves as a methyl ketone enolate equivalent is shown in (Eq. 3.23).



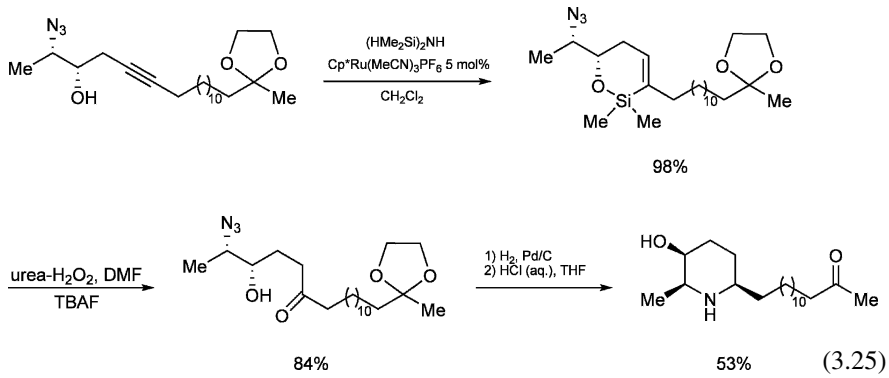
(3.23)

Epoxidation/oxidation sequence of the *endo*-cyclic hydrosilylation intermediates can furnish the hydroxyl ketone functionality to give diastereomerically pure *syn*-α,γ-dihydroxy ketones (Eq. 3.24), (usually obtained in protected form), however in some cases, the oxidative desilylation of cyclic epoxysilanes is complicated due to the resistance of the latter to oxidation [33].



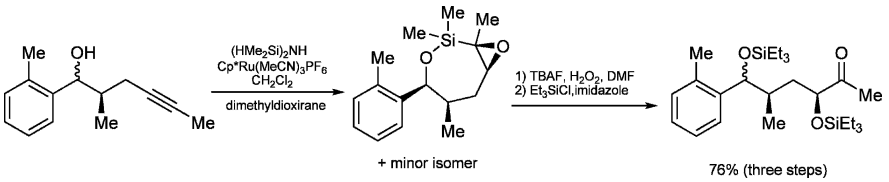
(3.24)

The utility of ruthenium-catalysed intramolecular hydrosilylation of homopropargyl alcohols for the selective installation of ketone functionality was proved in the synthesis of piperidine alkaloid – (+)-*spectaline* [33] (Eq. 3.25).



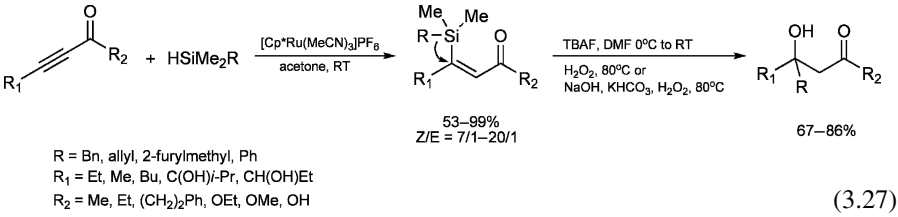
(3.25)

Similar intramolecular hydrosilylation – epoxidation – silane oxidation pathway applied to bishomopropargyl alcohols afforded the 1,4-diol derivatives (α,δ-dihydroxy ketones), best isolated as the bis-silyl ethers [33] (Eq. 3.26).



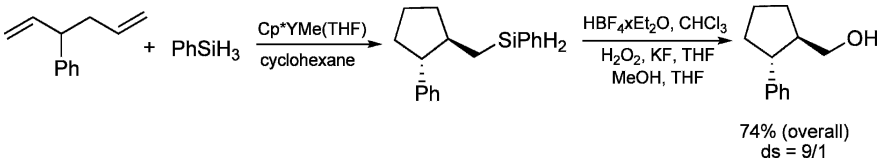
(3.26)

The regioselective [{Cp*Ru(MeCN)$_3$}PF$_6$]-catalysed *trans*-hydrosilylation of alkynyl carbonyl compounds such as alkynyl-substituted ketones and esters, together with a one-pot TBAF-promoted C—C bond formation by Si→C migration and subsequent silane oxidation, provides a new strategy for the synthesis of β-carbonyl-substituted tertiary alcohols [35] (Eq. 3.27).



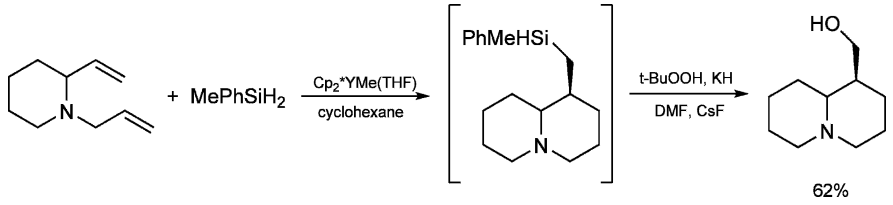
(3.27)

Early transition metal catalysts, despite their wide application in carbon—heteroatom double bond hydrosilylation, have been little used in sequential processes involving alkene or alkyne hydrosilylation. Yttrium-catalysed sequential hydrosilylation/cyclisation reactions of 1,5- and 1,6-dienes were reported by Molander et al. [36–38]. Despite the limited reactivity of the dihydrophenylsilyl group, the resulting silyl-substituted carbocyclic compounds have been shown as convenient sources for the subsequent Tamao-Fleming oxidation, which results in the formation of stereodefined cycloalkanols [36] (Eq. 3.28).

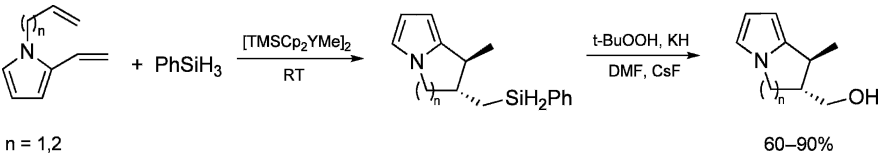


(3.28)

Similar sequential protocol has been applied in the one-pot synthesis of natural bicyclic compounds such as (±)-*epilupinine* [37] (Eq. 3.29) and 2,3-dihydro-1*H*-pyrrolizine derivatives [38] (Eq. 3.30)

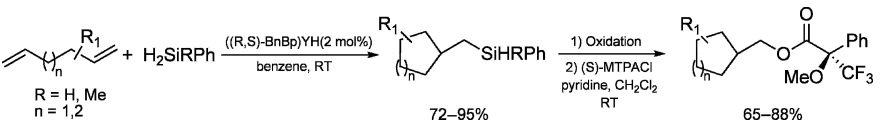


(3.29)



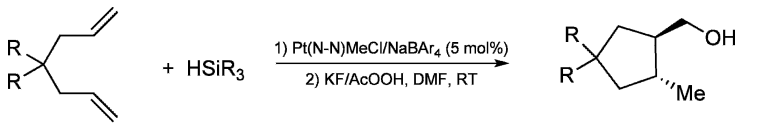
(3.30)

The silylated five- or six-membered cycloalkanes obtained *via* yttrium complex-catalysed: [((*R,S*)-BnBp)YH] (BnBp = $\{(OC_{10}H_6C_{10}H_6O)Si(C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2\}$) cyclisation/hydrosilylation of 1,5-hexadienes or 1,6-heptadienes can be transformed into corresponding esters using consecutive Tamao-Fleming oxidation and acylation [39] (Eq. 3.31).



(3.31)

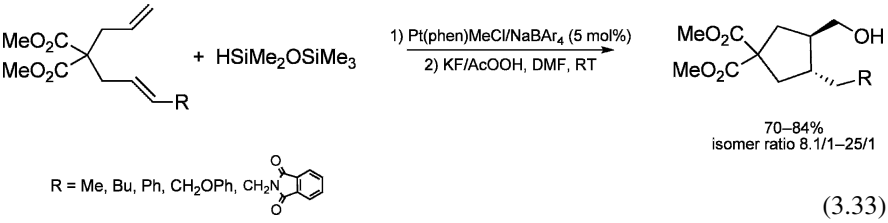
Pentasubstituted disiloxanes and silanes of the general formula $HSiMe_2CH_xPh_{3-x}$ (x = 1 or 2) reacted with a range of functionalised 1,6-dienes in the presence of [(*N-N*)Pd(Me)Cl] ((*N-N*) = 1,10-phenanthroline or (*R*)-(+)-4-isopropyl-2-(2-pyridinyl)-2-oxazoline) and $NaBAr_4$ ($Ar = 3,5\text{-}C_6H_3(CF_3)_2$) to form silylated carbocycles, which next could be oxidised with excess KF and peracetic acid to the corresponding cyclic alcohols in excellent yield with retention of stereochemistry [40–43] (Eq. 3.32).



R = CO_2Bn, CH_2OMe, CH_2OBn, CH_2OCOMe, $CH_2OCOt\text{-}Bu$,
R_3 = Me_2OSiMe_3, $Me_2OTBDPS$

(3.32)

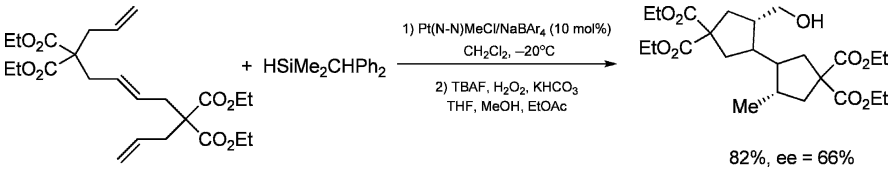
The compatibility of platinum-catalysed cyclisation/hydrosilylation with both terminal olefinic substitution and a range of functional groups allowed the synthesis of a number of vicinal difunctionalised cyclopentanes [42] (Eq. 3.33).



R = Me, Bu, Ph, CH_2OPh, CH_2N

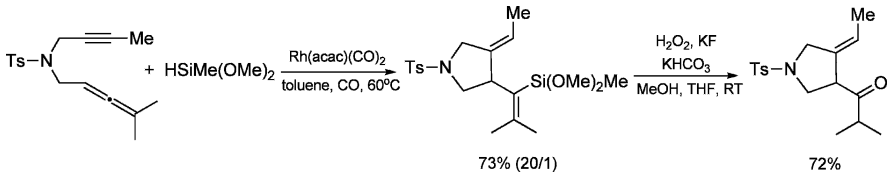
(3.33)

The cascade cyclisation/hydrosilylation protocol employing triene and benzhydryldimethylsilane followed by desilylative oxidation led to hydroxy-substituted bicyclopentane [42] (Eq. 3.34).



(3.34)

The oxidation of cyclic alkoxyvinylsilanes obtained *via* rhodium-catalysed silylcarbocyclisation of allenynes provided access to pyrrolidine isopropyl ketone derivative [44] (Eq. 3.35).



(3.35)

3.2 Hydrosilylation – Protodesilylation Protocol

The hydrosilylation-protodesilylation protocol is a useful method for stereoselective alkyne reduction to (*E*)-alkenes and is a complement to the *cis*-selectivity observed in the Lindlar reduction. The utility of this reaction sequence is attributed to the fact that many of the known methods for transforming alkynes to (*E*)-alkenes either have poor selectivity or are incompatible with common functional groups.

Recently, Trost [45] and Fürstner [46] independently, developed a general and mild procedure based on ruthenium-catalysed hydrosilylation/protodesilylation sequence. Trost et al. applied the combination of [{$Cp^*Ru(MeCN)_3$}PF_6]- catalysed internal alkyne hydrosilylation and cooper(I) iodide-inducted protodesilylation, which allows a net trans alkyne reduction for a wide variety of functionalised alkynes including esters, ketones and propargyl alcohols [45]. The intermediate alkenylsilanes were not isolated; however, the catalyst and the excess of silane had to be separated prior to the desilylation step by filtration and evaporation. Selected results are given in Table 3.3.

It has been noted that 1,1-disubstituted alkenylsilanes, which are difficult protodesilylation substrates, were smoothly cleaved to the terminal alkenes using CuI/TBAF system [45] (Eq. 3.36).

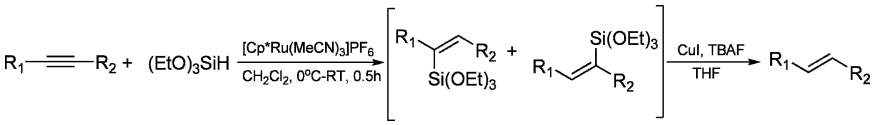
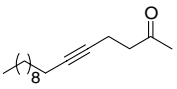
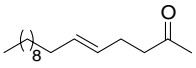
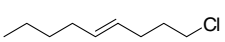
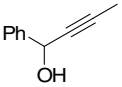
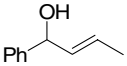
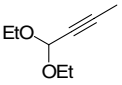
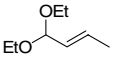
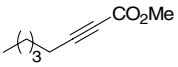
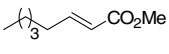
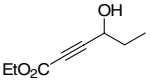
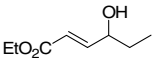
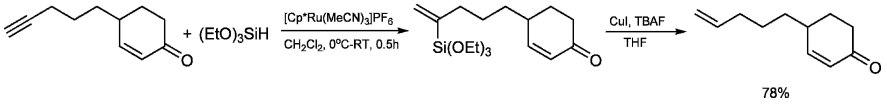


Table 3.3 (*E*)-selective reduction of internal alkynes

Alkyne	Product	Isolated yield (%)
		96
		59
		76
		67
		83
		80



(3.36)

Fürstner et al. reported a two-step protocol for the stereoselective synthesis of macrocyclic functionalised (*E*)-cycloalkenes from cycloalkynes (obtained from diynes *via* ring closing alkyne metathesis) using *trans*-selective hydrosilylation catalysed by $[\{Cp^*Ru(MeCN)_3\}PF_6]$ and following AgF-mediated protodesilylation [46, 47]. Selected results are presented in (Table 3.4).

The feasibility of this two-step method was also demonstrated in the stereoselective synthesis of (*E*,*E*)-dienes and (*E*,*E*)-cycloalkadienes [47] (Eq. 3.37).

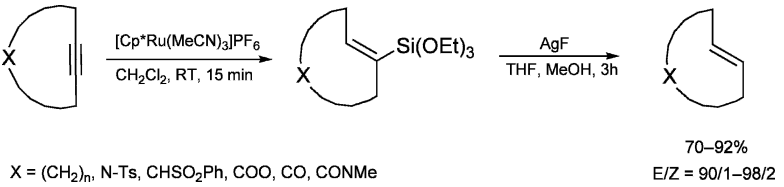
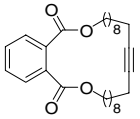
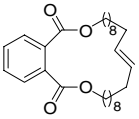
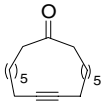
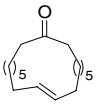
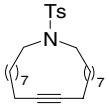
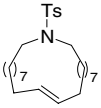
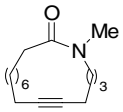
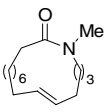
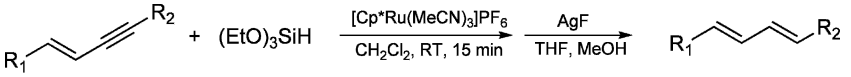


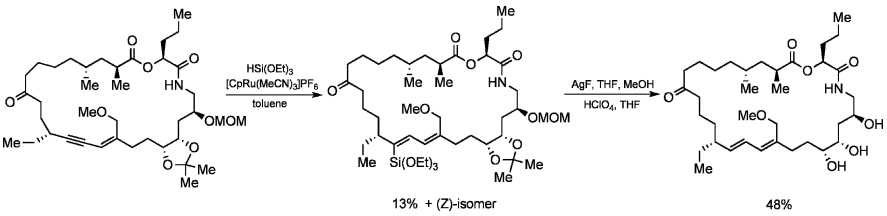
Table 3.4 (*E*)-selective reduction of cyclic alkynes

Cycloalkyne	Cycloalkene	E/Z	Isolated yield (overall %)
		90/10	76
		98/2	87
		98/2	65
		98/2	73
		95/5	78



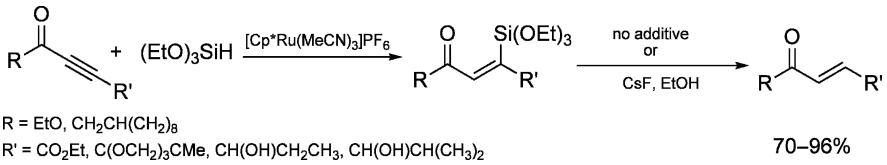
(3.37)

The strategy for the conversion of enynes into 1,3-dienes by a ruthenium-catalysed *trans*-hydrosilylation and subsequent protodesilylation has been recently applied (however, with limited success in terms of the selectivity) in total synthesis of antibiotic macrolide *myxovirescin A*$_1$ [48] (Eq. 3.38).



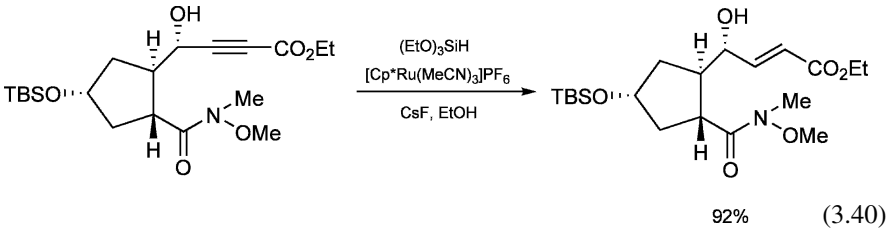
(3.38)

The hydrosilylation-protodesilylation methodology can be successfully applied to selective reduction of carbon—carbon triple bonds of functionalised alkynyl ketones to give (*E*)-α,β-unsaturated carbonyl compounds [49] (Eq. 3.39).



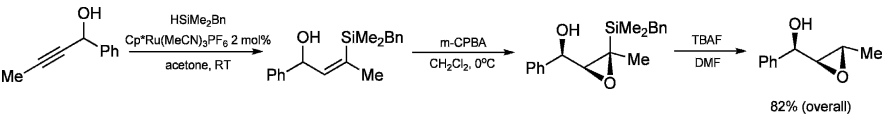
(3.39)

The optimised methodology was applied in the total synthesis of (+)-*brefeldin* as a new method for *trans*-selective alkyne reduction in the presence of other sensitive functional groups [49] (Eq. 3.40).



(3.40)

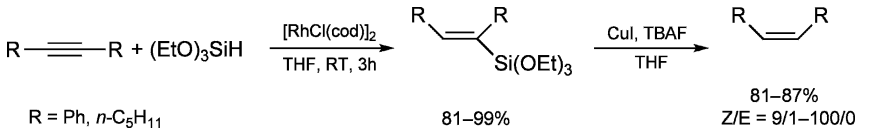
Another three-step process including consecutive ruthenium-catalysed hydrosilylation, epoxidation and protodesilylation furnishes *syn*-epoxy alcohols from propargyl alcohols [33] (Eq. 3.41).



(3.41)

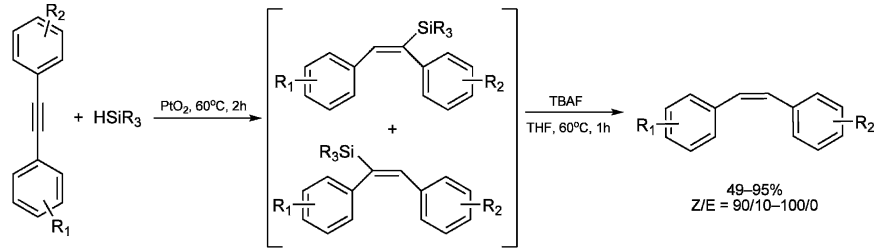
The hydrosilylation/protodesilylation protocol can be successfully applied as a stereoselective approach to (*Z*)-alkenes [50, 51]. It can be used not only for the

synthesis of geometrically pure (*Z*)-disubstituted alkenes, but also to confirm the hydrosilylation stereochemistry. An example is the rhodium-catalysed hydrosilylation of internal alkynes, whose stereochemical outcome was proved by treatment of the resulting (*E*)-alkenylsilanes with TBAF [50] (Eq. 3.42).



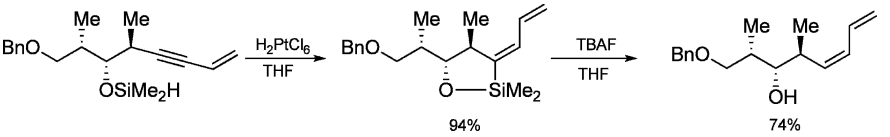
(3.42)

Very recently, mild and efficient method for the stereoselective synthesis of (*Z*)-stilbenes from diarylalkynes using PtO_2-catalysed hydrosilylation/TBAF-mediated protodesilylation procedure has been reported [51]. It was demonstrated that this reaction sequence could be realised in a one-pot way from various diarylalkynes (Eq. 3.43).



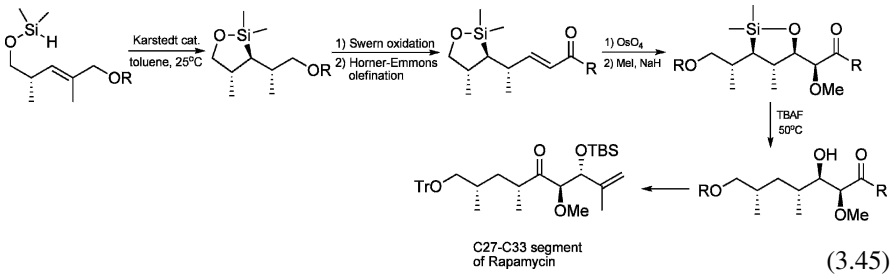
(3.43)

Intramolecular hydrosilylation–protodesilylation sequence has been used in several natural product syntheses. An interesting application of this sequential process is the transformation of enynes to 1,3-dienes reported by Marshall et al. [52] (Eq. 3.44). Enynes, prepared from homopropargyl alcohols, were subjected to platinum-catalysed intramolecular hydrosilylation and underwent subsequent silyl cleavage with TBAF to afford (*Z*)-1,3-dienes. This reaction sequence has been successfully applied to the synthesis of C17-C24 1,3-diene terminus of *Discodermolide* and its analogues.



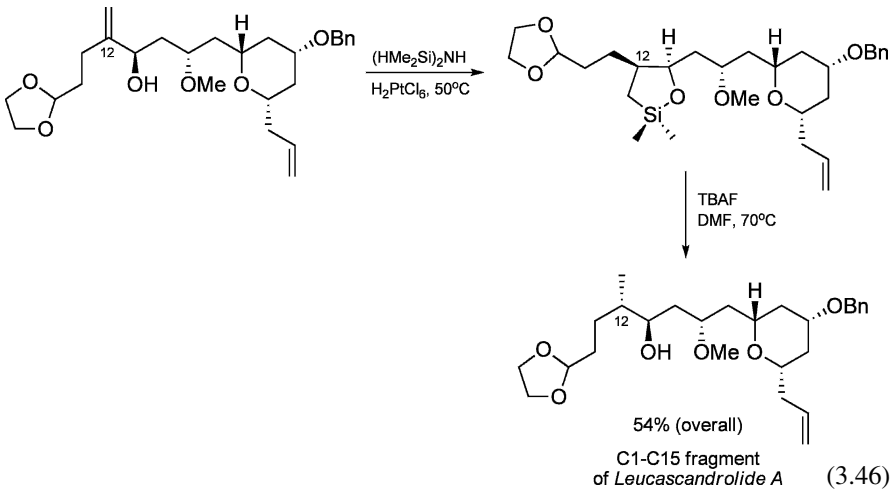
(3.44)

Intramolecular alkene hydrosilylation followed by protodesilylation can be used to control and relay asymmetry along an acyclic chain. The platinum-catalysed intramolecular hydrosilylation/protodesilylation protocol has been successfully applied in the synthesis of C27-C33 segment of immunosuppressant drug – *Rapamycin* [53, 54] (Eq. 3.45).



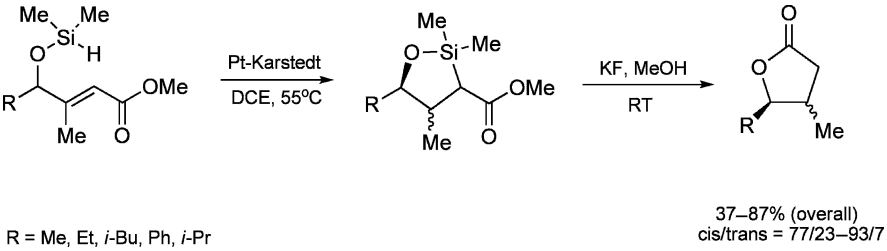
(3.45)

Intramolecular hydrosilylation/protodesilylation sequence was also applied in the stereoselective construction of the C1-C15 fragment of the marine macrolide *Leucascandrolide A* [55]. In this approach, the cyclic silyl ether, assembled *via* Pt-catalysed hydrosilylation, was designed to serve as a temporary template for the installation of the new C12 stereogenic centre (Eq. 3.46).



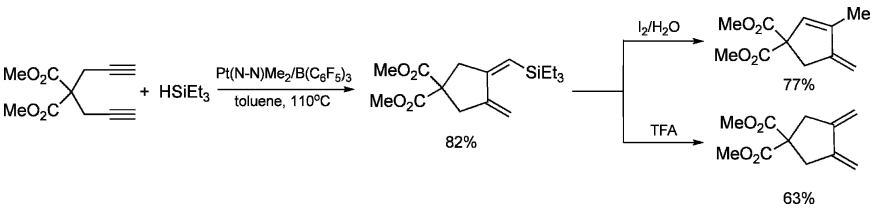
(3.46)

A study on intramolecular hydrosilylation of δ-hydroxy-α,β-unsaturated esters has been carried out. Platinum-catalysed intramolecular hydrosilylation of several 3-methyl-4-siloxy-2-butenoates followed by protodesilylation afforded *cis*-disubstituted lactones with modest stereoselectivity [56] (Eq. 3.47).



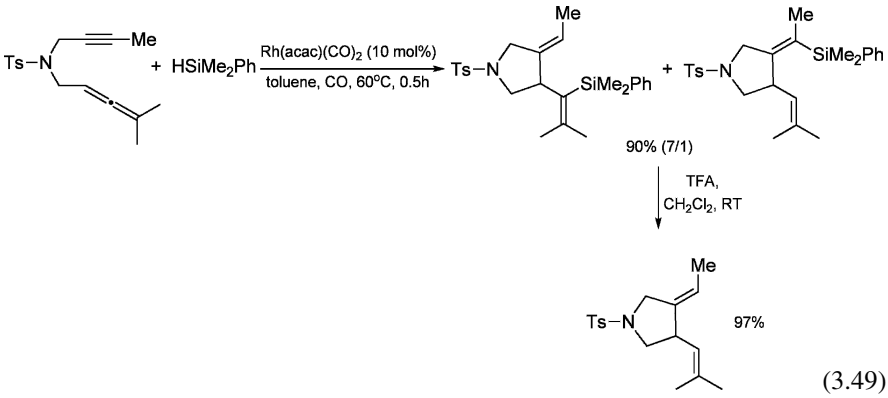
(3.47)

Application of the sequential platinum-catalysed cyclisation/hydrosilylation and protodesilylation processes led to methylenecyclopentane derivatives from 1,6-diynes [57] (Eq. 3.48). Treatment of the silylcarbocyclisation products with a mixture of iodine and water in benzene led to protodesilylation/isomerisation with formation of 1-methyl-5-methylenecyclopentene, whereas the use of trifluoroacetic acid (TFA) in protodesilylation step produced dimethylenecyclopentane derivative without isomerisation [57].



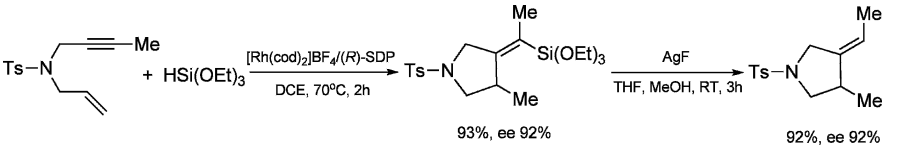
(3.48)

The trifluoroacetic acid-mediated protodesilylation of cyclic vinylsilanes obtained *via* rhodium-catalysed silylcarbocyclisation of allenynes provided access to cyclic 1,4-dienes [44] (Eq. 3.49).



(3.49)

Conjunction of the asymmetric 1,6-enyne silylcarbocyclisation with protodesilylation led to optically active methylenecyclopentane derivatives with high enantioselectivity [58] (Eq. 3.50).



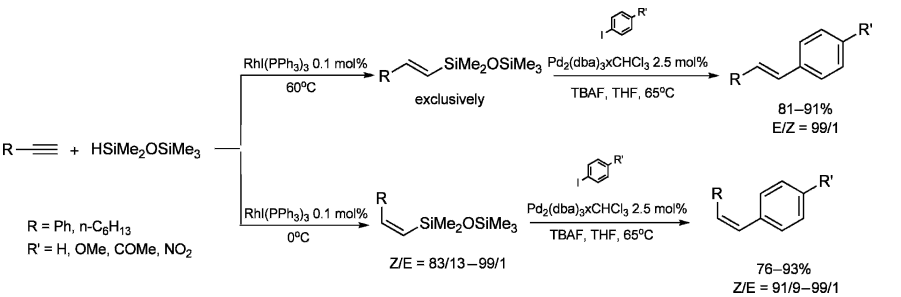
(3.50)

3.3 Hydrosilylation – Cross-Coupling Methodology

Silicon-based cross-coupling reaction (Hiyama coupling) has gained significant importance in synthetic organic chemistry as a reliable alternative to the Suzuki (boron), Stille (tin) and Negishi (zinc) couplings due to selective reactivity, stability and non-toxicity associated with organosilicon reagents [59–62]. Another beneficial aspect of the silicon-assisted cross-coupling reaction is the well established transition metal catalysed alkyne hydrosilylation, which makes a variety of unsaturated organosilicon precursors readily available in regio- and stereoselective manners. In this context, several independent protocols using the combination of transition metal catalysed stereoselective hydrosilylation – palladium catalysed cross-coupling sequence leading to stereodefined π-conjugated alkene derivatives have been successfully developed in the last decade.

The pioneering work of Hiyama [63,64] and Ito [65] groups reported consecutive Pt-catalysed hydrosilylation of alkynes by halo- or alkoxysilanes – Pd-catalysed cross-coupling reactions with aryl or alkenyl halides, requiring the sequential addition of the coupling partners and palladium catalyst.

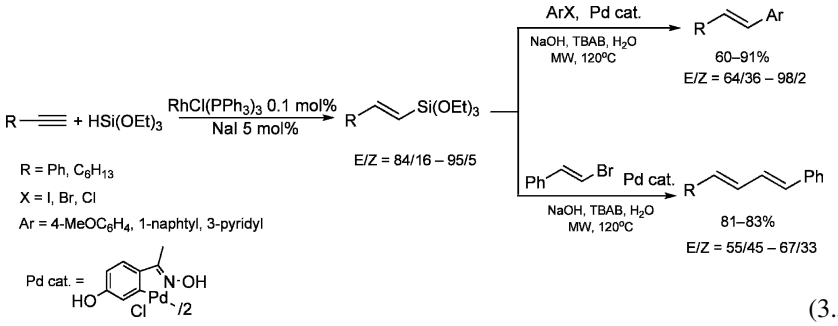
More recently Hiyama et al. applied the [$RhI(PPh_3)_3$] – catalysed stereodivergent hydrosilylation of terminal alkynes with pentamethyldisiloxane in the sequential synthesis of (*E*)- and (*Z*)-disubstituted alkenes [66]. In this strategy (*Z*)- and (*E*)- isomers of alkenylsiloxanes were independently synthesised from the same substrates, by switching the order of the addition of the reagents and reaction conditions. The obtained alkenylsiloxanes were then subjected to the stereospecific palladium-catalysed cross-coupling with aryl iodides to form alkenylarenes (Eq. 3.51).



(3.51)

Very recently, alkenyltriethoxysilanes, prepared *via* Wilkinson complex-catalysed hydrosilylation of terminal alkynes with triethoxysilane have been highly

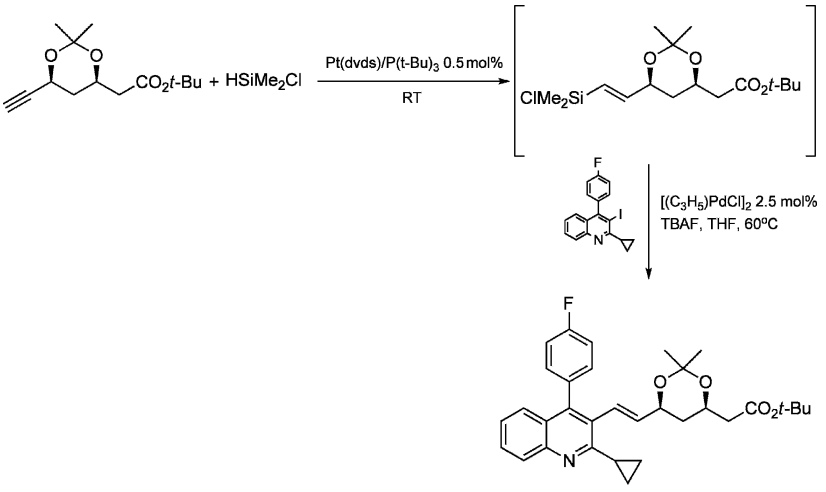
stereospecifically cross-coupled with aryl and alkenyl halides in water using sodium hydroxide as activator under microwave irradiation, affording unsymmetrical stilbenes, alkenylbenzenes and conjugated dienes, respectively [67] (Eq. 3.52).



(3.52)

An elegant application of the intermolecular hydrosilylation of terminal alkynes is the sequential hydrosilylation-Hiyama coupling strategy, reported by Denmark et al. [68]. The use of [Pt(dvds)/P(*t*-Bu)$_3$] catalyst allows near total control in the reaction of terminal alkynes with tetramethyldisiloxane. The in situ generated (*E*)-alkenylsiloxanes undergo a Pd-catalysed cross-coupling with aryl iodides to give (*E*)-disubstituted alkenes with good yields [68] (Table 3.5). The method is characterised by good functional group compatibility and perfect stereoselectivity (E/Z >99/1).

The synthetic potential of the [Pt(dvds)/P(*t*-Bu)$_3$] catalytic system has been proved in the total synthesis of an HMG-CoA reductase inhibitor NK-104, in which the one-pot (*E*)-selective hydrosilylation of alkyne precursor with a chlorosilane followed by the palladium-catalysed cross-coupling with 2,6-disubstituted aryl iodide were the key steps [63, 64] (Eq. 3.53).



(3.53)

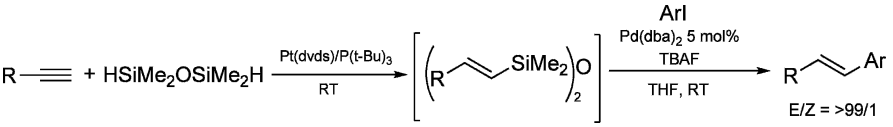
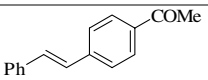
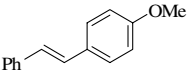
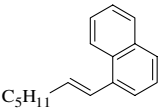
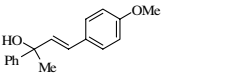
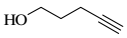
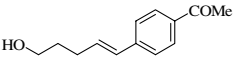
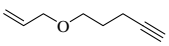
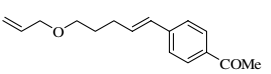
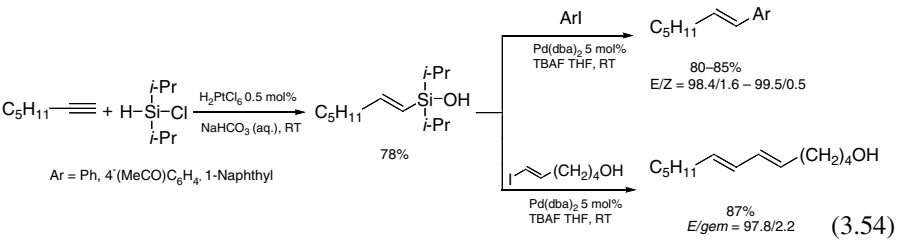


Table 3.5 Synthesis of (*E*)-disubstituted alkenes via sequential hydrosilylation – Hiyama coupling

Alkyne	Ar	Product	Isolated yield (%)
PhC≡CH	4-(MeCO)C_6H_4		89
PhC≡CH	4-(MeO)C_6H_4		74
$C_5H_{11}C$≡CH	1-Naphthyl		82
	4-(MeO)C_6H_4		79
	4-(MeCO)C_6H_4		89
	4-(MeCO)C_6H_4		78

Denmark et al. have also demonstrated, that (*E*)-heptenyldiisopropylsilanol, easily obtained *via* platinum-catalysed hydrosilylation of 1-heptyne, can undergo highly stereospecific, palladium-catalysed cross-coupling reaction with either aryl or alkenyl iodides under mild conditions [69] (Eq. 3.54).



(3.54)

A new hydrosilylation – silicon-based cross coupling protocol, that employs (*E*)-alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes as intermediates has been recently

reported by Hiyama et al [70, 71]. These highly stable alkenylsilanes, prepared by stereoselective platinum-catalysed hydrosilylation of functionalised alkynes using protected [(2-hydroxymethyl)phenyl]dimethylsilanes, underwent cross-coupling reaction with various aryl or alkenyl iodides to give functionalised conjugated arylethenes and dienes in highly stereoselective manner [71] (Table 3.6). The unique feature of this reaction sequence is that the silicon residue can be readily recovered and reused on a gram-scale synthesis.

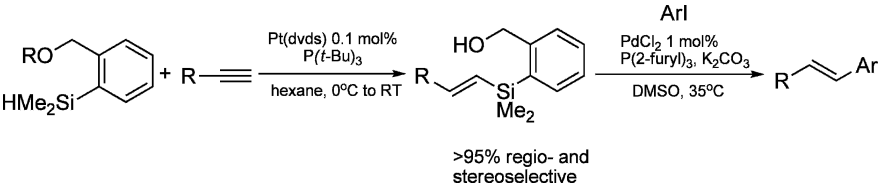
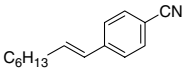
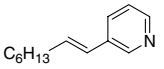
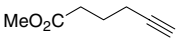
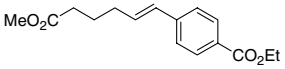
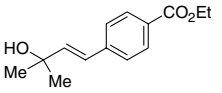
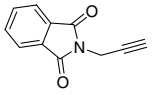
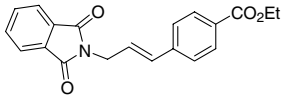
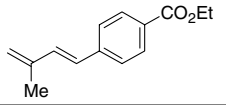
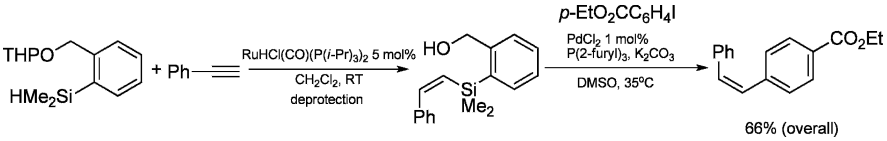


Table 3.6 Synthesis of (*E*)-disubstituted alkenes via sequential hydrosilylation – Hiyama coupling

Alkyne	Product	Isolated overall yield (%)
$C_6H_{13}C{\equiv}CH$		76
$C_6H_{13}C{\equiv}CH$		65
		62
		40
		67
		53

When ruthenium-hydride complex was used as hydrosilylation catalyst, isomeric (*Z*)-alkenylsilanes and consequently (*Z*)-alkenylarenes were produced [71] (Eq. 3.55).



(3.55)

Very recently, a one-pot stereoselective synthesis of conjugated disubstituted (*E*)-alkenes using the hydrosilylation/Hiyama cross-coupling sequence in the presence of bimetallic heterogeneous Rh-Pd catalyst has been reported [72]. The catalyst prepared from $[RhCl(PPh_3)_3]$, $[Pd(OAc)_2]$ and iodide ionic gel enables the synthesis of functionalised conjugated systems from readily available terminal alkynes without (*E*)-alkenylsilane intermediate isolation, with high yields and perfect stereoselectivities (Table 3.7).

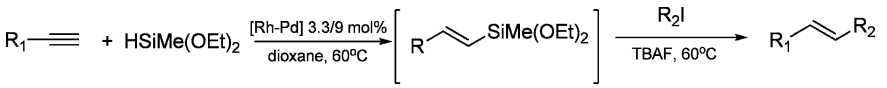
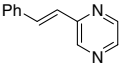
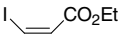
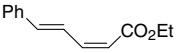
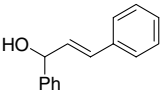
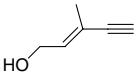
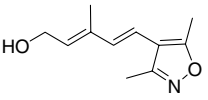
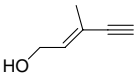
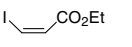
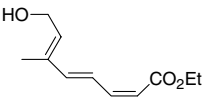
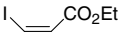
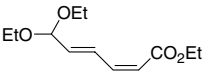
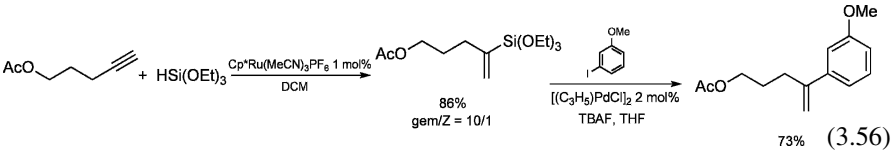


Table 3.7 Synthesis of substituted (*E*)-alkenes via one-pot Rh/Pt – catalysed hydrosilylation – Hiyama coupling

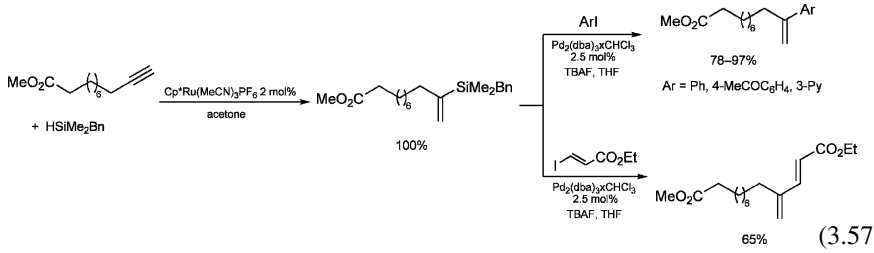
Alkyne	Iodide (R_2I)	Product	Isolated yield (%)
PhC≡CH			75
PhC≡CH			93
			96
			50
			95
			90

Geminal-substituted alkenes can be conveniently prepared from terminal alkynes using a combination of the ruthenium-catalysed hydrosilylation reported by Trost and the Pd-catalysed cross-coupling [29, 73]. Hydrosilylation of terminal alkynes in the presence of cationic cyclopentadienyl ruthenium(II) complex $[\{Cp^*Ru(MeCN)_3\}PF_6]$ gave α-alkenylsilanes in good to excellent yields, which next could be transformed into 1,1-disubstituted alkenes with high regioselectivity under standard cross-coupling conditions [29] (Eq. 3.56).



(3.56)

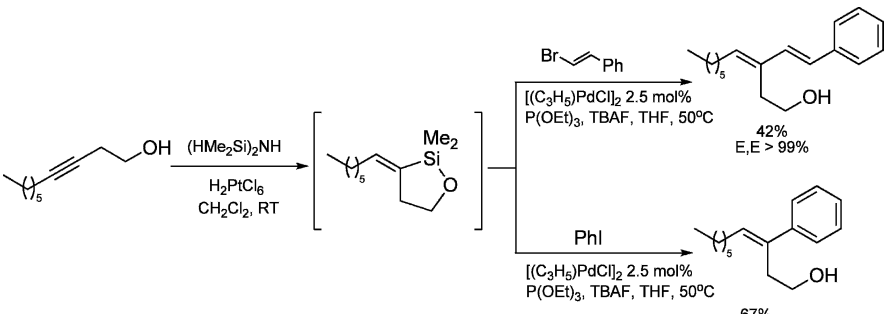
Although typically vinylsilanes with heteroatom substituents are necessary for efficient reactivity in cross-coupling processes, Trost et al. have recently disclosed the efficient Hiyama cross-coupling reaction of vinylsilanes bearing benzyldimethylsilyl groups. These compounds can be easily obtained by the ruthenium-catalysed "Markovnikov" hydrosilylation of terminal alkynes with benzyldimethylsilane. The palladium-catalysed cross-coupling of the obtained vinylsilanes with aryl or alkenyl iodides proceeds smoothly to afford geminal-substituted alkenes in regioselective manner [73] (Eq. 3.57).



(3.57)

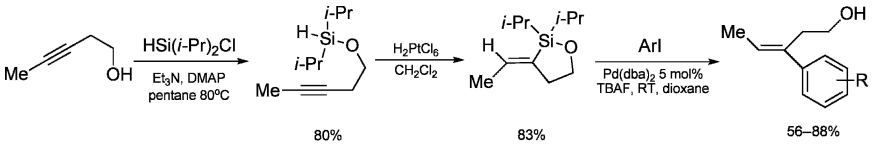
Recently, a series of studies have been reported on a combination of an efficient and stereo-controlled intramolecular hydrosilylation and a cross-coupling reaction [74–78]. Using this methodology, homopropargylic alcohols can be transformed into geometrically defined trisubstituted homoallylic alcohols *via* formal hydroarylation. As three steps of this transformation, i.e. alcohol silylation, hydrosilylation and C—C bond formation are mutually compatible, the reaction sequence can be carried out as a one-pot process, which is of great importance to organic synthesis.

The synthetic utility of the platinum-catalysed *exo-cis*-intramolecular hydrosilylation – palladium-catalysed cross-coupling sequence has been for the first time demonstrated by Tamao and Ito, who employed this strategy in the one-pot transformation of homopropargyl alcohols into stereodefined 3-aryl(alkenyl)-substituted (*E*)-homoallyl alcohols [65] (Eq. 3.58).



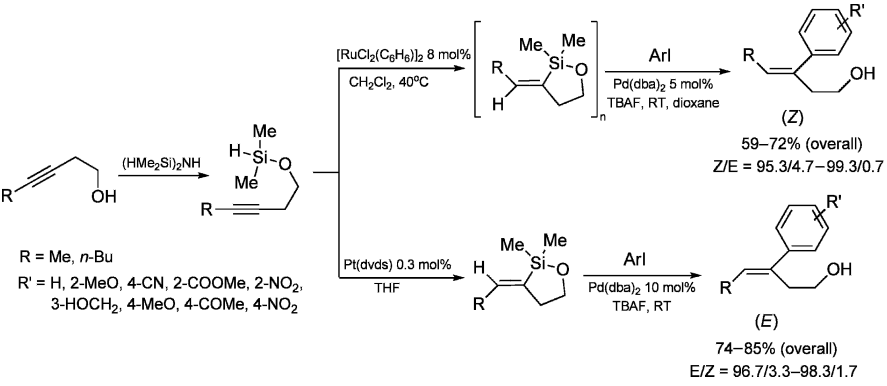
(3.58)

As trisubstituted homoallylic alcohol fragments are often encountered in natural products and are useful synthetic intermediates, much effort to develop their synthesis using sequential intramolecular hydrosilylation – cross-coupling methodologies have been made. Denmark et al. expanded the synthetical potential of platinum-catalysed *exo-cis* intramolecular hydrosilylation to obtain a series of (*E*)-3-aryl-3-penten-1-ols in highly stereoselective fashion and good yields [74] (Eq. 3.59).



(3.59)

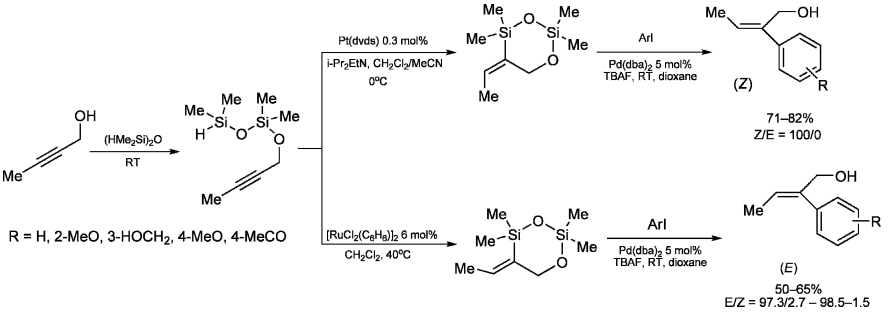
Denmark's group discovered the complimentary strategy to access the opposite geometrical isomers of homoallylic alcohols by using *exo-trans*-intramolecular hydrosilylation [75]. The unusual *anti*-addition was achieved in the presence of the ruthenium-arene complex: $[\{RuCl_2(C_6H_6)\}_2]$. The resultant (*Z*)-alkylidenesilacyclopentanes were then efficiently coupled (one-pot process) with aryl or alkenyl halides to give (*Z*)-trisubstituted homoallylic alcohols in good yields. As the stereochemical course of these reactions is defined by the configuration of *exo*-alkylidene intermediates, complimentary *cis*- (platinum) and *trans*- (ruthenium) hydrosilylation followed by stereospecific palladium-catalysed cross-coupling provide a general and predictable routes to functionalised (at 3-position) either (*E*) and (*Z*)-homoallylic alcohols [74–76] (Eq. 3.60).



(3.60)

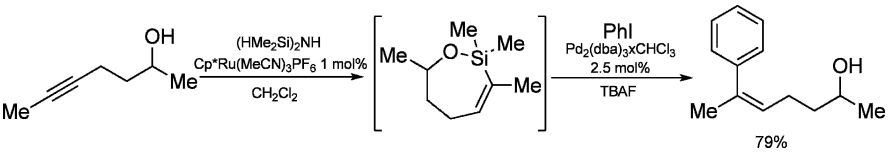
The ability to introduce silafunctional units in a controlled and stereoselective fashion acts well for the functionalisation of propargyl alcohols as well. Since the intramolecular hydrosilylation of silylated propargylic alcohols results in polymerisation due to the strain of oxasilacyclobutane intermediate, the use of an appropriate two-atom tether connecting the propargyloxy group to silylhydride moiety

is necessary to run the reaction successfully. An elegant approach to solve this problem using disiloxane tether has been recently described by Denmark and co-workers [76]. This approach involves the application of propargyloxytetramethyl-disiloxane (formed by copper-catalysed dehydrogenative silylation of propargyl alcohol derivative with tetramethyldisiloxane), which can participate in both *cis*-(platinum) and *trans*- (ruthenium) intramolecular hydrosilylation to afford cyclic six-membered (*E*)- and (*Z*)-*exo*-alkylidene carbosiloxanes respectively (Eq. 3.61). Subsequent stereospecific palladium-catalysed cross coupling processes led stereoselectively to functionalised (at 2-position) either (*E*)- or (*Z*)-2,3-disubstituted allylic alcohols.



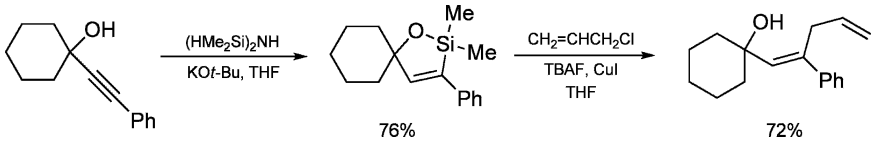
(3.61)

The sequence of ruthenium-catalysed intramolecular *trans*-hydrosilylation of substituted bishomopropargyl alcohol and subsequent cross-coupling provides an excellent method for introducing an aryl group at the alkyne carbon that is at a remote position from a hydroxyl group [30, 77] (Eq. 3.62).



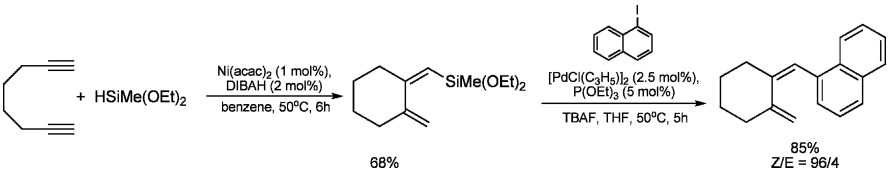
(3.62)

Oxasilacyclopentenes containing *endo*-cyclic bonds, easily obtained through potassium-*tert* butoxide catalysed intramolecular *trans*-hydrosilylation, could be transformed into 1,4-dienes under conditions developed by Takeda et al. [78] (Eq. 3.63).



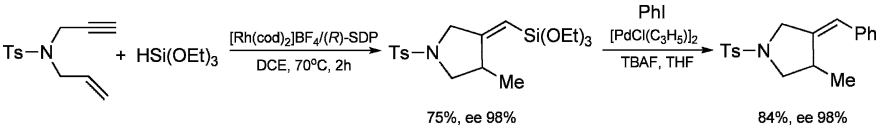
(3.63)

The application of the sequential cyclisation/hydrosilylation and cross-coupling reactions has been investigated as well. Tamao and Ito combined the consecutive Ni(0)-catalysed silylcarbocyclisation of 1,7-diynes with a cross-coupling reaction [79] (Eq. 3.64).



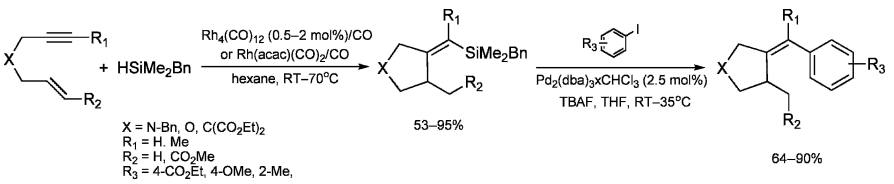
(3.64)

More recently, Zhou et al. described an enantioselective rhodium-catalysed silylcarbocyclisation of 1,6-enynes with a cross-coupling [58] (Eq. 3.65).



(3.65)

Denmark and co-workers reported the sequential rhodium-catalysed silylcarbocyclisation of a wide range of 1,6-enynes followed by palladium-catalysed cross-coupling reactions, to provide access to functionalised cyclopentanes or heterocycles with highly substituted *exo*-cyclic double bonds. 1,6-enynes reacted with benzyldimethylsilane in the presence of $[Rh_4(CO)_{12}]$ under CO atmosphere to afford five-membered rings bearing (*Z*)-alkylidenebenzylsilyl group, which then could be transformed into densely functionalised 3-(*Z*)-benzylidenecyclopentanes under mild cross-coupling conditions in high yields and complete stereoselectivities [80] (Eq. 3.66).

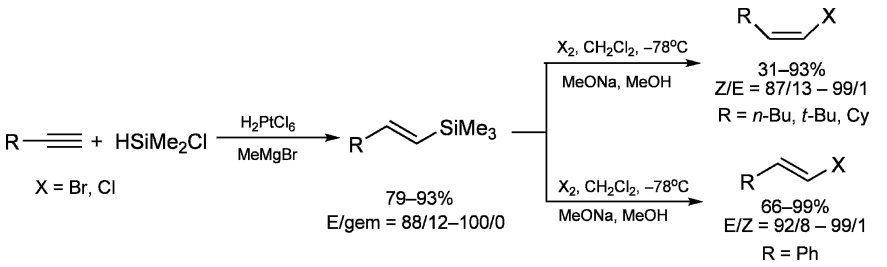


(3.66)

3.4 Miscellaneous Advanced Synthetic Methodologies Including Hydrosilylation

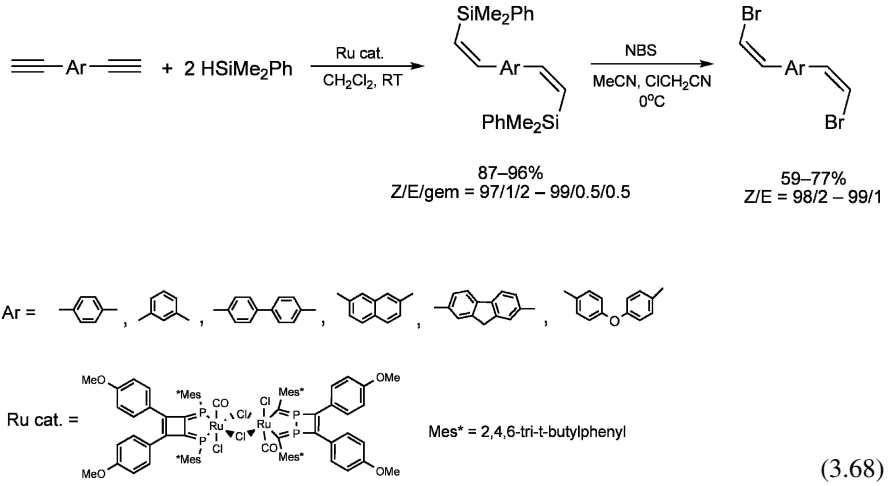
The sequential reactions described in the foregoing sections do not exhaust the synthetic potential of the hydrosilylation reaction in organic synthesis.

Hydrosilylation–halodesilylation sequence can be used for the stereoselective preparation of synthetically useful alkenyl halides from alkynes. Pioneering work of Miller et al., reported a combination of the platinum-catalysed *cis*-hydrosilylation and the chloro– or bromodesilylation of the resulting (*E*)-alkenylsilanes to give substituted 1-haloalkenes [81] (Eq. 3.67). When alkynes with alkyl or cycloalkyl groups were used, halodesilylation proceeded with inversion of configuration giving (*Z*)-alkenyl halides, whereas the presence of phenyl substituent changed the stereochemical outcome for retention of configuration to form (*E*)-styryl halides [82].



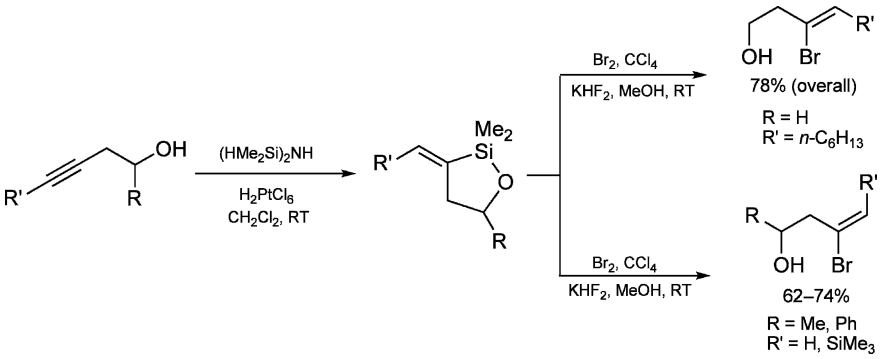
(3.67)

(*Z*,*Z*)-bis(2-bromoethenyl)arenes, the useful precursors for arylene-vinylene polymers can be successfully prepared by (*Z*)-selective hydrosilylation of dialkynylarenes by dimethylphenylsilane in the presence of ruthenium complex bearing diphosphinidenecyclobutene ligand, followed by stereospecific NBS-mediated bromodesilylation of the hydrosilylation products [82, 83] (Eq. 3.68).



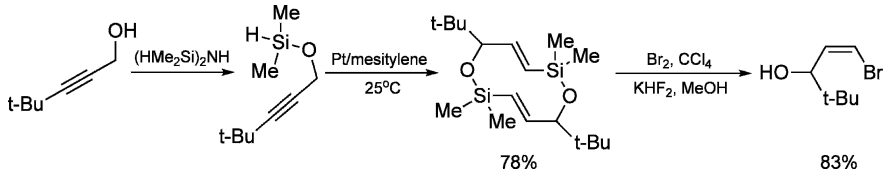
(3.68)

The platinum-catalysed intramolecular hydrosilylation of homopropargyl alcohols followed by bromodesilylation has been demonstrated by Tamao [24] and Caporusso [84] groups as a convenient route to bromoalcohols containing either (*Z*)- [24] or (*E*)-alkenyl [84] fragments (Eq. 3.69).



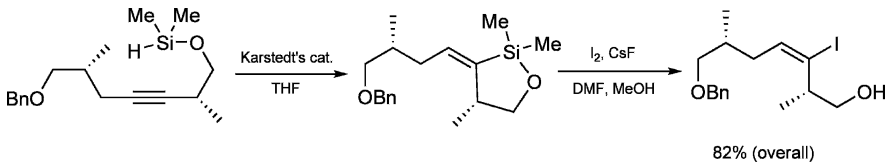
(3.69)

On the other hand, a combination of the Pt-catalysed intramolecular hydrosilylation of silylated propargyl alcohol derivative and bromodesilylation afforded (*Z*)-1-bromo-4,4-dimethyl-1-penten-3-ol [84] (Eq. 3.70).



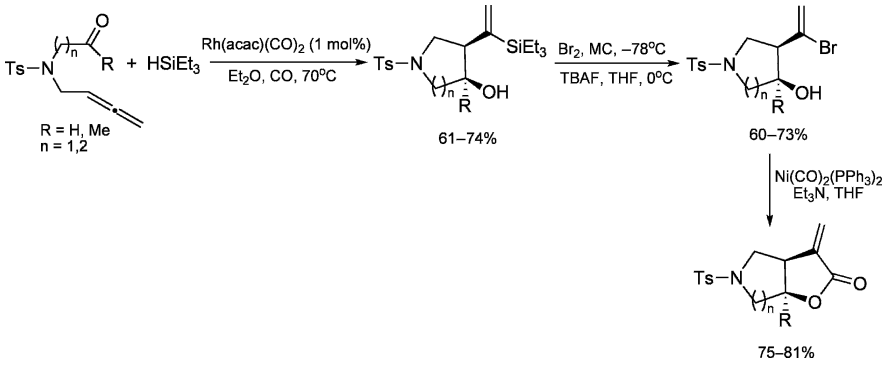
(3.70)

More recently, the intramolecular hydrosilylation–iododesilylation strategy has been used as a key step in the total synthesis of *neooxazolomycin* – oxazole-polyene *Streptomyces* antibiotic [85] (Eq. 3.71).



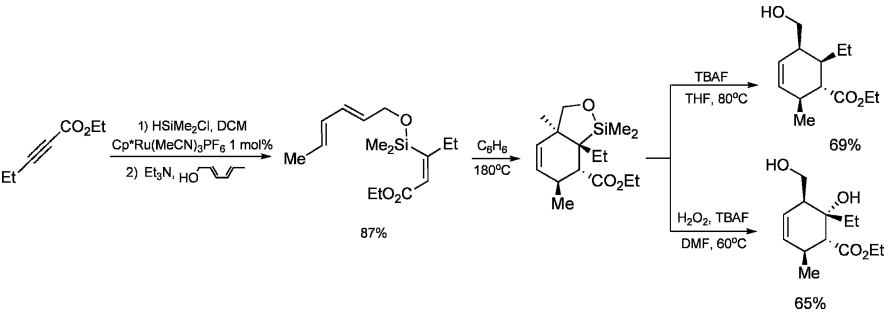
(3.71)

Cis-2-trimethylsilylvinylcyclopentanols and –cyclohexanols obtained through rhodium-catalysed silylcarbocyclisation of allenyl carbonyl compounds can serve as precursors to the synthesis of *cis*-bromovinylcycloalkanols and consequently α-methylene-γ-butyrolactones [86] (Eq. 3.72).



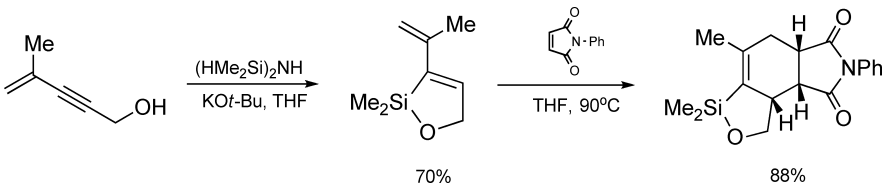
(3.72)

The use of ruthenium-catalysed hydrosilylation as an entry to the silicon-tethered Diels–Alder reaction has been reported [87, 88]. It has been demonstrated that the hydrosilylation products, (*Z*)-alkenylsilanes, can be easily transformed into bicyclic silyl ethers with four contiguous stereocenters *via* intramolecular Diels-Alder reaction [31] (Eq. 3.73). The resultant adducts could then be treated to protodesilylation or Tamao-Fleming conditions to furnish the cyclic primary alcohols or the diols, respectively [31].



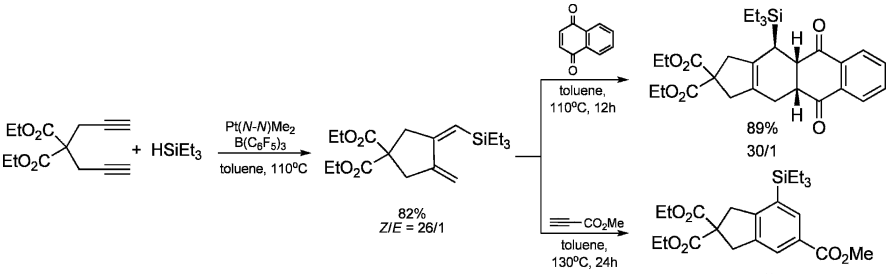
(3.73)

Another example illustrating the utility of hydrosilylation/Diels–Alder sequence has been recently reported by Welker et al. Intramolecular hydrosilylation of hydroxyl-substituted enynes led to silicon-containing 1,3-dienes, which then underwent efficient cycloaddition with substituted maleimide to give tricyclic compound [87] (Eq. 3.74).



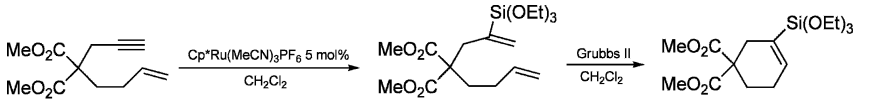
(3.74)

The silylated 1,2-dialkylidenecyclopentanes formed *via* platinum-catalysed cyclisation/hydrosilylation of 1,6-diynes undergo the Diels-Alder [4+2,] cycloaddition with a range of dienophiles including maleimides, quinones and methyl propiolates to yield polycyclic compounds with high *endo*-selectivity [57, 88] (Eq. 3.75).



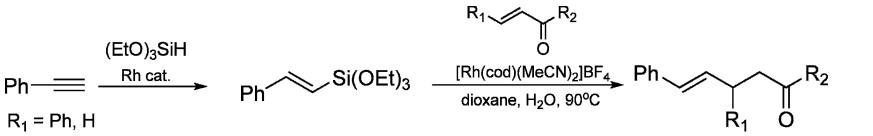
(3.75)

The products of ruthenium-catalysed internal alkyne *trans*-hydrosilylation (α-vinylsilanes) are active towards ring-closing metathesis with Grubbs' 2nd generation catalyst, yielding silicon-functionalised carbocyclic compounds that are amenable to further transformations [31] (Eq. 3.76).



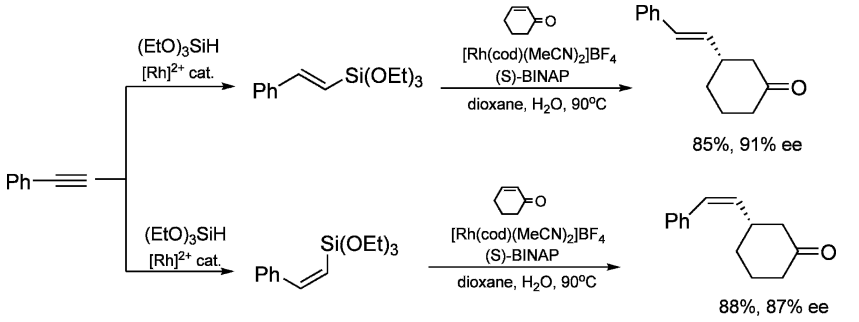
(3.76)

Alkenylsilanes are also useful as Michael acceptors in transition metal-catalysed conjugate addition reactions. (*E*)-Styryltriethoxysilanes, obtained from phenylacetylene using the hydrosilylation procedure reported by Ojima [89], have been subjected to rhodium-catalysed conjugate addition with α,β-unsaturated carbonyl compounds to give alkenyl-substituted ketones [90] (Eq. 3.77).



(3.77)

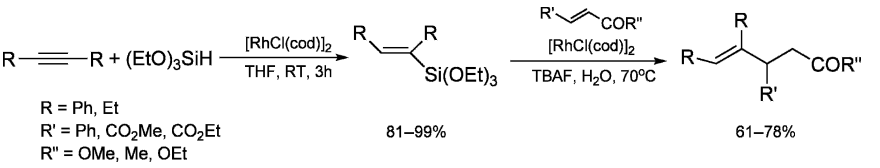
The asymmetric version of this process, proceeding in the presence of [{Rh(cod)$(MeCN)_2$}BF_4] and (S)-BINAP enables enantioselective introduction of both (*E*)- and (*Z*)-alkenyl groups into the β-position of ketones [91] (Eq. 3.78) by the use of stereodefined alkenylsilanes, prepared *via* dicationic rhodium complex-catalysed phenylacetylene hydrosilylation reported by Faller [92] (Chapter 2, Eq. 2.18).



(3.78)

The one-pot synthesis of cyclic α,β-unsaturated ketones involving the [{Rh((*S*)-BINAP)$(MeCN)_2$}BF_4]-catalysed asymmetric 1,4-addition of alkenylsilanes, generated by hydrosilylation of terminal alkynes, has been reported by Hayashi et al. [93].

The [{RhCl(cod)}$_2$]-catalysed hydrosilylation of internal alkynes followed by [{RhCl(cod)}$_2$]-catalysed conjugate addition with α,β-unsaturated carbonyl compounds such as unsaturated ketones and esters, has also been reported [44] (Eq. 3.79). The reaction can be carried out as a tandem process in one-pot under mild conditions to give multifunctionalised stereodefined alkenes directly from internal alkynes.



(3.79)

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Chapter 4
Asymmetric Hydrosilylation of Prochiral Alkenes and Their Derivatives

Abstract Asymmetric hydrosilylation of prochiral alkenes followed by Tamao-Fleming oxidation is a convenient method of synthesis of enantioenriched secondary alcohols. In this chapter asymmetric hydrosilylation of unsaturated carbon—carbon bond(s) in various families of reagents such as terminal and internal olefins, cycloolefins, 1,3-dienes, enynes and diynes as well as asymmetric intramolecular hydrosilylation of alkenylsilanes and cyclisation/hydrosilylation of non-conjugated dienes are reviewed. All these transformations proceed efficiently in the presence of palladium and to a minor extent in the presence of rhodium based complexes. Selected processes catalysed by yttrium and lanthanide complexes are also discussed. The chapter ends with brief presentation of some examples of free radical initiated asymmetric hydrosilylation.

Hydrosilylation of terminal olefins in the presence of platinum or rhodium complexes proceeds with *anti*-Markovnikov selectivity giving 1-silylalkanes. Formation of 2-silylalkanes containing a stereogenic carbon centre requires a catalytic system enabling reverse regioselectivity. The use of chiral catalysts in systems ensuring the desired regioselectivity can lead to formation of enantioenriched alkylsilanes. Subsequent oxidation of the carbon—silicon bond by using Tamao-Fleming oxidation protocol [1–4], which proceed with complete retention of configuration at the stereogenic carbon centre, allows efficient synthesis of chiral alcohols. The one pot asymmetric hydrosilylation / Tamao-Fleming oxidation sequence (equivalent to an enantioselective Markovnikov hydration of an olefin) have become one of the most useful, general methods for preparation of optically active alcohols from alkenes. Asymmetric 1,4-hydrosilylation of 1,3-dienes is another synthetically useful reaction as it leads to formation of enantioenriched allylsubstituted silanes, which are useful chiral allylation agents. Asymmetric hydrosilylation of carbon—carbon double bond is catalysed mainly by transition metal complexes. The protocols involve the use of catalyst generated *in situ* from a metal source and an optically active ligand or pre-synthesised. A high reaction rate and enantioselectivity can be achieved by realisation of an appropriate molecular architecture of a catalyst and suitable selection of reagents and reaction conditions. The first report on enantioselective hydrosilylation of olefins appeared in 1971. Formation of enantioenriched (ee = 5%)

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product in the reaction of 2-phenylpropene with methyldichlorosilane in the presence of *cis*-[$PtCl_2(C_2H_4)$] combined with (*R*)-benzylmethylphenylphosphine was communicated by Hayashi [5]. Since then new efficient and highly enantioselective catalytic systems have been developed. In this chapter the progress in the asymmetric hydrosilylation of unsaturated carbon—carbon bond that has been made since 1990 is reviewed. This topic is covered by a number of review articles [6–15].

4.1 Palladium-Based Catalysts

4.1.1 Hydrosilylation of Olefins

Palladium catalyst precursors combined with chelating diphosphine ligands such as CHIRAPHOS or BINAP do not exhibit catalytic activity in hydrosilylation of olefins. In 1991 Hayashi, reported the synthesis of an axially chiral monodentate phosphine ligand family based on 2-di(phenyl)phosphine-1,1'-binaphthyls (MOP's) (Fig. 4.1) [16, 17]. These ligands combined with palladium precursor were found highly active, regio- and enantioselective in the asymmetric hydrosilylation of terminal [16,18] and cyclic olefins [19,20] with trichlorosilane. High conversions were achieved by using as low as 0.01 mol % of the catalyst. Moreover, highly regioselective course of the hydrosilylation, unusual for the other transition metal-based catalysts, consistent with the Markovnikov rule was observed for linear 1-alkenes. Vinylcyclohexane, and terminal olefins bearing bulky group at the double bond undergo hydrosilylation with lower regioselectivity.

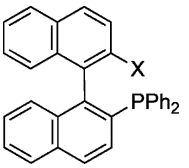


Fig. 4.1 X-MOP

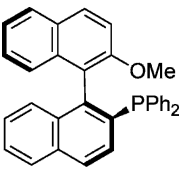


Fig. 4.2 (*S*)-MeO-MOP

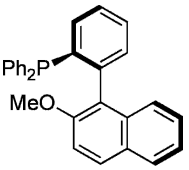
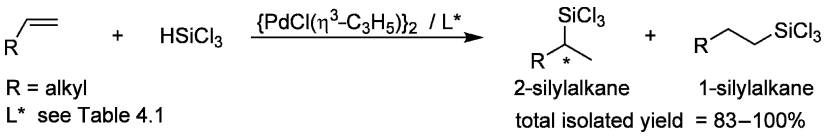
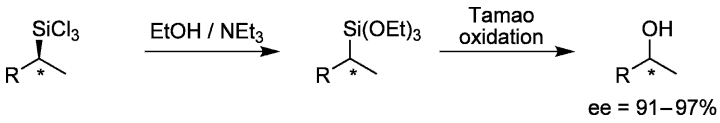


Fig. 4.3 (*S*)-NAPHEP

The X-MOP ligands tested (Fig. 4.1) (where X=OMe, O(*i*-Pr), OCH_2Ph, Et) gave almost identical results, indicating that the substituents X did not have significant effects on the catalytic activity and selectivity (Eq. 4.1). Subsequent alkoholysis and oxidation allows synthesis of respective alcohols with high regio- and enantioselectivity (Eq. 4.2). Recently, new axially chiral P-monodentate (or P,O-bidentate) biaryl ligands (NAPHEP) (Fig. 4.3) have been synthesised. Palladium catalysed hydrosilylation of terminal olefins with trichlorosilane in the presence of (*S*)-NAPHEP allows enantioselectivity (of the respective alcohol) exceeding 90%. However, the reaction proceeds with considerably lower regioselectivity (Table 4.1) [21].



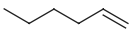
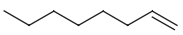
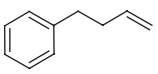
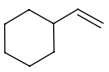
(4.1)



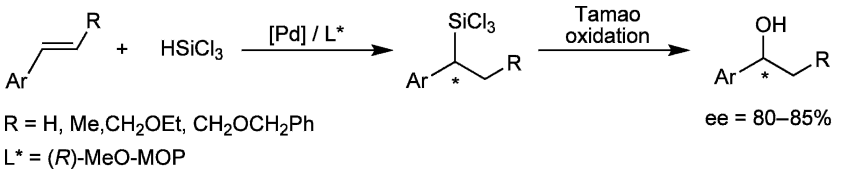
(4.2)

$[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$ combined with MeO-MOP (Fig. 4.2) was proved to be regio- and enantioselective in hydrosilylation of β-substituted styrenes with trichlorosilane (Eq. 4.3) [22]. 1-Aryl-1-silylalkanes were synthesised with very high regioselectivity and enantioselectivity ranging from 80 to 85%.

Table 4.1 Palladium catalysed asymmetric hydrosilylation of terminal olefins in the presence MOP ligands

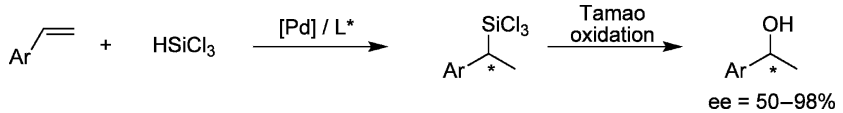
Substrate	Ligand	Yield[a] [%]	regioisomers ratio[b]	Ee[c] [%] (config.)	Ref.
	Fig. 4.2	91	89/11	94 (*R*)	[16]
	Fig. 4.3	61	76/24	91 (*R*)	[21]
	Fig. 4.2	83	93/7	95 (*R*)	[16]
	Fig. 4.1, X = O(*i*-Pr)	88	90/10	91 (*R*)	[16]
	Fig. 4.1, X = Et	80	90/10	93 (*R*)	[16]
	Fig. 4.3	59	77/23	93 (*R*)	[21]
	Fig. 4.2	90	81/19	97 (*S*)	[16]
	Fig. 4.3	53	65/35	93 (*R*)	[21]
	Fig. 4.2	100	66/34	96 (*R*)	[16]

Reaction conditions: 0.1 mol% $[\{PdCl(\eta^3\text{–}C_3H_5))_2]$, 24 h, 40°C, neat, [Pd]:[L] 1:2, [C C]:[$HSiCl_3$] 1:1.2; [a] of silyl derivative (mixture of regioisomers); [b] [α-adduct]/[β-adduct]; [c] determined after oxidation.



(4.3)

Although simple terminal alkenes such as 1-octene have been efficiently converted into the corresponding secondary alkyl alcohols with enantioselectivity exceeding 90% by use of a palladium catalyst coordinated with MeO-MOP (Fig. 4.2), the hydrosilylation of styrene derivatives has not resulted in enantioselective transformation. Therefore, new MOP derivatives containing different substituents at 2'-position of the naphthyl moiety were prepared and tested for their applicability as ligands. Surprisingly, (*S*)-2-diphenylphosphino-1,1′-binaphthyl (H-MOP) (Fig. 4.4) appeared to be particularly effective for the enantioselective palladium-catalysed hydrosilylation of styrenes to give (after Tamao oxidation) the corresponding benzylic alcohols with high enantiomeric purity ranging from 89 to 96% ee (Eq. 4.4) (Table 4.2) [23]. High enantioselectivity was also observed for structurally related monodentate chiral phosphine ligand (Fig. 4.5) (Table 4.2) [24]. Replacement of the phenyl substituent with the methyl groups in the structure of the ligand has resulted in a significant decrease in the enantioselectivity (Table 4.2). Enantioselectivities reported for the hydrosilylation of styrenes with trichlorosilane in the presence of ligand (Fig. 4.6) ranged from 10 to 50% depending on the substrate [25].



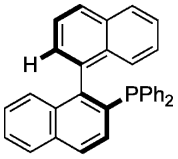
(4.4)

Table 4.2 Palladium catalysed asymmetric hydrosilylation of styrene in the presence of MOP ligands

Ligand	Time [h]	Temp. [°C]	Yield [%][a]	Ee [%][b] (config.)	Ref.
Fig.4.2	44	5	100	71 (*R*)	[23]
Fig.4.4	32	–10	92	94 (*R*)	[23]
Fig.4.4	32	5	100	92 (*R*)	[26]
Fig.4.5	24	0	–	91 (*R*)	[24]
Fig.4.6	24	40	91	10 (*S*)	[23]
Fig.4.7	70	r.t.	100	72 (*S*)	[27]
Fig.4.8	10	0	78	95 (*R*)	[28]
Fig.4.9	40	25	70	50 (*S*)	[29]
Fig.4.10	12	0	100	93 (*S*)	[30]
Fig.4.11	24	–20	85	98 (*S*)	[30]

Reaction conditions: 0.1 mol% [{PdCl(η^3–C_3H_5)}$_2$]; [Pd]:[L] = 1:2, [C=C]:[$HSiCl_3$] = 1:1.2; [a]of silyl derivative; [b]determined after oxidation.

Fig. 4.4



(*S*)-H-MOP

Fig. 4.5

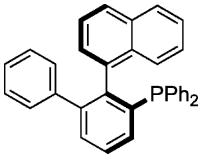
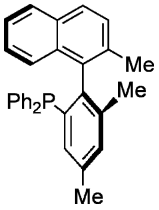


Fig. 4.6

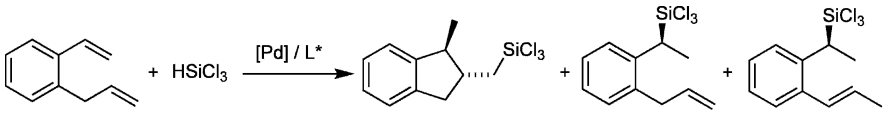


(*S*)-2-diphenylphosphino-2'-diphenylphosphinyl-1,1'-binaphthalene (*S*)-BINAPO (Fig. 4.7) has been tested as a chiral inducer in the Pd-catalysed asymmetric hydrosilylation of styrene. The reaction performed in the neat substrate gave quantitative conversion with complete regioselectivity for the branched isomer affording after oxidative work-up, (*S*)-1-phenylethanol in 18% ee. The ee increased up to 72% when the reaction was run in benzene [27]. A 2'-Sb-substituted 2-phosphano-1,1'-binaphthyl (Fig. 4.8) combined with $[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$ catalyses hydrosilylation of styrene to give (after oxidative work up) 1-phenylethanol with 78% yield and 95% ee. No perceptible enantioselectivity was observed for 2,2'-antimony substituted derivative [28]. The structural analogue with sulphur in position 2' (Fig. 4.9) in the presence of suitable Pd-complexes catalyses asymmetric hydrosilylation of styrene with trichlorosilane leading (after oxidation) to (*S*)-1-phenylethanol with 90% regioselectivity and 50% ee [29].

Further structure optimisation of the MOP ligand family involved modification of diphenylphosphino group [30]. Several chiral monophosphine ligands, (*R*)-2-diarylphosphino-1,1'-binaphthyls (Fig. 4.10), (where Ar=C_6H_5, 4-C_6H_4(OMe), 4-$C_6H_4(CF_3)$, 3,5-$C_6H_3Me_2$, 3,5-$C_6H_3Cl_2$, 3,5-$C_6H_3(CF_3)_2$) have been tested in the palladium-catalysed asymmetric hydrosilylation of styrene with trichlorosilane (Table 4.2) [30]. The highest enantioselectivity was observed for $[\{PdCl(\eta^3\text{-}C_3H_5)_2\}_2]$ / (*R*)-2-bis[3,5-bis(trifluoromethyl)phenyl]phosphino-1,1'-binaphthyl

(Fig. 4.11), system which gave (*S*)-1-phenylethanol with 93% yield and 98% ee after oxidation of the hydrosilylation product.

The same system efficiently catalyses asymmetric hydrosilylation of substituted styrenes to give (after oxidation) the corresponding chiral benzylic alcohols with the yields 81–92% and selectivities up to 98% ee (Table 4.2) [30, 31]. The hydrosilylation of 2-allylstyrene results in formation of a mixture of cyclic and linear products (Eq. 4.5).



[Pd] = [{PdCl(η^3-C_3H_5)$_2$}$_2$]
L* see Fig. 4.11

yield = 35%
ee = 91% (1*S*,2*R*)

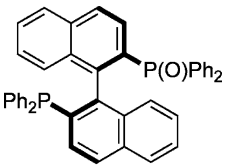
yield = 31%
ee = 95% (*S*)

yield = 8 %
ee = 95 % (*S*)

(4.5)

On the basis of the mechanistic studies, the hydrosilylation of styrene with trichlorosilane catalysed by palladium complexes coordinated with a tertiary phosphine ligand has been proposed to proceed according to the Chalk and Harrod mechanism which involves oxidative addition of Si—H bond to palladium complex (**1**) with formation of **2**, hydropalladation of an olefin on hydride(silyl)(olefin)palladium complex (**2**) generating alkyl(silyl)palladium species (**3**) and reductive elimination of the alkyl and silyl fragments from **3** forming a hydrosilylation product and regenerating complex **1** (Scheme 4.1) [30].

In 2002 Hayashi reported efficient and practical catalytic asymmetric synthesis of 1-aryl-1,2-diols. The method involves successive platinum- and palladium-catalysed hydrosilylation of arylacetylenes with trichlorosilane leading to bis(silyl)ethanes and subsequent Tamao oxidation (Eq. 4.6) [32]. Asymmetric hydrosilylation step utilises highly enantioselective catalytic system with MOP ligand (Fig. 4.11). A variety of 1-aryl-1,2-diols were obtained with moderate to high yields 50–87% and high enantiomeric excess ranging from 94 to 98%. Alkylsubstituted acetylenes cannot be converted into the corresponding 1,2-diols by this method.



(*S*)-BINAPO

Fig. 4.7

Fig. 4.8

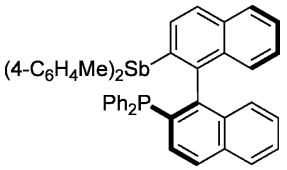


Fig. 4.9

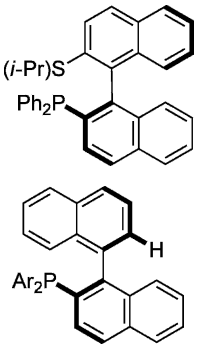


Fig. 4.10

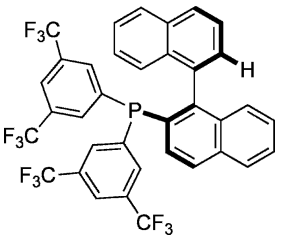
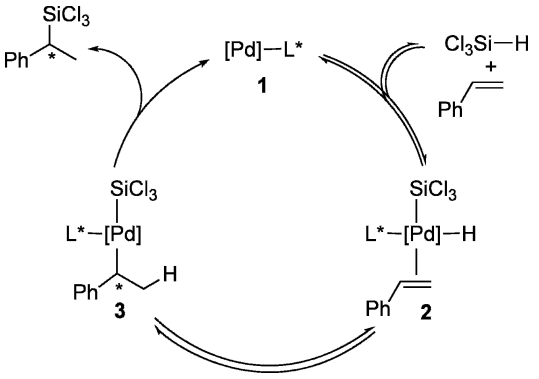
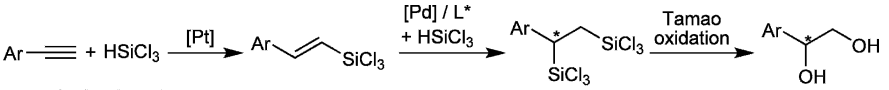


Fig. 4.11



Scheme 4.1 Mechanism of asymmetric hydrosilylation of styrene in the presence of palladium complexes



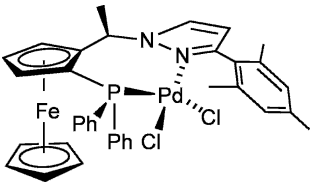
[Pt] = [{$PtCl_2(C_2H_4)$}$_2$]

[Pd] = [{$PdCl(\eta^3\text{-}C_3H_5)$}$_2$], L* see Fig. 4.11

(4.6)

The use of chiral ferrocenyl phosphine amine ligands in Pd-catalysed hydrosilylation of olefins was first reported by Hayashi [33]. In 1998 Togni reported applications of non-racemic ferrocenyl phosphine amine ligands in asymmetric hydrosilylation [34]. Hydrosilylation of styrene with $HSiCl_3$ in the presence of palladium complex (Fig. 4.12) permits (after oxidation step) the synthesis of the corresponding (*S*)-1-aryl alcohols with 39–71% yield and up to 67% of enantiomeric excess (Table 4.3). Pronounced effect of electronic properties of the substituents at phenyl ring was observed for a series of 4-substituted styrenes [34].

Fig. 4.12



Detailed theoretical investigation of the mechanism of palladium-catalysed hydrosilylation indicated that the reaction proceeds in agreement with the classical Chalk-Harrod mechanism, according to which the active catalyst of hydrosilylation is a (silyl)hydride palladium complex [35]. The factors determining the enantioselectivity in this system have been rationalised by performing mixed QM/MM Car-Parrinello molecular dynamics simulations with styrene and 4-(dimethylamino) styrene as unsaturated substrates [36]. A family of aryl monophosphine ferrocene ligands (MOPF) (Fig. 4.13) described by Pedersen were tested in combination with Pd source in asymmetric hydrosilylation of styrene with trichlorosilane and found to exhibit slightly better activity and selectivity. Hydrosilylation of styrene in the presence of ligand (Fig. 4.13a) and subsequent oxidation allow synthesis of 1-phenylethanol with 73% yield and 70% ee (Table 4.3) [37]. Development of the Pd / MOPF system resulted in a further increase in enantioselectivity. In the

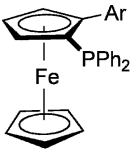
Table 4.3 Palladium catalysed asymmetric hydrosilylation of styrene with trichlorosilane in the presence of planar chiral ligands

Catalytic system	Temp. [°C]	Time [h]	Yield[a] [%]	Ee[b] [%] (config.)	Ref.
Fig. 4.12	–	–	63	63.4 (*S*)	[34]
$[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$ / Fig. 4.13a	r.t.	36	73	70 (*S*)	[37]
$[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$ / Fig. 4.14	r.t.	5.5	100	90 (*S*)	[38]
$[PdBr(\eta^3\text{-}C_3H_5)\}_2]$ / Fig. 4.16	–50	48	–	92 (*S*)	[39]
$[PdBr(\eta^3\text{-}C_3H_5)\}_2]$ / Fig. 4.17	–40	48	–	87 (*S*)	[39]
$[PdCl_2(cod)]$/Fig. 4.18	r.t.	48	99	73	[40]

Reaction conditions: 0.05–0.5 mol% $[Pd_2]$; [Pd]:[L*] = 1:2; [styrene]:[$HSiCl_3$] = 1:1.2 – 1:1.5; [a]of silyl derivative; [b]determined after oxidation.

presence of 4-methoxyphenyl- (Fig. 4.14) or 1-naphthyl-substituted ferocenylphosphine (Fig. 4.15), (*S*)-1-phenylethanol was formed with ee 90 and 86%, respectively. Very high turnover frequency (exceeding 180 000 h^{-1}) was achieved by tuning the [Pd]/MOP ratio [38].

Fig. 4.13



(*S*)-MOPF
a Ar = Ph
b Ar = 2-C_6H_4OMe

Fig. 4.14

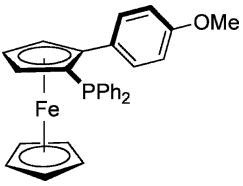
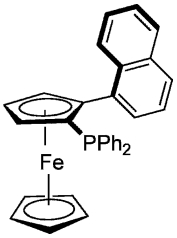


Fig. 4.15



A family of planar chiral bidentate ligands were synthesised via modifications of the aromatic ring in arene tricarbonyl chromium complex and tested in palladium catalysed asymmetric hydrosilylation of styrenes with trichlorosilane. High yields (73–92%) and enantioselectivities have been observed for thiophene and furan derivatives (Figs. 4.16 and 4.17) as ligands (Table 4.3) [39].

Fig. 4.16

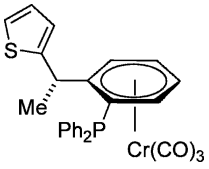
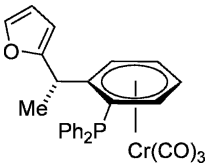
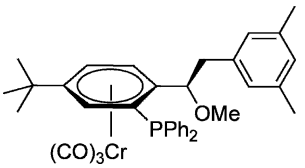


Fig. 4.17

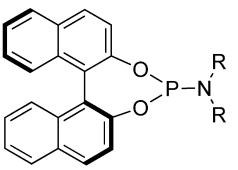


Similar complexes (e.g. Fig. 4.18) exhibit lower enantioselectivity in the palladium-catalysed asymmetric hydrosilylation of styrene (Table 4.3) [40]. The identity of benzylic substituent was found to have a significant effect on the enantioselectivity of the resulting catalysts. Planar chirality plays an important role in the outcome of the reaction. Removal of the tricarbonylchromium(0) unit from the structurally optimised phosphine ligand leads to reduced enantioselectivities.

Fig. 4.18



Phosphoramidite ligands introduced by Feringa (Fig. 4.19) characterised by axially chiral BINOL structure in combination with a phosphorus–nitrogen bond were modified by introduction of chiral substituents at the nitrogen (Fig. 4.20) and tested in the palladium catalysed hydrosilylation of styrenes with trichlorosilane [41]. Reaction proceeds highly regio- and enantioselectively for a variety of substituted aromatic alkenes. After efficient Tamao oxidation step a range of benzylic alcohols of high optical purity were obtained (Table 4.4). A similar system containing chiral spirophosphoramidite ligand with a 1,1'-spirobiindane scaffold (Fig. 4.21) exhibits a similar activity and enables the synthesis of the corresponding alcohols with ee up to 99.1% (Table 4.4) [42].

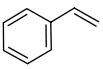
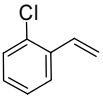
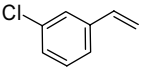
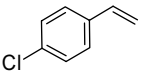
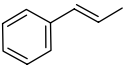


(*S*)-isomer

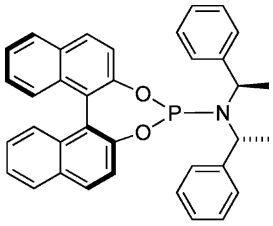
Fig. 4.19

In 2003 Tamura and Fujihara reported the catalytic activity of palladium nanoparticles stabilised by chiral BINAP (for (*S*)-BINAP see Chapter 10, Fig. 10.14) in the asymmetric hydrosilylation of styrene with trichlorosilane [43]. Hydrosilylation / oxidation sequence led to formation of 1-phenylethanol with ee up to 95% for reaction carried out at 0°C. In contrast, [{PdCl(η^3-C_3H_5)}$_2$] / BINAP system did not

Table 4.4 Palladium catalysed asymmetric hydrosilylation of styrene with $HSiCl_3$ in the presence of phosphoramidite ligands

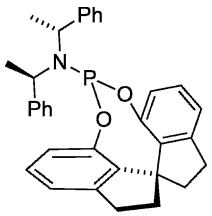
Styrene	Ligand	Temp. [°C]	Time [h]	Yield[a] [%]	Ee[b] [%] (config.)	Ref.
	Fig. 4.20	20	16	87[c]	99 (*R*)[c]	[41]
	Fig. 4.21	r.t.	2	99	97 (*R*)	[42]
	Fig. 4.20	r.t.	7	88	99.1 (*R*)	[42]
	Fig. 4.20	20	60	91[c]	98 (*R*)[c]	[41]
	Fig. 4.21	r.t.	9	86	95 (*R*)	[42]
	Fig.4.21	r.t.	3	90	96 (*R*)	[42]
	Fig. 4.20	40	40	91[c]	98 (*R*)[c]	[41]
	Fig. 4.21	r.t.	36	86	95 (*R*)	[42]

Reaction conditions: 0.125 mol% $[\{PdCl(\eta^3\text{–}C_3H_5)\}_2]$; [Pd]:[L]=1:2; [C=C]:[$HSiCl_3$]=1:2; [a]of silyl derivative; [b]determined after oxidation; [c]0.1 mol% $[\{PdCl(\eta^3\text{–}C_3H_5)\}_2]$; [Pd]:[L]=1:2; [C=C]:[$HSiCl_3$]=1:1.2



(*S*,*R*,*R*)-isomer

Fig. 4.20

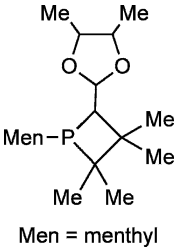


(*R*,*R*,*R*)-isomer

Fig. 4.21

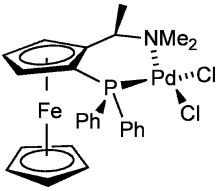
catalyse the reaction even at elevated temperature [44]. Electron-rich chiral phosphines – P-menthylphosphetanes having several chiral centres, (e.g., Fig. 4.22) exhibit modest enantioselectivity (up to 24% ee) in palladium-catalysed hydrosilylation of styrene [45, 46]. The observed enantioselectivities have been found to depend on the relative configurations of the sequence of the chiral centres.

Fig. 4.22

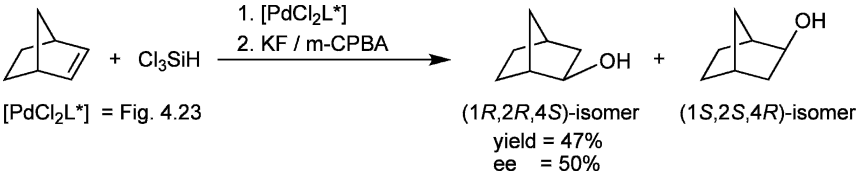


Men = menthyl

Fig. 4.23



Asymmetric hydrosilylation of norbornene was first reported by Hayashi for catalytic system utilizing ferrocenylphosphine (Eq. 4.7) [33]. The ferrocenyl ligand containing phosphine and pyrazole as donors (Fig. 4.24) combined with $[PdCl_2(cod)]$ exhibits moderate activity and modest to very high enantioselectivity in the hydrosilylation of norbornene with $HSiCl_3$.



[PdCl2L*] = Fig. 4.23

(1*R*,2*R*,4*S*)-isomer
yield = 47%
ee = 50%

(1*S*,2*S*,4*R*)-isomer

(4.7)

In the presence of $[PdCl_2(cod)]$ combined with ligand (Fig. 4.25) (*1R*, *2R*, *4S*)-2-norbornanol has been obtained with 50% yield and 99.5% ee [34].

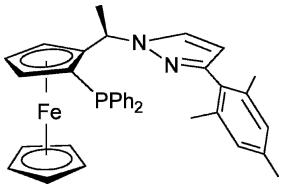
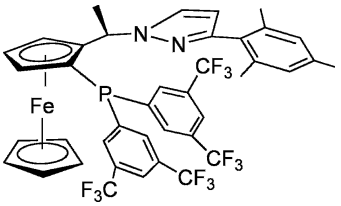
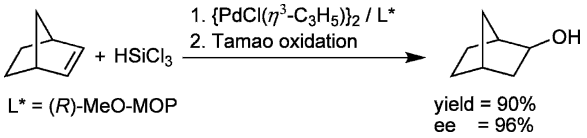


Fig. 4.24

Fig. 4.25

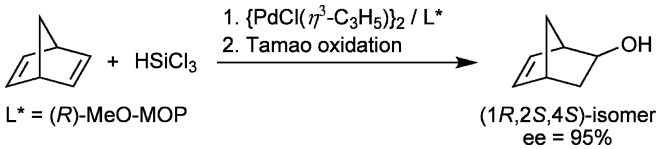


Efficient hydrosilylation of norbornene with trichlorosilane has been reported in the presence of (*R*)-MeO-MOP (for (*S*)-enantiomer see Fig. 4.2) combined with palladium catalyst precursor [19]. Asymmetric hydrosilylation followed by Tamao oxidation led to *exo*-2-norbornanol (eq. 4.8) The method was successfully tested for dimethylester derivative of norbornene and for bicycle[2.2.2]octene-6.



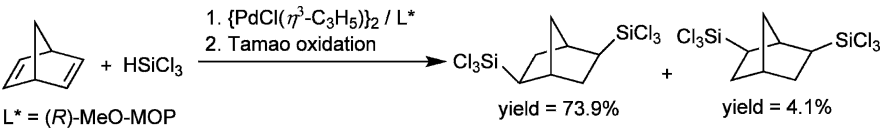
(4.8)

Monofunctionalisation of nornornadiene by hydrosilylation in the presence of palladium MOP catalyst leads to chemo- and enantioselective formation of *exo*-2-(trichlorosilyl)-5-norbornene (Eq. 4.9).



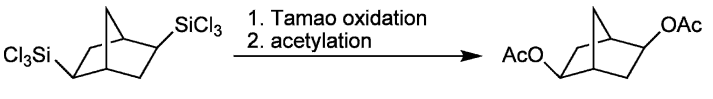
(4.9)

Hydrosilylation of both double bonds of norbornadiene can be easily achieved by using an excess (2.5 equiv.) of silane. In such conditions, enantioselective addition takes place resulting in formation of a mixture of two isomers with overall yield of 78% (Eq. 4.10) [19].



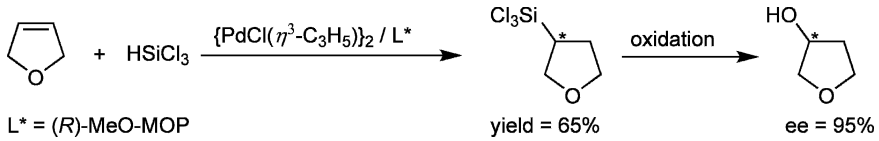
(4.10)

Oxidation of bis(silyl)norbornane followed by acetylation of the respective diol gives diacetate with ee exceeding 99% (Eq. 4.11).



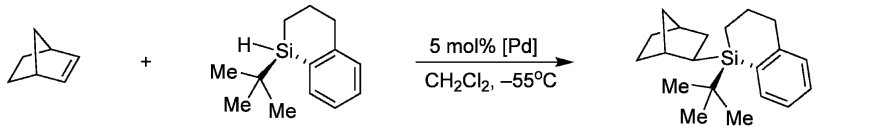
(1*R*,2*S*,4*R*,5*S*)-isomer
ee > 99% (4.11)

Hydrosilylation of dihydrofuran derivatives including 7-oxabicyclo[2.2.1] heptenes with trichlorosilane in the presence of Pd / (*R*)-MeO-MOP proceeds enantioselectively to give the respective products with ee up to 95% [20]. Treatment of 2,5-dihydrofuran with trichlorosilane followed by oxidative cleavage of the carbon–silicon bond by the modified Tamao protocol yields the corresponding alcohol with 95% of enantiomeric purity (Eq. 4.12).



L* = (*R*)-MeO-MOP
yield = 65%
ee = 95% (4.12)

Chirality transfer from silicon to carbon with perfect stereoselectivity was reported by Oestreich. Silane with silicon centred chirality undergoes hydrosilylation with norbornene and its derivatives in the presence of non-chiral palladium cationic phenanthroline complex [Pd(phenanthroline)Me(OEt_2)][B{3,5-$C_6H_3(CF_3)_2$}$_4$] [47]. In the reaction, the silicon reagent with the silicon-centred chirality induces the carbon centred chirality during the intermolecular formation of a carbon—silicon bond to a prochiral substrate. Reaction (Eq. 4.13) is a rare example of asymmetric amplification in the reagent-controlled reactions. Enantiometric excess determined for the obtained norbornylsilane was higher than the optical purity of the starting silane.



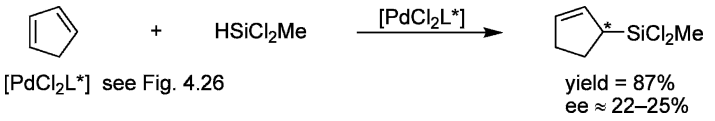
ee = 85%
yield = 58%, exo/endo = 99/1
de = 99%, ee = 93% (4.13)

The mechanism of intermolecular chirality transfer via a two-silicon cycle has been investigated by means of stereoisotopochemical probes in catalytic crossover experiments [48]. Application of silicon-stereogenic silanes in asymmetric catalysis has been summarised and discussed by Oestreich [49, 50].

4.1.2 Hydrosilylation of 1,3-Dienes

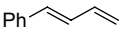
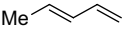
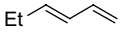
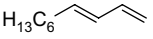
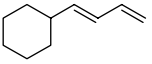
Palladium catalysed hydrosilylation of 1,3-dienes is an important method for synthesis of allylsilanes. In the presence of palladium-based catalysts the silanes containing electron withdrawing substituents at silicon usually undergo 1,4-

hydrosilylation to give allylsilanes with high regioselectivity. Enantioenriched allylsilanes are used as chiral allylating reagents as they readily react with a wide variety of electrophiles. The first examples reported by Hayashi, concerned the hydrosilylation of 1,3-cyclopentadiene with dichloromethylsilane catalysed by PPFA palladium complex (Fig. 4.23) producing allylsilane with 24% ee (Eq. 4.14) (Table 4.5) [51].



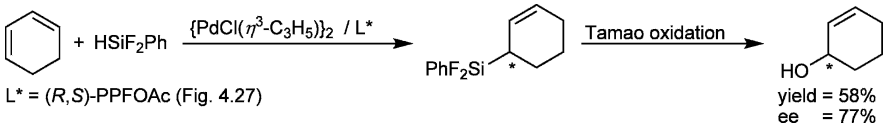
(4.14)

Table 4.5 Palladium catalysed asymmetric hydrosilylation of 1,3-dienes in the presence of PPF ligand family

Substrate	Catalyst / catalytic system	Temp. [°C]	Time [h]	Yield[a] [%]	Ee[b] [%] (config.)	Ref.
	Fig. 4.23	30	20	87[c]	13[c] (*S*)	[51]
	$[PdCl_2L^*]$, L* = Fig. 4.26	–	–	87[d]	60[d] (*S*)	[52]
	$[PdCl_2(PhCN)_2]$ / L* L* see Fig. 4.27	r.t.	20	58	77 (*S*)	[53]
	Fig. 4.23	r.t.	20	–	69 (*S*)	[53]
	Fig. 4.23	r.t.	20	–	69 (*S*)	[53]
	Fig. 4.23	r.t.	20	–	69 (*S*)	[53]
	$[PdCl(\eta^3\text{-}C_3H_5)_2]$ / L* L* see Fig. 4.28	–5	168	72[d]	93[d] (*S*)	[54]
	$[PdCl(\eta^3\text{-}C_3H_5)_2]$ / L* L* see Fig. 4.28	–5	168	75[d]	90[d] (*S*)	[54]

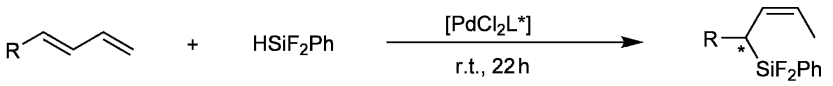
Reaction conditions: 0.01 – 0.1 mol% [Pd]; [Pd]:[L*] = 1:1 or 1:2; $HSiF_2Ph$, [diene]:[silane]=1:1.2 or 1:2; [a]of silyl derivative; [b]determined for alcohols; [c]$HSiCl_2Me$ was used; [d]$HSiCl_3$ was used.

Ligand modification by introduction of perfluoroalkyl group at the nitrogen (Fig. 4.26) enabled the synthesis of (*R*)-3-trichlorosilylcyclopentene with 60% ee [52]. 1,3-Cyclohexadiene undergoes palladium catalysed asymmetric hydrosilylation with difluorophenylsilane (Eq. 4.15) in the presence of (*R*,*S*)-PPFOAc (Fig. 4.27) or (*R*,*S*)-PPFOH. The respective cyclohexenylsilanes were obtained with moderate to high yield. In the subsequent Tamao oxidation the corresponding alcohols were formed in enantiomeric excess up to 77% (Eq. 4.15) (Table 4.5) [53]. Enantioselectivity was remarkably affected by the substituents at the silyl group and the highest ee values were observed for $HSiF_2Ph$.



(4.15)

(*R*,*S*)-PPFOAc (Fig. 4.27) was also used in the palladium catalysed hydrosilylation of acyclic 1,3-dienes (Eq. 4.16) (Table 4.5) [53].



R = Me, Et, Ph
L* = (*R*,*S*)-PPFA

ee = 69%

(4.16)

Bis(ferrocenyl)monophosphine (Fig. 4.28) used in combination with palladium complex in asymmetric hydrosilylation of linear 1,3-dienes allowed to obtain enantioselectivities up to 93% ee (Table 4.5) [54].

Fig. 4.26

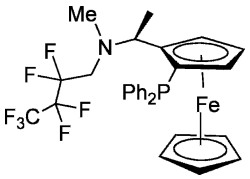
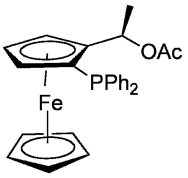
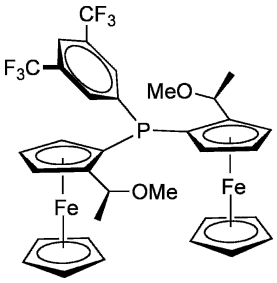


Fig. 4.27

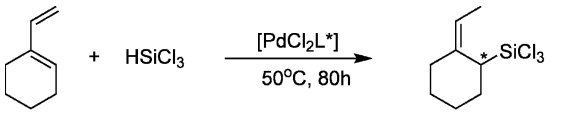


(*R*,*S*)-PPFOAc

Fig. 4.28



Hydrosilylation of 1-vinylcycloalkenes with $HSiCl_3$ in the presence of (Fig. 4.26) gave (*Z*)-1-ethylidene-2-(trichlorosilyl)cyclohexane (Eq. 4.17) [55].



(4.17)

β-(*N*-sulphonylamino)alkylphosphines (Figs. 4.29, 4.30, 4.31 and 4.32) were utilised as ligands in asymmetric hydrosilylation of 1,3-cyclopentadiene with Cl_2MeSiH.

Fig. 4.29

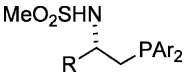


Fig. 4.30

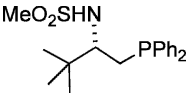


Fig. 4.31

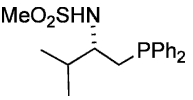
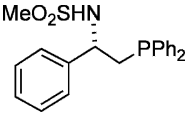
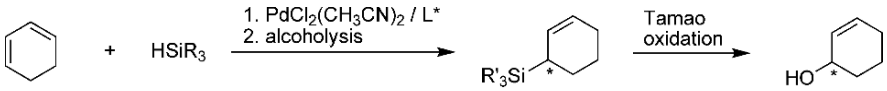


Fig. 4.32

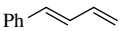


Corresponding products were obtained with enantiomeric excess up to 75.8% [56, 57]. β-(*N*-Sulphonylamino)alkylphosphine (Fig. 4.32) combined with $[PdCl_2(MeCN)_2]$ catalyses hydrosilylation of selected cyclohexadienes with a number of chlorosubstituted silanes to give allylsilane in moderate yield (Eq. 4.18) [58].



(4.18)

Table 4.6 Palladium catalysed asymmetric hydrosilylation of 1,3-dienes in the presence of MOP ligands

Diene	Ligand (L*)	Temp. [°C]	Time [h]	Yield[a] [%]	Ee[b] [%] (config.)	Ref.
	Fig. 4.37	25	90	73	57 (*R*)	[52]
	Fig. 4.35	20	120	99	80 (*R*)	[61]
	Fig. 4.2, (*R*)-isomer	20	14	100	39 (*R*)	[61]
	Fig. 4.37	–20	72	89	90 (*S*)	[62]
	Fig. 4.38	–30	168	75	91 (*S*)	[64]
	Fig. 4.35	20	150	99	51 (*R*)	[61]
	Fig. 4.33	20	12	96[c]	66[c] (*S*)	[60]
	Fig. 4.34	20	3	94[d]	56[d] (*R*)	[60]
	Fig. 4.38	0	168	53	79 (*S*)	[64]

Reaction conditions: 0.02 – 0.5 mol% [{$PdCl(\eta^3\text{–}C_3H_5)\}_2$]; [Pd]:[L*]=1:2; $HSiCl_3$, [diene]:[$HSiCl_3$]=1:1.2; [a]of silyl derivative ; [b]determined for alcohols; [c]$HSiFPh_2$ was used; [d]$HSiClPh_2$ was used.

Hydrosilylation / Tamao oxidation sequence enabled the synthesis of the corresponding alcohols with enantiomeric excess up to 84% (Eq. 4.18). Enantioselectivity was found to be sensitive to the stereoelectronic properties of the silyl group. Formation of racemic alcohol was observed for the reaction performed with $HSiCl_3$. Electron rich chiral phosphetane ligands were tested in the palladium catalysed asymmetric hydrosilylation of cyclopentadiene with trichlorosilane. The enantiomeric excess was demonstrated to be highly dependent on the relative configurations of chiral centres. In the presence of P(*R*),C(*R*) (*R*,*R*)-isomer of phosphetane acetal (Fig. 4.22), (*S*)-3-(trichlorosilyl)cyclopentene was formed with 65% ee [45, 46]. Efficient chiral ligands for the asymmetric hydrosilylation of terminal alkenes [17, 59], cyclic alkenes [19, 20] and styrene derivatives [22, 23], i.e., (MeO-MOP) (Fig. 4.2) and (H-MOP) (Fig. 4.4) were moderately effective in asymmetric hydrosilylation of 1,3-dienes (Table 4.6). Hydroxysubstituted MOP (Fig. 4.33) used in hydrosilylation of 1-phenyl-1,3-butadiene with $HSiPh_2F$ allows the synthesis of respected allylsilane with 66% ee. Exchange of OH substituent for OSi(*t*-Bu)Me_2 (Fig. 4.34) has reversed the enantioselectivity of the reaction and enabled the synthesis of (*R*)-isomer with ee up to 56% [60]. 4,4'-Biphenanthryl analogue of MeO-MOP (Fig. 4.35) was found to be an efficient ligand for asymmetric hydrosilylation of cyclic 1,3-dienes (Table 4.6) [61].

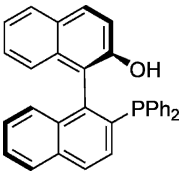


Fig. 4.33

Fig. 4.34

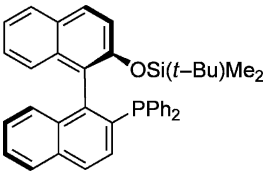
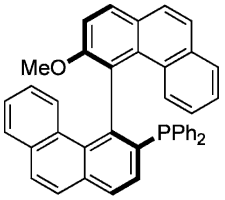


Fig. 4.35



(*R*)-MOP-phen

MOP ligands containing aryl group at position 2' of 2-(diphenylphosphino)-1,1'-binaphthyl skeleton (Fig. 4.36) are effective in the palladium catalysed asymmetric hydrosilylation of cyclic 1,3-dienes with trichlorosilane [62].

Fig. 4.36

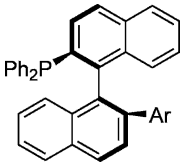


Fig. 4.37

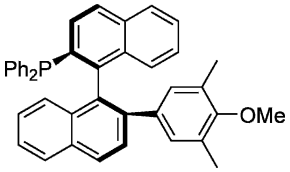
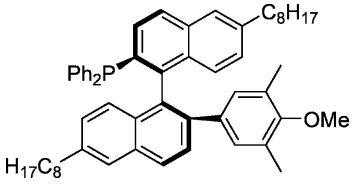
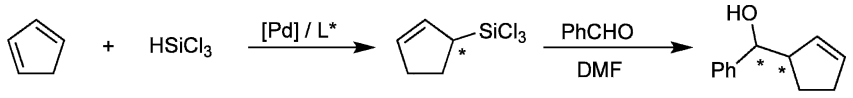


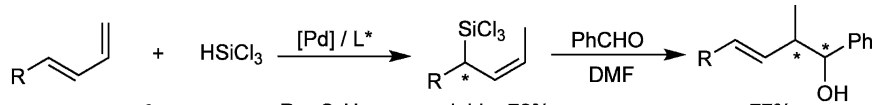
Fig. 4.38



The respective allylsilanes were obtained with high yield and up to 90% ee. The highest enantioselectivity was observed for ligand bearing 4-(methoxy)-3,5-(dimethyl) phenyl group at position 2 (Fig. 4.37). Enantiomeric excess was measured for the product obtained by subsequent treatment of 3-silylcyclopentene (or silylcyclohexene) with benzaldehyde according to the Kobayashi protocol (Eq. 4.19) [63].



(4.19)

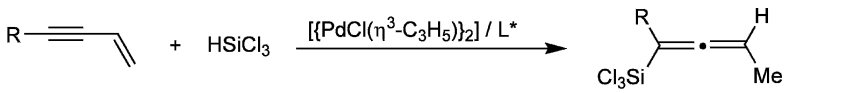


(4.20)

Introduction of two *n*-octyl groups at positions 6 and 6' of the (*R*)-2-(diphenylphosphino)-2'-aryl-1,1'-binaphthyl skeleton (Fig. 4.38) improves the solubility of palladium–phosphine catalyst in the reaction medium at low temperatures [64]. It remains active in the asymmetric hydrosilylation of linear and cyclic 1,3-dienes with trichlorosilane performed at −30°C. In such conditions hydrosilylation of cyclopentadiene followed by the reaction with benzoic aldehyde (Eq. 4.19) gives the respective alcohol with ee up to 91%. The related hydrosilylation of (*E*)-1,3-decadiene and subsequent treatment with benzaldehyde (Eq. 4.20) gives at 0°C (*S, R*)-(*E*)-2-methyl-1-phenyl-3-decen-1-ol with ee up to 79% (Table 4.6) [64, 65].

4.1.3 Hydrosilylation of Enynes

1-Buten-3-ynes containing various types of substituents at position 4 undergo the palladium-catalysed asymmetric 1,4-hydrosilylation with trichlorosilane to give axially chiral allenylsilanes [66]. Monoferrocenylmonophosphine (Fig. 4.39) and bis(ferrocenyl)monophosphine ligand (Fig. 4.40) used with [{PdCl(η^3-C_3H_5)}$_2$] were found to enable the highest enantioselectivity of all ligands tested (Eq. 4.21).

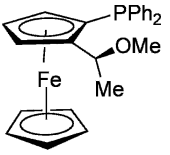


(4.21)

It has been found that the selectivity strongly depends on the steric bulkiness of the substituents. No formation of allenylsilanes was observed for 1-buten-3-ynes containing substituents at positions 1 or 2. The proposed mechanism of the reaction involves hydropalladation of the terminal alkene and formation of a π-propargylsilylpalladium intermediate [66]. In the presence of iron phosphametallocene (Fig. 4.41) 5,5-dimethyl-1-hexen-3-yne undergoes hydrosilylation with

trichlorosilane with 82% yield to give the corresponding allenylsilane with ee = 92% [67].

Fig. 4.39



(*S*,*R*)-PPFOMe

Fig. 4.40

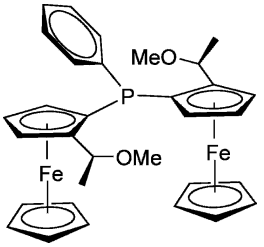
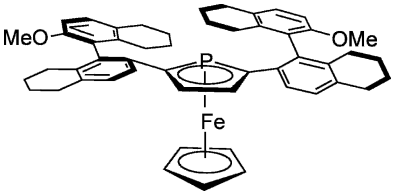
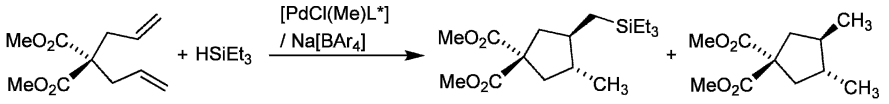


Fig. 4.41



4.1.4 Cyclisation / Hydrosilylation

Functionalised 1,6-dienes in the presence of stoichiometric amounts of triethylsilane undergo palladium catalysed cyclisation/hydrosilylation to form silylated cyclopentanes [68]. A number of cationic palladium complexes containing enantiomerically pure bidendate nitrogen ligands were screened as catalysts for asymmetric cyclisation/hydrosilylation of 1,6-dienes. The reaction leads to formation of silylmethyl-substituted carbocycle and is often accompanied by the cycloisomerisation product (Eq. 4.22).



[PdCl(Me)L*] see Fig. 4.42
Ar = 3,5-$C_6H_3(CF_3)_2$

(4.22)

Optically active palladium bis(oxazoline) complexes (eg. Fig. 4.42) catalyse the cyclisation/hydrosilylation of dimethyl diallylmalonate and triethylsilane to form mixtures of silylated carbocycle and carbocycle in moderate yield. Organosilicon product was formed with up to 72% ee. The optically active palladium pyridine-oxazoline complexes (eg. Fig. 4.43) catalyse the asymmetric cyclisation/ hydrosilylation of dimethyl diallylmalonate and $HSiEt_3$ to form exclusively the silylated product in good yield and with up to 91% ee [69, 70].

Fig. 4.42

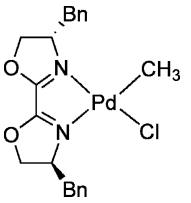
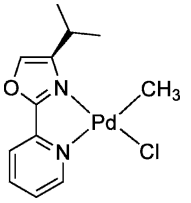


Fig. 4.43



The enantioselectivity was observed to increase with the increasing steric bulk of the silane. The notable increase in enantioselectivity (up to 95% ee) relative to the results obtained for $HSiEt_3$, $HSiMe_2Et$ and $HSiMe_2(t\text{-Bu})$ was observed when employing $HSiMe_2OSi(t\text{-Bu})Ph_2$ [71]. Pentamethyldisiloxane reacts with a range of functionalised dienes to form the corresponding silylated carbocycles in good yield (79–93%) and with good diastereo- (de up to 98%) and enantioselectivity (ee = 75–82%). Synthesised silylated carbocycles were demonstrated to undergo oxidative cleavage of the C—Si bond under mild conditions with retention of stereochemistry to form the corresponding alcohols [71–73]. The effect of the silane structure on the yield and enantioselectivity of the cyclisation / hydrosilylation / oxidative cleavage has been tested. Some limitations associated with the use of disiloxanes were largely avoided through the employment of benzhydryldimethylsilane, which enables synthesis of silylated carbocycles with good yields (81–100%) and enantioselectivities (86–95% ee). Carbocycles bearing benzhydryldimethylsilyl group can be easily oxidised in good yield (71–98%) under mild conditions. The protocol tolerates a range of functional groups and substitution at olefinic and allylic positions. It allows the synthesis of spiro and tethered bicyclic compounds [72]. The development and mechanistic study of the cyclisation / hydrosilylation of functionalised dienes catalysed by cationic palladium(II) complexes has been summarised by Widenhoefer [74].

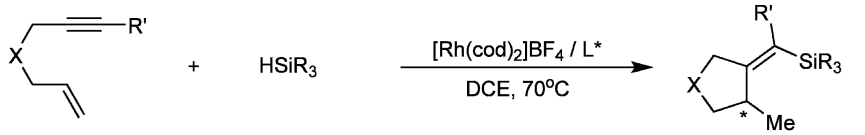
4.2 Rhodium-Based Catalysts

4.2.1 Hydrosilylation of Olefins

Hydrosilylation of terminal olefins in the presence of rhodium complexes suffers from low regioselectivity. The reaction leads to formation of the mixture of α- and β-adducts. Since 1990 no remarkable progress has been made in designing a more selective catalyst. For example asymmetric addition of alkoxysilanes to styrene derivatives in the presence of chiral bis(oxazolinyl)phenyl–rhodium complex leads to formation of a mixture of regioisomers, with the isomer ratio typically close to 1:1. For selected reagents an excess of 2-silyl derivatives (up to 77:23) and high enantioselectivity (up to 95% for the α-adduct) were observed [75].

4.2.2 Hydrosilylation of Enynes and Diynes

Asymmetric cyclisation / hydrosilylation of 1,6-enynes catalysed by a cationic, rhodium diphosphine complex leads to enantioselective formation of silylated alkylidenecyclopentanes. When non-racemic BIPHEMP (Fig. 4.44) was used as a ligand, the respective products were obtained with up to 92% ee (Table 4.7) [76].



X = NTs, $C(CO_2Et)_2$, $C(CO_2Me)_2$, $C(CN)_2$
SiR_3 = $SiEt_3$, $SiEt_2Me$, $SiPr_3$, $SiMe_2Ph$, $SiMePh_2$, $Si(OMe)_3$, $Si(OEt)_3$
R' = H, Me
L* = (*R*)-SDP (Fig. 4.45)

yield = 48 – 93%
ee = 92 – 99.5%

(4.23)

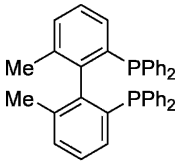
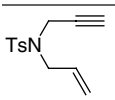
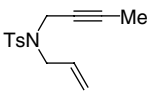
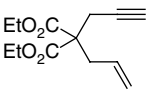
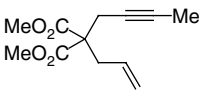
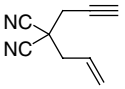


Fig. 4.44 BIPHEMP

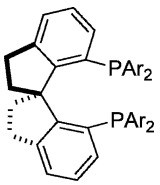
The same process in the presence of rhodium cationic complex $[Rh(cod)_2]BF_4$ combined with spirodiphosphine (SDP) (Fig. 4.45) leads to efficient and enantioselective formation of silylalkylidene, cyclopentane and pyrrolidine derivatives (up to 99.5% ee) (Eq. 4.23) (Table 4.7) [77].

The silyl group of this tandem hydrosilylation / cyclisation reaction products can be easily converted into other functional groups by standard methods, e.g. palladium catalysed cross-coupling, which was reported to proceed with a slight decrease in enantiopurity [77].

Table 4.7 Asymmetric cyclisation hydrosilylation of 1,6-enynes catalysed by a cationic rhodium diphosphine complexes

Substrate	Ligand	Temp. [°C]	Time [h]	Yield [%]	Ee [%]	Ref.
	$[Rh(cod)_2]BF_4$ / L* L* see Fig. 4.45	70	2	60[a]	98[a]	[77]
	$[Rh(cod)_2]SbF_6$ / L* L* see Fig. 4.44	70	–	73[b]	80[b]	[76]
	$[Rh(cod)_2]BF_4$ / L* L* see Fig. 4.45	70	2	93[c]	92[c]	[77]
	$[Rh(cod)_2]BF_4$ / L* L* see Fig. 4.45	70	2	67[c]	96[c]	[77]
	$[Rh(cod)_2]SbF_6$ / L* L* see Fig. 4.44	70	1.5	81[a]	92[a]	[76]
	$[Rh(cod)_2]BF_4$ / L* L* see Fig. 4.45	70	2	50	99.5	[77]

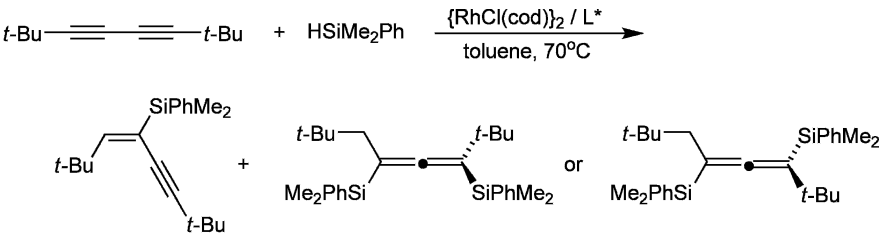
Reaction conditions: 5 mol% [Rh], [Pd]:[L*]=1:1.2, $HSiEt_3$, [enyne]:[$HSiR_3$]=1:5; [a]$HSiEt_3$; [b]$HSiMePh_2$; [c]$HSi(OEt)_3$.



(*R*)-SDP

Fig. 4.45

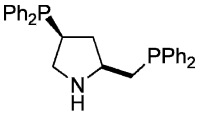
The rhodium catalysed hydrosilylation of butadiynes in the presence of chiral phosphine ligands leads to the formation of axially chiral allenes (Eq. 4.24). Enantiomeric excess up to 22% was achieved for ligand (*S*,*S*)-PPM (Fig. 4.46) combined with [{RhCl(cod)}$_2$] [78, 79].



L* = (*S*,*S*)-PPM (Fig. 4.46)

(4.24)

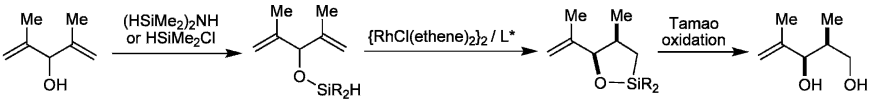
Fig. 4.46



(*S*,*S*)-PPM

4.2.3 Intramolecular Hydrosilylation

Asymmetric intramolecular hydrosilylation of allylic alcohols followed by Tamao-oxidation affords optically active 1,3-diols (Eq. 4.25), which are useful synthetic intermediates for the synthesis of the natural products such as polypropionate derivatives. (*R*,*R*)-DIOP (see Chapter 10, Fig. 10.9) and (*R*)-BINAP (for (*S*)-isomer see Chapter 10, Fig. 10.14) in combination with $[\{RhCl(ethene)_2\}_2]$ or $[\{RhCl(cod)_2\}_2]$ were found active in the process. Under the optimized conditions, essentially complete diastereoselectivity (*syn*:*anti* > 99:1) and high enantioselectivity (up to 93%) have been observed [80].

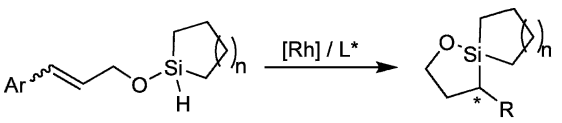


L* = (*R*,*R*)-DIOP
R = 3,5-$C_6H_3Me_2$

yield = 93%,
syn / *anti* = 99 / 1
ee = 93%

(4.25)

Rhodium(I) cationic complex combined with chiral diphosphine ligands such as (*S*)-BINAP (Chapter 10, Fig. 10.14) and (*S*,*S*)-CHIRAPHOS (Fig. 4.47) efficiently and rapidly catalyse the intramolecular hydrosilylation of a wide range of silyl ethers (Eq. 4.26) (Table 4.8) [81, 82].

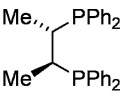


n = 1, 2
L* = (*R*,*R*)-DIOP or (*S*)-BINAP

yield = 61 – 100%
ee = 74 – 97%

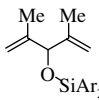
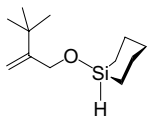
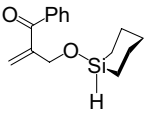
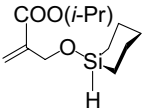
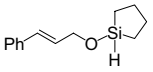
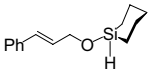
(4.26)

Fig. 4.47



(*S*,*S*)-CHIRAPHOS

Table 4.8 Intramolecular asymmetric hydrosilylation of allyl silyl ethers

Substrate	Ligand	Temp [°C]	Time [h]	Yield [%]	Ee [%] (config.)	Ref.
 Ar = 3.5-$C_6H_3Me_2$	[{RhCl(ethene)$_2$}$_2$] / (*R*,*R*)-DIOP	30	11 days	66[a]	93[a]	[80]
	[Rh{(*S*)-BINAP)}(solv.)$_2$](ClO_4)	25	<0.08	100[b]	96[b] (*R*)	[83]
	[Rh{(S)-BINAP}(solv.)$_2$](ClO_4)	25	<0.08	100[b]	96[b] (*S*)	[83]
	[Rh{(*S*)-BINAP}(solv.)$_2$](ClO_4)	25	0.08	100[b]	87[b] (*S*)	[83]
	[Rh{(*S*)-BINAP}](ClO_4)	25	0.08	75[c]	97[c] (*R*)	[80, 82]
	[Rh{(*S*)-BINAP}](ClO_4)	25	1.5	75[c]	96[c] (*R*)	[80, 82]

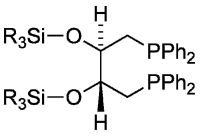
Reaction conditions: *2–2.5 mol% [Rh_2], [Rh]:[DIOP]=1:1.3–1.5; [b] mol% [Rh]; [c]2 mol% [Rh].

High enantioselectivities (up to 97%) were observed for hydrosilylation of olefins bearing terminal aryl substituent at double bond in the presence of [Rh{(*S*)—BINAP}](ClO_4) (Table 4.8). Terminal alkyl substituents were found to retard the reaction. Oxidative cleavage of the hydrosilylation products was demonstrated to give chiral diols.

Allyl silyl ethers bearing tertiary group, acyl or ester substituents in position 2 are effectively hydrosilylated in the presence [Rh{(*S*)-BINAP}(solvent)$_2$](ClO_4) [83]. Chemical yields and enantioselectivities are sensitive to the solvent employed. Proper combinations of the substrate and the solvent enable formation of the corresponding products with high chemical yields and enantioselectivities 4.27 (Table 4.8).

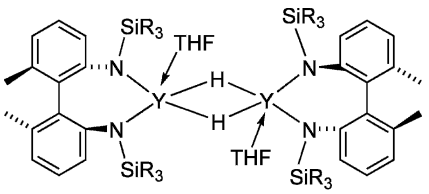
The mechanism of asymmetric catalytic intramolecular hydrosilylation was studied in detail by Bosnich with the use of specifically labelled deuterated substrates and [Rh(diphosphine)]$^+$ catalysts [84, 85]. On the basis of the results obtained it was suggested that hydrosilylation proceeds via olefin insertion into the metal—silyl bond rather than into the metal—hydrogen bond. The turnover-limiting and enantioselective steps are believed to be the silyl olefin insertion. The axially chiral spirosilane – 5-silaspiro[4.4]nonane derivative was obtained via intramolecular hydrosilylation of bis(alkenyl)silane (Eq. 4.27) [86]. In the presence of [{RhCl(1,5-cyclohexadiene)}$_2$] combined with chiral diphosphine ligands (SILOP) (Fig. 4.48) reaction proceeds highly diastereo- and enantioselectively.

Fig. 4.48



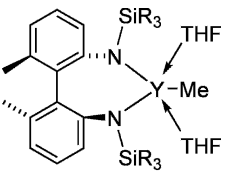
(*R*,*R*)-SILOP
a $SiR_3 = SiMe_3$
b $SiR_3 = SiMe_2(t\text{-Bu})$
c $SiR_3 = Si(i\text{-Pr})_3$
d $SiR_3 = SiPh_3$

Fig. 4.49

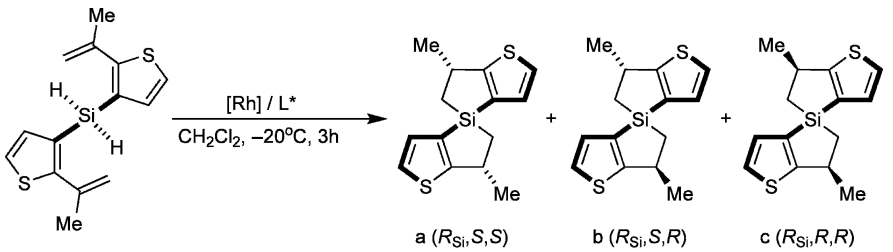


$SiR_3 = SiMe_2(t\text{–Bu})$

Fig. 4.50



$SiR_3 = SiMe_2(t\text{–Bu})$



[Rh] = [{RhCl(1,5-cyclohexadiene)}$_2$]
L* = (*R*,*R*)-SILOP

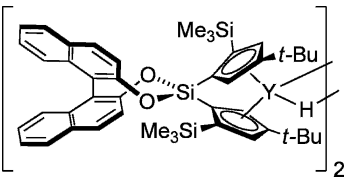
yield = 81%, ee = 99% yield = 1.7% traces

(4.27)

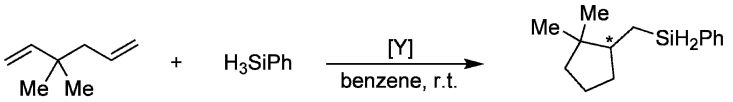
4.3 Yttrium-Based Catalysts

Dimeric yttrium hydride (Fig. 4.49), generated from monomeric methyl complex (Fig. 4.50) by the treatment with phenylsilane, catalyses hydrosilylation of norbornene with $PhSiH_3$ to give quantitatively 2-silylnorbornane with 90% ee [87]. This system is the first example of the use of a d^0 metal complex bearing no

Fig. 4.51



Cp ligands in the catalytic hydrosilylation of olefins. Kinetic studies support a mechanism consistent with the generally accepted one for hydrosilylation catalysed by early transition metal species, involving rapid olefin insertion into the Y—H bond followed by a slow σ-bond metathesis of the resulting yttrium-alkyl with Si-H bond of silane. Yttrocene hydride (Fig. 4.51) exhibits catalytic activity in the asymmetric cyclisation / hydrosilylation of α,ω-dienes (Eq. 4.28) [88]. The cyclisation of 1,5-hexadienes and 1,6-heptadienes results in the formation of five- and six-membered rings, respectively, with low to moderate enantioselectivities.



[Y] see Fig. 4.51 yield = 95%, ee = 50% (4.28)

4.4 Lanthanides-Based Catalysts

Marks reported the catalytic hydrosilylation of olefins with H_3PhSi using the organolanthanide precatalysts (Fig. 4.52) [89]. For terminal olefins, the hydrosilylation rate and regioselectivity of α-addition are enhanced by openness of the metal ligation sphere and increasing lanthanide ion radius. For styrene derivatives complete regioselectivity (consistent with the Markovnikov's rule) and up to 99% ee was observed. An increase in the reaction rate by electron donating substituents in position 4 of the ring was observed. The hydrosilylation mechanism is discussed in terms of the hydride/alkyl cycle involving a rapid exothermic olefin insertion into the Ln—H bond followed by turnover-limiting Si-H / Ln-alkyl σ-metathesis.

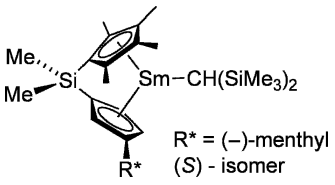


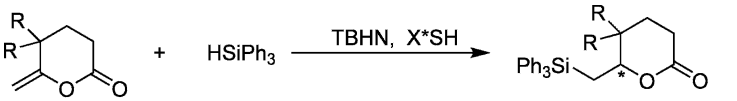
Fig. 4.52

4.5 Miscellaneous Metal-Based Catalysts

A report appeared on high activity of calcium complexes in hydrosilylation of styrene with phenylsilane [90, 91]. However, corresponding asymmetric transformation led to poor enantioselectivity.

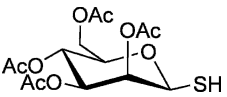
4.6 Free-Radical Initiated Hydrosilylation

Enantioselective radical-chain hydrosilylation of a number of cyclic prochiral terminal olefins with triphenylsilane in the presence of a catalytic amount of enantiomerically pure thiols and di-*tert*-butyl hyponitrite (TBHN) as initiator was reported by Roberts (Eq. 4.29) [92–94]. A number of non-racemic thiols were investigated and the highest enantiomeric excesses (up to 95%) were achieved using the tetra-*O*-acetyl derivatives of 1-thio-β-D-glucopyranose and 1-thio-β-D-mannopyranose (Fig. 4.53). The α-anomers of the pyranose thiols were ineffective in mediating of enantioselective hydrogen-atom transfer.

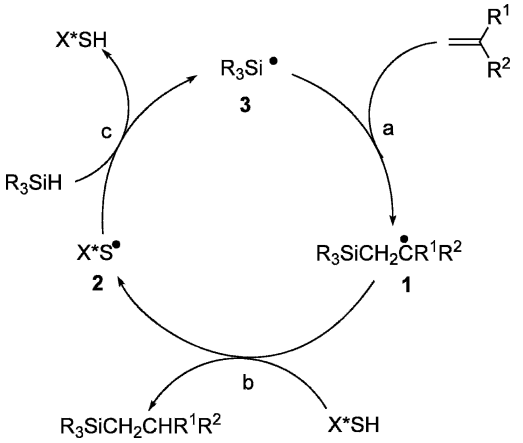


(4.29)

Fig. 4.53



According to the mechanism proposed (Scheme 4.2) radical **1** is formed by addition of the silyl radical **3** to the alkene (step **a**). In the presence of a thiol, direct transfer of a hydrogen atom from the silane to radical **1** is replaced by a more rapid hydrogen transfer from the thiol. The resulting radical **2** interacts subsequently with silane in step **c** to form silyl radical **3** and thiol. If radical **1** is prochiral and the thiol is optically active, step **b** can be enantioselective.



Scheme 4.2 Enantioselective radical-chain hydrosilylation mechanism

It was demonstrated that the silyl derivatives obtained undergo oxidative desilylation to the corresponding alcohol and acetate with no loss of enantiopurity.

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Part II
Hydrosilylation of Carbon–Carbon Multiple Bonds in Polymer Chemistry and Materials Science

Chapter 5
Functionalisation and Cross-Linking of Organosilicon Polymers

Abstract This chapter presents the progress made over the last two decades in the modification (functionalisation) of polysiloxanes as well as curing of polysiloxanes via catalytic hydrosilylation. Well-defined silicones have been prepared by hydrosilylation of functional olefins with polymethylhydrosiloxanes predominantly in the presence of Pt-based catalysts to make a whole branch of materials for adhesives binders, ceramic and dielectric coatings, encapsulates, membranes, sealants and a lot more. On the other hand, the addition of polyfunctional silicon hydrides to poly(vinyl)organosiloxane leads to effective cure of silicon rubber. Pt-complex or other TM-complexes but yet usually Karstedt's catalyst with various inhibitors added to reduce or temporarily inhibit its catalytic activity in the cross-linking, reported since 1990 are compiled. Fast cure can be also effected by radiation methods. Most patents describe the procedures for preparing silicon rubber used for dental materials, improving adhesion to metal, glass and plastics, electric insulators, membranes and many others.

Polysiloxanes (silicones) are the most popular representatives of silicon polymers not only among organosilicon polymers but also among inorganic ones. Silicones, due to their unique properties, have found a great number of applications to almost all branches of industry. For a few years, the future of silicones has been associated with their functionalised derivatives [1]. Modification of polysiloxanes with organic functional groups is intensively developed in order to obtain polymers of specific properties or to make them chemically active, which will increase the number of new potential applications. It has been estimated that at present the share of organofunctional siloxanes in the world silicone market reaches about 15% [2]. The subchapter gives a comprehensive review of the most popular functionalised silicones, obtained via hydrosilylation, and main directions of their applications. In the Subchapter 5.2, hydrosilylation is discussed as a tool for crosslinking of silicone rubber, since it finds increased application to the rubber manufacture due to its many technological and economic advantages. In patents published during the last two decades, procedures for the preparation of silicon rubbers of special properties and applications were described. Information on new catalytic systems, reported since 1990, involving transition metals (mostly platinum complexes) and various

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inhibitors aimed at reducing temporarily their catalytic activity, has been compiled in this subchapter.

5.1 Modified Organosilicon Polymers and Their Applications

Functionalised silicones include those having functional groups (FG) at one end (a) or at both ends (b) of siloxane chain as well as in a side chain linked to the main siloxane chain (see Fig. 5.1). The latter case includes homopolymers (c) and copolymers (d) with controlled content of dimethylsiloxane fragments.

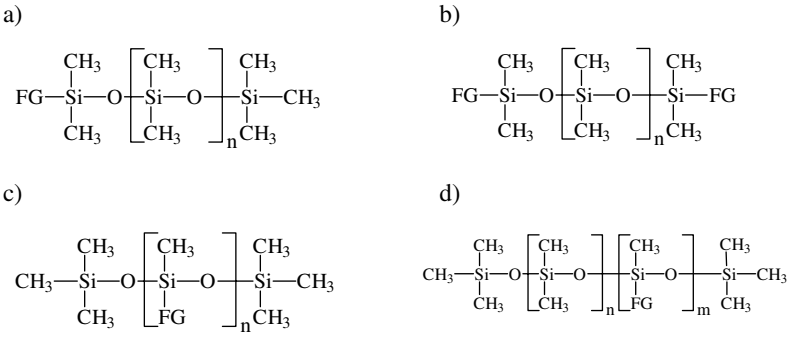
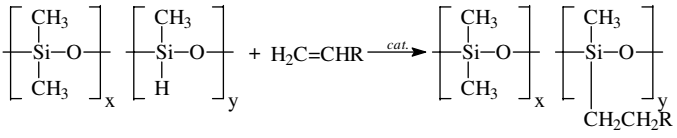


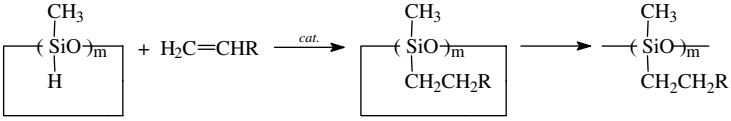
Fig. 5.1

The most important, efficient and widely applied method of functional group introduction to a polysiloxane chain is the Si—H bond addition to functional group-containing unsaturated compounds, i.e. the process of hydrosilylation according to (Eq. 5.1):

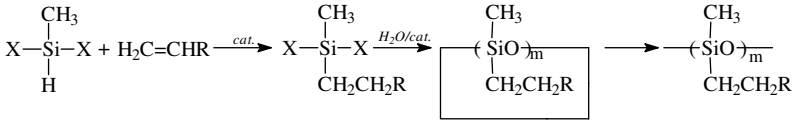


(5.1)

Hydrosilyl group-containing starting materials can be siloxane polymers, cyclic siloxane oligomers as well as a monomeric silane with Si-H function and two hydrolysable substituents at silicon atom. Substituted cyclic siloxanes or monomeric silanes (after their addition to a functional olefin) can undergo further polymerisation via ring-opening polymerisation (Eq. 5.2) or polycondensation (Eq. 5.3):



(5.2)



(5.3)

Although hydrosilylation accompanies each method of siloxane functionalisation, this subchapter will be limited to the processes of direct hydrosilylation of olefins with polyhydrosiloxanes.

Hydrosilylation, contrary to hydrolytic polycondensation or ring-opening polymerisation, proceeds in a neutral medium and the "purity" of the process (there is no evolution of HCl, which occurs in polycondensation process) is its major advantage, therefore, in the case of many organic functional groups (sensitive to strongly acidic or strongly basic media), it is the only method for siloxane functionalisation. To achieve the target properties of the modified polysiloxanes, a great variety of functional groups may be introduced in the side chains of organosilicon polymers.

Typical silicones contain methyl (rarely ethyl) groups at silicon atoms that results in their characteristic hydrophobic properties. Although alkyl group can hardly be considered as a functional group, longer alkyl chains (from C_8 to C_{40}), linked to the silicon atoms of the polysiloxane chain, can significantly modify the physicochemical properties of the initial silicones, thanks to a possibility of penetration into organic systems, both monomeric and polymeric ones. Polysiloxanes, modified in such a way, show considerably greater affinity to organic compounds, than the typical polymethylsiloxanes.

Polysiloxanes subjected to side chain modification with groups capable of crosslinking under the influence of light (acryl, epoxy, vinyl or styrenic ones) make the next important class of polysiloxanes, whose main applications have been reviewed [3].

Another class of modified polysiloxanes is that of liquid crystal polysiloxanes [4]. Depending on the mesogenic group-, linked to the polysiloxane chain, the above compounds show a variety of properties, thereby a variety of applications as well. Some of them can be used as biomedical materials [5] to control penetration of drugs, others have been proposed as solid phases for high performance chromatography, when enantiomer separation is required [6] or as optoelectronic and optical materials [6].

One of more popular groups of modified silicones is that of fluorinated polysiloxanes. They have found application in many areas, first and foremost, to those requiring hydrophobic and organophobic properties in addition to chemical inertness and resistance to high and changing temperatures. Liquid fluorosilicones can be used as moistening oils, hydraulic liquids, leather, textiles and glass coatings, as well as foam inhibitors. Elastomers can find their applications as components of sealants, protective coatings (e.g. in fuel tanks) and electric insulators. The greatest consumers of such elastomers are automotive and aircraft industries. In a review paper on fluorosiloxanes [7], different applications of such compounds were listed, e.g. as surfactants, gels, coatings, adhesives, sealants, rubbers and elastomers.

Siloxane chain can be modified also by amino functional groups, mainly $(CH_2)_3NH_2$ or $(CH_2)_3NHCH_2CH_2NH_2$, epoxycarbofunctional groups – most frequently glycidyl or epoxycyclohexyl ones, as well as by polyether groups $(CH_2)_n$—$(OCH_2CH_2)_m$—. Recently, a growing interest has been observed in polysiloxanes modified with different derivatives of carbohydrates and fatty acids. All functionalised silicones, mentioned above, have been obtained in the hydrosilylation processes.

Hydrosilylation has been widely applied to the introduction of fluorine-containing groups to polysiloxanes, e.g. the first commercially available poly(3,3,3-trifluoropropylmethyl)siloxane, was manufactured by hydrosilylation of 3,3,3-trifluoropropene with methyldichlorosilane in the presence of H_2PtCl_6, followed by hydrolytic polycondensation of the product obtained [8].

$$CF_3{-}CH{=}CH_2 + HSi(CH_3)Cl_2 \xrightarrow[2.\ H_2O]{1.\ H_2PtCl_6} {-}\!\!-\!\!\left(\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_2CH_2CF_3\end{array}\right)_m\!\!-\!\!- \qquad (5.4)$$

Polysiloxanes containing longer alkylfluorinated [9] and fluoroalkyl etheric [10] chains were obtained in an analogous way. As a result of the electropositive nature of silicon, the stability of polymers fluorinated at the α or β positions is low. Therefore, siloxanes are usually fluorinated at the γ-position.

Poly(hydro, methyl)siloxane homopolymers and copolymers have been used in hydrosilylation of fluorinated olefins, containing both alkyl groups [11–14], alkyl esters [15], aryl esters [16] and alkyl or fluoroalkyl ethers [17–19]. In all cases the catalyst of the reactions mentioned was H_2PtCl_6, except for the reaction of aryl esters, in which cobalt complexes played the role of catalyst [16].

The synthesis of fluorosilicone having highly fluorinated alkyl side chains (heptadecafluorodecyl, heptadecafluoroundecyl, heptadecafluorooxatetradecyl) based on the hydrosilylation of fluorinated olefins with polyhydromethylsiloxane has been reported [20, 21]

The synthesis of photocrosslinkable fluorinated polydimethylsiloxanes was carried out through the direct hydrosilylation of allyl-2-(perfluorohexyl)ethyl ether and allyl methacrylate with copoly(dimethyl, methylhydro)siloxane in the presence of Speier catalyst [22, 23].

Other examples of modified silicones, obtained by hydrosilylation, are poly(methyl, alkyl)siloxanes, the so-called silicone waxes which, due to their hydrophobising, moisturising and glazing properties have found a number of valuable applications.

Alkylsilicones easily form mixtures with other organic compounds and are characterised by good lubricating properties, reduction in surface tension of many non-aqueous solvents and are capable of oiling soft metals (aluminium, zinc, copper), elastomers and rubber. Alkyl derivatives, containing C_8 groups can be applied as plasticisers of polyolefins. The moisturising and softening effect, in addition to

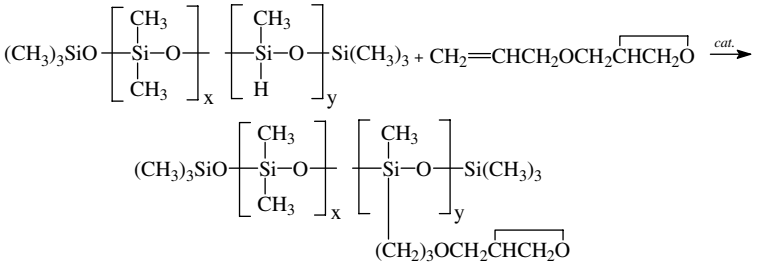
biological inertness, excellent oiliness and spreading, predisposes them to the use in cosmetic industry as components of many preparations. There are also examples of application of alkylpolysiloxanes to other areas: as hydrophobising and softening agents for fibres [24, 25], as lubricants and oils [26–28], motor oils and fuels for two-stroke engines [29], brake fluids [30], foam inhibitors for diesel oil [31], surfactants for paints and varnishes [32], agents for masonry protection against moisture, preparations for surface maintenance in household, car cosmetics [32], leak stoppers for toners [33], coatings of heated shafts (Xerox machines and laser printers) [34], abrasive compounds [35, 36], agents for assembly of printing plates [37], agents for modification of surfaces of fillers for polyamide resins [38], detergents for dishwashers [39].

Reports on the polysiloxanes containing siloxane fragments with other chains, in additions to the monomeric units with alkyl groups, appear more and more frequently in literature, e.g. emulsifiers, surfactants that contain alkyl and polyether chains [32, 40], additives to herbicides that have alkyl and amino group-containing monomers [41]. In most cases, the role of hydrosilylation catalysts is played by transition metal complexes, those of platinum in particular [42–49]. The hydrosilylation processes were also carried out in the presence of supported platinum catalysts, using hydrophobic styrene-divinylbenzene copolymer [50–52] and activated carbon as supports [50, 53]. Platinum complexes show a high catalytic activity for hydrosilylation of olefins, however, some impurities present in reagents lead to catalyst deactivation. The catalysts that are characterised by a higher resistance to poisoning are rhodium complexes. Rhodium siloxide complexes are one of the most efficient catalysts for hydrosilylation processes, even at room temperature [54–57].

In the last few years biphasic reactions employing ionic liquids have gained increasing importance. Nowadays, many reactions are known to proceed in biphase systems using ionic liquids, whereas only a few examples of catalytic hydrosilylation by polysiloxanes have been reported so far. Such catalytic systems are based on platinum [58–60] and rhodium siloxide complexes [50, 61–64], immobilised mainly in immidazolium salts as ionic liquids.

Polysiloxanes can also be modified by introducing various groups capable of crosslinking under the influence of light via hydrosilylation of respective organic derivatives with poly{(dimethyl)(methylhydro)}siloxanes [3, 65, 66]. This class of compounds includes a whole range of modified silicones containing such groups as e.g. acryl [67], epoxynorbornene [68] or glycidyl and epoxycyclohexyl ones [69–72]. Epoxycyclohexyl group is more reactive than glycidyl group, easily reacts with nucleophilic agents when initiated thermally or chemically, e.g. undergoes crosslinking with amines.

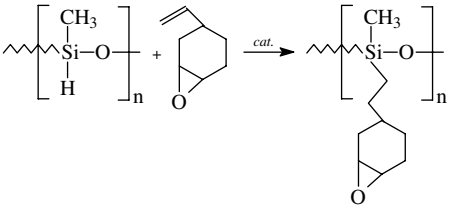
Epoxy derivatives of silicones are obtained via hydrosilylation with (poly, oligo) hydromethylsiloxanes of allyl glycidyl ether, most often in the presence of platinum catalyst [73], but salts of quaternary amine $Bu_4N^+Br^-$ [74] also show catalytic activity in the reaction discussed:



(5.5)

The above reaction was also carried out in the presence of analogous catalytic systems like those ones used for the synthesis of silicone waxes, i.e. rhodium siloxide complexes [54–57] and Pt or Rh complexes immobilised in ionic liquids, mentioned earlier [50, 58, 62–64].

Hydrosilylation enables addition of epoxycyclohexyl group as well:



(5.6)

In this case, hydrosilylation of vinylepoxycyclohexane competes with polycondensation that proceeds with epoxy ring opening [70]. Addition of various polyhydrosiloxanes to vinylepoxycyclohexane occurs efficiently in the presence of a whole range of catalysts (complexes of Co, Ru, Rh, Pt, Ni) [75, 76] Rhodium complexes, especially Wilkinson catalyst [$Rh(PPh_3)_3Cl$] and polymer-bound Wilkinson's catalyst are used quite freequently [77–83] however, platinum complexes are used most often [84, 85], mainly Speier catalyst [86–93], Karstedt's catalyst [94–100] and Lamoreaux catalyst [45].

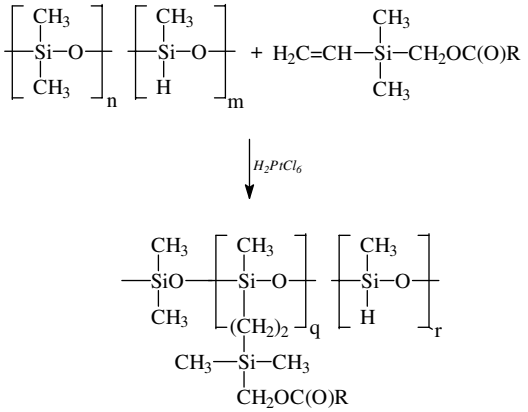
Epoxy functional siloxanes have been well known and used in a lot of various applications for many years, However, due to high reactivity, these compounds are more valuable as substrates than as final products. Epoxy siloxane has a good reactivity in cationic polymerisation [77] and is easily polymerised by both photo- or thermally-induced polymerisation. A number of epoxyfunctional (poly)siloxanes have been synthesised via hydrosilylation of allyl glycidyl ether or 1,2-epoxy-4-vinyl-cyclohexane by oligo or polysiloxanes [77, 86–88, 94, 95], which were subsequently crosslinked with diamines [94] or with diglycidyl ether of bisphenol-A [95].

In a few cases, the siloxanes containing (besides epoxy group) also electron-transfer photosensitizer such as N-vinyl carbazole, N-allyl carbazole, vinyl antracene or benzyl ether, have been synthesised [79, 80].

Other mixed polysiloxanes containing both epoxy and fluoroalkyl [98], poly (ethylene oxide) [90] acrylates [83] or nitrile functional groups [91] have also

been obtained via hydrosilylation. Finally, the high reactivity of the oxirane ring of epoxides makes it possible to obtain a wide range of compounds such as ionic silicone surfactants [101]. Epoxy functional siloxanes obtained in the hydrosilylation processes have been used for the synthesis of surface-active quaternary amino polyfluorosiloxanes [99], bis(methoxylhydroxyl)-functionalised polysiloxanes [100], pol(imide-siloxane) [92] and alkylsulphonated siloxanes [102].

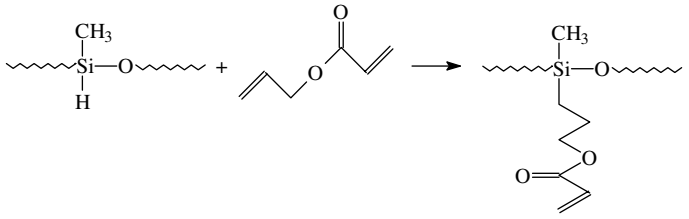
Organosilicon vinyl derivatives with groups capable of crosslinking are also subject for hydrosilylation, e.g. vinyl esters [103]:



where m = q + r;

R = Ph−CH=CH−;  −CH=CH−; Ph−CH=CH−CH=C(CN)− (5.7)

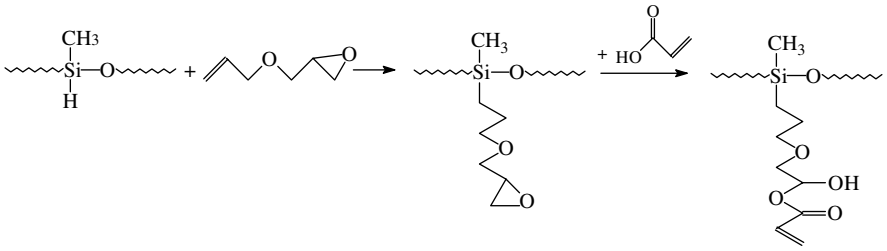
Numerous polysiloxanes with side groups, containing ethers, esters [104] (acid-sensitive groups) or carbamates [105] have been synthesised in hydrosilylation processes, usually in the presence of H_2PtCl_6 or Pt/C as catalysts [74, 106]. In this way a lot of silicones bearing acrylic groups have been prepared [107–111]. Among them, one can find examples of the direct hydrosilylation of allyl (met)acrylate with methyl-hydrogen siloxanes [46, 66, 112, 113]:



(5.8)

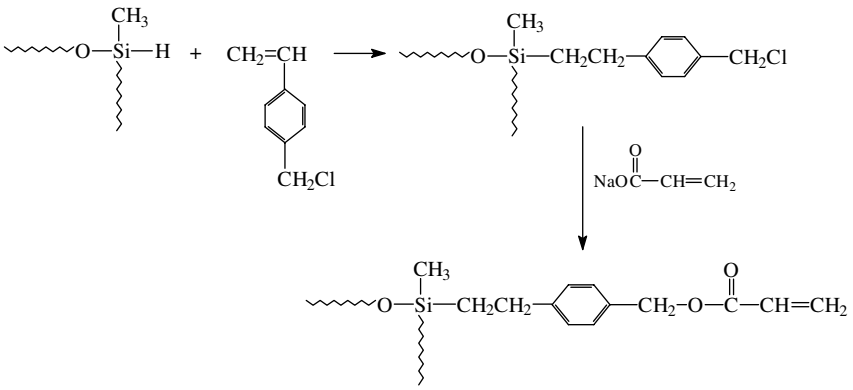
The synthesis of photocrosslinkable fluorinated polydimethylsiloxanes by introduction of acrylic pendant group via hydrosilylation has been described [22]. The indirect methods for synhesis photocrosslinkable acrylic silicones are known. The

first step in most of them is the hydrosilylation of allyl glycidyl ether by H-siloxanes, followed in the second step by esterification with acrylic acid [114–116]:



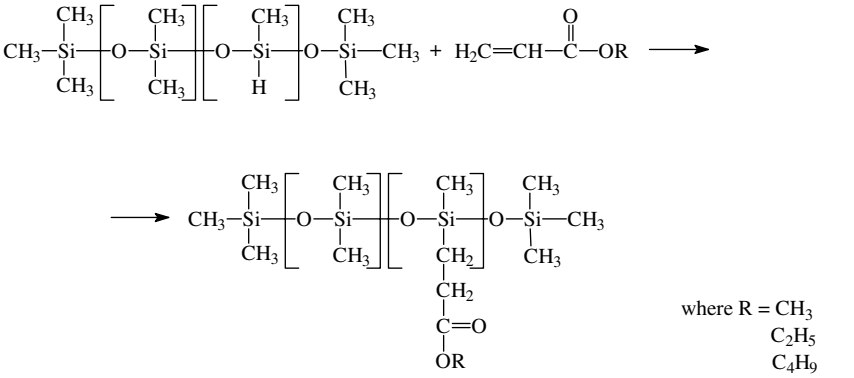
(5.9)

Another example of such a process is the hydrosilylation of vinylbenzyl chloride, followed by nucleophilic substitution of chlorine by acrylic group [117]:



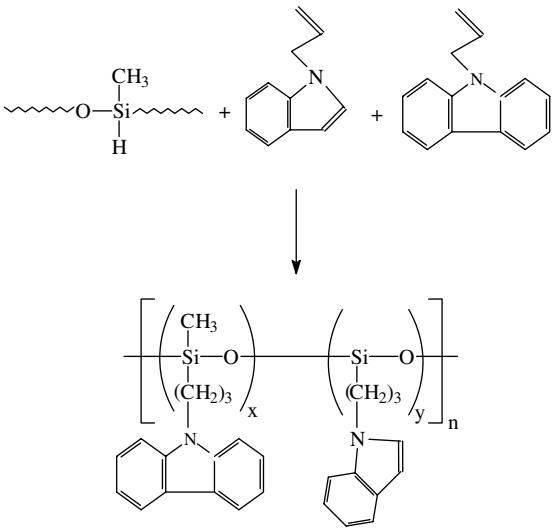
(5.10)

The "untypical" addition of Si-H to CH_2=CH- from acrylic group, between polysilaethers and acrylic acid [118] or polysiloxanes and alkyl acrylate [119], has also been described:



(5.11)

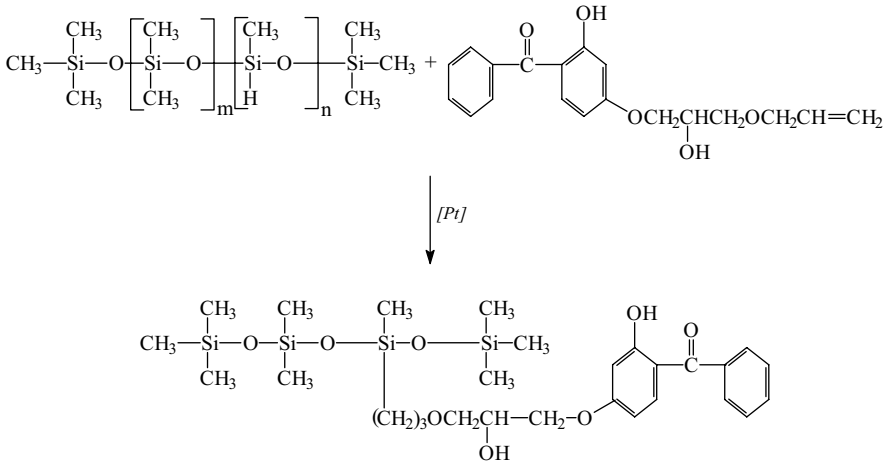
In the past decade, growing attention has been focused on the development of organic nonlinear optical chromophore-containing polymeric materials because of their potential photonic applications in telecommunication, optical data storage, and optical information processing. Because of this interest, several multifunctional polysiloxanes containing electro-optical chromophores and charge-transporting agents have been prepared for the photorefractive applications. Among them, the most popular are polysiloxanes with indole and carbazolyl groups as side chains, which are synthesised by hydrosilylation of a mixture of allylindole and allylcarbazole in the presence of dichlorodicyclopentadiene platinum [Cp_2PtCl_2] as a catalyst [120–125]:



(5.12)

The product of this reaction was modified, using post azo coupling reaction of p-nitrobenzenediazonium fluoroborate [120,121] or p-ethylsulphonylbenzenediazonium fluoroborate [122] towards the indole rings. The product could also be partially formylated under the standard Vilsmeier reaction conditions, and these formyl groups with high reactivity were condensed with cyanoacetylated chromophores [124, 125]. In these compounds, carbazoyl group offers the charge-transporting agent and azodye group acts as the electro-optical chromophore.

Polysiloxanes with pending benzophenone derivative side group are functional ultraviolet light absorbing polymeric materials [126–128]. They have been used as components for sun screening cosmetics and drugs, or as additives in various anti-UV coatings, and functional textile finishing preventing photo-degradation induced by sunlight. One example of such compounds is a functional polysiloxane, synthesised by hydrosilylation of polyhydromethylsiloxane with 2-hydroxy-4-(β-hydroxy-γ-allyloxy)propyloxy benzophenone in the presence of Speier catalyst [128], according to the equation:



(5.13)

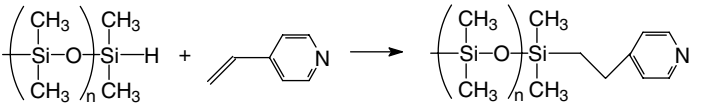
There are also examples of modification of polysilanes via hydrosilylation, however they are very rare. One of them describes the synthesis of blue-emissive, water-soluble, conjugated polymers based on the polysilanes with amino-terminal groups. The compounds of this kind are very attractive as sensing materials (for DNA, RNA and metal ions), due to their high sensitivities to analytes. The water-soluble properties are endowed by grafting quaternized ammonium [129] (or other hydrophilic group) side chain to a conjugated polymer, however in the first step polysilane with an Si-H group react with 2-(dimethylamino)ethyl methacrylate through hydrosilylation and then it is quaternised with CH_3I [130]. Another example of polysilane modification described the synthesis of polysilanes bearing thienyl groups on the appended sila-alkyl side chains [131], according to the equation:

where **R** = $SiThCl_2$, $CH_2SiThCl_2$, $SiTh_2Me$, CH_2SiTh_2Me; Th =

(5.14)

These compounds are used for generation and stabilisation of silver nanoparticles. In the above examples, the hydrosilylation reactions were catalysed by AIBN (2,2'-azobisisobutyronitrile) as the free radical initiator. The common hydrosilylation catalysts, such as transition metal complexes are not effective in this reaction, because they also cause degradation of the polysilane chain. The free radical hydrosilylation, with AIBN, provides a very mild process for selectively substituting the Si—H bonds [132].

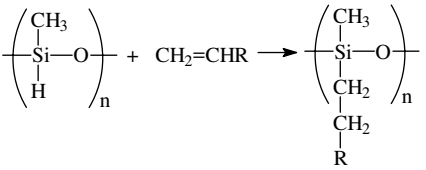
Finally, modified polysiloxanes were used as catalyst supports. Supercritical carbon dioxide ($scCO_2$) is, potentially, a relatively green alternative to commonly used organic solvents, however, low solubility of many catalysts in $scCO_2$ makes a barier to its employment as a reaction solvent. Furthermore, siloxane-based polymers are generally soluble in $scCO_2$ and have high chemical stability. Hydrosilylation of vinyl pyridine by polysiloxane, enabled obtaining a product capable of coordination with metal atom via terminal pyridine moiety [133] and the obtained catalyst is soluble in $scCO_2$.



(5.15)

One of the most important groups of polysiloxanes modified via hydrosilylation is that of polysiloxane bearing liquid –crystalline side chains. These compounds have been very popular for almost 30 years [134]. A large number of recent publications, proves that the interest in these compounds is even increasing. Liquid crystal polymers (LCP), due to their specific properties, can be used for various practical applications, especially in the electronics industry [6, 135]. LCP can be used in a variety of electro-optical, opto-optical, magneto-optical or thermo-optical devices.

The hydrosilylation is a very powerful tool for synthesis of the compounds of this type. Analysing this great number of publications, one can conclude, that most of them describe the properties of the LCP obtained and that the methods of the synthesis are almost the same. Most of the processes are catalysed with the use of platinum complexes, mainly Karstedt's catalyst, H_2PtCl_6 and $[Cp_2PtCl_2]$. The considerable difference between these processes is the type of mesogens which are added to the siloxane chain. The Table 5.1 presents a few examples of mesogens which have been used in the processes of hydrosilylation in the recent years [136–145]

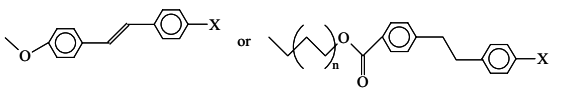
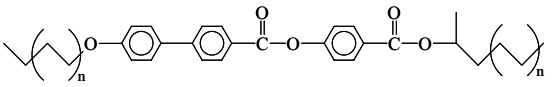
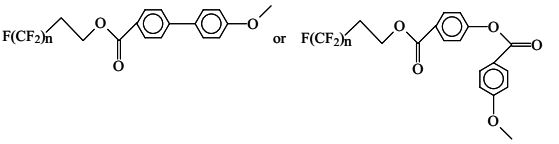
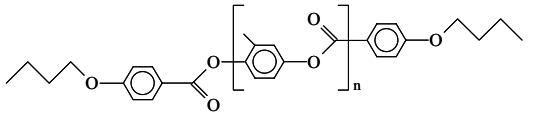
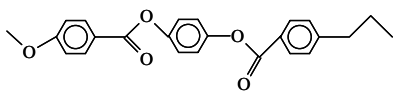
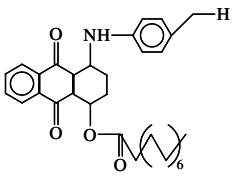
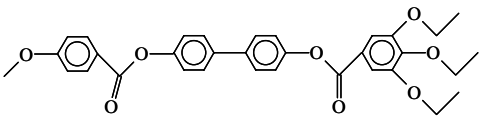
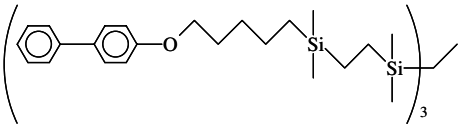


(5.16)

Hydrosilylation was conducted with the use of linear [136–145], cyclic [139, 146], and hyperbranched [146–148] polysiloxanes as well as silicone resins [149]. There are also examples of hydrosilylation with the use of silsesquioxanes [150–152]. Recently, much attention has been paid to cholesteric or chiral nematic liquid crystals with a unique property of selective reflection of circularly polarised light [145, 153–158].

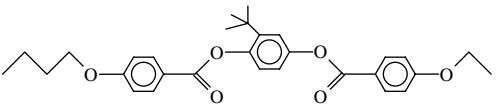
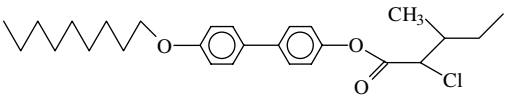
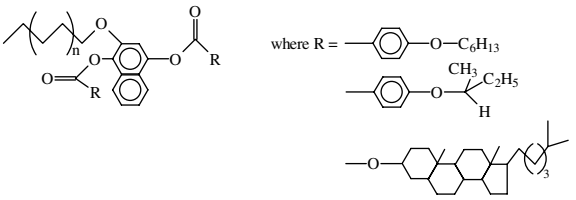
In addition, liquid crystalline elastomers (LCE) which are lightly crosslinked polymers have become very common. They exhibit both rubber-like elasticity and anisotropic liquid crystalline behaviour between the glass temperature and that

Table 5.1 Examples of mesogenes, used in the hydrosilylation processes

R	Cat	[Ref]
	Cp_2PtCl_2	[136]
	Karstedt's	[137]
	H_2PtCl_6	[138]
	$PtCl_2(cod)$	[139]
 and 	H_2PtCl_6 in THF	[140]
	H_2PtCl_6 in THF	[141]
	Karstedt's	[142]

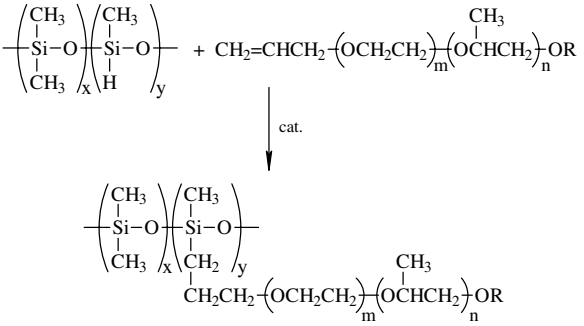
(Continued)

Table 5.1 (Continued)

R	Cat	[Ref]
	Karstedt's	[143]
	Karstedt's	[144]
	Karstedt's	[145]

of the liquid crystalline to isotropic phase transition [139, 144, 157–161]. This combination enables producing materials with a number of unique optical, mechanical and piezoelectric properties. The compounds of this kind were synthesised by a one-step hydrosilylation of a mesogenic monomer and a flexible crosslinking agent.

Due to high usefulness of products of polysiloxane addition to polyethers, the ways of their synthesis have been subjects of many patents. Most of them are based upon hydrosilylation catalysed by platinum complexes: H_2PtCl_6 in 2-propanol [162], H_2PtCl_6 in butanol [162], Pt/C [163], Karstedt's catalyst [164, 165]. Applying hydrosilylation to an allyl-functionalised PEO (polyethylene oxide) or PPO (polypropylene oxide) block, a variety of surfactants with different block lengths (resulting in various relative molar ratios of the blocks) have been synthesised with high yields [166–173]:



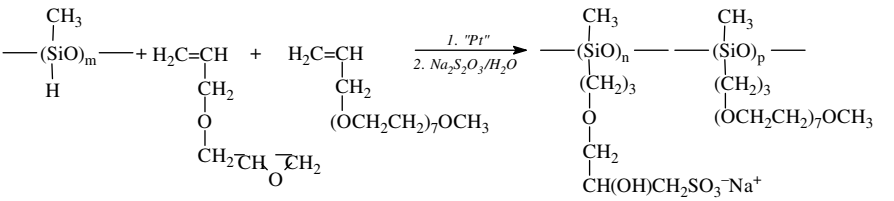
(5.17)

Reduction in surface tension, foam improving properties, ability to form emulsions in aqueous systems, solubility in water while maintaining properties characteristic of polydimethylsilicones (lubricating ability, thermal stability) have determined a whole range of applications of this class of products [166–168]. The first, and the largest yet, commercial application of silicone polyethers is in production of polyurethane foams [174–177].

Moreover, main trends in polyether applications are in woodworking, cosmetic and pharmaceutical industries, in which polyethers serve as components of many preparations. Moreover, they are applied as detergents for dish-washers, agents for surface maintenance, components of bonding agents, glues and insulations for electronic parts, components of car cosmetics, surfactants for paints and inks, compatibilising agents for thermoplastic silicone-polyamide elastomers, agents improving silicone dispersion in epoxy resins, components of liquid finishes for fibres and textiles, components of textile softeners, components of sealings and construction packings, foam inhibitors, frothing agents, emulsifiers, lubricants, moisteners, herbicide additives.

More and more reports have appeared on polyethersiloxanes containing monomeric units with other groups, e.g. alkyl ones (emulsifiers, surfactants, herbicide additives), amine groups (softeners, herbicide additives), epoxy and glycidyl groups (softeners).

Polyether groups are often introduced to the polysiloxane chain together with glycidyl ether and the product is then esterificated to give ionic polymer [178–181]:



(5.18)

In recent years, polymer electrolytes have received considerable attention for their potential application in modern electronics.

Since 1973 it has been well known that poly(ethylene oxide) (PEO) can be used as ion conductor upon doping with salt, however, there are difficulties associated with the development of highly conductive (PEO) electrolytes for ambient temperature applications because of their crystalline nature. The concept of combining stable, flexible polysiloxanes (with relatively low glass transition temperature) with PEO has led to the development of a variety of polymeric structures with the expressed aim of increasing conductivity. In the last few years, a number of copolymers with comb [182, 183], double-comb [184–186], cyclic [187, 188] and cross-linked structures [189–196] have been synthesised and investigated as possible candidates for both liquid and solid polymer electrolytes. All of these compounds were synthesised by hydrosilylation of poly(methylhydrosiloxane) with

appropriate poly(ethylene oxide) allyl ether, catalysed by platinum compounds, i.e., H_2PtCl_6,[Cp_2PtCl_2] or Karstedt's catalyst.

Very recently, other types of silicone electrolytes, of the general formula (5.2), based on the hydrosilylation processes, were synthesised containing besides (PEO) also other substituents, i.e. sulphate salt [197], trimethoxysilylpropyl group [198], cyclic carbonate [199], quaternary ammonium groups [200] or propyl cyanide [201–203] (see Fig. 5.2).

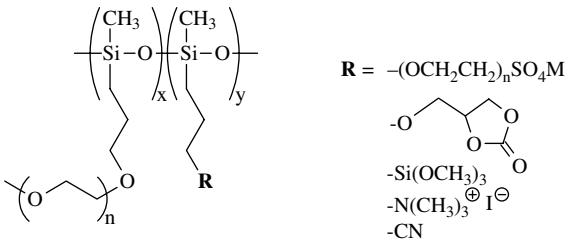


Fig. 5.2

These product show improved conductivity. However one of the highest conductivities ever observed in liquid "polymer" electrolytes is that of the low viscosity compounds, i.e., tetra- or trisiloxane with oligo(ethylene oxide) chain [204]

Silicone polyethers are the most common silicone surfactants, however presently various research teams are aimed at replacing of polyethers by carbohydrates. The widely available carbohydrates represents the main part of renewable resources and could be considered to function as predetermined breaking points during biodegradation of hybrid materials.

In the 1990's the carbohydrate modified silicones were developed as a novel class of hydrophilic modified silicones and are now ready for marketing and industrially available, mainly as ingredients of cosmetic formulations.

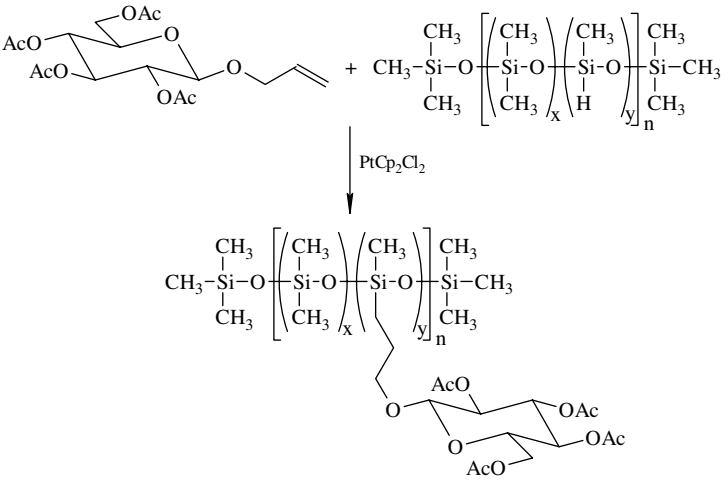
Carbohydrate-modified siloxanes seem to be interesting candidates for surface-active biocompatible materials. Amphiphilic block copolymers containing carbohydrates can enhance solubility of hydrophobic drugs and may facilitate the delivery of drugs to the target cell, on the basis of biological recognition procedure [205–207]. Their use as transdermal penetration enhancers [208], cosmetic formulations [209, 210], surfactants [211–215] and self-assembling polymers [216, 217] or stabilizers for polycaprolactone nanoparticles [218, 219] have also been reported.

There are three main pathways for synthesis of compounds of this type, i.e., in the reactions of amino-functionalised silicones and sugar lactone, of epoxy-functionalised silicones and sugar amines and hydrosilylation of allyl modified carbohydrates.

In most of the latter reactions, poly(dimethyl-co-hydromethyl)siloxanes have been used, giving access to the comb structure [216, 217, 220–226], however a few examples of chain-end-modified polysiloxanes have also been reported [208, 215].

Mono-, di- and oligosaccharides (glucose, galactose, maltose, cellobiose, lactose, maltotriose and maltoheptaose) were converted by a simple two-step reaction

(β-acetylation and allyl glycosilation) into active compounds allowing the polymer analogues addition to random poly(dimethyl-co-hydromethyl)siloxanes [216, 217, 223, 224] according to the equation:

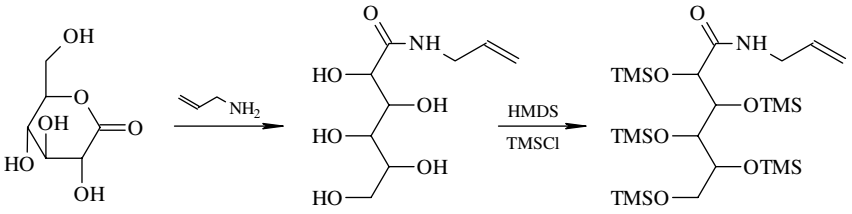


(5.19)

The hydrosilylation processes were catalysed by dicyclopentadienylplatinum(II) dichloride. Alkyldisiloxane and oligomethylsiloxanes containing glucose or cellobiose moiety at a terminal group were prepared by hydrosilylation of appropriate allyl derivatives by alkyltetramethyldisiloxane or hydrosilylterminated oligodimethylsiloxane in the presence of bis(benzonitrile)platinum dichloride as a catalyst [208, 227]. Similar reaction but using polysiloxane was catalysed by Speier's catalyst [215].

Carbohydrate-modified siloxane were also synthesised starting from allyloxyethyl mannopyranoside and either telechelic H-ended polysiloxanes [218], tetramethylcylotetrasiloxane [219] or poly(dimethyl-co-hydromethyl)siloxanes [218], catalysed by Karstedt's catalyst. These compounds were tested as stabilizers in nanoparticle formulations with poly(caprolactone) and polysulphone.

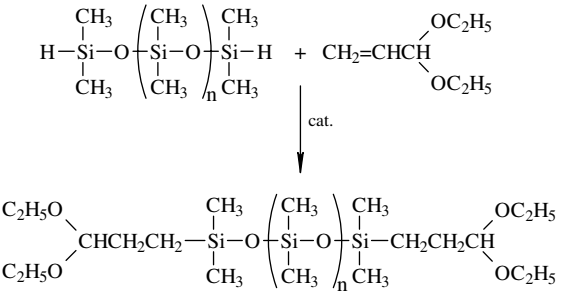
A series of well-defined polysiloxanes with pendant sugar units were prepared by hydrosilylation of the trimethylsilyl-protected allylamides of gluconic acid [228], according to (Eq. 5.20):



(5.20)

As reported [216], the common catalyst such as Speier's catalyst and dicyclopentadienyl platinum chloride showed no catalytic activities in the hydrosilylation reactions of this type because of the amide linkage in N-allylaldonamides, poisoning these catalysts. However, platinum dioxide PtO_2 apperad to be a powerful hydrosilylation catalyst in this reaction [228].

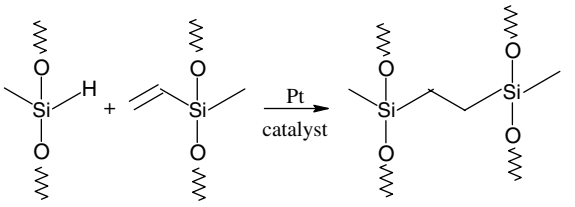
Another, indirect method for the synthesis of "sweet" silicones is also available, i.e., by acid catalysed transacetalation between an acetal functional siloxane and glucose [229]. Acetal functional siloxanes as starting materials can be synthesised in good yields by addition of Si-H functional siloxanes to acrolein diethylacetal, catalysed by Karsted's catalyst, according to the equation:



(5.21)

5.2 Silicone Curing

The addition of polyfunctional silicon hydrides to poly(vinyl)organosiloxane activates the curing of silicone rubber. The commonest activated curing method is based on the hydrosilylation reactions of polydiorganosiloxanes containing small numbers of vinyl groups and Si-H groups (usually end – blocked by them) [230].



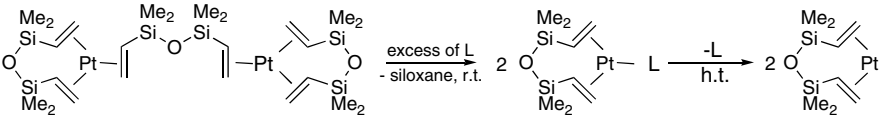
(5.22)

Since the reaction results in a high conversion and is free from side reactions this curing method can be used as a model application of network topology theories. The reaction product is usually characterised by an exceptionally high tensile strength, toughness and low porosity. Numerous papers have appeared containing mechanistic considerations based mainly on kinetic measurements, but also taking into account the physicomechanical properties of silicone elastomer [231]. The replacement of methyl groups by ethyl or phenyl in α, ω-dihydropolysiloxane

and α, ω-divinylpolydimethylsiloxane leads to a marked decrease in the rate of vulcanisation by hydrosilylation.

Hexachloroplatinic acid and other platinum complexes are mainly used as soluble catalysts for the additive cure of such polymers. The most active catalyst used recently for vulcanisation of silicon rubber based on polysiloxanes containing vinyl and Si-H groups is a platinum–alkenylsiloxanes complex, mainly the platinum(0)–vinylsiloxane complex (Karstedt's catalyst) [232]. An important approach to the activated cure of silicone rubber makes use of various inhibitors added to the platinum catalyst to reduce, or temporarily inhibit, its catalytic activity. The catalyst is usually added to the reaction mixture in quantities related to the number of unsaturated (e.g. vinyl) substituents in the polysiloxane.

It is now rather clear, the inhibitors act as ligands, which block the hydrosilylation reaction by coordination to the metal centre, but under the conditions employed for the cure, release the active catalyst.



L = inhibitor

(5.23)

However recent density functional computations study on the main cycle for Karstedt's catalysed cross-linking of silicones via hydrosilylation indicate that the reaction proceeds readily at ambient conditions with a barrier for the cycle on the order of 18 kcal/mol [233]

Basing on semiempirical methods to estimate solubility parameters, the authors conclude that all commonly used inhibitors cannot interfere with the polymerisation by binding to the catalytic center. The inhibitors are not soluble in the substrate but form liquid globules which physically isolate the catalyst from substrate i.e. the role of the inhibitors is to phase-separate the catalyst. From the substrate where they should depend only weakly on the inhibitors binding energy to the catalyst.

From catalytic point of view new co-activators (accelerators, promotors) of the catalyst (precursor) have been in the last two decades revealed to reduce in ppm levels of platinum required to effect hydrosilylation curing. The numerous unsaturated organic compounds e.g. esters, alcohols, ketones, sulphoxides, phosphines, phosphates, nitriles and hydroperoxides and others [49, 234–246] have been reported as

where, R = CH_3, C_2H_5, $CH_2CH_2OCH_3$, $CH(CH_3)CH_2OCH_3$, Ph, -CH=CH_2

Fig. 5.3

platinum catalysts inhibitors during the cure of silicone rubber through addition processes. The unsaturated diesters, e.g. maleates and fumarates (Fig. 5.3) are the most important and commonly used platinum inhibitors in industrial curing processes, and have been described in many papers and patents (for review see [230,231,247]). Various unsaturated hydrocarbons containing alkynyl function were used as effective inhibitors, e.g: dicarboxyacetylene esters such as [246] (Fig. 5.4).

Fig. 5.4

alcohols [245] (Fig. 5.5)

Fig. 5.5

diols [238] (Fig. 5.6)

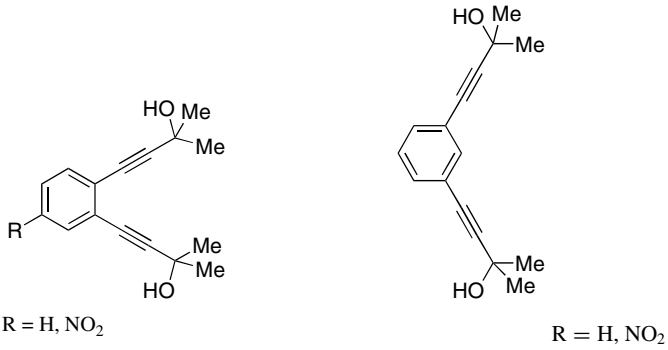


Fig. 5.6

or alkynes [245] (Fig. 5.7)

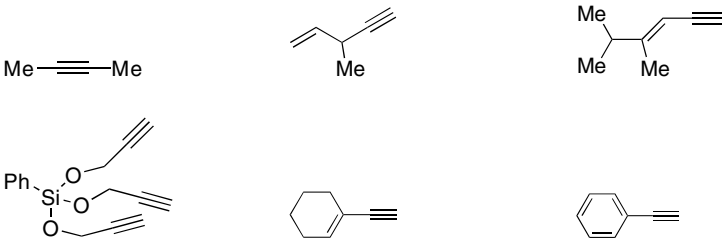


Fig. 5.7

Derivatives containing multiple bonds betwen nitrogen atoms have also been used as curing inhibitors e.g. azodicarbonyl compounds [239, 240] (Fig. 5.8) or triazoline dienes [241, 242].

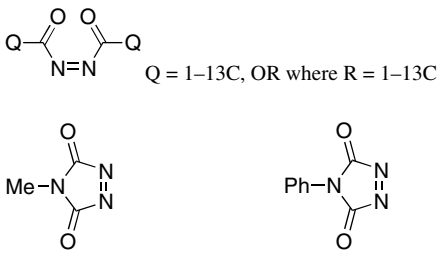


Fig. 5.8

Organophosporous compounds such as phosphines, phosphites as well as amine-N-oxides and sulphoxides as inhibitors of platinum group metal-containing hydrosilylation catalysts are claimed to delay curing compositions in the absence of oxygen and Si-H reactive hydroxylated compounds [248]. Well-defined platinum complexes with phosphite ligands have also been employed as catalysts of this process [249]. An inhibiting system consisting of phosphite with organic peroxide has been recently patented [250].

Other platinum complexes also exhibit high activity in the curing of polysiloxanes containing vinyl groups at elevated temperatures. For example, the curing of the catalyst composition is achieved by exposing them to molecular oxygen, which activates Pt catalyst and simultaneously deactivates the inhibitor [251]. The silane cure accelerator additives such R_2SiH_2 or $RSiH_3$ play the same role as molecular oxygen [252]. Treatment of the curing mixture containing H_2PtCl_6 precursors with base (sodium bicarbonate) also exhibits higher hydrosilylation catalyst activity [253]. Preparation of a platinum catalyst by reacting a platinum halide with organic compound having at least one -C≡C- group in the presence or absence of a base leads to formation of a Pt-complex which promotes the hydrosilylation (also curing) [245]. Hydrosilylation catalysts derived from cyclodextrin organometallic platinum and palladium inclusion compounds have been effectively used in command-cure applications [254–257] Co, Rh as well Pd complexes are also effective catalysts mentioned in patent claims quoted. Ni analog of Karstedt's catalyst was also found as a soluble catalyst for curing of polysiloxanes via hydrosilylation [258].

Instead of the catalyst inhibitors the method of microcapsulated platinum group catalyst has been effectively used. The catalyst is encapsulated within one or two layers of thermoplastic organic polymers such as cyclodextrines [255, 259–262] (Fig. 5.9).

$$\begin{aligned}
&\mathrm{Pt(COD)Cl_2} + \beta\text{-CD} \rightarrow \beta\text{-CD-Pt(COD)Cl}_2\\
&\mathrm{Pt(COD)Me_2} + \beta\text{-CD} \rightarrow \beta\text{-CD-Pt(COD)Me}_2\\
&\mathrm{CpPtMe_3} + \beta\text{-CD} \rightarrow \beta\text{-CD-PtCpMe}_3\\
&\mathrm{Pt(MeCp)Me_3} + \beta\text{-CD} \rightarrow \beta\text{-CD-Pt(MeCp)Me}_3
\end{aligned} \tag{5.24}$$

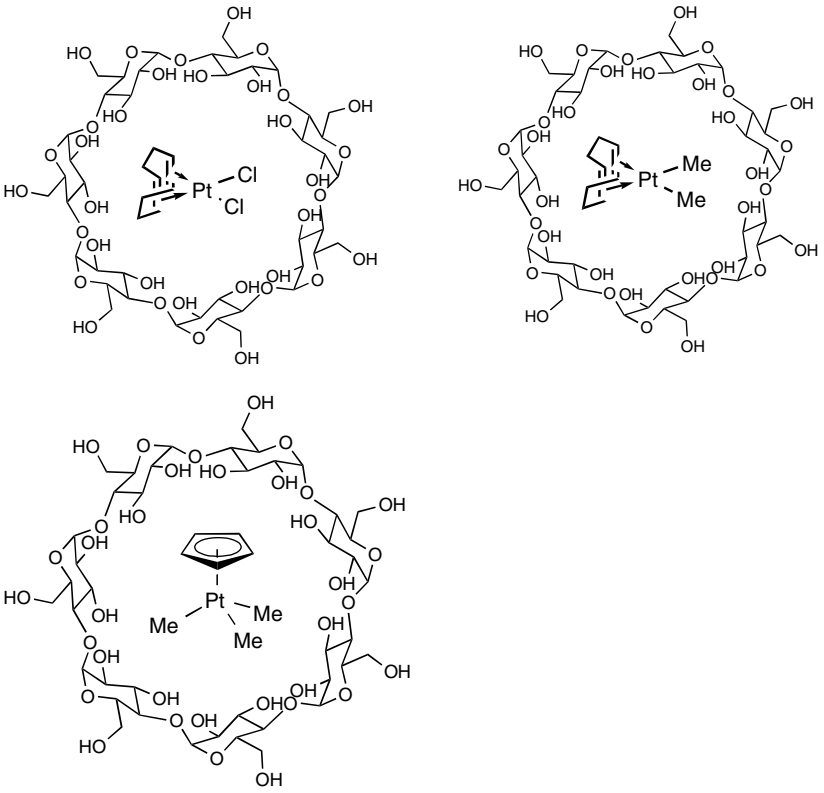


Fig. 5.9

The microcapsules can be incorporated into storage–stable one–part polysiloxane compositions that cure at the given temperature.

The fast cure can be also effected by accessible radiation methods (UV, electron beam, microwaves, actinic radiation) as well as free radical initiation system, e.g. azo-containing initiators [263].

As mentioned above, Boardman used (η^5-cyclopentadienyl) trialkylplatinum (IV) complex as photohydrosilylation catalyst particularly in the hydrosilylation cure [264–267]. Also β-dicarbonyltrialkylplatinum(IV) complexes are able to photoactivate efficiently hydrosilylation curing [268]. The homogeneous character of hydrosilylation is pointed out. Under irradiation the complexes are decomposed via

a triplet excited state and a radical stage into an active hydrosilylation catalyst and finally into less reactive colloidal platinum.

Well recognised maleate and fumarate as thermal inhibitors of Pt complexes were also used in photoinitiated curing reactions with good results [269].

Compounds with multiple bonds between nitrogen e.g. azodicarbonyl compounds [270] and aryl alkyl triazenes (R-C(O)-N=N-C(O)-R) (R=alkyl, alkoxyl) and R-N=N-N(H)-R (where R=alkyl aryl) [241] were also used as inhibitors in UV-activated curing processes. Kishi described the use of isocyanides RCNO (where R=t-Bu, Cy, Ph, benzyl, 4-ClP, 4MeOPh) as inhibitors in the photoactivated addition curing [271].

The reology of the systems can also vary widely, ranging from dip–cures to liquid injection molding (LIM) and conventional heat cure rubber (HCR) processing. Vinyl terminated polydimethylsiloxane polymers (viscosity >200 cSt) are typically crosslinked by methylhydrosiloxane – dimethylsiloxane copolymer with 15–50 mole % of polymethylhydrosiloxane. The catalyst is usually a complex of platinum in alcohol, xylene, divinylsiloxanes or cyclic vinylsiloxanes. The system is mostly prepared in two parts (part A – vinylsiloxane + Pt (5–10 ppm), part B – hydrosiloxane + inhibitor, generally 0.01–50 ppm). Apart from temperature, also moderators and inhibitors are used to control the work time. Moderators (e.g. tetravinyltetramethylcyclotetrasiloxane) slow Pt catalysis. Inhibitors stop the platinum catalyst, they are volatile or are decomposed by heat or light (UV).

A hydrosilylation catalyst improving the self stability and fast curing capability of silicone compositions was provided by preparation of Pt complex in a heat-fusible compound having a melting point of 40–200°C and containing an aliphatic unsaturated bond carbonyl, carboxyl or thioether radical in a molecule [272]. Emulsion of liquid Pt-catalyst in surfactant containing water is also employed as the hydrosilylation curing catalyst [273]. On the other hand, organic iron and aluminum compounds, e.g. iron [111] octylate and aluminium alkoxides used as scavangers of transition metal Pt, Pd, Rh catalyst poison have also been patented [274].

A Pt-catalyst can be obtained by condensing Pt-vapour in a mixture of an aromatic compound and a vinyl siloxane compound using metal vapour synthesis, resulting in the formation of a solid matrix and followed by its melting to obtain a Pt-containing solution [275].

Hydrosilylation crosslinking of silicone rubber has been increasingly used in rubber manufacture because of many technological and economic advantages. The composition and proportion of both polysiloxane components as well as the catalyst used (mostly Pt-complex-based), determine the quality of the vulcanisate and in particular allow obtaining materials of given properties and for special applications. Among the recent patents, some describe procedures for preparation of silicon rubber excellently improving its chemical and temperature resistance [276] mechanical properties such as tensile strength and high tear strength [277] gas permeability [278] and other desirable properties of gels [279–287]. In particular, fluorinated curable silicone composition cure into a gel with improved chemical and solvent resistance [288, 289]. They constitute protective coating of such commonly used materials as optical displays, textiles, metals, stone, wood and leather. Of particular interest have been the compositions usually comprising alkoxy ter-

minated polysiloxanes and the methods of the in situ formation of hydrosilylation cross-linked films related to the production of materials being long-lasting flexible, transfer-resistant and water proof [290, 291].

Special focus of cured organopolysiloxanes have been recently observed on optoelectronic and semiconductor materials having a high refractive index, optical transmission and adhesion to various substrates. They are used as protective coating agents for semiconductor elements in photocoupless, light emitting diodes (LED), solid-state image sensors and other optical semiconductor devices [292–319]. Curable compositions for the conductive material include also organic polymers containing at least one alkenyl group in a molecule [320–322].

Numerous patents of two last decades are focused on organopolysiloxane compositions containing predominantly typical Pt-complex as catalyst and, additionally, adhesion promoting compositions (usually silane coupling agents with carbon substituted functional groups), improving adhesion to metal, glass, plastics and other inorganic materials [323–342] and also the release of adhesive materials [343]. Electrically conductive silicone adhesives can be produced from silicone adhesives containing a conductive filler [344]. A silicone based hot melt encapsulant material is applied in photovoltaic cells [345]. Silicone rubber composition can be useful in the sealing and encapsulation of electric and electronic parts e.g. preventing or retarding those parts from corrosion with sulphur-containing gel [346]. Exemplary high viscosity cure-silicone based thermal interface material can be useful to absorb the heat from a central processing unit (CPU) of a computer and transfer the heat to the heat sink thereby cooling the CPU [347]. Silicone rubber compositions are also reported as multicomponent systems involving two-step curable addition, cross-linkable mixer-suitable silicone materials [348]. They are used as discoloration–resistant compounds, gas-separating siloxane membranes, electric insulators, gasoline and oil-resistant fluorinated silicone elastomer [349–351]. Cured silicones are used as dental materials having rigid and/or voluminous group and great flexured strength [352] as well as the sheets for surgical bandages [353]. Cross-linked silicone can also be used in lithography [354, 355] for drug delivery [356] and for preparation of polymer dispersed liquid crystals [357, 358]. Cured silicones as well as Si-C-O compositions have been used as silicone materials operating as a negative electrode active material for non-aqueous electrolyte secondary cells [359]

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Chapter 6
Hydrosilylation Polymerisation

Abstract The catalytic hydrosilylation of difunctional organosilicon monomers containing alkenyl- or alkynyl-groups and/or Si—H bonds has become a versatile synthetic tool for obtaining saturated or unsaturated organosilicon polymers bearing the Si—C bonds in the backbone. These important polymeric products have been prepared through two main routes: the intermolecular hydrosilylation polymerisation of alkenyl(alkynyl)hydrosilanes and the polyhydrosilylation of α,ω-dienes or diynes with dihydro-substituted organosilicon compounds. The chapter covers recent achievements on the synthesis of saturated polycarbosilanes and polycarbosiloxanes as well as unsaturated polycarbosilanes or related σ-π conjugated polymers using transition metal catalysed hydrosilylation polymerisation.

The catalytic hydrosilylation of difunctional organosilicon monomers containing alkenyl groups and/or Si—H bonds leads to formation of saturated organosilicon polymers. These polymeric products, depending on their structure or the degree of branching – have recently been applied as precursors of ceramic materials characterised by truly unparalleled resistance to chemical and mechanical factors. Recently, polycarbosilanes and related polymers have also attracted increasing attention for their applicability in heat-resistant materials (coatings, paints or prepergs) and moulding materials [1].

On the other hand, hydrosilylation of difunctional organosilicon monomers containing alkynyl groups and/or Si—H bonds leads to formation of unsaturated polycarbosilanes or related σ-π conjugated polymers. These polymeric products, also known as poly(silylenevinylene)s or poly(arylene-silylene-vinylene)s (where monomers with aromatic functionalities are polymerised) have gained increasing attention for their potential applications to optoelectronic devices, heat-resistant materials and ceramic materials. Such silicon-containing σ-π conjugated polymers are expected to be photoresistant and photo- and electroluminescent materials featuring high processability, because they are more flexible and soluble than classical conjugated organic polymers without silicon.

Hydrosilylation polymerisation leading to polycarbosilanes (polycarbosiloxanes) may be carried out by means of the following processes:

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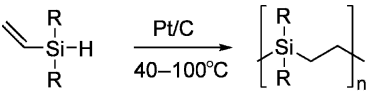
– intermolecular hydrosilylation of monomers containing both alkenyl (alkynyl) groups and Si—H bonds in the molecule
– polyaddition of dihydro-substituted organosilicon monomers to dialkenyl-(dialkynyl)-substituted organosilicon compounds.
– polyaddition of dihydro-substituted organosilicon compounds to dienes or diynes and their functionalised derivatives

6.1 Hydrosilylation Polymerisation of Monomers Containing C=C Bonds

6.1.1 Intermolecular Hydrosilylation of Alkenyl(hydro)silanes

The intermolecular hydrosilylation leading to oligomeric polycarbosilanes was extensively studied as early as in the 1950s. [2, 3] (Eq. 6.1)

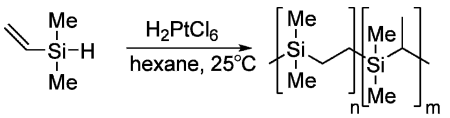


R = Me, Et, Ph

M_w = 990–2300 (6.1)

The interest in the methods of synthesis of saturated polycarbosilanes has dramatically raised after it became obvious that the compounds discovered were excellent preceramic materials due to the fact that in the reaction of pyrolysis carried out at temperatures of over 1000°C, silicon carbide (β–SiC) [4] was yielded. While continuing the research on the reaction of catalytic polyhydrosilylation of diorganovinylsilanes initiated in 1950s and 1960s, Corriu devised a method of synthesis of poly(dimethylsilyl)ethylene by utilizing the intermolecular hydrosilylation of dimethylvinylsilane in the presence of H_2PtCl_6 [5, 6]. The number-average molecular weights of the oligomers obtained varied from 960 in hexane to 5500 in chlorobenzene with 64–78% yields.

The poly(dimethylsilyl)ethylene formed was distinguished by an irregular structure since it incorporated $-Si(Me)_2CH_2CH_2-$ fragments (70–85%) as well as branched ethylidene units between silicon atoms (Eq. 6.2).

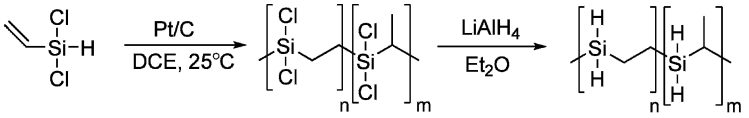


M_w = 3700, n/m = 7/3 (6.2)

Poly(dimethylsilyl)ethylene containing only ethylene units between silicon atoms was successfully synthesised *via* Karstedt's complex-catalysed hydrosilylation of vinyldimethylsilane to get oligomers of $M_w = 4100$ [7]. Photoactivated [$Pt(acac)_2$]-catalysed hydrosilylation polymerisation of vinyldimethylsilane leading to

higher-molecular weight oligomers of irregular structure (M_w up to 12,300) has also been reported [8].

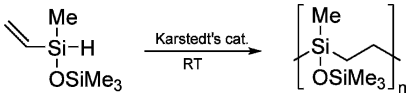
Poly(silyl)ethylene, which does not contain aliphatic substituents at the silicon atoms, is a particularly interesting preceramic material as it contains silylene groups (SiH_2), which thermodecompose relatively easily. Poly(silyl)ethylene was obtained by platinum-catalysed hydrosilylation of dichlorovinylsilane, followed by $LiAlH_4$ reduction of the oligomer obtained [9]:



M_w = 1200, n/m = 68/32 (6.3)

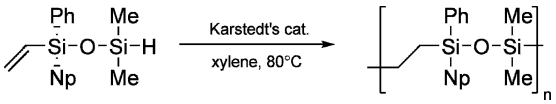
Optimising the reaction conditions by replacing the 1,2-dichloroethane (DCE) for chlorobenzene, as well as utilizing the hexachloroplatinic(IV) acid instead of heterogeneous platinum catalyst made it feasible to obtain the oligomers of identical structures, characterised, however, by the higher average molecular weight M_w = 3960 [6].

The intermolecular hydrosilylation of methyl(trimethylsiloxy)vinylsilane (Eq. 6.4) leads to the formation of siloxy-functionalised poly(silyl)ethylene [10]. The process gives substantial yields in the presence of Karstedt's catalyst, leading in turn to the formation of oligomeric products, which features M_w = 1100 and the polydispersity index (PDI) M_w/M_n = 1.4.



(6.4)

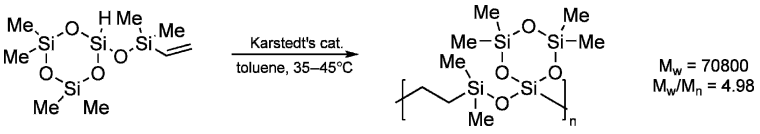
Platinum-divinyltetramethyldisiloxane complex was also utilised as a catalyst of the polyhydrosilylation of optically active (*S*)-1-phenyl-1-naphthyl-1-vinyl-3,3-dimethyl-1,3-disiloxane [11] (Eq. 6.5). In this reaction, stereoregular, isotactic polycarbosiloxanes with almost β-addition units (>99%) of molecular weight M_n = 2920 and M_w/M_n = 1.57 were produced.



(6.5)

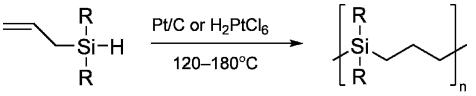
It is worth noting that the application of the racemic difunctional siloxane in the reaction described results in the formation of atactic product with inferior physicochemical properties (M_n = 2400, M_w/M_n = 2.11).

Cyclic siloxanes containing both Si—H bond and vinyl group have also been applied in the Karstedt's complex-catalysed hydrosilylation polymerisation [12,13]:



(6.6)

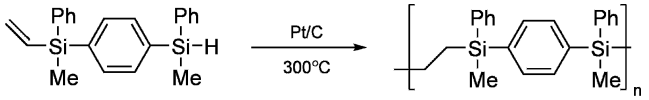
The research on the reaction of intermolecular hydrosilylation leading to the formation of saturated polycarbosilanes, was, however, not limited to vinylsilanes, but it also covered some other alkenyl-substituted organosilicon compounds. An example is the hydrosilylation polymerisation of halo- or alkyl(aryl)-substituted allylsilanes in the presence of Pt/C or H_2PtCl_6 giving oligomeric products (M_w = 1100–4100) [14, 15]:



R = Me, Et, Ph, Cl, F (6.7)

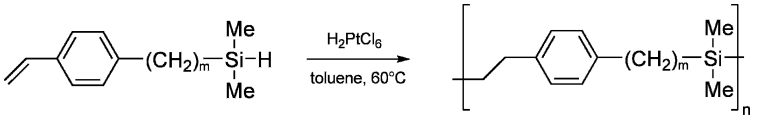
Hyperbranched polycarbosilanes with allyl end groups were also synthesised *via* hydrosilylation polymerisation of diallylmethylsilane in the presence of Karstedt's catalyst [16]

The pioneering study in the field of the synthesis of phenylene-silylene-alkylene polymers was published by Znamenskaya and co-workers, who presented the outcome of their research on intermolecular hydrosilylation of 1-(methylphenylvinylsilyl)-4-(methylphenylsilyl)benzene in the presence of platinum on carbon [17]:



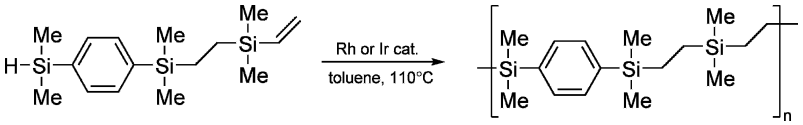
(6.8)

Hydrosilylation polymerisation of ω-(dimethylsilyl)alkyl-substituted styrenes has also been reported [18] (Eq. 6.9).



(6.9)

More recently, polycarbosilanes containing arylene units in the backbone have been synthesised *via* intermolecular hydrosilylation of difunctional carbosilane in the presence of dimeric [{M(μ-OSiMe$_3$)(cod)}$_2$] or monomeric [M(OSiMe$_3$)(cod)(PCy$_3$)] rhodium and iridium siloxide complexes [19]:



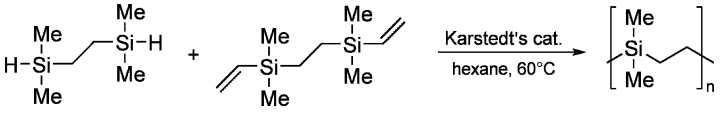
(6.10)

The most attractive results were achieved in the presence of dimeric rhodium siloxide catalyst. In this reaction, polycarbosilanes with molecular weights as high as $M_w = 102,000$ were obtained (in comparison to the reaction with platinum catalyst giving compounds of $M_w = 14,000$).

6.1.2 *Polyaddition of Dihydro-Substituted Organosilicon Compounds to Organosilicon Dienes*

The polyaddition of dihydro-substituted organosilicon compounds to dialkenyl-substituted organosilicon compounds, running in the presence of transition metal complexes represents another type of synthesis of saturated organosilicon polymers employing hydrosilylation [20]. The possibility of regulating the molar ratio of the substrates used in the reaction makes this method useful not only to obtain linear polycarbosilanes of defined structure, but also to produce polymers of specific terminal groups, which may react with multifunctional organosilicon cross-linking agents leading to the formation of polymer materials of branched structure.

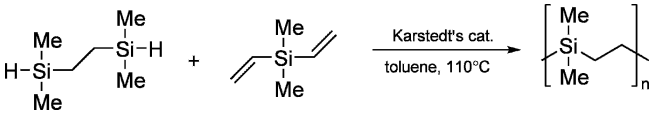
Catalytic polyaddition of dihydrosilanes to organosilicon dienes has been used to obtain poly(silyl)ethylene [21] (Eq. 6.11). Polyaddition of 1,2-bis(dimethylsilyl) ethane to 1,2-bis(dimethylvinylsilyl)ethane, occurring effectively in the presence of Karstedt's catalyst, led to oligomers of molecular weights ($M_n = 25,000$, $M_w/M_n = 3.4$) higher than those formed by means of intermolecular hydrosilylation of vinyldimethylsilane.



(6.11)

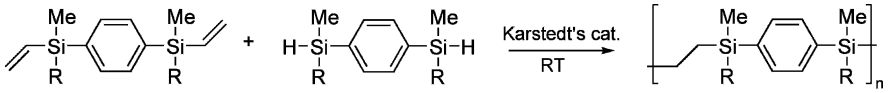
By using the excess of one of the reagents in the reaction described, two difunctional oligomers (of the average molecular weights ranging from $M_n = 1100$ to $M_n = 7600$) were obtained, which were in turn used in the hydrosilylative cross-linking by tetravinylcyclotetrasiloxane, tetravinylsilane or (when terminal vinyl groups were present in the oligomer chain) tetrahydrocyclotetrasiloxane in the presence of Karstedt's catalyst. The obtained cross-linked oligomers were characterised by much better physicochemical properties, however, the data on their molecular weight are lacking [21].

An alternative way of poly(dimethylsilyl)ethylene synthesis consists in the reaction between divinyldimethylsilane and 1,2-bis(dimethylsilyl)ethane in the presence of Pt-Karstedt's catalyst (Eq. 6.12). In this case the highest molecular weight was $M_w = 9000$ [7].



(6.12)

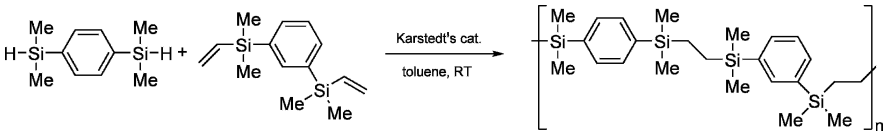
Tsumura and co-workers reported the results of the hydrosilylation of 1,4-bis(diorganosilyl)benbenes with 1,4-bis(diorganovinylsilyl)benzenes in the presence of Karstedt's catalyst [22] (Eq. 6.13). The incorporation of an aromatic unit into the polymer chain improves both the mechanical and thermal properties and reduces the risk of depolymerisation to small cyclic compounds at elevated temperatures.



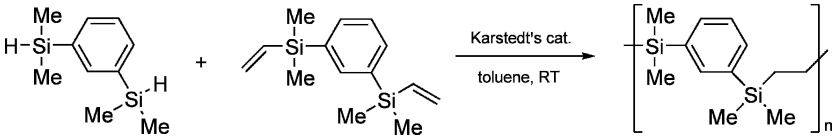
(6.13)

When the monomers with phenyl substituents at the silicon atoms were used, the reaction led to the formation of an oligomer of the molecular weight $M_n = 7000$ ($M_w/M_n = 1.8$), whereas the use of methyl derivatives led to the formation of oligomers with the molecular weight $M_n = 15,000$ ($M_w/M_n = 2.0$) [22].

Replacement of 1,4-bis(dimethylvinylsilyl)benzene by 1,3-bis(dimethylvinylsilyl)-benzene in the reaction with 1,4-bis(dimethylsilyl)benzene leads to the formation of oligomer of the molecular weight $M_n = 9200$ ($M_w/M_n = 2.4$) (Eq. 6.14), whereas in the reaction of 1,3-bis(dimethylvinylsilyl)benzene with 1,3-bis(dimethylsilyl) benzene, the oligomer of a higher molecular weight $M_n = 17,000$ ($M_w/M_n = 1.9$) [23–26] can be obtained (Eq. 6.15):

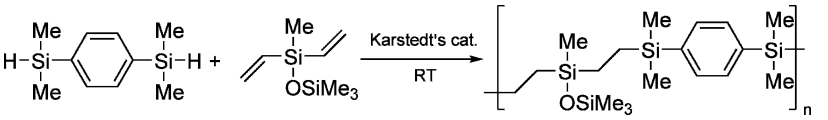


(6.14)



(6.15)

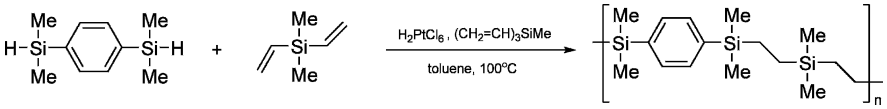
The reaction of 1,4-bis(dimethylsilyl)benzene with 1,1-divinyl-1,3,3,3-tetramethyldisiloxane run in the presence of Karstedt's catalyst led to formation of aromatic polycarbosilane ($M_n = 11,000$, $M_w/M_n = 3.9$) bearing siloxy groups at the silicon atoms [10]:



(6.16)

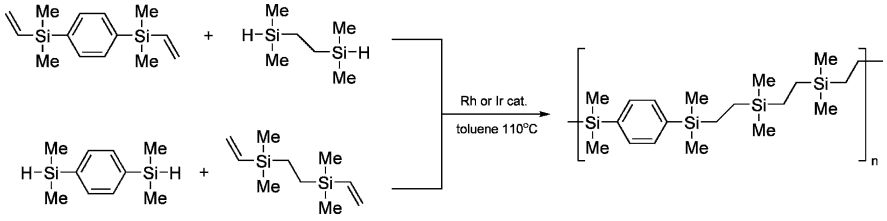
1,4-Bis(dimethylsilyl)benzene was also hydrosilylated with divinyldisilanes in the presence of Speier's catalyst, however the structure of the resulting polymers was found to be disturbed due to the side reaction involving the Pt-catalysed cleavage of Si—Si bonds [27].

High-molecular weight polycarbosilanes were obtained by hydrosilylation of dimethyldivinylsilane with 1,4-bis(dimethylsilyl)benzene in the presence of methyltrivinylsilane (Eq. 6.17). As a result of the reaction catalysed with H_2PtCl_6, the polymers of the average molecular weights reaching $M_w = 113,000$ [28] were synthesised:



(6.17)

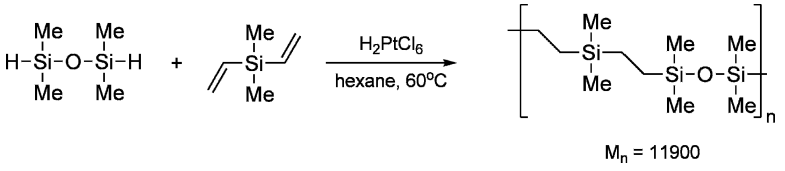
Application of dimeric and monomeric rhodium and iridium siloxide complexes of the general formula $[\{M(\mu\text{-}OSiMe_3)(cod)\}_2]$ and $[M(OSiMe_3)(cod)(PCy_3)]$ (M = Rh, Ir) as catalytic systems in the hydrosilylation polymerization of 1,4-bis(dimethylvinylsilyl)benzene with 1,2-bis(dimethylsilyl)ethane or 1,2-bis(dimethylvinylsilyl)ethane with 1,4-bis(dimethylsilyl)benzene led to obtain linear poly (phenylene-silylene-ethylene)s with molecular weights ranging from $M_w = 6200$ to $M_w = 20,200$ [19] (Eq. 6.18):



(6.18)

By substituting one of the difunctional carbosilanes with a dihydrosiloxane or divinylsiloxane, polycarbosiloxanes can be obtained, differing from their polycarbosilane analogues in the thermal and mechanical properties [20]. The organosilicon polymers of this type, containing both Si—O and Si—C bonds in their backbones are also called "hybrid silicones". As polycarbosiloxanes have been shown to have properties intermediate between those of linear polydimethysiloxanes and saturated hydrocarbons, recently they have been synthesised to improve thermal and fuel resistance properties of classical silicones.

One of the first examples of the synthesis of polycarbosiloxanes using hydrosilylation polymerisation was reported by Boileau and co-workers [21] (Eq. 6.19 and 6.20):



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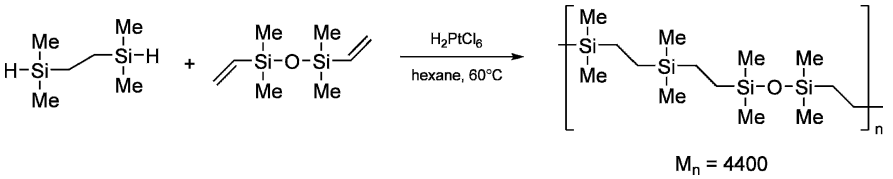
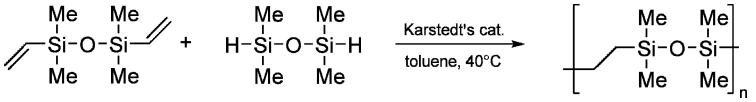


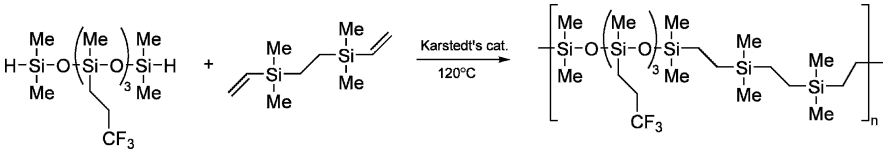
(6.20)

Dvornic and co-workers used Karstedt's complex-catalysed hydrosilylation polymerisation reaction between divinyltetramethyldisiloxane and tetramethyldisiloxane to prepare polycarbosiloxanes with a high molecular weight (M_w up to 76,000) [29] (Eq. 6.21). The kinetics and mechanism of the formation of these polycarbosiloxanes have been recently also investigated [30]



(6.21)

More recently, a series of trifluoropropyl-substituted polycarbosiloxanes showing unique chemical stability have been prepared by Pt-Karstedt's complex-catalysed polyhydrosilylation of dihydropentasiloxane containing three trifluoropropyl groups with various divinyl-substituted organosilicon compounds [31, 32] (Eq. 6.22–6.24). The GPC analysis of the resulting polymers proved that high molecular weights polymers can be obtained (M_w = 14, 100–47,600, M_w/M_n = 2.0–4.3)



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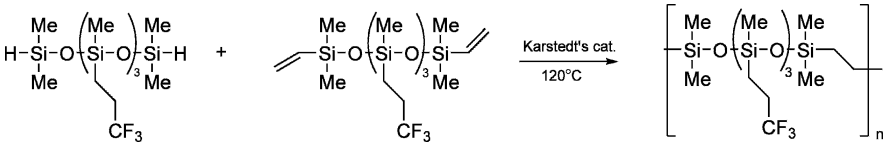

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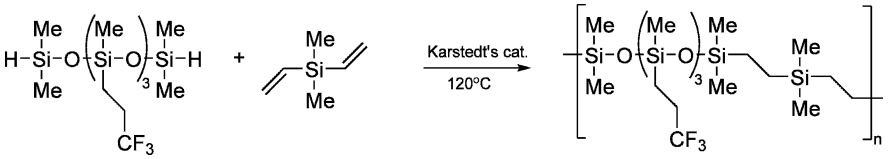
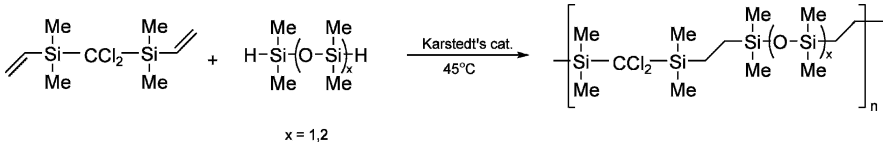


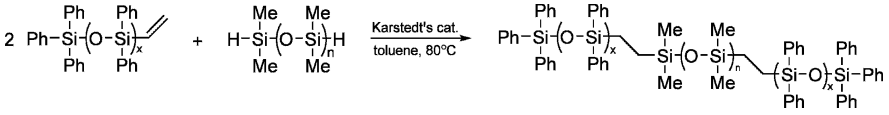
(6.24)

Halogenated polycarbosiloxanes (M_w = 14,500–26,700, PDI = 1.62–1.68) have been successfully prepared using platinum-complex catalysed hydrosilylation polyaddition of tetramethyldisiloxane to dihalo(vinyldimethylsilyl)methanes [33, 34] (Eq. 6.25):



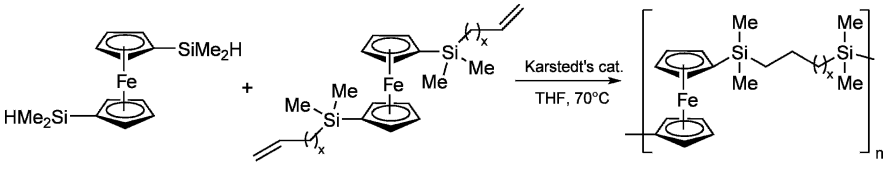
(6.25)

Triblock siloxane copolymers of molecular weights ranging from M_w = 15,000 to M_w = 52,000 (PDI = 1.4–1.8), were conveniently prepared by polyhydrosilylation of α,ω-bis(hydro)polydimethylsiloxane with α-vinylpolydiphenylsiloxane [35, 36] (Eq. 6.26):

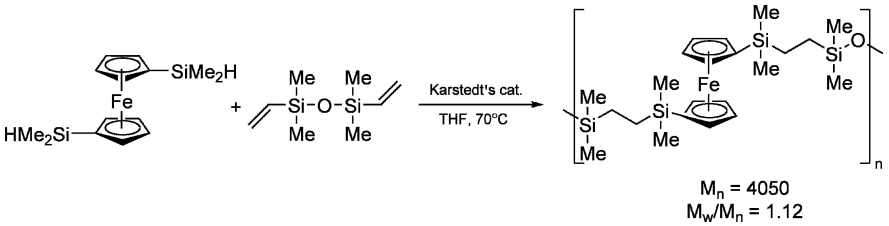


(6.26)

Very recently, dimethylsilyl-substituted ferrocenes have been used to produce new iron-containing organometallic polymers *via* hydrosilylation with dialkenyl-substituted ferrocenes (Eq. 6.27) or divinyltetramethyldisiloxane (Eq. 6.28) respectively, in the presence of Karstedt's catalyst [37]:



(6.27)

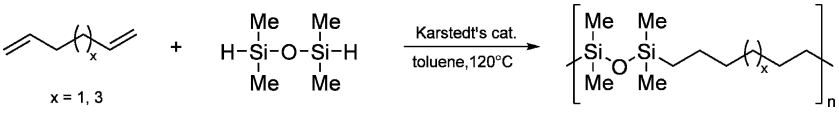


(6.28)

6.1.3 Polyaddition of Dihydro-Substituted Organosilicon Compounds to Dienes

Polyaddition of organosilicon dihydrides to dialkenyl-substituted organic compounds also known as hydrosilylation copolymerisation, leads to obtain polycarbosiloxanes with functionalised organic segments.

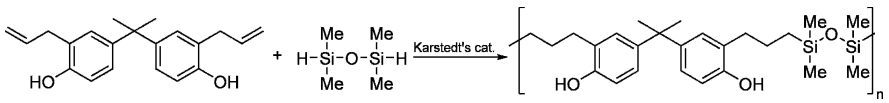
Weber et al., reported the Karstedt's complex-catalysed polyaddition of dihydrosiloxanes to simple α,ω-dienes such as 1,7-octadiene or 1,5-hexadiene [38, 39] (Eq. 6.29). The molecular weight of the polymers formed was limited by platinum-catalysed isomerisation of terminal C—C double bonds to the unreactive internal double bonds, and varied from $M_w = 7500$ to 11,500.



(6.29)

The kinetics of the $PtCl_2$-catalysed polyhydrosilylation of divinylbenzene by tetramethyldisiloxane was studied by Buchmeiser and co-workers [40]. Radical polyhydrosilylation of divinylperfluorohexane with dihydrodisiloxane or dihydrotrisiloxane proceeding in the presence of *tert*-butyl peroxide was reported [41, 42]

Hydrosilylation polymerisation of 2,2′-diallyl bisphenol A with tetramethyldisiloxane or hexamethyltrisiloxane to produce carbosiloxane polymers containing bisphenol fragments ($M_w = 27,000$) has been reported by Mathias et al. [43] (Eq. 6.30):

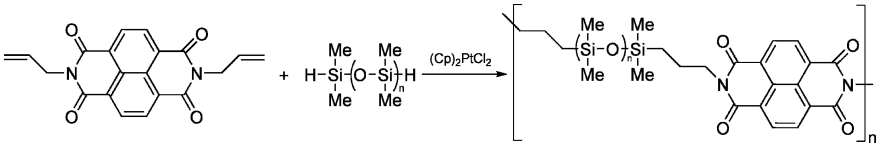


(6.30)

A similar reaction was performed between 2,2′-diallyl bisphenol A [44,45] or fluorinated 2,2′-diallyl bisphenol A [46] with hydride-terminated polydimethylsiloxanes which led to polymers of possible use as chemical sensors.

Poly(imidesiloxanes) have been prepared through catalytic polyaddition hydrosilylation of α,ω-bis(hydro)polydimethylsiloxanes with unsaturated imides (Eq. 6.31)

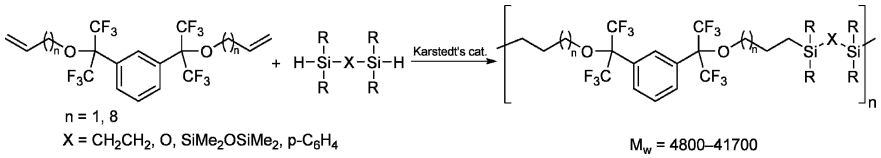
[47–50]. An example is the reaction of linear dihydro polysiloxane with *N,N'*-diallyldiimide in the presence of platinum cyclopentadiene complex [47]:



(6.31)

More recently poly(arylene-siloxylene)-polyimide thermoplastic elastomers have been synthesised through polyhydrosilylation of allyl-terminated oligoimides with α,ω-bis(hydro)silarylene-siloxanes in the presence of hexachloroplatinic acid or Karstedt's catalyst [51–53].

Platinum catalysed hydrosilylation polymerisation was also used to prepare fluorine-containing hybrid materials bearing crosslinkable units in the backbone (Eq. 6.32). The best results were obtained using supercritical carbon dioxide [54].



n = 1, 8

X = CH_2CH_2, O, $SiMe_2OSiMe_2$, p-C_6H_4

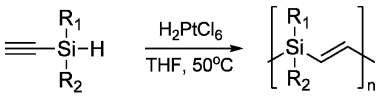
M_w = 4800–41700

(6.32)

6.2 Hydrosilylation Polymerisation of Monomers Containing C≡C Bonds

6.2.1 Intermolecular Hydrosilylation of Alkynyl(hydro)silanes

The results of the intermolecular hydrosilylation of the range of ethynylhydrosilanes in the presence of H_2PtCl_6 as a catalyst were reported by Barton and co-workers [55] (Eq. 6.33):



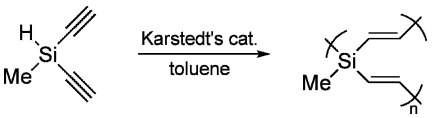
R_1=Me, Et, Ph

R_2=Me, Et

(6.33)

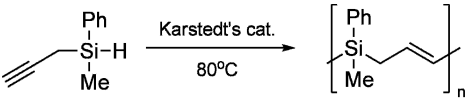
As a result, stereoregular polymers with *trans*-vinylene units of the molecular weights ranging from $M_w = 30,000$ to 85,000 and $M_w/M_n = 2,5–4,8$ were formed. Optimisation of the conditions of the reaction with diethylethynylsilane, which included applying high temperature (160°C) and increased duration of the reaction,

made it possible to obtain higher-molecular weight polymer of $M_w = 110,700$, characterised, however, by unusually high polydispersity index ($M_w/M_n = 36$). Hyperbranched unsaturated organosilicon polymers (molecular weights ranging from 2720 to 3090) possessing pendant ethynyl groups has been also prepared *via* Karstedt's complex-catalysed hydrosilylation polymerisation of diethynylmethylsilane [56] (Eq. 6.34):



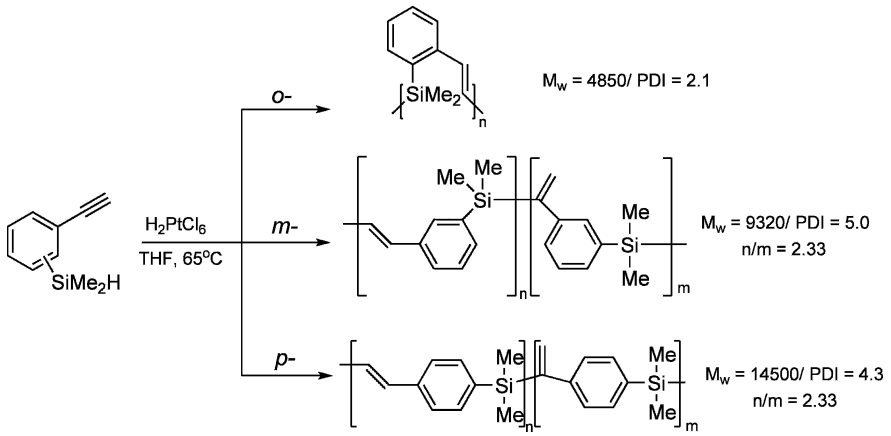
(6.34)

Replacement of ethynyl group for propargyl in the substrate, makes it feasible to obtain a polymer with propenylene units between silicon atoms in the chain [57] (Eq. 6.35):



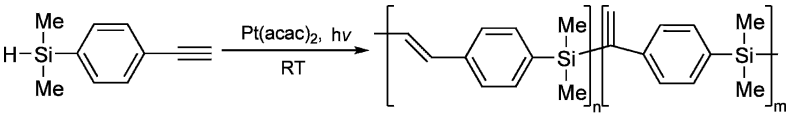
$M_w = 15600$, $M_w/M_n = 2.52$ (6.35)

Kim and Shim reported the intermolecular hydrosilylation polymerisation of *o*-, *m*- and *p*-(dimethylsilyl)phenylacetylenes in the presence of H_2PtCl_6 to get the corresponding poly(dimethylsilylene-phenylene-vinylene)s [58]. While *orhto*-substituted monomer produced only polymer (69% yield) with regular (*E*)-1,2-vinylene units, the hydrosilylation of *m*- and *p*-silylphenylacetylenes led to obtain polymers containing two isomeric (*E*)-vinylene and vinylidene fragments with 89 and 67% yield, respectively (Eq. 6.36):



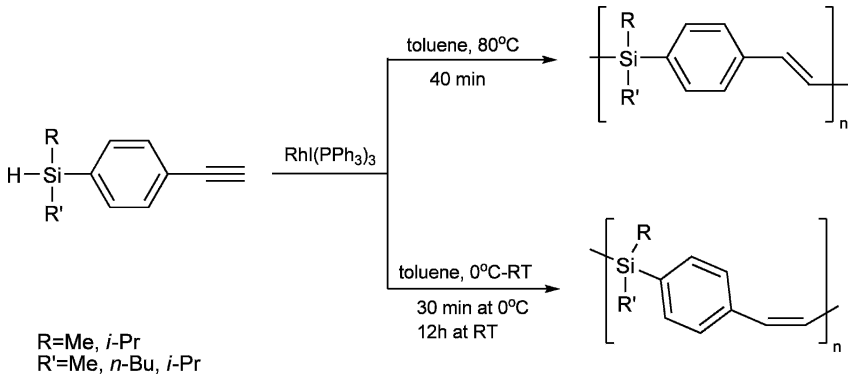
(6.36)

Similar silicon-containing unsaturated polymers containing both the (*E*)-vinylene and vinylidene units between silicon atoms and phenylene rings, have been synthesised using the [$Pt(acac)_2$]-catalysed photoactivated hydrosilylation of 4-(dimethyl silyl)phenylacetylene [59] (Eq. 6.37):



Mw = 16900, M_w/M_n = 2.5 (6.37)

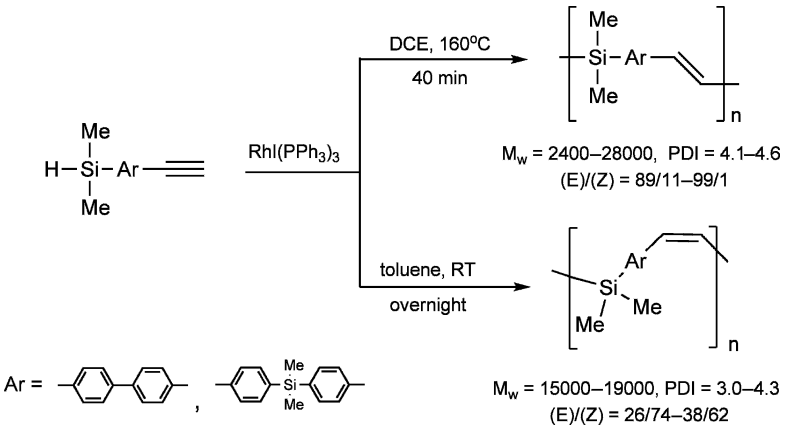
Polyhydrosilylation of 4-(dimethylsilyl)phenylacetylene using [$RhI(PPh_3)_3$] as the catalyst afforded, depending on the reaction conditions, highly regio- and stereoregular poly(dimethylsilylene-phenylene-vinylene)s containing 98% *cis*- and 99% *trans*-vinylene moieties, respectively [60, 61] (Eq. 6.38):



(6.38)

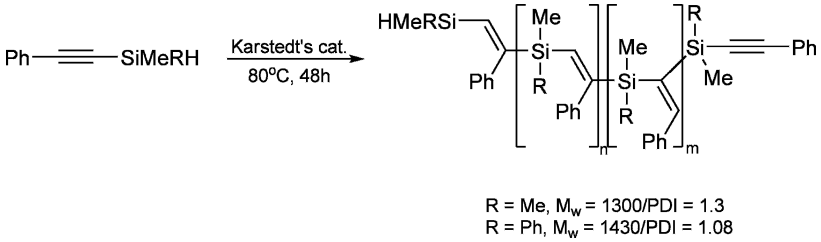
Depending on the substituents at the silicon atom, the linear, stereoregular (*E*)-polycarbosilanes of an average molecular weight ranging from $M_w = 43,000$ ($M_w/M_n = 3.2$) (for two methyl groups) up to $M_w = 46,000$ ($M_w/M_n = 4.2$) (for methyl and *n*-butyl substituents) were obtained. The molecular weights of the (*Z*)-poly(silylene-phenylene-vinylene)s were slightly lower and ranging from $M_w = 31,000$ ($M_w/M_n = 2.6$) for polymers containing butylmethylsilylene units to $M_w = 33,000$ ($M_w/M_n = 3.6$) for dimethylsilylene polymers.

This stereoselective rhodium-catalysed approach has been also successfully exploited in the synthesis of both (*E*)- and (*Z*)-poly(dimethylsilylene-arylene-vinylene)s containing biphenylene and phenylenesilylenephenylene units [62] (Eq. 6.39):

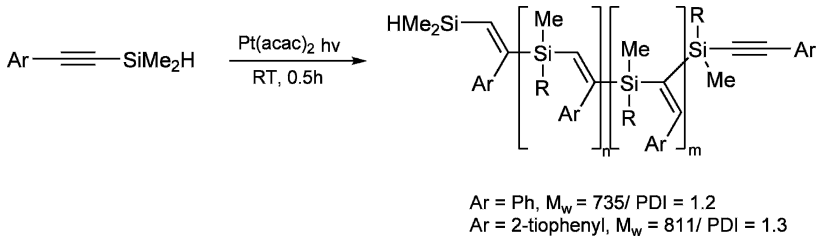


(6.39)

Photoluminescent silylene-vinylene oligomers with pedant aromatic groups containing both conjugated and *cross*-conjugated segments have been obtained *via* Karsted [63] (Eq. 6.40) or [Pt(acac)$_2$]-catalysed [58] (Eq. 6.41) polyhydrosilylation of 1-(silyl)-2-arylacetylenes:

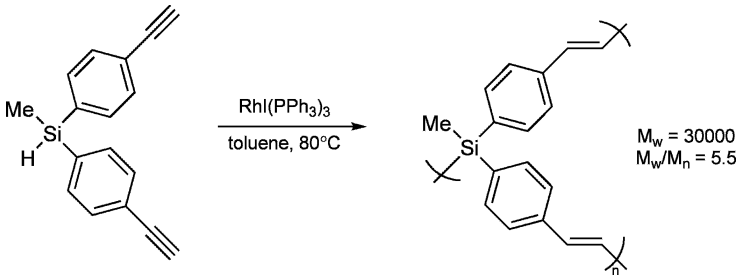


(6.40)

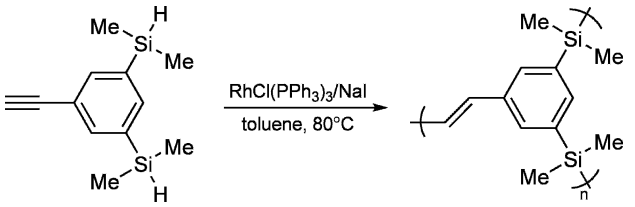


(6.41)

Regio- and stereoregular σ-π conjugated hyperbranched polymers, containing 95% *trans*-vinylene units, were prepared from rhodium-catalysed intermolecular hydrosilylation of di(4-ethynylphenyl)methylsilane (Eq. 6.42) or 1,3-bis(dimethylsilyl) phenylacetylene (Eq. 6.43) [64, 65]:



(6.42)

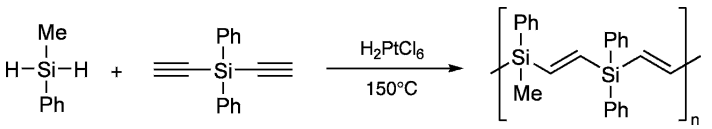


(6.43)

6.2.2 Polyaddition of Dihydrosilanes to Diynes

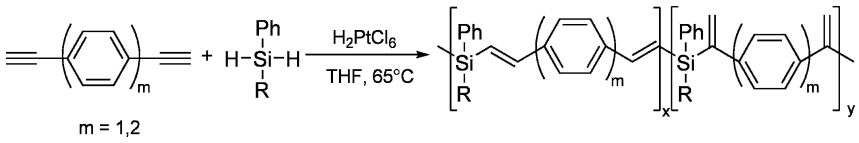
Despite the fact that an easier and more feasible method of the synthesis of the unsaturated polycarbosilanes seems to be the reaction of intermolecular polyhydrosilylation of alkynylhydrosilanes, (stoichiometry need not be considered, unlike for polyaddition of two monomers) there are also many reports on the reaction of various dihydrosilanes with diynes or dialkynyl-substituted organosilicon compounds. However, the possibility of regulating the molar ratio of the substrates used in the reaction makes this method useful not only to obtain linear unsaturated polymers of defined structure but also to produce polymers of specific terminal functionalities, which may react with multifunctional cross-linkers leading to the formation of polymer materials of complex spatial and/or branch structure.

The reaction of methylphenylsilane or diphenylsilane with diethynyldiphenylsilane, carried out in the presence of hexachloroplatinic(IV) acid could serve as an example of synthesis of silylene-vinylene oligomers with the molecular weight of $M_w < 17,000$ [66] (Eq. 6.44):



(6.44)

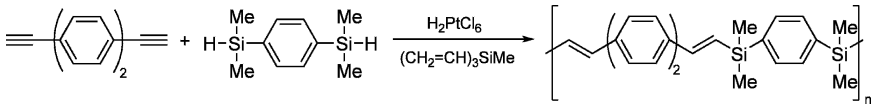
Kim and co-workers devised a method of the synthesis of oligo(silylene-arylene-vinylene)s based on polyaddition of dihydrosilanes to 1,4-diethynylbenzene or 4,4'-diethynylbiphenyl in the presence of H_2PtCl_6 [67] (Eq. 6.45):



(6.45)

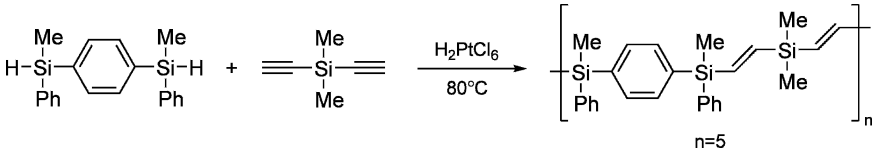
Depending on the substituents at the silicon atom and the type of the diyne applied, the oligomers of different molecular weights ranging from $M_w = 3000$ ($M_w/M_n = 1,9$) (the reaction of diphenylsilane with 4,4'-diethynylbiphenyl) up to $M_n = 9200$ ($M_w/M_n = 3.1$) (the reaction of methylphenylsilane with 4,4'-diethynylbiphenyl) were obtained. The ratio of the number of (*E*)-vinylene to vinylidene groups in the oligomers chain varied within: $x/y = 0,82–0,96$ and it was the highest for the phenyl substituents, which can be explained by the steric effect induced by these groups.

Rickle, reported the outcomes of the hydrosilylation of 4,4'-diethynylbiphenyl with 1,4-bis(dimehylsilyl)benzene in the presence of small amounts of metyltrivinylsilane (cross-linking agent) and H_2PtCl_6 (Eq. 6.46); however the article cited lacked complete spectroscopic and gel-permeation chromatography characterisations of the resulting polymers [28].

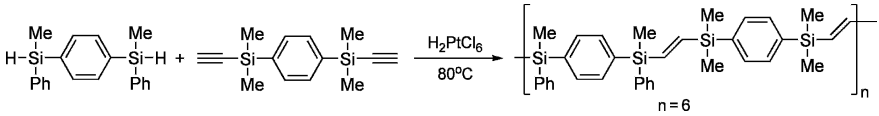


(6.46)

It is worth stressing that the polyhydrosilylation of the monomers of similar structures runs in the presence of H_2PtCl_6, but without a cross-linking agent leads only to the formation of oligomeric penta- or hexamers [68] (Eq. 6.47 and 6.48):



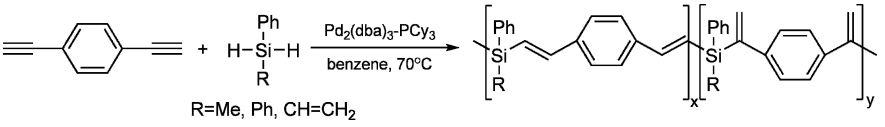
(6.47)



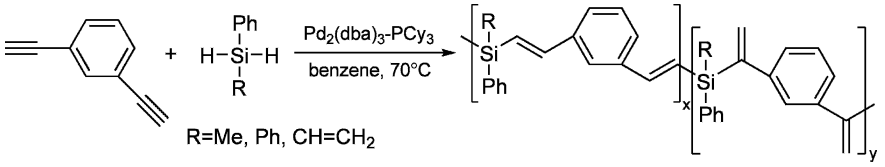
(6.48)

The polycarbosilanes of similar structures but of higher average molecular weights may be obtained in the reaction of 1,4-diethynylbenzene or 1,3-diethynylbenzene with phenylhydrosilanes in the presence of the catalytic system of $[Pd_2(dba)_3$-$PCy_3]$ (dba-dibenzylideneacetone) [69,70] (Eq. 6.49 and 6.50). Palladium-catalysed polyhydrosilylation, however, did not run with such a high selectivity as when the complexes of platinum were applied. The hydrosilylation of 1,4-diethynylbenzene

with methylphenylsilane leads to formation of polymeric product of the average molecular weight of $M_w = 49,000$ ($M_w/M_n = 6,6$), whereas the reactions with diphenylsilane and phenylvinylsilane (Pd catalysis promotes only the C≡C hydrosilylation, so polymers containing vinyl substituents could be made) give the polymers of $M_w = 53,000$ ($M_w/M_n = 6,8$) and $M_w = 20,000$ ($M_w/M_n = 4,6$), respectively. The application of 1,3-diethynylbenzene in the reaction with the three above-mentioned silanes makes it possible to obtain polymers whose molecular weights, however, do not exceed, $M_w < 20.000$.

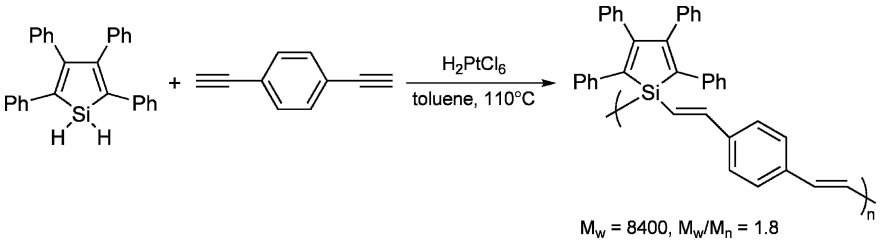


(6.49)

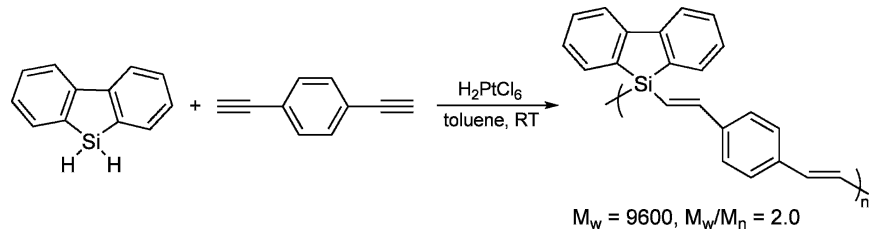


(6.50)

Very recently, the synthesis and fluorescence properties of (*E*)-stereoregular 1,1-silole- (Eq. 6.51) and 1,1-silafluorene-phenylene-divinylene polymers (Eq. 6.52) have been reported [71]:



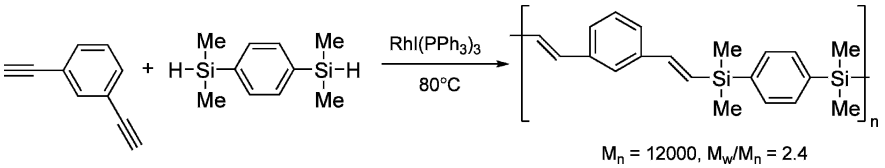
(6.51)



(6.52)

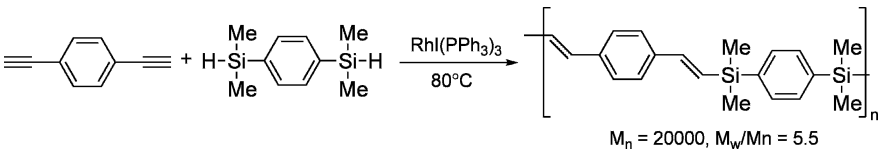
The polyaddition of 1,4-bis(dimethylsilyl)benzene and 1,3-bis (dimethylsilyl)-benzene to aromatic diynes has been carried out in the presence of rhodium(I)

complexes (Eq. 6.43). Mori et al., have found that the above-mentioned dihydrosilanes in the reaction with 1,4-diethynylbenzene or 1,3-diethynylbenzene, catalysed by $[RhI(PPh_3)_3]$, form stereoregular (*E*)-silylene-arylene-vinylene polymers with excellent regio- and stereoselectivity ($E/Z = 96{:}4$) [72] (Eq. 6.53 and 6.54):



$M_n = 12000$, $M_w/M_n = 2.4$

(6.53)

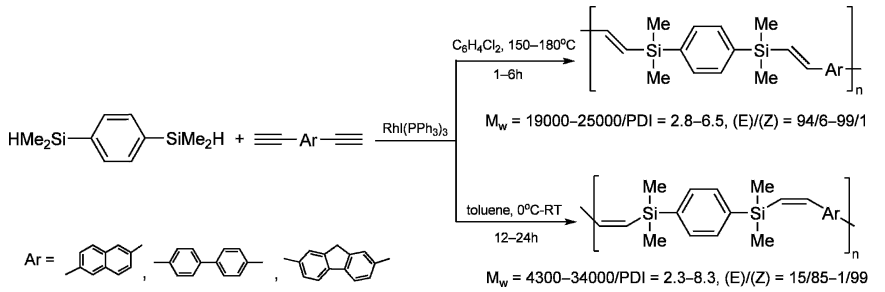


$M_n = 20000$, $M_w/Mn = 5.5$

(6.54)

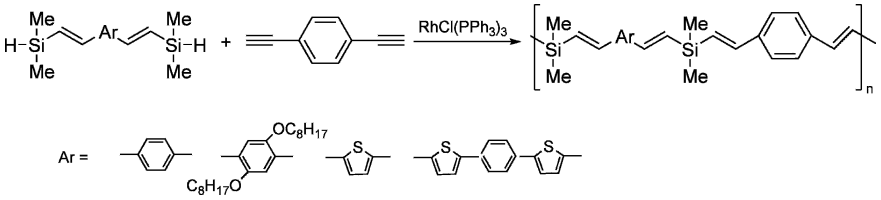
The authors have also found that the use of $[RhI(PPh_3)_3]$ as a catalyst for the polyhydrosilylation reaction furnishes (*E*)- and (*Z*)-poly(silylene-arylene-vinylene)s in stereochemically divergent manners by switching the order of the addition of the reagents and reaction conditions [72]. When the reactants and catalyst were heating together (*E*)-polycarbosilanes were formed, while pre-acting catalyst and dihydrosilane followed by diyne addition afforded polymers containing (*Z*)-vinylene units selectively.

The hydrosilylation polymerisation of 1,4-bis(dimethylsilyl)benzene with 4,4'-diethynylbiphenyl, 2,7-diethynylfluorene and 2,6-diethynylnaphthalene in the presence of $[RhI(PPh_3)_3]$ has been reported [73] (Eq. 6.55). Similarly to the intermolecular hydrosilylation methodology, (*E*)- poly(silylene-arylene-vinylene)s with average molecular weights ranging from $M_w = 19,000$ to 25,000 were obtained by polyaddition performed in dichlorobenzene at 150–160°C, whereas (*Z*)-polymers with M_w from 4300 to 34,000 were synthesised in toluene at room temperature.



(6.55)

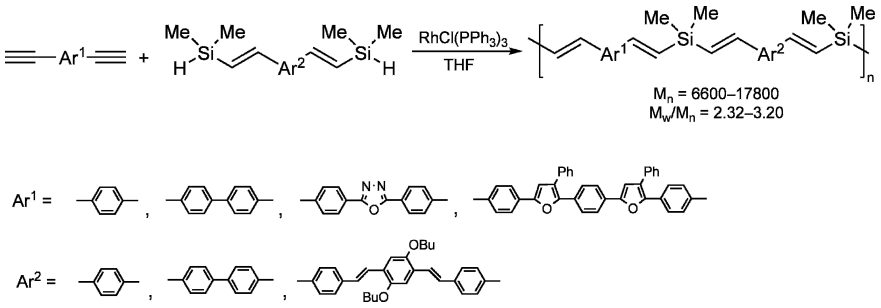
The Wilkinson complex – $[RhCl(PPh_3)_3]$, turned out to be an efficient catalyst in the reaction of hydrosilylation polyaddition of a wide range of aromatic organosilicon hydrides with 1,4-diethynylbenzene [74, 75]:



(6.56)

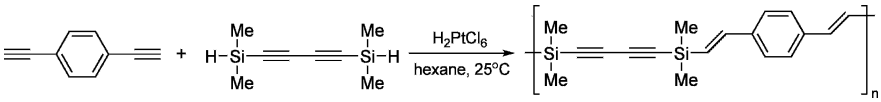
The average molecular weights which were obtained were between $M_n = 2100$ (oligomers containing dialkoxyarylene fragments) and $M_n = 10,600$ (oligomers yielded in the reaction of 1,4-bis(2-(dimethylsilyl)ethenyl)benzene with 1,4-diethynylbenzene).

More recently a range of stereoregular silylene-spaced divinyloligoarene copolymers have been synthesised by [$RhCl(PPh_3)_3$]-catalysed hydrosilylation of bis(ethynyl)arenes with bis(silanes) [76–78] (Eq. 6.57):



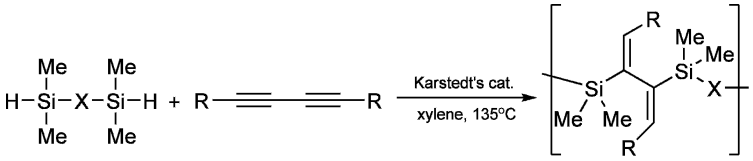
(6.57)

Unsaturated polycarbosilanes containing the π-conjugated triple bonds in the molecule were obtained by means of the reaction of polyaddition of 1,4-bis (dimethylsilyl)-1,3-butadiyne with 1,4-diethynylbenzene [79, 80] (Eq. 6.58). In this reaction, however, only the oligomeric products were obtained, and the number of mers in the oligomer chain was 7 at maximum.



(6.58)

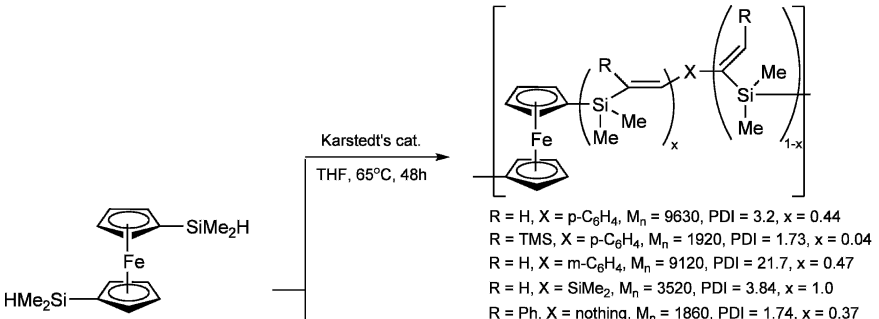
Photoluminescent silylene-arylene-vinylene polymers with pedant aromatic or alkyl groups containing both conjugated and cross-conjugated segments have been recently obtained *via* Karstedt's complex-catalysed hydrosilylation polymerisation of 1,3-diynes with bis-silylhydrides [81, 82] (Eq. 6.59):



R = Bu, X = C_6H_4-O-C_6H_4, M_w = 17600, PDI = 2.45
R = Bu, X = C_6H_4, M_w = 19800, PDI = 2.47
R = Ph, X = C_6H_4-O-C_6H_4, M_w = 6500, PDI = 2.50
R = Ph, X = C_6H_4, M_w = 4130, PDI = 2.31

(6.59)

A number of low molecular weight silylene-arylene-vinylene polymers containing ferrocene fragments have been synthesised by Sheridan and co-workers using hydrosilylation of various diynes with 1,1'-bis(dimethylsilyl)ferrocene in the presence of either Karstedt's complex (highly (*E*)-vinylene products are obtained) or [$RhI(PPh_3)_3$] (polymers with mostly (*Z*)-vinylene units) catalyst [83, 84] (Eq. 6.60). The ferrocenylene-silylene polymers of this type have attracted much attention due to their capacity to act as catalysts, ion exchange resins, conducting polymers or chemical sensors.



R = H, X = p-C_6H_4, M_n = 9630, PDI = 3.2, x = 0.44
R = TMS, X = p-C_6H_4, M_n = 1920, PDI = 1.73, x = 0.04
R = H, X = m-C_6H_4, M_n = 9120, PDI = 21.7, x = 0.47
R = H, X = $SiMe_2$, M_n = 3520, PDI = 3.84, x = 1.0
R = Ph, X = nothing, M_n = 1860, PDI = 1.74, x = 0.37

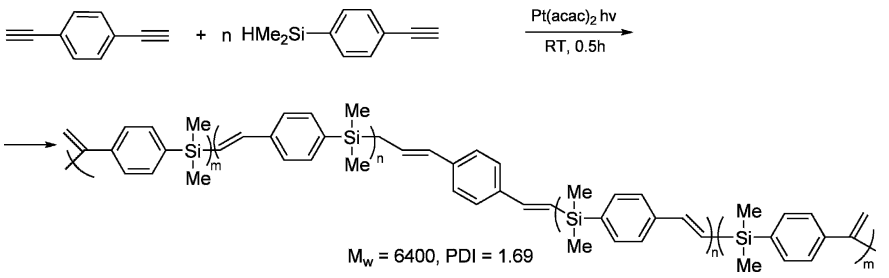
X = p-C_6H_4, M_n = 4660, PDI = 14.8, x = 0.07
X = m-C_6H_4, M_n = 3650, PDI = 2.69, x = 0.11

(6.60)

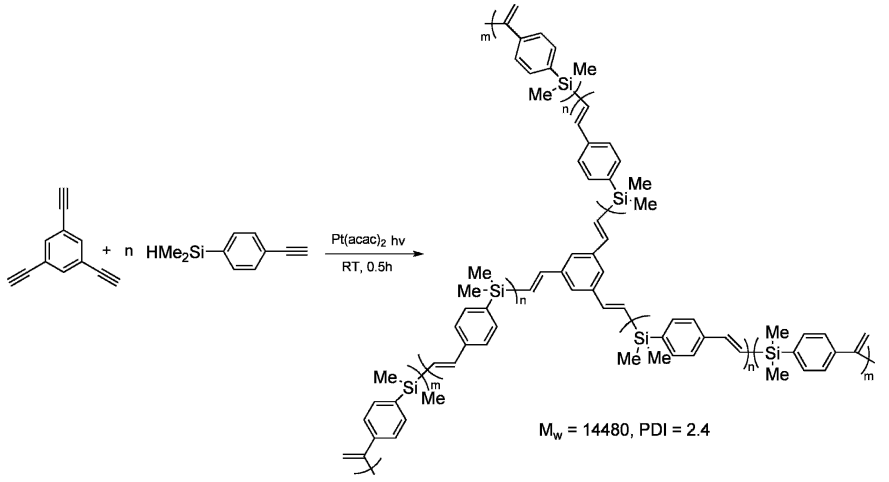
Tanaka and co-workers reported the synthesis of ill-defined unsaturated branch polymers containing silsesquioxane units *via* hydrosilylation polymerisation of octakis(hydrosilsesquioxane) with diynes [85]. More recently, well-defined linear unsaturated polymers from Karstedt's complex-catalysed hydrosilylation polymerisation of double-decker-shaped silsesquioxane with diynes including 1,4-bis (phenylethynyl)benzene, 1,9-bis(phenylethynyl)antracene and 1,4-diethynylbenzene

of the molecular weights $M_w = 11,900–29,100$ ($M_w/M_n = 2.9–4.9$) were successfully synthesised [86].

Neckers et al. have synthesised linear (Eq. 6.61) and star (Eq. 6.62) photoluminescent copolymers containing silylene-phenylene-vinylene units using excess (10:1 or 50:1) of 4-(dimethylsilyl)phenylacetylene and 1,4-diethynylbenzene or 1,3,5-triethynylbenzene, respectively, using [$Pt(acac)_2$]-catalysed photohydrosilylation [59]:



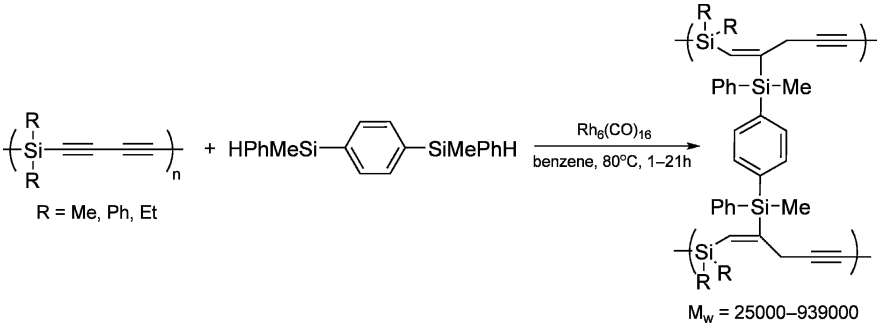
(6.61)



(6.62)

Recently, new cross-linked silylene-divinylene compolymers with organoboron segments have been obtained using palladium-catalysed ($Pd_2(dba)_3/PCy_3$) polyhydrosilylation of the mixture of diynes (*p*- or *m*-diethynylbenzene) and triynes (1,3,5-triethynylbenzene or 1,3,5-triethynylborazine) with methylphenylsilane [87] or platinum-catalysed polyhydrosilylation of 1,3,5-triethynylborazine by *p*- and *m*-bis(dimethylsilyl)benzene [88].

High-molecular weight, branched structures have been also obtained through the regiospecific [$Rh_6(CO)_{16}$]-catalysed hydrosilylation reaction of 1,4-bis(methylphenylsilyl)benzene with poly(silylene-diethynylene)s [81, 89] (Eq. 6.63):



(6.63)

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Chapter 7
Functionalised (Poly)silsesquioxanes and Silicon-Containing Dendrimers

Abstract Functionalised (poly)silsesquioxanes which can be considered as organicmodified silica and silicon-containing dendrimers with their highly branched, tree-like structure offer special properties. They have inspired many chemists to develop new materials and nanomaterials and their several applications have been explored.

The syntheses of such compounds via hydrosilylation processes are described in this chapter.

Functionalised (poly)silsesquioxanes and silicon-containing dendrimers are belong to the most rapidly developing branches of organosilicon chemistry.

Hydrosilylation reactions using hydridosilsesquioxanes as the starting precursors have been used to prepare a number of interesting new adducts, proving a particularly high versatility of this method of functionalisation of silsesquioxanes.

On the other hand, a combination of hydrosilylation with alkenylation (usually allylation and vinylation) or ethynylation and with alcoholysis has provided powerful protocols for the rapid and efficient synthesis of silicon-containing dendrimers, mostly carbosilanes, carbosiloxanes and carbosilazanes, also dendritic poly(silanes) and poly(siloxanes).

7.1 Functionalised Silsesquioxanes

The term "silsesquioxanes" refers to all the structures with the empirical formula $(RSiO_{1.5})_n$, where R is a hydrogen or any alkyl, aryl, alkylene, arylene or organofunctional derivative. Such compounds are synthesised by hydrolytic condensation of trifunctional silanes, including alkoxy- or chlorosilanes, silanols and silanolates. The trifunctional nature of the silsesquioxane moieties allows formation of a variety of structures (see Fig. 7.1) ranging from oligomeric cages (c) through ordered ladder-like structure (b) to three dimensional network structure (a):

A related family of polyhedral silsesquioxanes can be prepared by base-catalysed equilibration of tetrafunctional monomers. However, they are functionalised silicates (called spherosilicates) (d) rather than silsesquioxanes. Moreover, they show many similarities to silsesquioxanes and arouse great interest because of the possibilities of their applications.

B. Marciniec (ed.), *Hydrosilylation,* Advances in Silicon Science,
DOI 10.1007/978-1-4020-8172-9_7,

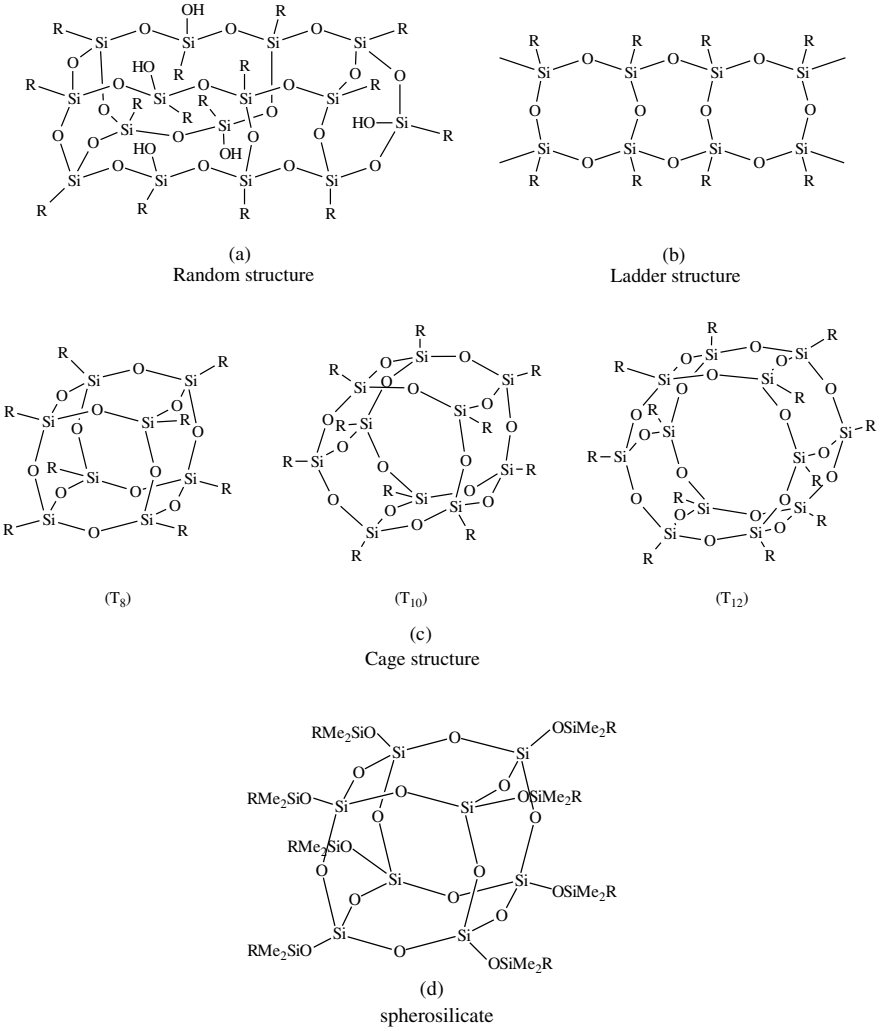
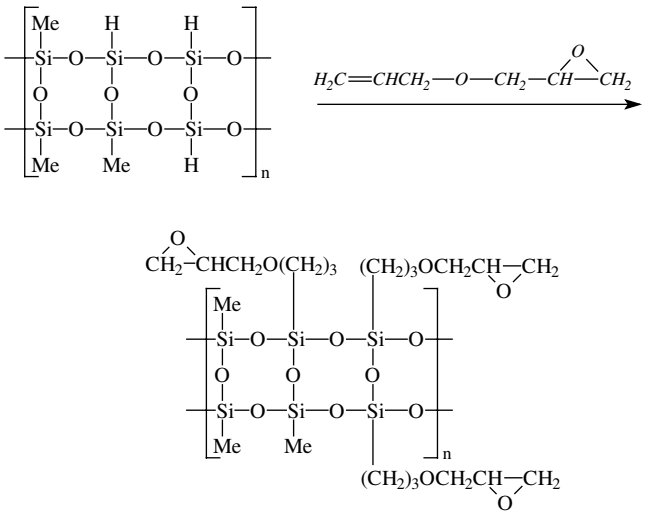


Fig. 7.1

In the last two decades several excellent reviews have been published of the properties and various possibilities of application of all kinds of silsesquioxanes [1–12]. One of the most important and useful classes of such compounds are hydridosilsesquioxanes which are excellent precursors of functionalised silsesquioxanes [13, 14] and spherosilicates [15, 16].

Polyhedral silsesquioxane (POSS) feedstocks, which have been functionalised with various reactive organic groups, can be incorporated into virtually existing polymer system through either grafting or copolymerisation. An example is the

preparation of copolymethylepoxysilsequioxane by grafting allyl glycidyl ether to a ladder-like polysilsesquioxane via the hydrosilylation reaction, catalysed by $[Cp_2PtCl_2]$ [17], according to (Eq. 7.1):



(7.1)

Ladder-like copolymethylaminopropylsilsesquioxane [18], acrylic/ silsesquioxane hybrid optical materials [19] and liquid crystalline polysilsesquioxane [20, 21] are synthesised in a similar way, using the same catalytic system. The hydrosilylation reaction of poly(hydridosilsesquioxane) with vinyl alkyl ethers, in the presence of Karstedt's catalyst leads to obtainig a product which is an excellent dielectric coating material [22].

Recently, in order to get highly ordered, ladder-like polysilsesquioxanes, a new method named "stepwise coupling polymerisation", has been introduced. In this method 1,4-phenylenediamine, used as a pre-coupling agent, plays the role of a template of the hydrogen-bonding interaction [23–25]. In the first step, appropriate organofunctional silanes are synthesised by hydrosilylation of the corresponding allylic derivatives with trichlorosilane (or trialkoxysilane), in the presence of $[Cp_2PtCl_2]$ as a catalyst, followed by the reaction with diamines. Using this method, a series of ladderlike polymers have been synthesised, including those having the following side-groups: bromophenyl [26], aryl ester [27, 28], amino [29], chloromethylphenyl [30] and also hydrido [31] and allyl [32] groups.

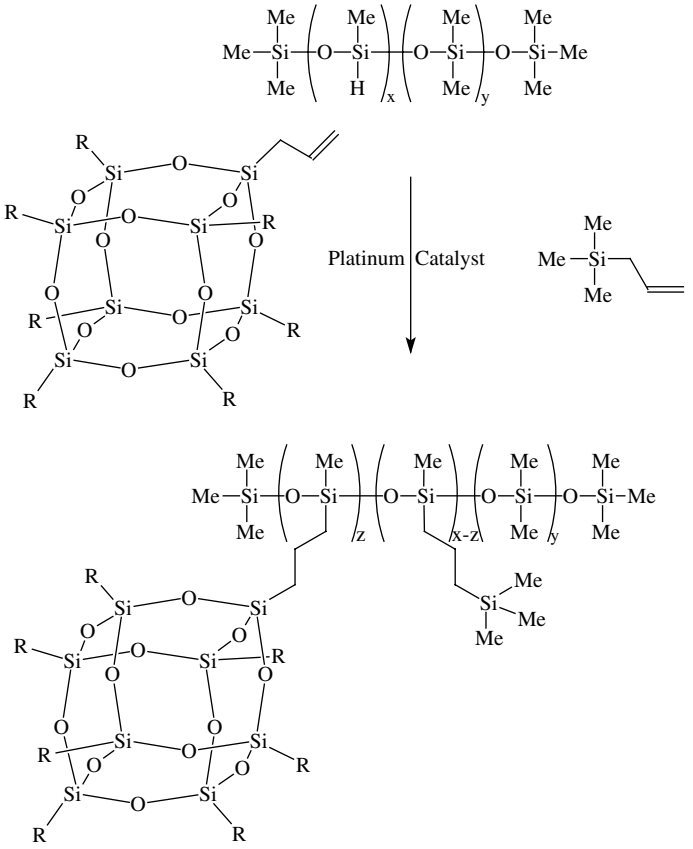
Although, various applications of ladder-like silsesquioxanes have been found in the past few years, much more attention is paid to the silsesquioxanes with specific cage structures, often referred to as polyhedral silsesquioxanes, (POSS), from which the most popular are octafunctional octasilsesquioxanes T_8. An octasilsesquioxane offers eight reactive sites, which can be functionalised differently, however, most of

the works have so far concentrated on the homofunctionalised species. Incomplete or partial functonalisation of the octafunctional silsesquioxane can also be achieved [32–34]. The methods of preparation of monosubstituted POSS, their properties and applications have recently been summarised in [9, 11].

The POSS-methacrylate homopolymer, obtained from propyl methacrylate substituted POSS monomer containing seven cyclohexyl or cyclopentyl group, is a transparent brittle plastics with high thermal stability [35].

Functionalised octasilsesquioxanes with different numbers of methacrylate or epoxy groups form thermally- and photo-curable monomers, which are interesting as precursors in the processing of composites [36–39].

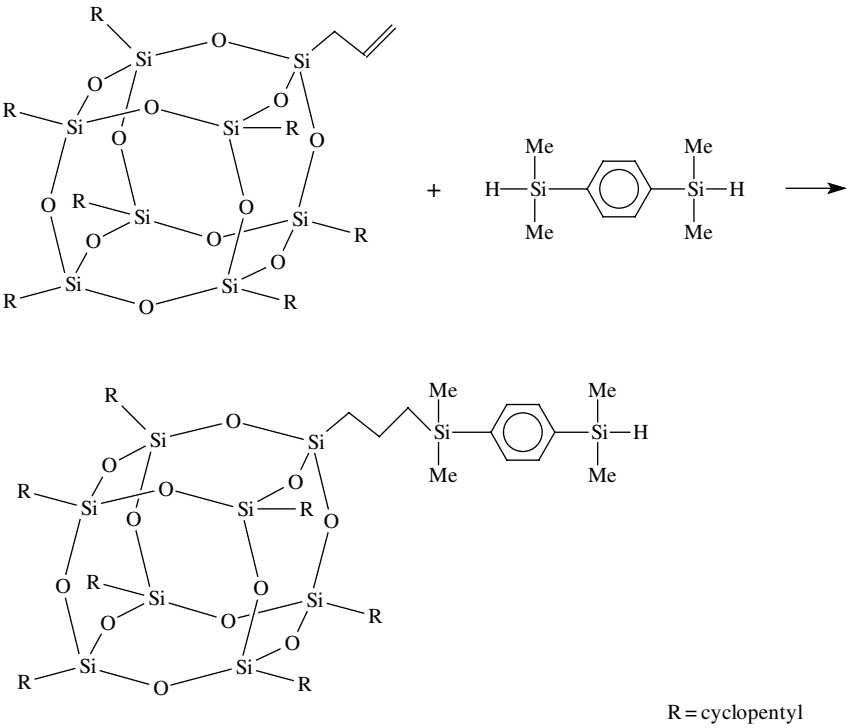
Monosubstituted POSS are grafting with polysiloxanes involved the hydrosilylation of allyl substituted POSS monomers with poly(dimethyl, hydridomethyl)siloxane, in the presence of platinum catalyst [40, 41], according to (Eq. 7.2):



(7.2)

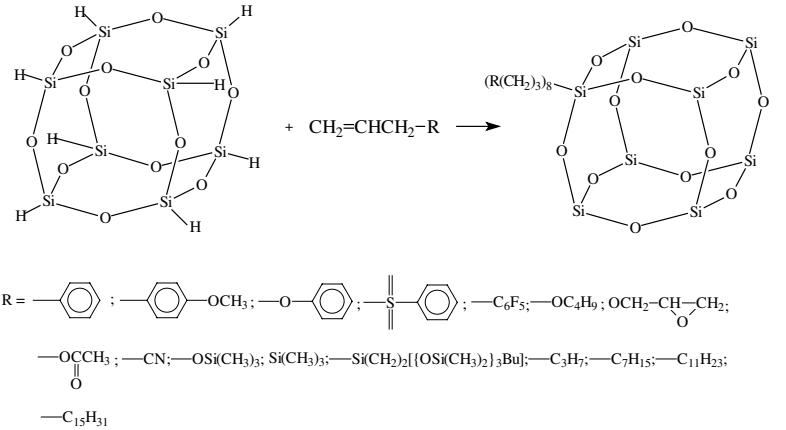
Thermal analysis of this polymer has shown that POSS units could promote a special type of chair formation in combustion process of POSS-containing or-

ganic thermoplastics or thermosets. Monoallyl POSS was also hydrosilylated by bis(dimethylsilyl)benzene, in the presence of Karstedt's catalyst, and then the product was grafted with unsaturated polymers via hydrosilylation [42]:



(7.3)

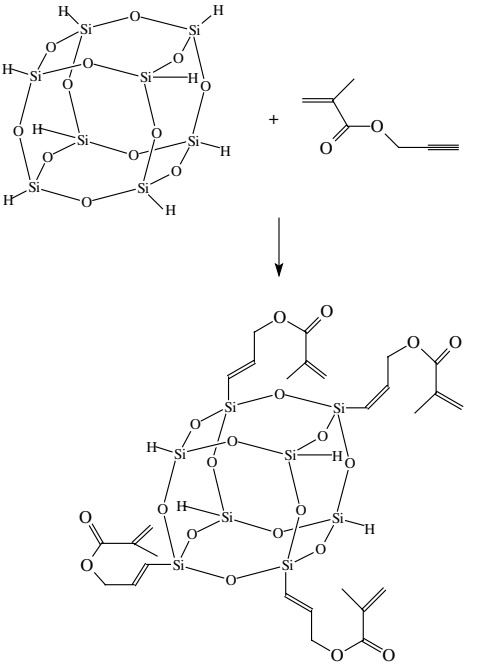
Among silsesquioxanes, octa(hydridosilsesquioxane) $[H_8(SiO_{1.5})_8]$ (T_8H) and octa(hydridospherosilicate) $[(HSiMe_2O)_8(SiO_{1.5})_8]$ ($H_8M_8Q_8$) are the best (and the most popular) raw materials for transformations. Especially the latter is recently regarded as very attractive, because, comparing with T_8H, its synthesis is much easier and effective. It is also more reactive and soluble in a large number of solvents. Hydrosilylation reactions using T_8H as the starting precursor have been used to prepare a number of interesting new adducts, illustrating that this method of functionalisation of silsesquioxanes, in comparison with other two methods, i.e., hydrolytic condensation of corresponding functionalised propyltrialkoxysilanes and nucleophilic substitution of the chlorine atoms of octakis[(3-chloropropyl)silsesquioxane] is the most versatile [13, 43, 44]:



(7.4)

Many papers describe the preparation of epoxy octa-substituted silsesquioxanes, used as nanocomposites of epoxy resins, by the hydrosilylation reaction. Epoxy functionalised silsesquioxane monomers have been synthesised via hydrosilylation of allyl glycidyl ether or vinyl epoxycyclohexane by both T_8H [45–48] and $H_8M_8Q_8$ [49–55], catalysed by platinum dicyclopentadiene or Karstedt's catalyst.

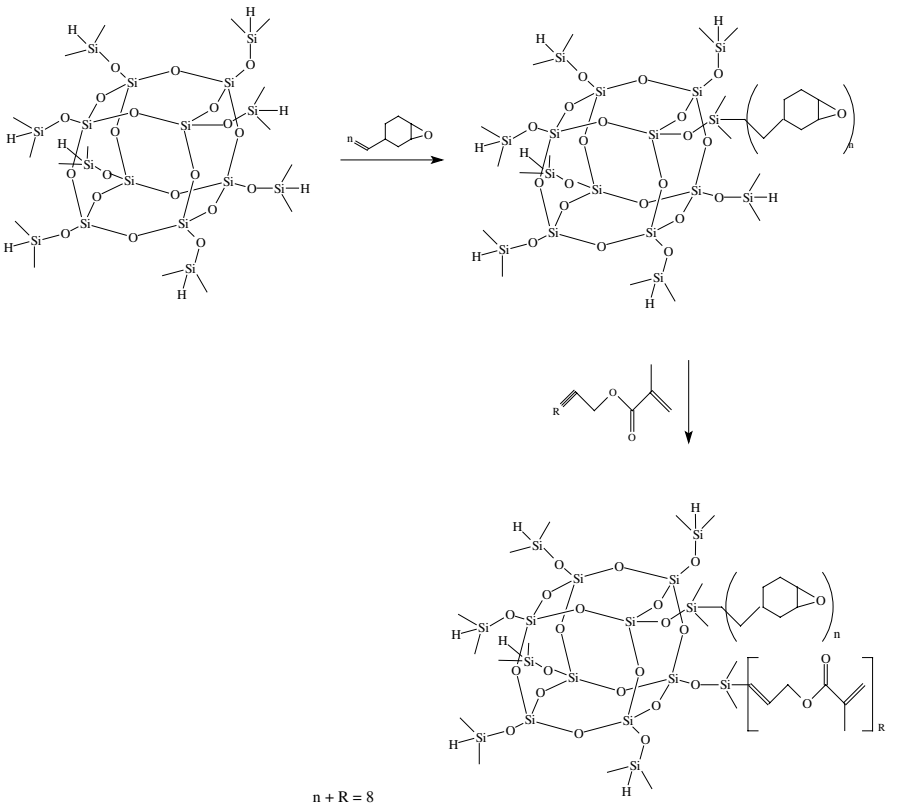
Methacrylates are another group for functionalisation of silsesquioxanes, which is very frequently reported. The hydrosilylation of propargyl methacrylate by T_8H, catalysed by $[Cp_2PtCl_2]$, leads to a number of partially and fully substituted derivatives of T_8H [37]:



(7.5)

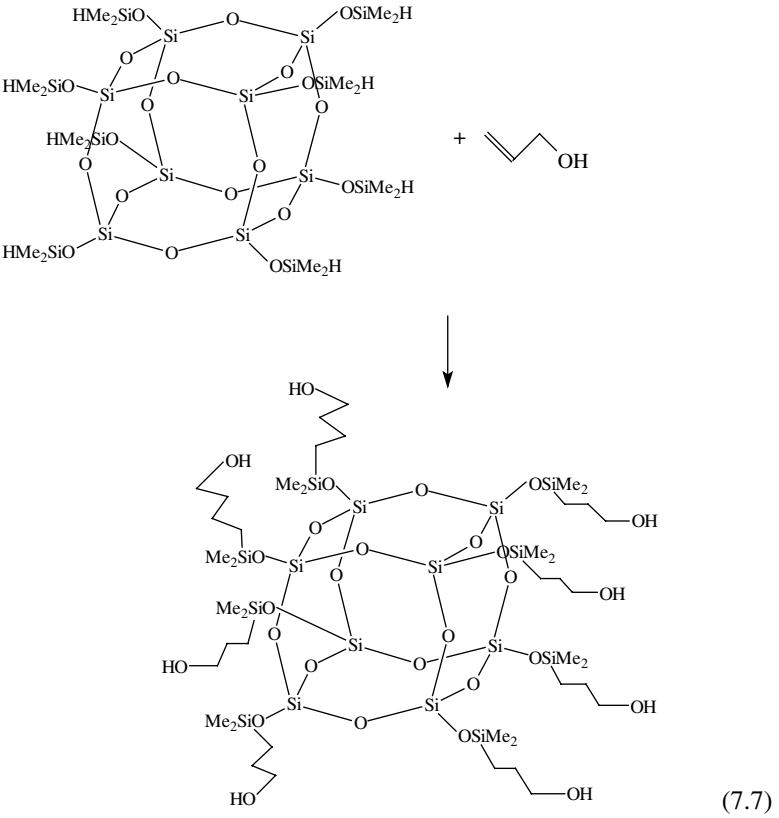
It was also reported that in the same reaction, catalysed by Karstedt's catalyst, only gel was obtained [39].

Various silsesquioxane core-based nanocomposites, used in dental applications, with varying amounts of methacrylate and/or epoxide groups were prepared via Karstedt's catalysed hydrosilylation of di(propylene glycol) allyl ether methacrylate, propargyl methacrylate, and 4-vinyl-cyclohexene epoxide combination with $H_8M_8Q_8$ [56–58]:



(7.6)

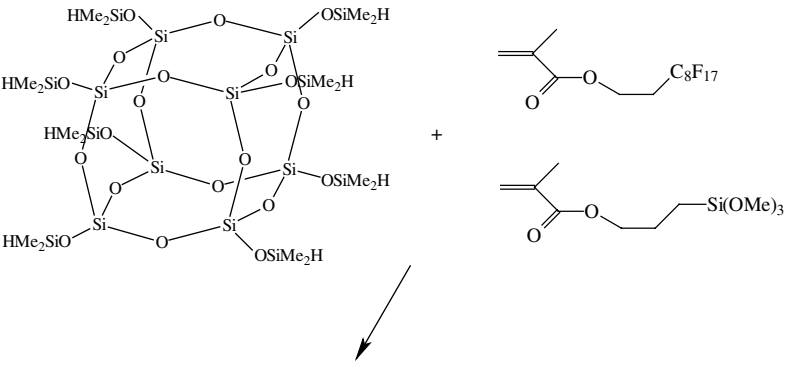
Methacryloxyfunctional silsesquioxanes were also obtained in a two-step reaction via octahydroxy functionalised silsesquioxane synthesised in the hydrosilylation reaction of allyl alcohol with $H_8M_8Q_8$, in the presence of Karstedt's catalyst [59]:

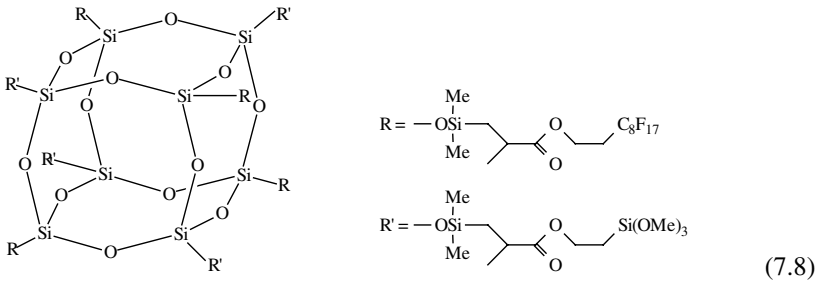


(7.7)

The reaction of the above product with methacroyl chloride [59] or methacroyl anhydride [60] gives the desired methacryloxyfunctional product.

Recently, the hydrosilylation of a mixture of perfluoromethylmethacrylate and trimethoxysilylmethylmethacrylate equivalent by $H_8M_8Q_8$ has been reported, where the methylmethacrylate double bond was used to append different functionalities on the cube with the concomitant loss of methacrylate functionality [61], according to (Eq. 7.8):

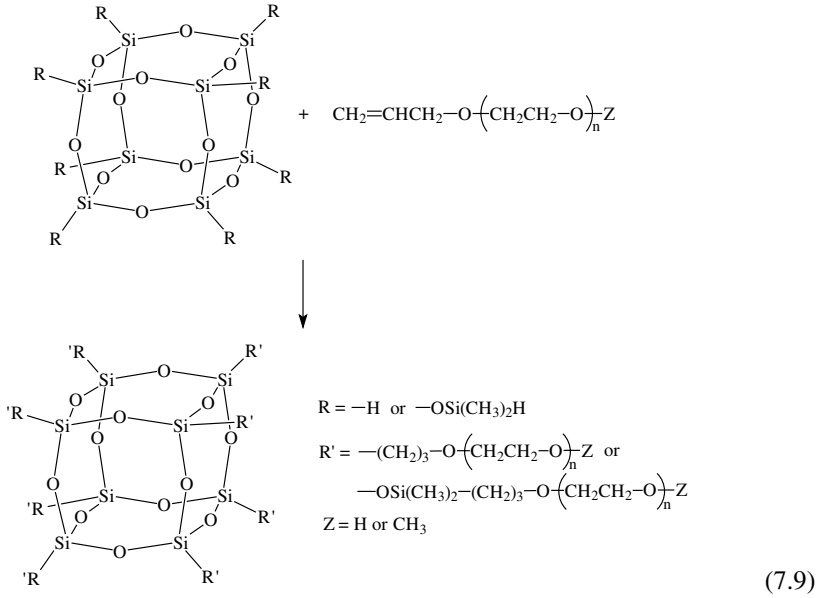




(7.8)

The octasilsesquioxane cage has been successfully derivatised by platinum-catalysed hydrosilylation reaction of the alkene functionality of appropriate laterally substituted mesogenic moieties to yield liquid -crystalline silsesquioxanes [38, 62–69].

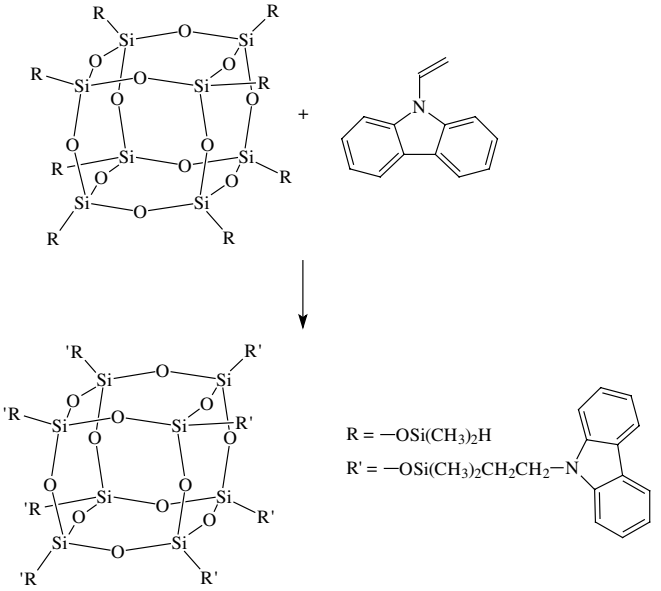
Very recently, a homologue series of poly(ethylene glycol)s PEG (with various chain length) – substituted octasilsesquioxanes have been prepared by hydrosilylation of unsaturated PEGs with both $H_8M_8Q_8$ and T_8H, in the presence of Karstedt's catalyst [70–76], according to (Eq. 7.9):



(7.9)

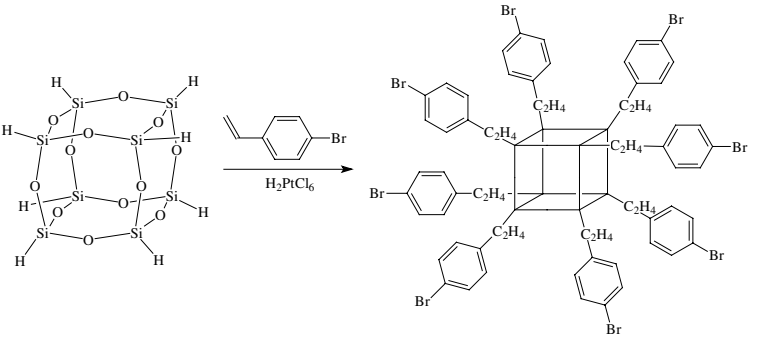
These compounds were used as a template for the preparation of nanoporous polyimide films [71] or as a solid polymer electrolyte for lithium batteries [74]. Such compounds are also very hydrophilic and can be readily dispersed in polar monomers, mostly thanks to the solubilising effect of the modified corners of the POSS cage. Some other functionalised silsesquioxanes containing isocyanate [77] chloroethyl alkyl ether [78] or benzoxazine [79] have been reported.

A few of functionalised silsesquioxanes have shown unique photoluminescence [80] or optolectronic properties [81]. The first of them has been synthesised by hydrosilylation reaction of $H_8M_8Q_8$ with 9-vinylcarbazole, in the presence of Karstedt's catalyst:



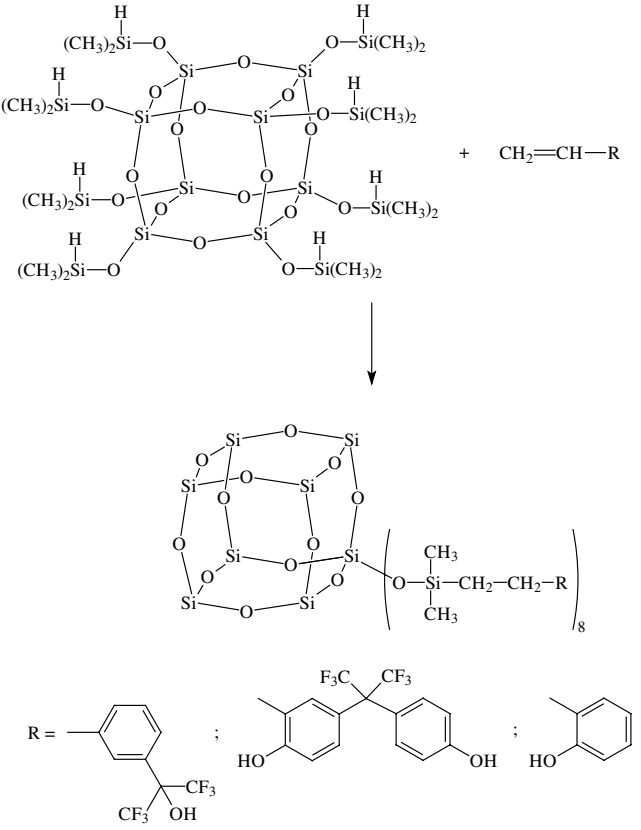
(7.10)

Another one has been obtained in the reaction of octa[(bromophenyl)ethyl]silsesquoxane (obtained via hydrosilylation of vinylbromophenyl with T_8H), according to (Eq. 7.11)) and polydioctylfluorene.



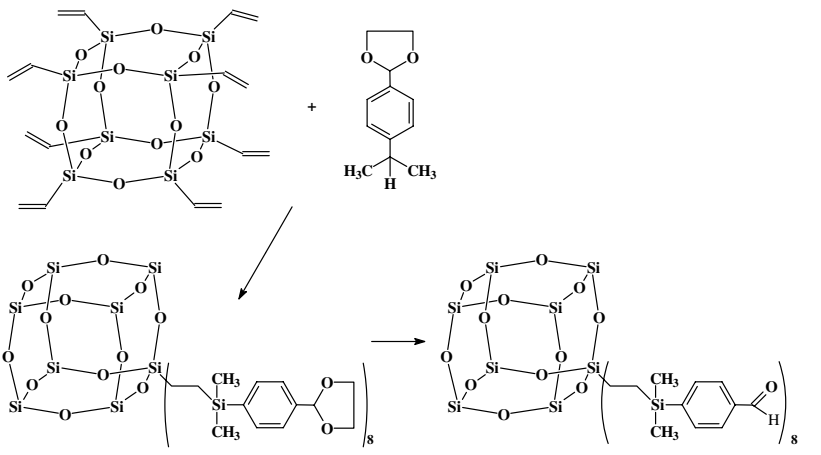
(7.11)

Hydrosilylation process was also used for the synthesis of a series of POSS nanofilling compounds functionalised with hydrogen-bond acidic sensor group [82]:



(7.12)

Finally, some examples of the hydrosilylation reaction employing octavinyl silsesquioxanes have been described, such as the synthesis of octaaldehyde POSS species via platinum catalysed hydrosilylation of octavinyl POSS with protected aldehyde silane (with dioxolane functionality) [83], according to (Eg 7.13):



(7.13)

7.2 Organosilicon Dendrimers

Dendrimers are globular, nano-scaled macromolecules with a particular architecture composed of three distinct domains: (1) a central core which is either a single atom or an atomic group having at least two identical chemical functions, (2) branches stemming from the core, made of repeated units having at least one branch junction, whose repetition is organised in a geometrical progression that results in a series of radially concentric layers called generations, and (3) many terminal functional groups, generally located in the exterior of the macromolecule, determining the properties of dendrimers.

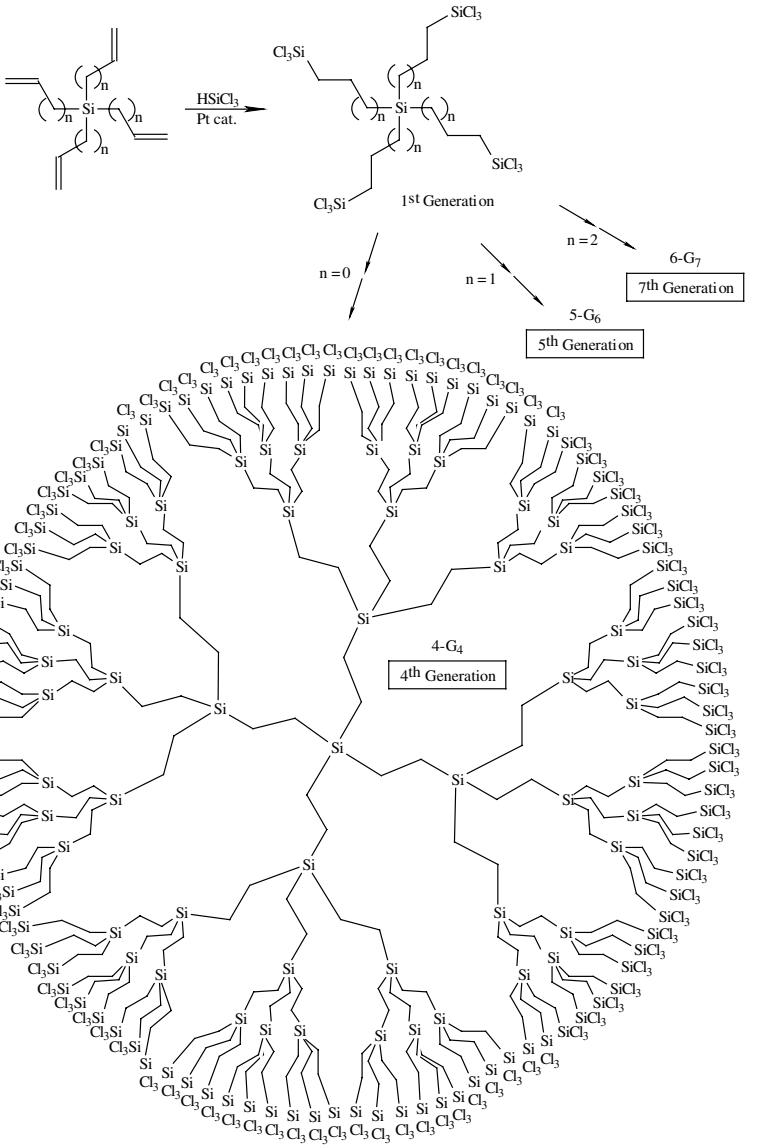
In the last decades there has been a rapid development in the synthesis and application of dendrimers. A few thousand of publications including some reviews [84–89] have been devoted to the characterisation of dendrimers, however, not only research reports are growing in number each year, but there is also a concomitant explosion in the patent literature from 2 patents in 1981–1985, 51 in 1991–1995 to over 1000 in the period of 2001–2005 [89]. The pecularities of dendritic molecules with their highly branched (monodispere), tree-like structure offer special properties (and a variety of functions). Dendrimers are widely investigated as supports for functional groups and metal fragments, which can be localised at the core or at the periphery. They have inspired many chemists to develop new materials and their several applications have been explored [90, 91]. Currently there is significant interest in dendrimers in view of their potential applications, including light harvesting and energy transfer, nanoscale catalysis, chemical sensors, unimolecular micelles, enzyme mimics, encapsulation of guest molecules, molecular recognition, diagnostic agents, and gene and drug delivery [92–94].

Dendrimers are generally prepared using either a divergent method or convergent one. In the first one, dendrimers are built stepwise from a small polyfunctional core, through the reiteration of sequence reactions, which allow construction of dendrimers layer after layer (generation after generation). The convergent method consist of the branching of dendrons (branched polymeric arms) employing the reactivity of their core.

Organosilicon chemistry offers a number of high yield, and selective reactions that are suitable for dendrimer construction. A combination of hydrosilylation with alkenylation (usually allylation and vinylation) or ethynylation and with alcoholysis gives powerful protocols for the rapid and efficient synthesis of silicon-containing dendrimer, mostly carbosilanes, carbosiloxanes and carbosilazanes, also dendritic poly(silanes) and poly(siloxanes) [86, 95–98].

Among the organosilicon dendrimers, carbosilane dendrimers have been by far the most investigated group. The first carbosilane dendrimer was reported as early as 1978 by Fetters and co-workers [99], however, the field really opened up in the 1990s after the seminal contributions by van der Made and van Leeuven, et. al. [100], Roovers et al. [101], Muzafarov et al. [102], as well as by Seyferth's group [103]. The most popular core molecules are tetraallylsilane and tetravinylsilane allowing to obtain dendrimers with spherosymmetrical topology.

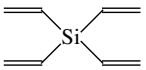
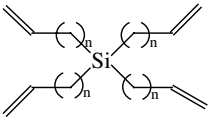
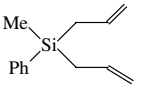
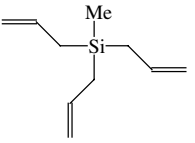
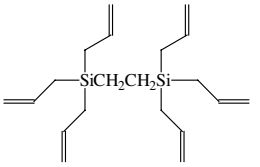
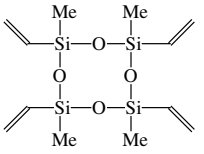
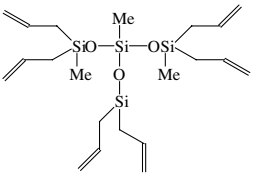
Starting from the central core with four alkenyl groups, the dendrimer is constructed using repeating sequences of alternating hydrosilylations with chlorosilanes as the core, $HSiCl_3$ as the hydrosilylation reagent and allyl magnesium bromide as the ω-alkenylation reagent to obtain dendrimers up to the fifth generation [100] according to (Eq. 7.14):



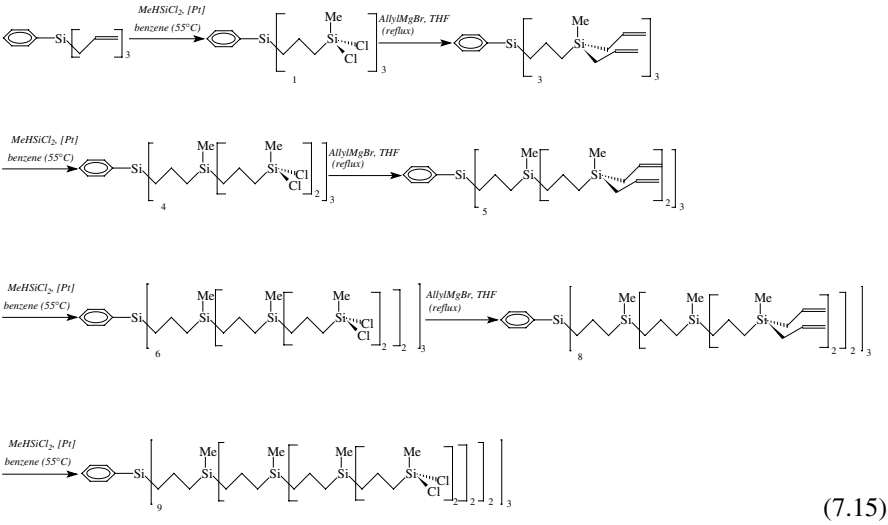
(7.14)

Numerous reports on the synthesis of carbosilane dendrimers with alkenyl end groups and with various core molecules (besides allyl- and vinyl-silanes also tetravinyltetrasiloxane) have been published. Most of such examples are presented in Table 7.1. The general synthetic strategy of all carbosilanes reported is based mainly on the divergent approach.

Table 7.1 Examples of substrates used for syntheses of carbosilane dendrimers

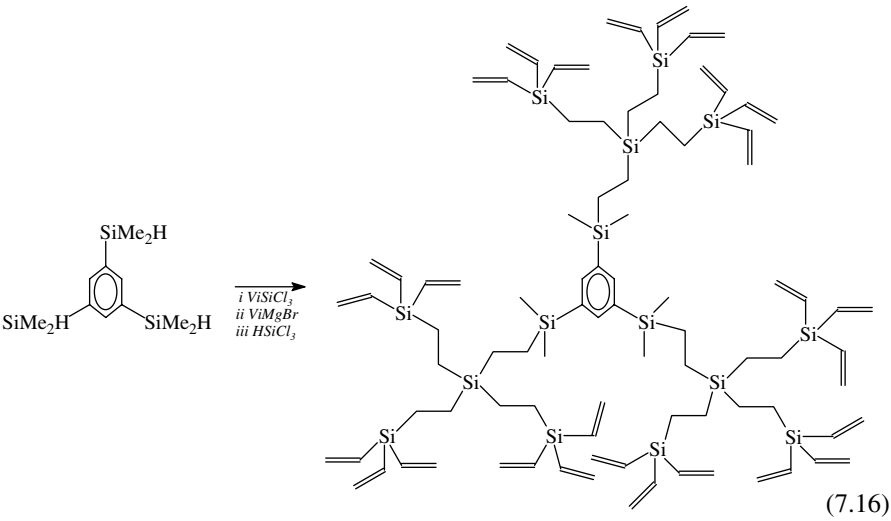
Core	Hydrosilylation reagents	Alkenylation agent	Generation	Ref.
	$HSiCl_3$	$CH_2{=}CHCH_2MgBr$	3rd	[103]
	$HSiMeCl_2$	$CH_2{=}CHCH_2MgBr$	4th	[101]
	$HSiCl_3$	$CH_2{=}CHCH_2MgBr$	n=0, 3rd n=1, 5th n=8, 7th	[100, 104]
	$HSiCl_3$	$CH_2{=}CHCH_2MgBr$	4th	[105]
	$HSiCl_3$	$CH_2{=}CHCH_2MgBr$	2nd	[106]
	$HSiMeCl_2$	$CH_2{=}CHCH_2MgBr$	3rd	[107, 108]
	$HSiCl_3$ $HSiMeCl_2$	$CH_2{=}CHCH_2MgBr$ $CH_2{=}CHCH_2MgBr$	3rd 4th	[–109 111]
	$HSiMeCl_2$	$CH_2{=}CHCH_2MgBr$	7th	[112]

Core phenylated first-fourth generation dendrimers were synthesised from tri-(allyl)phenylsilane by an alternating sequence of hydrosilylation and allylation steps [113, 114], according to (Eq. 7.15):



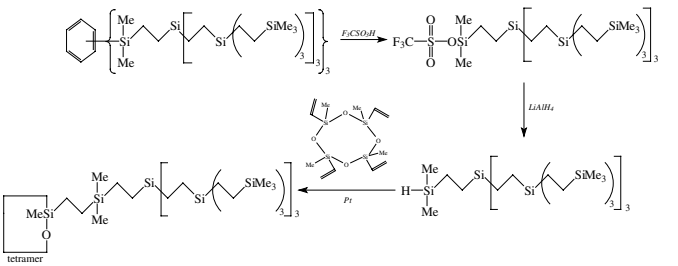
(7.15)

However, dendrimers of this type were also synthesised using 1,3,5-tris(dimethylsilyl)-benzene as a core molecule instead of allylsilane [97]:



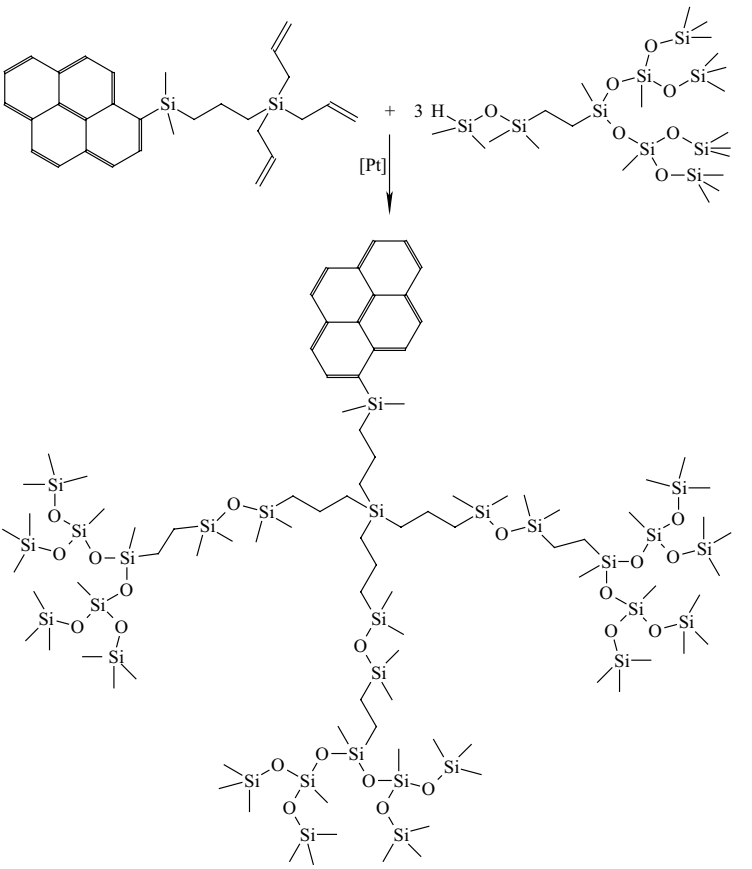
(7.16)

The introduction of phenyl groups on carbosilane dendrimers allows their acidolytic conversion to highly reactive triflato groups, which, in turn, are readily substituted by anionic nucleophiles or by hydride. Such products were used for convergent synthesis of other dendrimers [97]. The resulting carbosilane hydride was attached to a tetravinylcyclotetrasiloxane, according to (Eq. 7.17):



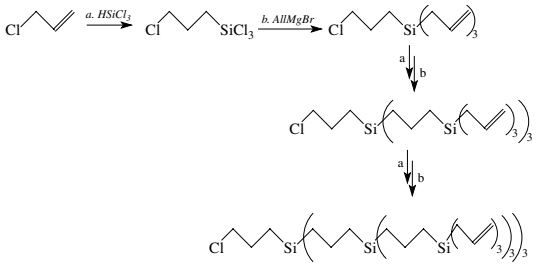
(7.17)

An analogous combination of divergent and convergent methods was also used for the synthesis of siloxane-carbosilane dendrimers [115–117]. An example of such synthesis [116] is presented in (Eq. 7.18):



(7.18)

Recently, the convergent syntheses of three generations of carbosilane dendrimeric carbodiimides have been reported [118]. The wedge-type building blocks were synthesised in a divergent way, starting from allyl chloride and a repetitive sequence of hydrosilylation with $HSiCl_3$ and a Grignard reaction with allylmagnesium bromide. The hydrosilylation process was catalysed by an uncommon catalyst, i.e., $[(Bu_4N)_2PtCl_6]$:



(7.19)

In the next step, chlorides were converted into several reactive groups, having both electrophilic and nucleophilic properties ultimately leading in a convergent way to dendrimers containing a carbodiimide in the core. Such dendrimers successfully mediated cyclisation of dipeptides that are difficult to ring-close with traditional methods.

A very interesting product has been synthesised in the reaction of tetrakis(phenylethynyl)silane with methyldichlorosilane or dimethylchlorosilane as the hydrosilylating reagents and lithium phenylacetylide as nucleophilic substitution reagent [119]. Such a reaction leads to the formation of the third generation dendrimer (see Fig. 7.2)

Very recently, carbosilane dendrimers using $Ph_2Si(CH_2CH{=}CH_2)_2$ and $Si(CH_2CH{=}CH_2)_4$ as the core molecules have been divergently synthesised by alternative hydrosilylation using dichloromethylsilane and alkenylation with allylmagnesium chloride [120]. These compounds were employed as crosslinkers for silicone rubber.

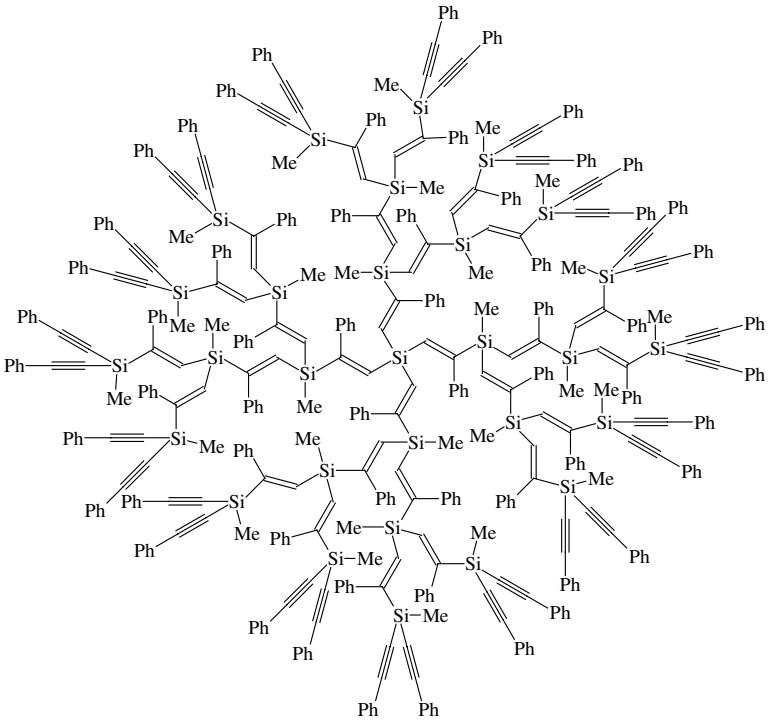
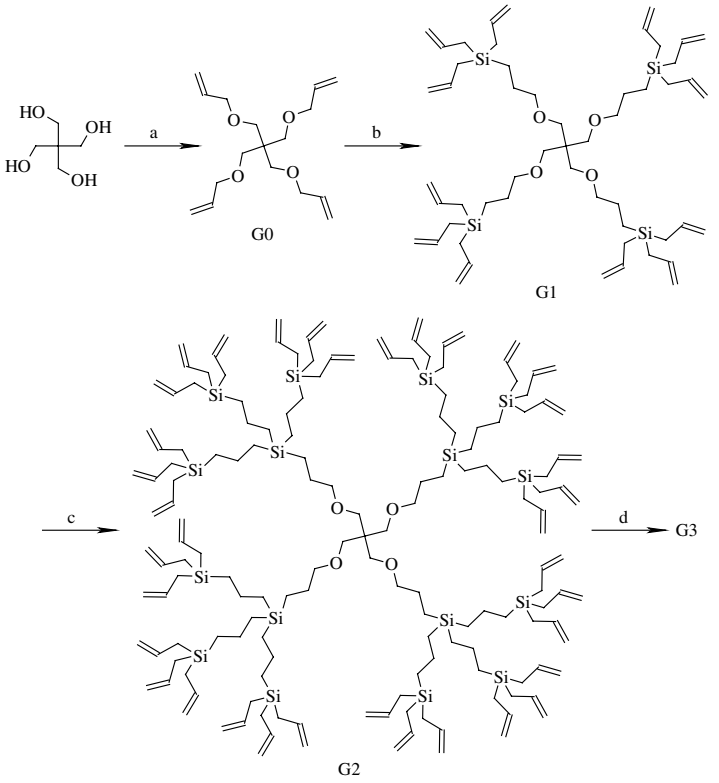


Fig. 7.2

A series of novel pentaerythritol-based carbosilane dendrimers has been synthesised. Using pentaerythritol-based tetraallyl ether as core molecule, the dendrimers have been prepared up to the third generation. This is the first example of carbosilane dendrimers with the central carbon atom [121]:

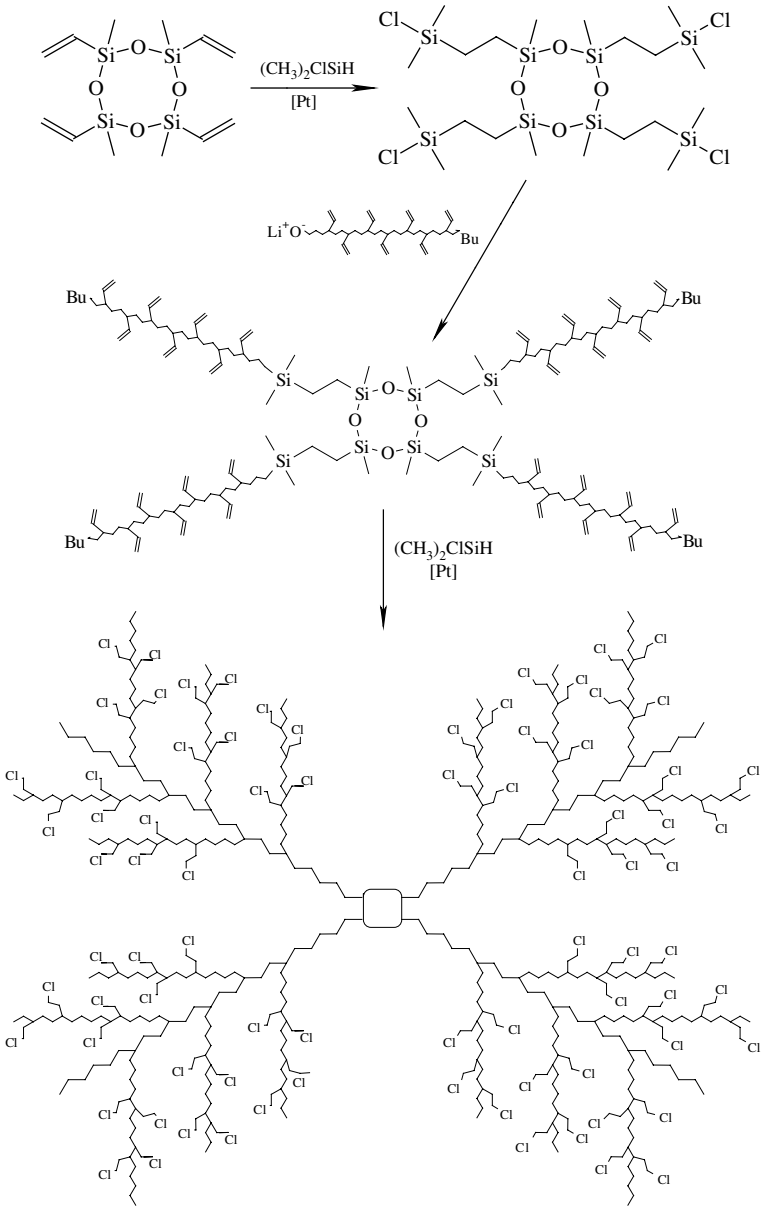


a = $CH_2=CHCH_2Br$, NaOH, THF;
b, c, d = 1) $HSiCl_3$, [Pt]-Karstedt, THF 2) $CH_2=CHCH_2MgBr$, THF; (7.20)

Carbosiloxane dendrimers are generally synthesised using methyldichlorosilane as hydrosilylating agent and allyl alcohol as the nucleophilic substitution reagent. These reactions were carried out using tetravinyltetramethylcyclotetrasiloxane [108, 122, 123], 1,2-bis(triallyloxysilyl)ethane [108], and tetra(allyloxy)silane [124] as core molecules.

A few examples of the preparation of the dendrigrafts based on the polysiloxane have been reported [125–129]. Such compounds are very interesting due to the unusual static and dynamic flexibility of their chains which may easily adopt many conformations. One of such examples describes the synthesis of 3-chloropropyl functionalised dendrigraft polysiloxanes [130]. This process consists of the hydrosilylation of vinyl-ended star, comb, or dendritic branched polysiloxane core with $HSiMe_2Cl$ which generates reactive silyl chloride groups. These groups are used for the termination of the 3-chloropropylmethylsiloxane living polymer to attach it to

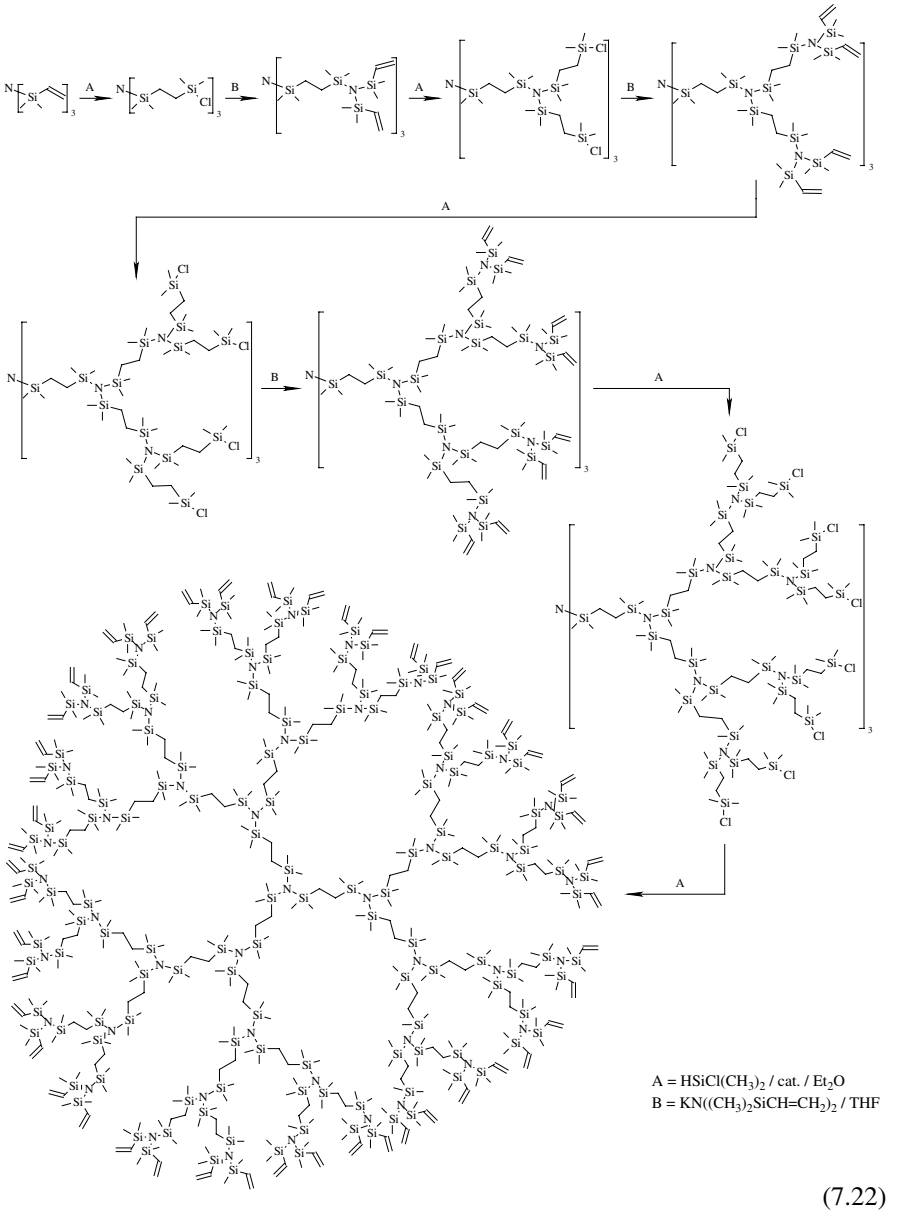
the core, followed by functionalisation via the nucleophilic substitution of chlorine, e.g. by tertiary amines:



(7.21)

The carbosilazane dendrimers are very rare among the oganosilicon dendrimers. Only a few researchers have paid attention to dendritic and hyperbranched polycarbosilazanes [131–134]. In most of these cases, tris(vinyldimethylsilyl)amine was used as the core molecule, chlorodimethylsilane as the hydrosilylating reagent

and lithium- (or potassium [132, 133]) bis(dimethylvinylsilyl)amide [131] as the nucleophilic substitution reagent. Utilising alternating hydrosilylation and nucleophilic substitution, dendrimers of up to fourth generation were obtained:



(7.22)

The synthesis of hyperbranched polysilazane occurrs in a different way [134], via hydrosilylation polymerisation of appropriate monomers, such as bis(N,

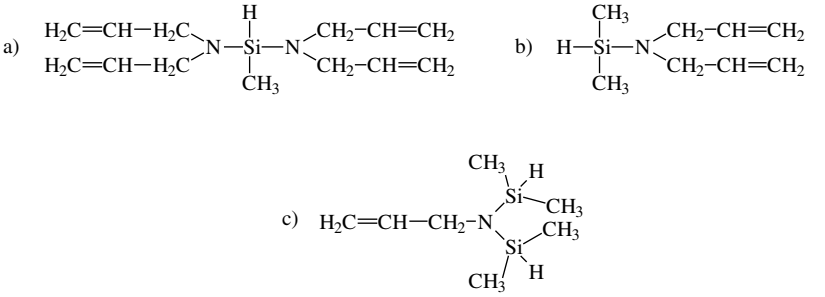


Fig. 7.3

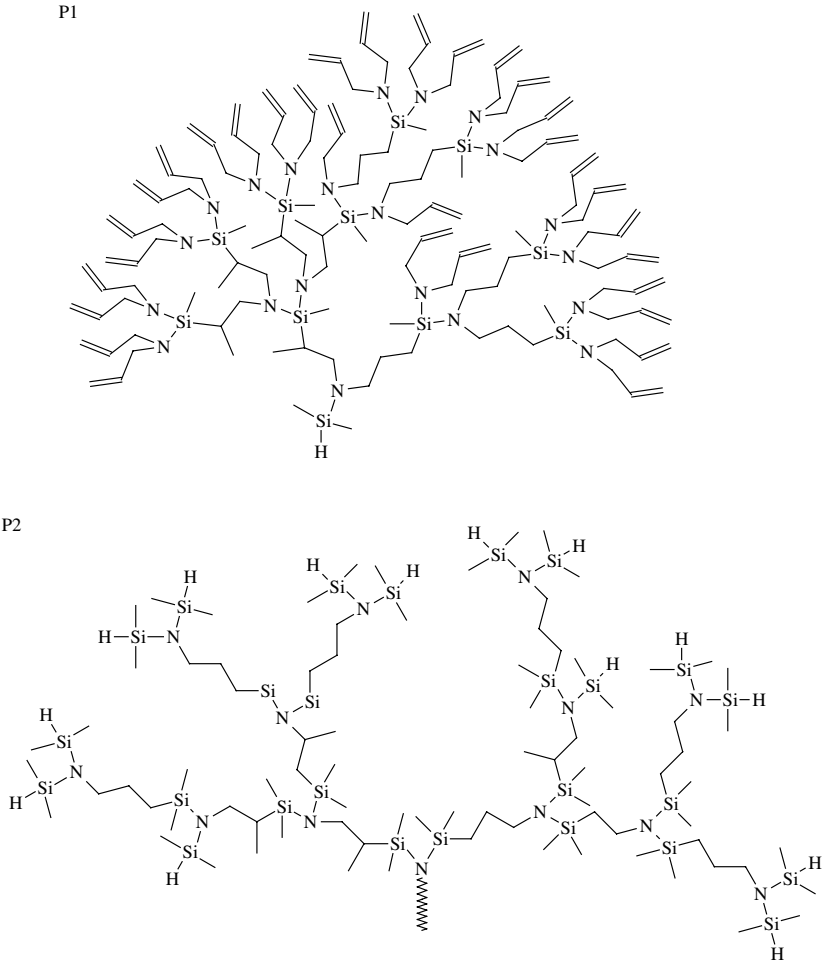


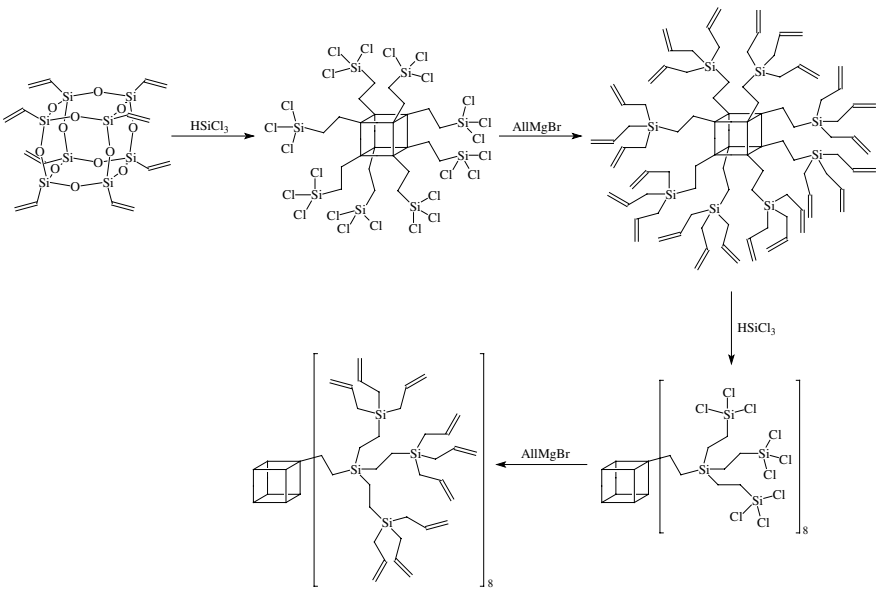
Fig. 7.4

N-diallylamino) methylsilane (a), (N,N-diallylamino)dimethylsilane (b) or N,N-bis-(dimethylsilyl)allylamine (see Fig. 7.3):

The following figures (see Fig. 7.4) present polymers which have been obtained from the monomer (a) - P1, and (c) - P2. It is very interesting that in all of these hydrosilylation reactions, catalysed by H_2PtCl_6, only α-adduct has been formed:

Generally, synthesis of dendrimers often requires many repetitive steps in order to build the dendrimers outwards leading to multi-step and often low yield preparations. This problem can be partially overcome by the use of polyhedral oligomeric silsesquioxane (POSS) molecules as the core of dendrimers. Using the POSS cube as a framework, the dendrimer can be built out in three dimensions leading to a very globular structure which, by the second generation, has 72 end groups suitable for functionalisation with a catalytic species [135].

Therefore, for the synthesis of such dendrimers, octa(hydrido)- (T_8H) and octa(vinyl)- (T_8Vi) silsesquioxane have been used. In the first case, the hydrosilylation of tris(allyl)pentaerythritol by T_8H leads to obtaining the silsesquioxane with eight hydroxyl groups available for further functionalisation [15]. However, most of POSS-based dedrimers have been synthesised using octa(vinyl)octasilsesquioxane [135–138]. A number of POSS-based dendrimer molecules with functionality ranging from terminal silane (Si-H), silanol(Si-OH), aromatic aldehyde, carboxylic acid, Schiff base groups [135, 139] hydroxyl [136] and phosphines [137, 138] have been prepared. Otherwise, the chlorosilyl- and allyl-derivatised dendrimers (which then undergo functionalisation) have been synthesised via repetitive hydrosilylation/allylation (vinylation) of vinyl-functionalised POSS, according to (Eq. 7.23):



(7.23)

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Chapter 8
Organosilicon – Organic Hybrid Polymers and Materials

Abstract Hybrid organic-organosilicon materials, obtained by the combination of molecular organic and organosilicon components, have been considered potentially attractive for the purpose of development of new materials with distinct and specific properties, if compared to single organic and organosilicon constituents. One of the most useful methods for the synthesis of such materials is based on hydrosilylation processes. In this chapter, hydrosilylation is discussed in the aspects of its use for organic polymer modification and syntheses of multiblock and segment polymers. Another part of this chapter is devoted to the manufacture of nanocomposite, *via* hydrosilylation by using functionalised silsesquioxanes as fillers. Finally, the application of hydrosilylation processes to functionalisation of surfaces of materials as well as silicon single crystals and porous silicon is presented.

8.1 Functionalisation of Unsaturated Organic Polymers by Silicon Compounds

The hydrosilylation reaction of unsaturated polymers offers a useful and convenient method for preparing silane-modified polymers which may find potential applications as rubber materials, adhesives and drug delivery agents [1]. The hydrosilylation of vinyl- or allyl-containing organic monomers or macromonomers by hydrosilanes or hydrosiloxanes can lead to block or graft copolymers and hybrid materials. The hydrosilylation of unsaturated polymers (e.g. polybutadiene, polyisoprene, polyesters, other polyenes, polycarbonates) with silane having hydrolysable substituents at silicon atoms leads to the formation of polymeric systems with enhanced activity toward mineral fillers [2]. Both $>C{=}C<$ as well as $>C{=}O$ bonds are capable of hydrosilylation. This modification is connected with a reversed use of the silane (siloxane) coupling agents. Trialkoxysilyl groups are commonly incorporated into the polymers by Pt-catalysed hydrosilylation of internal or terminal olefinic bond.

B. Marciniec (ed.), *Hydrosilylation,* Advances in Silicon Science,
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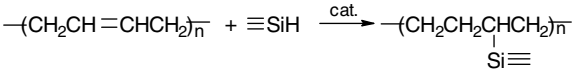
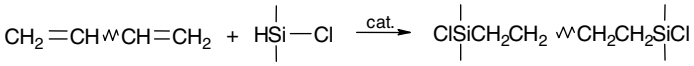


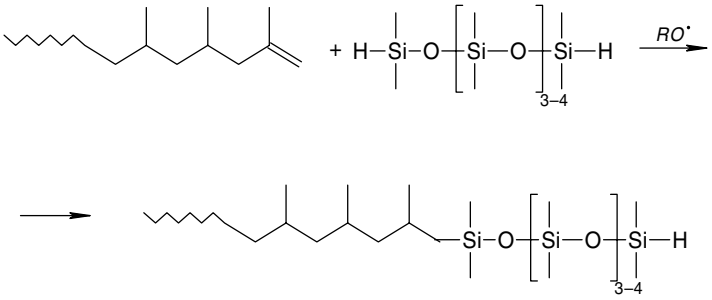
(8.1)

The hydrosilylation of polyisobutylene telomers by various chlorohydrosilanes proceeds after the substitution of chlorine atom by living polystyrene anions Pst^- to a variety of glassy rubber block co-polymers [3]:



(8.2)

The hydrosilylation has been investigated as a possible method for polymer functionalisation in the solution [4–6] but also in the melt-phase. For example, the melt-phase hydrosilylation of polypropylene was performed by both noncatalytic free radical method [7–10]:

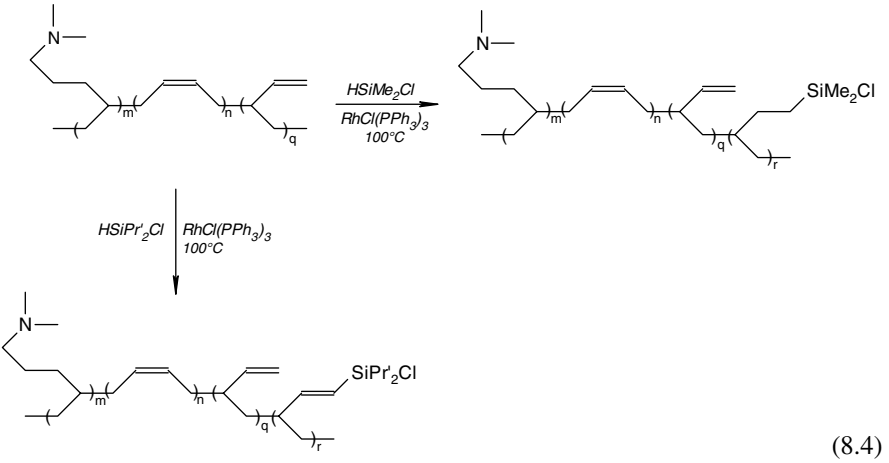


(8.3)

and also in the presence of platinum (Karstedt's) catalyst [7, 11]. In this case, a peroxide cocatalyst, such as *t*-buthylhydroperoxide, is necessary to maintain the catalytic activity.

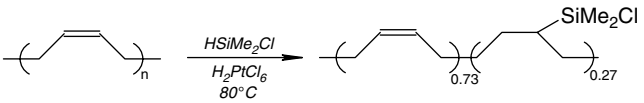
Polybutadiene is one of the most popular and commonly modified unsaturated polymers. Its availability at various molecular weight ranges and well-defined microstructures make it a practical choice for catalytic modification [2]. Hydrosilylation of polybutadiene by tri(alkyl, aryl)silane ($HSiEt_3$, $HSiBu_3$, $HSiPhMe_2$) in the presence of Wilkinson catalyst [$Rh(PPh_3)_3Cl$] leads to the formation of a mainly anti-Markovnikov product [12]. Similarly, the hydrosilylation of butadiene copolymers with styrene (SBR) and nitrile (NBR) was also examined and the influence of functional groups was studied [13]. In the case of SBR, the reaction occurred via a typical anti-Markovnikov addition contrary to the reaction of NBR, in which Markovnikov addition was observed.

The effect of the kind of hydrosilane on the product formation was also described. For example, the reaction of aminomethylated polybutadiene with $HSiMe_2Cl$ resulted in the expected anti-Markovnikov product, however, when the same reaction was performed with $HSi^{i}Pr_2Cl$, the vinyldiisopropylsilane product was formed [14], according to (Eq. 8.4):



(8.4)

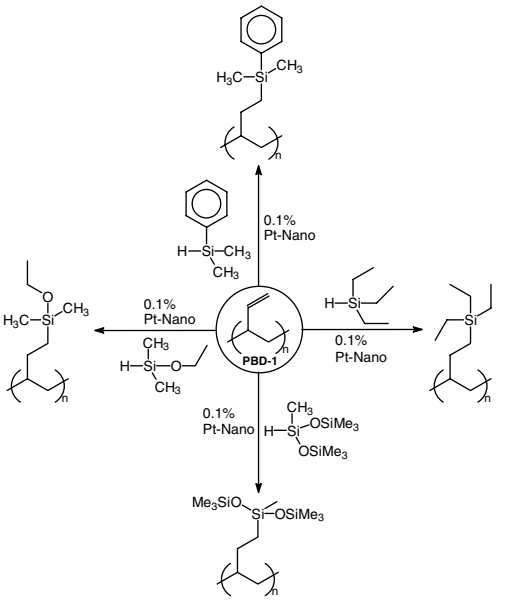
Rhodium catalyst showed activity in the above reaction, however, the majority of reactions of hydrosilylation of polybutadiene examined were performed in the presence of platinum catalysts, mainly hexachloroplatinic acid [2, 4, 15–17]. In the Pt-catalysed reaction, unlike the Rh system, formation of some of the internal 1,4-adduct was observed:



(8.5)

Hydrosilylation of polybutadiene by hydropolysiloxane was also used for the synthesis of polyethylene-graft-poly(dimethylsiloxane copolymers). Such a product was obtained via hydrosilylation of polybutadiene, catalysed by $[Pt\{(Et)_2S\}Cl_2]$, followed by hydrogenation [18].

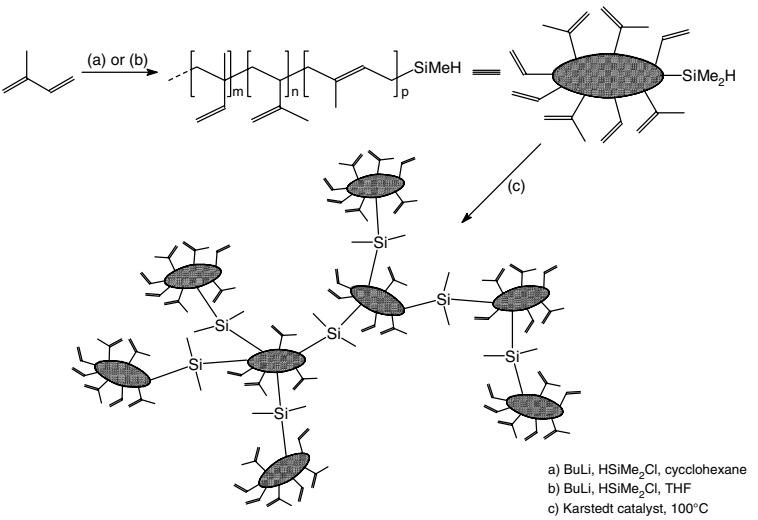
Very recently, the first example of a highly selective, mild, and clean synthetic route to silyl-functionalised organic polymers, has been reported [19]:



(8.6)

These products were obtained by hydrosilylation of polybutadiene, using readily synthesised and recyclable platinum nanoclusters as catalysts.

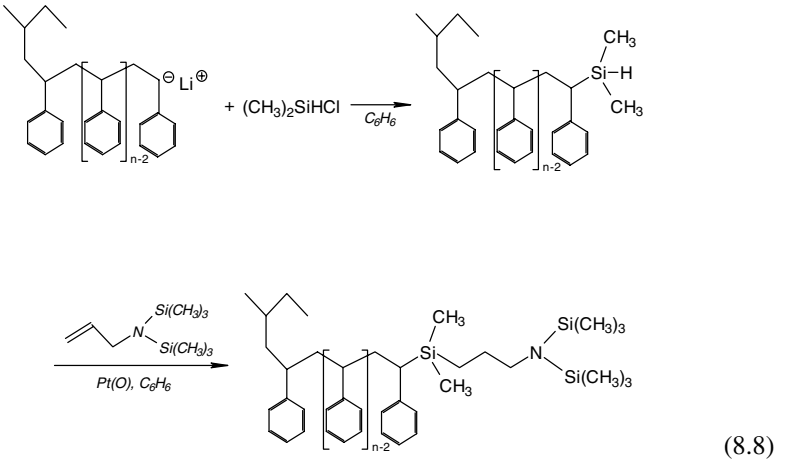
Synthesis of branched polyisoprenes was carried out by a Pt catalysed hydrosilylation of silane end-functionalised macromonomers [20], according to (Eq. 8.7):



(8.7)

The synthesis of macromonomers was achieved by anionic polymerisation of isoprene and subsequent end-capping of the polymers by addition of chlorodimethylsilane to the living carbanions.

Similar methodology was used for the synthesis of amine functionalised poly styrene via hydrosilylation of allylamines with silyl hydride functionalised polystyrene [21] according to (Eq. 8.8):

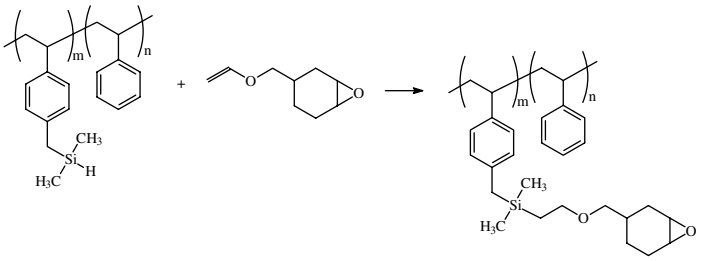


(8.8)

Silyl hydride functionalised polystyrene was also used for synthesis of maltoheptaose-block-polystyrene, via hydrosilylation [22].

Trialkylsilanes were used for photoinduced pattering of electroluminescent polymers, e.g., under UV irradiation. Trialkylsilanes selectively saturate the vinylene groups in poly(p-phenylenevinylene)-type polymers, while leaving aromatic units virtually unaffected [23]. In contrast to the other methods, in that with trialkylsilanes it is possible to achieve photochemical pattering under non-toxic and odourless conditions.

Many, highly reactive silicone–epoxy oligomers for cationic photopolymerisations were also synthesised, using linear [24–29] and hyperbranched H-siloxanes [29–31] or polystyrene having Si-H as a pendant group [32]:



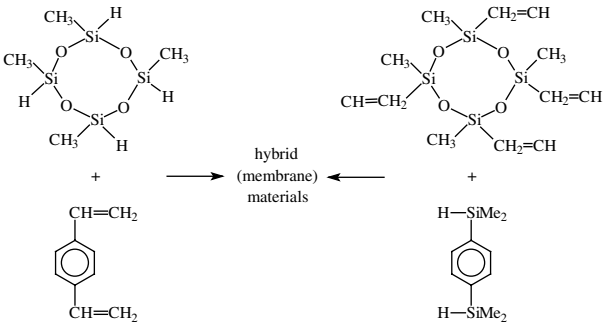
(8.9)

Decorative and protective coatings, printing inks, and adhesives are just a few examples of those commercial uses of photoinitiated cationic polymerisations. These compounds contain both 1,2-epoxycyclohexyl group [24–27, 31, 32] and glycidyl group [25, 30], as well as oxetane and trioxane groups [28, 29].

8.2 Organosilicon-Organic Multiblock and Segmented Polymers

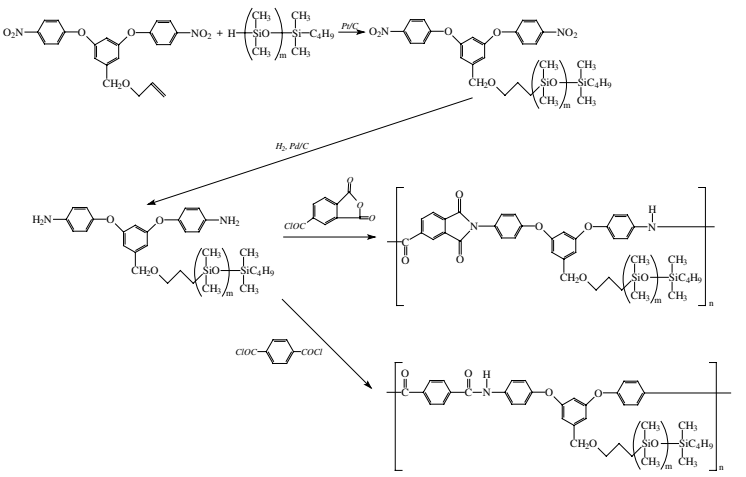
Hybrid organic-inorganic materials, obtained by combinations of molecular organic and inorganic components, have been considered as potentially attractive for the purpose of developing new materials [33–37]. The most obvious advantage of inorganic –organic hybrids is that they can favourably combine the often dissimilar properties of organic and inorganic components in one material. Because of many possible combinations of components, this field is very creative, giving an opportunity to invent an almost unlimited set of new materials with distinct and specific properties. Various compounds consisting of organic and inorganic parts can be classified as hybrid materials. Generally, they are divided into two classes of hybrid materials. Class I are those that show weak interactions between the two phases, i.e., interpenetrating networks (IPNs), in which inorganic and organic network interpenetrate each other without strong chemical interactions. Class II hybrid materials are those which show strong chemical interactions between the components, i.e. the inorganic and organic (poly)mers are covalently connected with each other. The latter class includes the whole group of silicone-organic multiblock or segmented copolymers. The hydrosilylation processes belong to the common methods for the synthesis of both classes of hybrid materials, which are involved in either monomer synthesis, or in catalysing the copolymerisation reaction itself. A considerable group of silicone-organic hybrid copolymers can be obtained in the process of hydrosilylation polymerisation, between α, ω- dihydrido(poly)siloxanes and α, ω-alkenes (alkynes) or their functional derivatives. Some examples of such reactions have been described in Chapter 6.

Several hybrid polymers have been investigated as membrane materials for gas separation processes [38, 39]. Most of the membrane materials are polymers with high Tg value which promotes low gas flow but high selectivity for gas separations. However, an ideal membrane material should be characterised by good permeability /ideal selectivity relationships. Such properties are shown by polycyclic silicone membranes obtained from 1,3,5,7-tetravinyl, 1,3,5,7-tetramethylcyclotetrasiloxane (and tetraallyl- or tetravinylsilane) and 1,4-bis(dimethylsilyl)benzene [40] or from divinylbenzene and 1,3,5,7-tetramethylcyclotetrasiloxane [41] via hydrosilylation catalysed by Karstedt's catalyst.



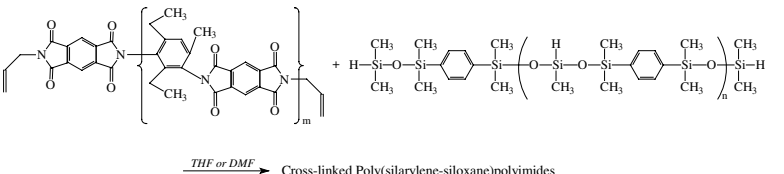
(8.10)

The hydrosilylation process, catalysed by Pt/C, was used for the synthesis of macromonomers, such as 3,5-bis(4-aminophenoxy)benzyloxypropyl-terminated polysiloxane. Its polycondensation with trimellitic anhydride chloride and terephthaloyl chloride yielded the siloxane-grafted poly(amide-imide) copolymers, from which a highly permeable and durable membrane material for pervapouration has been obtained [42, 43], according to (Eq. 8.11):



(8.11)

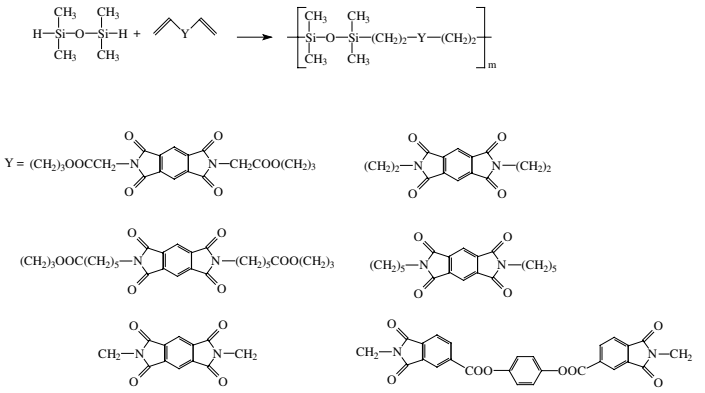
The oligoimide was also used for a synthesis of polyimide – polyhybridsiloxane block copolymers [44, 45] (and their fluorinated counterparts [46, 47]). A very similar system was used for the synthesis of cross-linked poly(silarylene-siloxane)-polyimides in the hydrosilylation of allyl – terminated oligoimides with hydride – functional silarylene-siloxanes, catalysed by hexachloroplatinic acid, [48]:



(8.12)

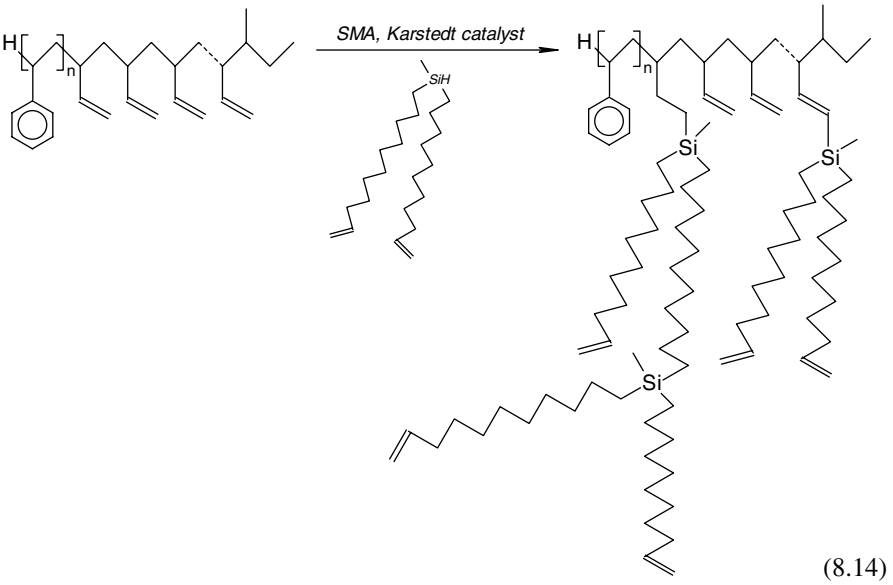
This high-performance polymeric material, which has outstanding thermal and chemical resistance, may be found useful in such fields as aeronautics, microelectronics and composites.

A series of poly(siloxane imide)s was synthesised by polyhydrosilylation of N,N-dialkenylimides with 1,1,3,3-tetramethyldisiloxane [49]:



(8.13)

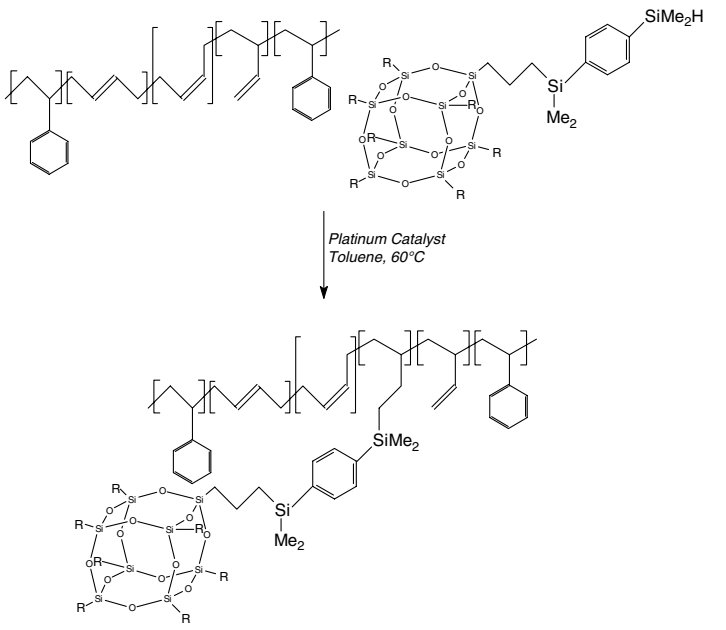
Some of these products showed liquid crystalline properties. The novel linear-hyperbranched diblock copolymers with narrow polydispersities, based on the grafting of methyldiundecen-10-yl silane onto a polystyrene-block-polybutadiene copolymers, were prepared by hydrosilylation catalysed by Karstedt's catalyst [50, 51]:



(8.14)

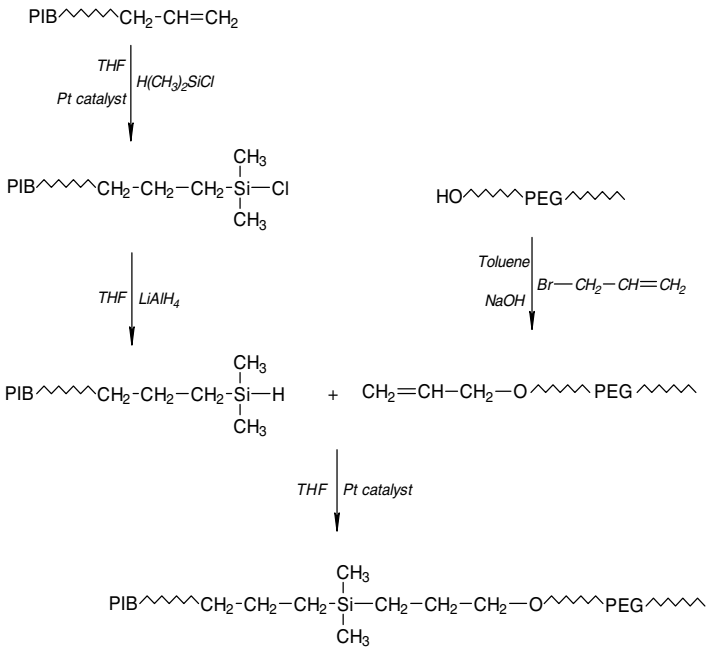
The polymers prepared in the bulk polymerisation of styrene and methyl methacrylate, in the presence of multifunctional silanes, can be functionalised by the reaction of hydrosilylation and further used in the synthesis of block copolymers [52]. The organosilicon hydrides play the role of chain-transfer –agents in such radical polymerisation.

Modification of triblock copolymer of polystyrene-polybutadiene-polystyrene by hydrosilylation with hydride-functional POSS derivative leads to the formation of novel hybrid materials [53]:



(8.15)

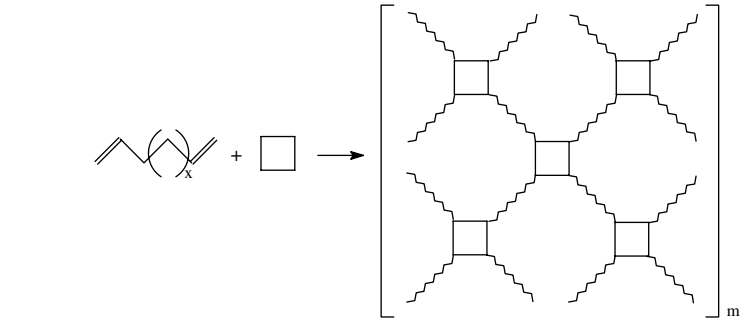
Hydrosilylation process has been used for coupling of poly(ethylene glycol) with polyisobutylene [54], according to (Eq. 8.16):



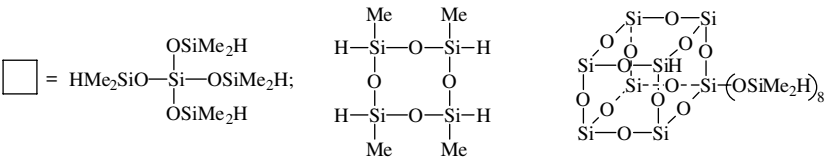
(8.16)

The synthetic strategy involved Karstedt's catalysed hydrosilylation of allyl-telechelic poly(ethylene glycol)s with PIB-Si$(CH_3)_2$H, which was also obtained via hydrosilylation of polyisobutylene, followed by hydrogenation.

Some organic-inorganic hybrid polymers with network structures have been developed by means of the hydrosilylation reaction of multi-functionalised crosslinking reagents containing Si-H or vinyl group [40,41,55–57]. For example, a series of organic –inorganic hybrid gels have been synthesised from siloxane (tetrakis(dimethylsiloxy)silane -TDSS and tetramethylcyclotetrasiloxane –TMCTS) or silsesquioxane (octakis(dimethylsiloxy)octasilsesquioxane –POSS) crosslinking reagents and α,ω-non-conjugated dienes via a hydrosilylation reaction with a Karstedt's catalyst [58], according to (Eq. 8.17):



x = 1, 2, 3

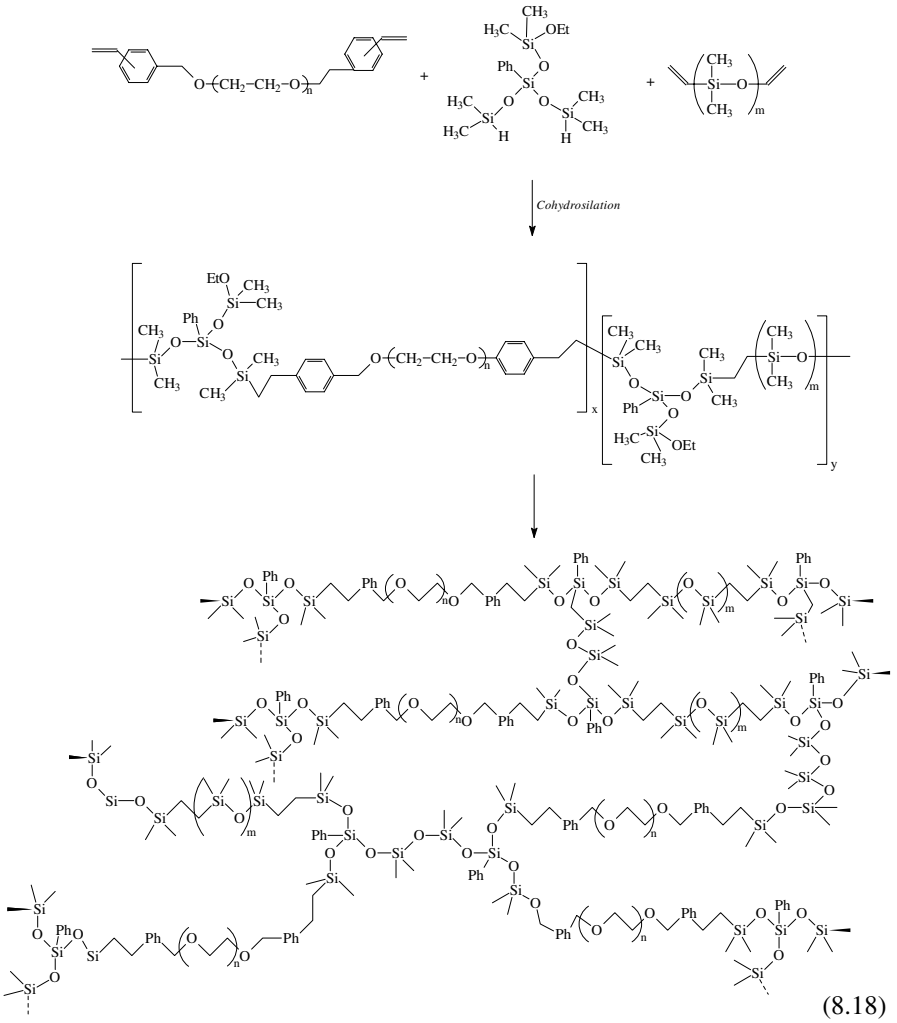


TDSS TMCTS POSS (8.17)

The gelation and structure of the organic –inorganic hybrid gels depended on both the stretched molecular length of the diene (the critical gel concentration decreased as the diene length increased) and the molecular structure of the crosslinking reagent (the critical gel concentration decreased in order TDSS > TMCTS > POSS).

There are also examples of synthesis of amphiphilic conetworks (APCN), i.e., networks consisting of well defined hydrophilic poly(ethylene glycol) and hydrophobic polydimethylsiloxane [59–62]. One of such conetworks was achieved by the use of dual-purpose extender/crosslinker, PhSi$(OSiMe_2H)_2\{OSiMe_2(OEt)\}$, whose first function was to extend the incompatible prepolymers into random functional multiblocks (via hydrosilylation catalysed by Karstedt's catalyst), and

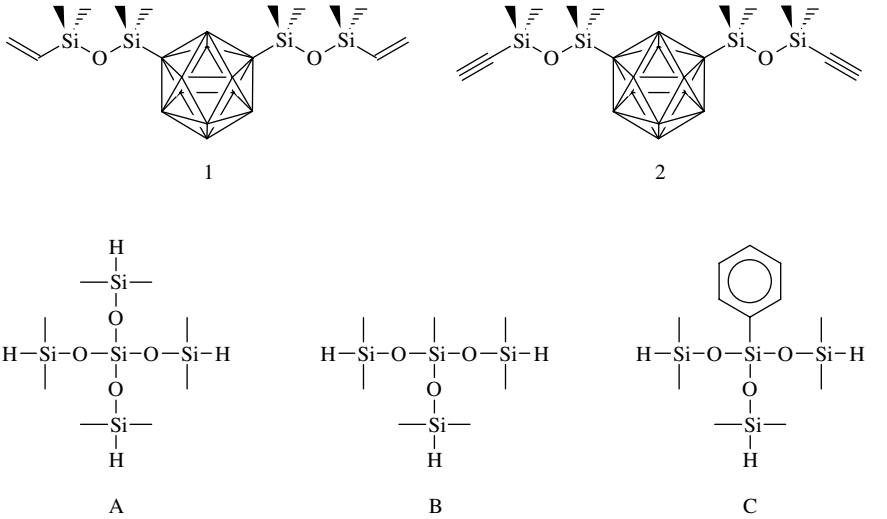
subsequently, to crosslink them by condensing the Si(OEt) functions [62], according to (Eq. 8.18):



(8.18)

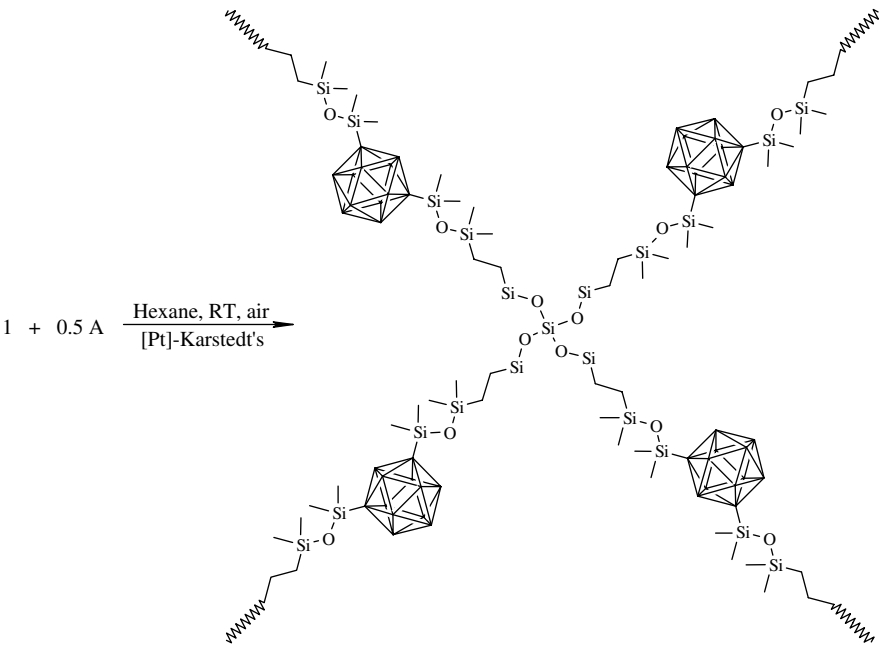
Such networks exhibit desirable chemical, mechanical and biological properties for selective medical applications, e.g. as hydrogels, material of contact lenses, etc.

High temperature thermally and thermooxidatively stable elastomeric network polymers were obtained by the Karstedt's catalysed hydrosilylation reactions of a monomeric vinyl (or ethynyl)-containing carboranylenesiloxane and three-branched siloxane crosslinker monomers (see Scheme 8.1) [63]:



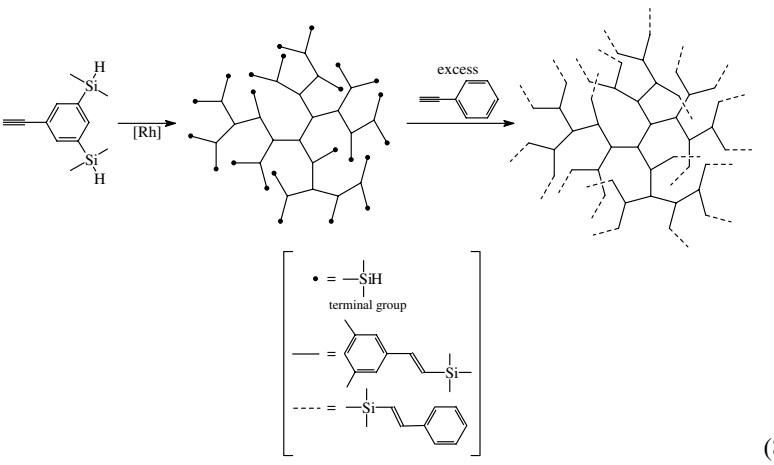
Scheme 8.1 Carboranylene siloxanes (1 and 2) and siloxane crosslinkener monomers (A, B and C) for synthesis of thermally stable elastomeric network polymers

For example, the flexible and transparent films of the saturated elastomeric network polymers were synthesised from 1 and A:



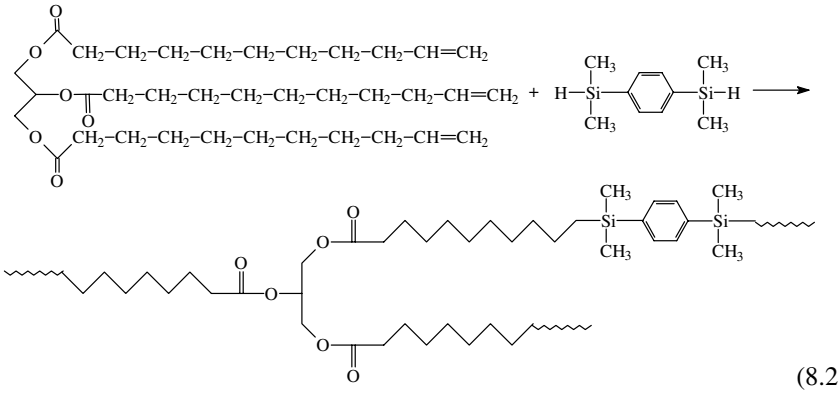
(8.19)

Silicon-containing σ-π conjugated polymers having a silylenevinylene moiety, have been promising for the use as semiconductors, photo- and electroluminescent materials. The majority of polymers of this type have been synthesised by the hydrosilylation reactions of bis(dialkylsilyl)arenes with diethynylarenes, catalysed by Rh complexes, mainly $[RhCl(PPh_3)_3]$/NaI or $[RhI(PPh_3)_3]$ [64–67]. In order to obtain such polymers, a new AB_2-type monomer, m-bis(dimethylsilyl)phenylacetylene has been obtained. The hydrosilylation (in the presence of $[RhCl(PPh_3)_3]$/NaI), and subsequent aerial oxidation of the monomer provided a transparent homogeneous gel film, which emitted quite intense blue light when excited at the change-transfer absorption wave-length [68]:



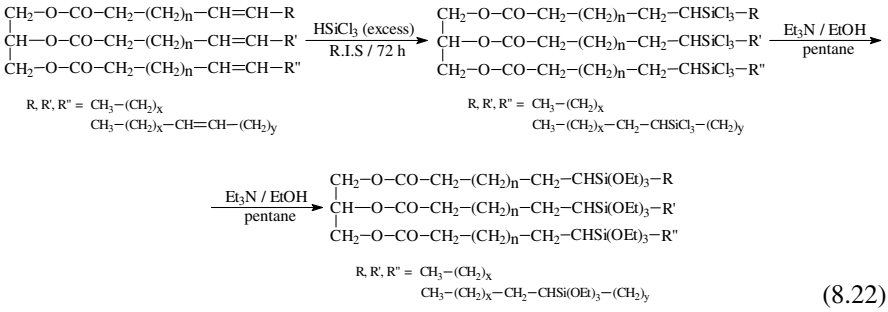
(8.20)

Very recently, there has been great interest in organic-inorganic hybrid materials obtained from renewable resources. The preparation of polymeric materials from renewable resources is of great economic and ecological significance. Oils and fats are one of the most important renewable materials, since they offer a large number of possibilities for application which can be rarely met by petrochemistry. Although the hydrosilylation of olefins has been widely studied, a few reports have appeared on the fatty acid esters [69–72]. One of the examples is, the hydrosilylation of 10-undecenoyl triglyceride with multihydridosilyl moieties, such as 1,4-bis(dimethylsilyl)benzene, tetrakis(dimethylsiloxy)silane and tetramethylcyclotetrasiloxane, in the presence of Karstedt's catalyst [73]:



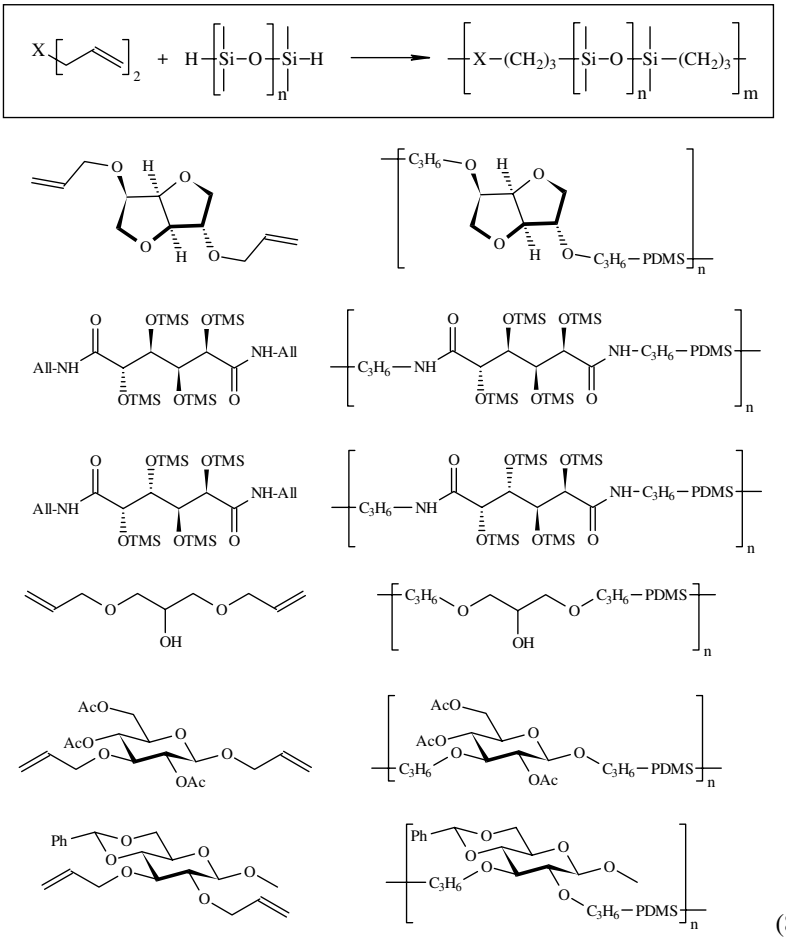
(8.21)

The materials obtained showed good transparency and promising properties for optical applications. Another example describes the hydrosilylation of various terminal and internal C=C double bonds in triacylglycerol fish oils, which was performed under radical initiation sequence (RIS). The product synthesiesed, after ethanolysis, gave the sol-gel processable triethoxysilyltriacylglycerol, which led to hybrid materials [74]:



(8.22)

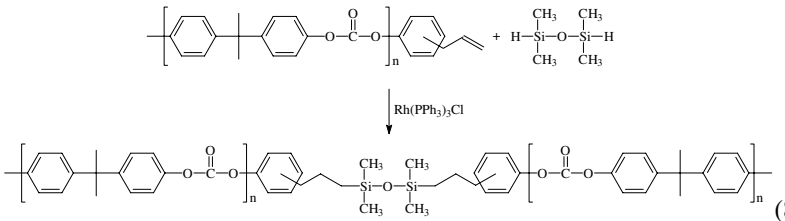
Carbohydrate-modified polysiloxanes are another, very important group of hybrid materials. Some examples of such modified, comb structure, polysiloxanes are presented in Chapter 6.1. However there are also a few examples of carbohydrate-segmented polydimethylsiloxane block copolymers. A series of such compounds have been synthesised by hydrosilylation of bisallylsubstituted carbohydrate derivatives with hydrodimethylsilyl-terminated polysiloxane, in the presence of Speier catalyst [75], according to (Eq. 8.23):



(8.23)

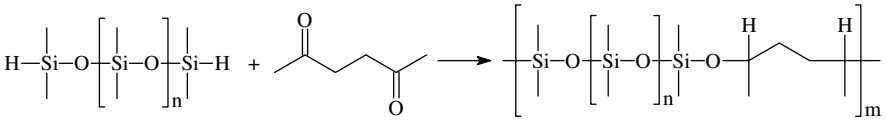
Polydimethylsiloxane-modified chitosans, due to their unique properties such as biocompatibility and biodegradability, are of particular interest for use as biomaterials. The synthesis is based on the reaction of an epoxy functional polysiloxanes (obtained via hydrosilylation) and chitosan in an acidic aqueous solution [76].

Hydrosilylation was also used for synthesis of silylated polycarbonates or polycarbonate-disiloxane-polycarbonate triblock copolymers. Such reactions, between allyl-terminated polycarbonatres and H-Si moieties (silane or siloxane) were efficiently catalysed by Wilkinson catalyst [77]:



(8.24)

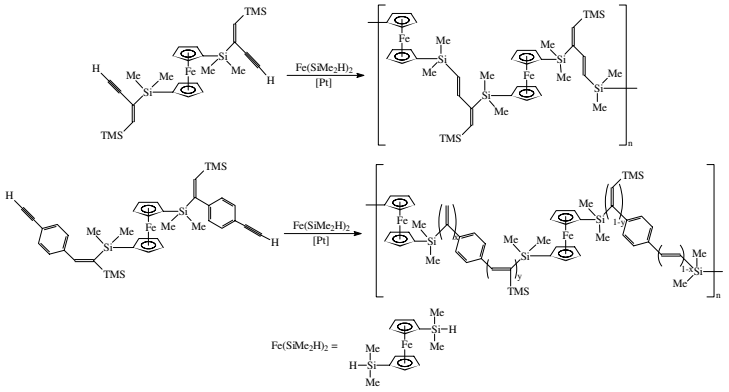
The hydrosilylation polymerisation of aliphatic ω-dimethylsilyloxy ketones or α,ω-diketones with α,ω-dihydridooligodimethylsiloxanes gave unsymmetrical or symmetrical poly(silyl ether)s, respectively [78]:



(8.25)

These reactions were catalysed by specially activated ruthenium complex. Styrene activates $[RuH_2(CO)(PPh_3)_3]$ by removal of hydrogen (producing of ethylbenzene) and one PPh_3 ligand, which leads to coordinately unsaturated active catalyst $[Ru(CO)(PPh_3)_2]$.

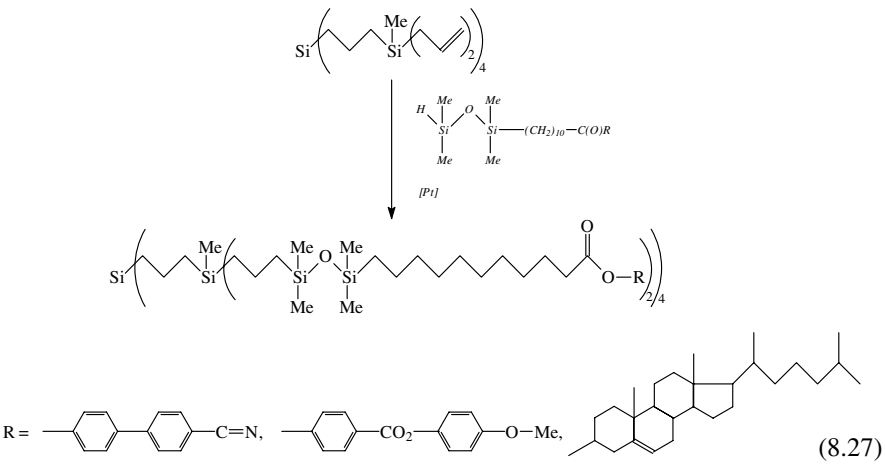
Finally, there are some examples of synthesis of ferrocene-containing polymers, obtained by hydrosilylation of dialkynes and ferrocene-containing bis-enynes with 1,1'-bis(dimethylsilyl)ferrocene using Karstedt's catalyst and $RhI(PPh_3)_3$, [79]:



(8.26)

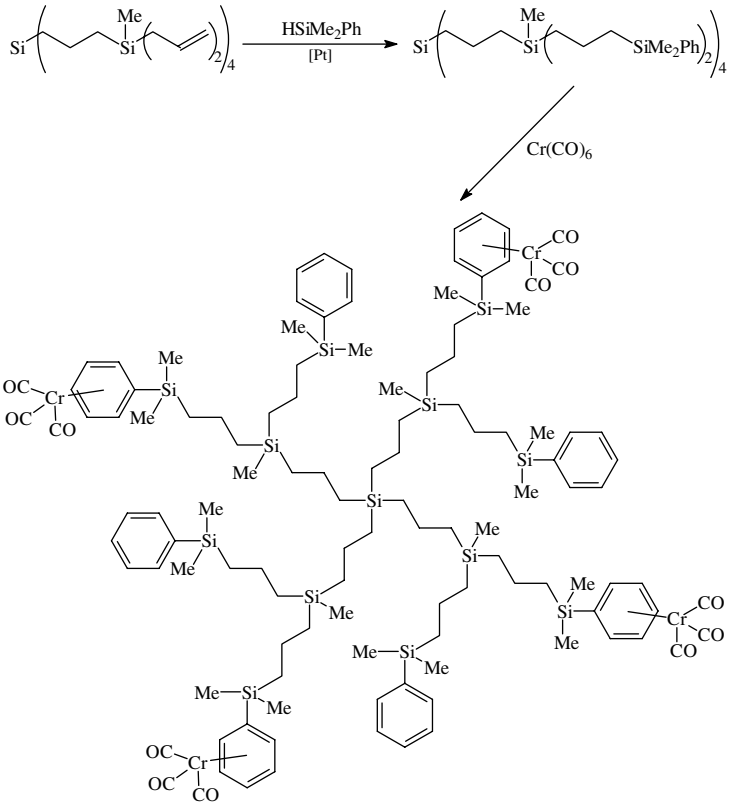
Most of the known organosilicon dendrimers contain alkenysilyl or halosilyl endgroups, which can undergo various transformations yielding a wide range of dendrimers functionalised at peripheral sites. From among such transformations, the substitution of the chlorine atom of the Si-Cl end groups by various nucleophilic agents, and the addition of compounds with labile hydrogen (e.g. silanes, boranes, mercaptanes, phospines) to Si-alkenyl groups, are the most important. A halosilyl group can also be readily reduced with $LiAlH_4$ giving a Si-H group [80], which is a basic substrate, besides vinyl groups, for functionalisation via hydrosilylation. However, organosilane used for functionalisation is different from those used for the construction of a dendrimer.

The hydrosilylation of a vinyl-terminated carbosilane dendrimers with a mesogen –functionalised organosilanes leads to formation of dendrimers exhibiting mesomorphic behaviour [81]:



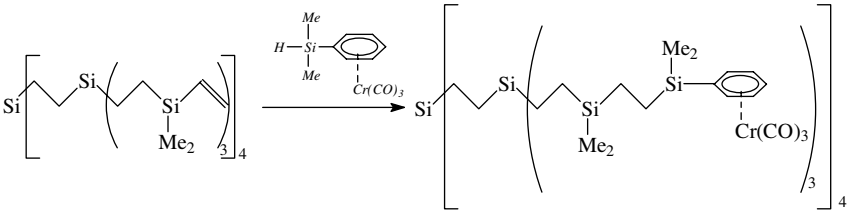
(8.27)

Some organosilicon dendrimers have been functionalised by organometallic moieties. For example, dendrimers, containing (arene)(tricarbonyl) chromium complex, in peripheral sites, have been synthesised in the reaction of vinyl-terminated dendrimers with dimethylphenylsilane, followed by the reaction with $[Cr(CO)_6]$ [81]:



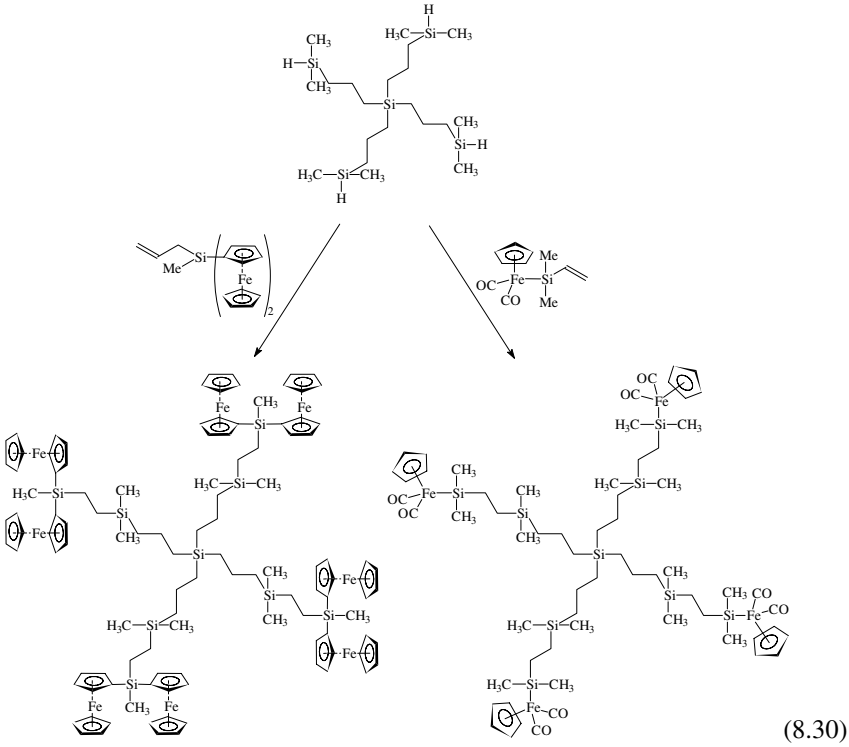
(8.28)

or in the reaction with dimethylsilylbenzenechromium tricarbonyl [82]:



(8.29)

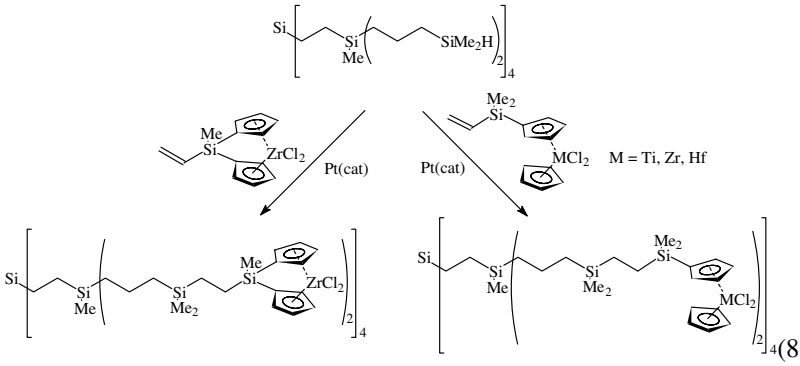
Another type of organometallic derivatives of dendrimers are ferrocene-functionalised dendrimers. Poly(ferrocenyl)based macromolecules are very useful as electrode mediators, electrochemical sensors, as materials for the construction of electronic devices, non-linear optical systems and as chiral ligands for asymmetric catalysis [83, 84]. Such compounds have been synthesised by hydrosilylation of the vinyl-functionalised silicon bridged biferrocene CH_2 =CHSiMe[Fe(η^5-C_5H_4)(η^5-C_5H_5)]$_2$ [85–87] or silyl iron complex [(η^5-C_5H_5)Fe(CO)$_2$ {$SiMe_2$(CH=CH_2)}] [88]:



(8.30)

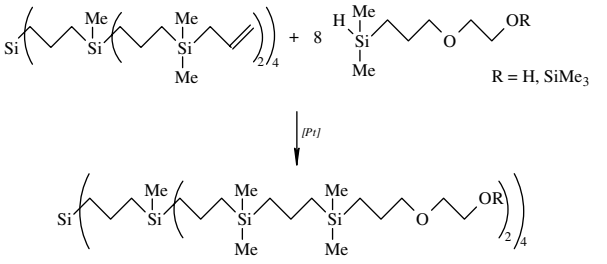
The synthesis of poly(bis(imino)pyridyl)iron(II) metalladendrimer has also been reported [89].

Hydrosilylation of other vinyldimethyl-substituted metallocene (i.e. titanocene, hafnocene, zirconocene) has also been reported [82]:



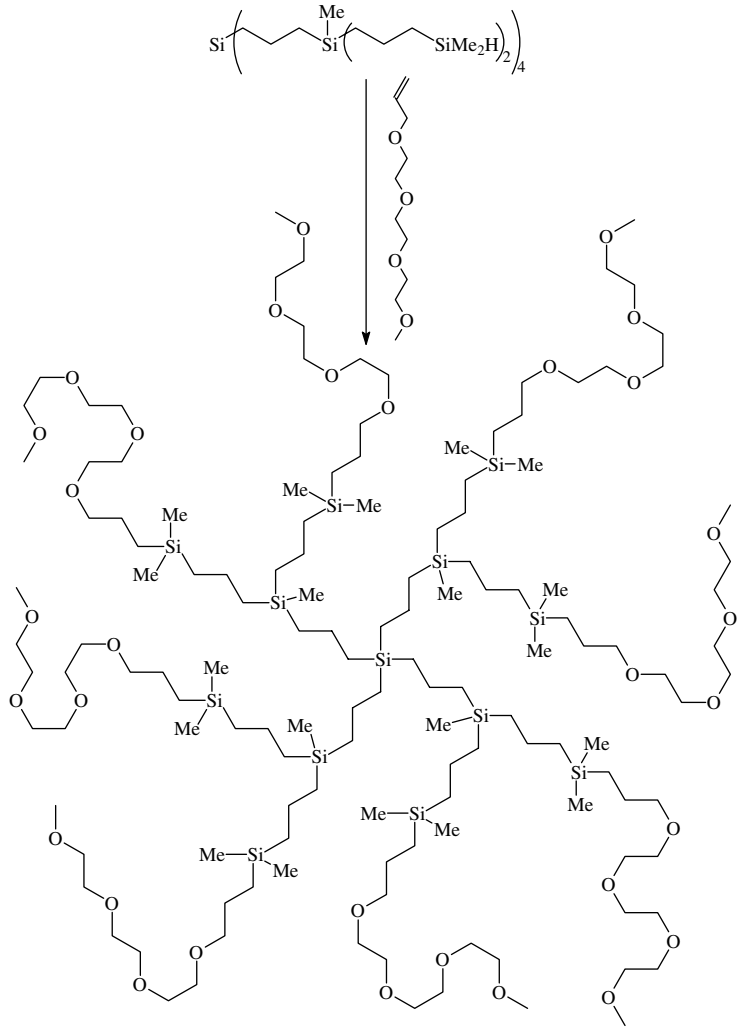
(8.31)

Carbosilane dendrimer periphery can be modified with different polar and amphiphilic groups. An example of such syntheses is that of hydroxyl group containing dendrimers via hydrosilylation of allyl terminated dendrimers with functionalised silane containing a protected hydroxyl group, followed by its deprotection [90]:



(8.32)

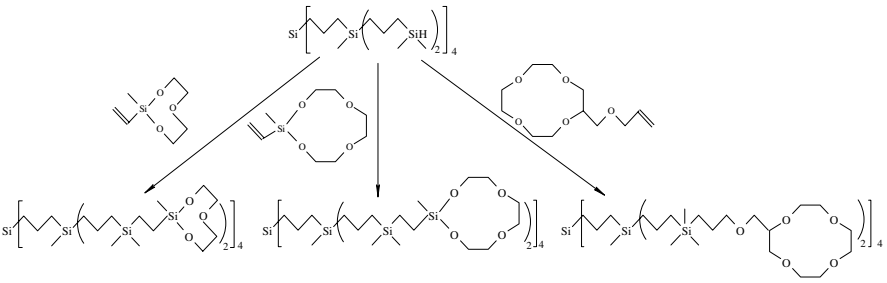
Poly(ethylene glycol) is another polar group that can be attached to carbosilane dendrimers. The hydrosilylation of allyl functionalised poly(ethylene glycol) monomethyl ether with the respective Si-H terminated dendrimers leads to the second generation of functionalised dendrimers [91–93]:



(8.33)

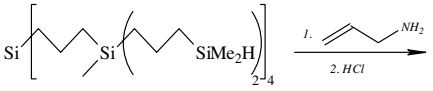
These compounds can be used as ionophores in chemical sensors.

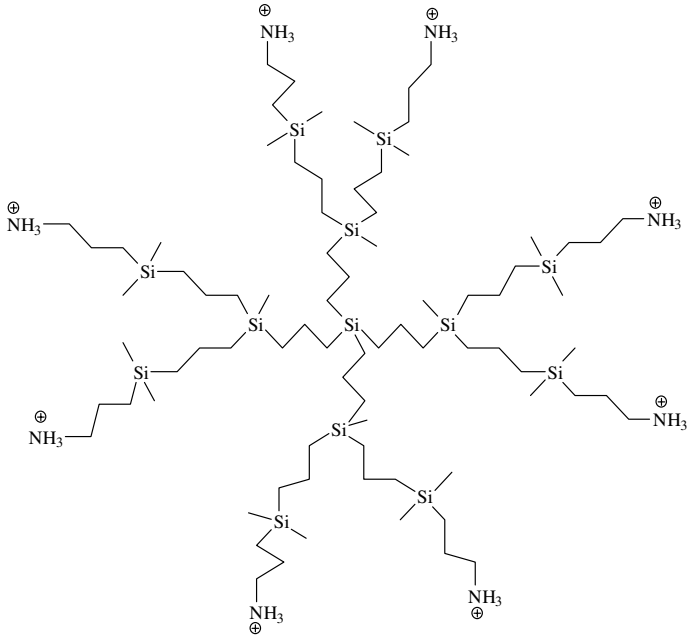
Similarly, carbosilane dendrimers with end-grafted silacrown- and crown-ether units have been synthesised [94], via hydrosilylation of the respective vinyl or allyl derivatives of crown-ethers:



(8.34)

Very recently, the syntheses of novel amine- or ammonium-terminated carbosilane dendrimers have been reported [95]. These compounds have been obtained by hydrosilylation of allylamine with Si—H bonds of the dendritic system, in the presence of Speier's catalyst, and subsequent quaternisation with HCl:

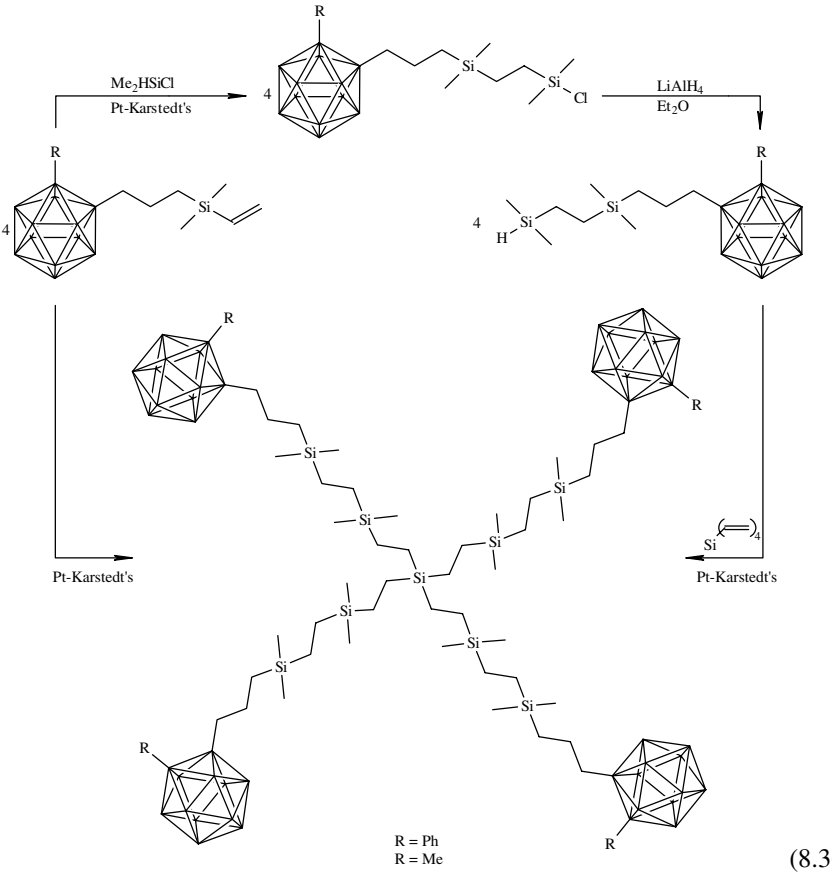




(8.35)

These new ammonium-terminated carbosilane dendrimers (soluble and stable in water), are promising for biomedical applications, such as drug carriers, controlled drug liberation, as antigen carriers or as vehicles for nucleic acids.

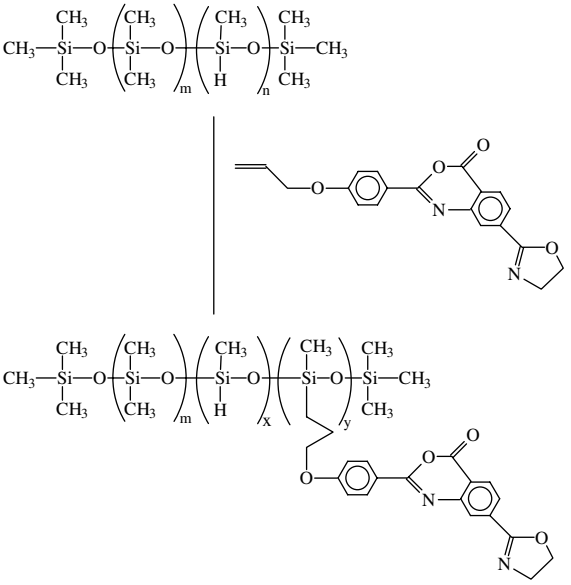
A final example of functionalisation of organosilicon dendrimers is the synthesis of carboranyl-containing carbosilane dendrimers [96–98]. Because of their versatility, carboranes, have been an ideal group for the preparation of stable, agile and suitable building block that are subsequently attached to a core molecule. These compounds were synthesised using two different approaches. The first is the divergent approach, involving the hydrosilylation of allyl or vinyl-substituted carborane derivatives with the first generation of carbosilane dendrimers containing peripheral Si-H functions, or the convergent strategy requiring the synthesis of Si-H functionalised carboranyl building blocks, to be attached, in the last step, to the tetravinylsilane core:



(8.36)

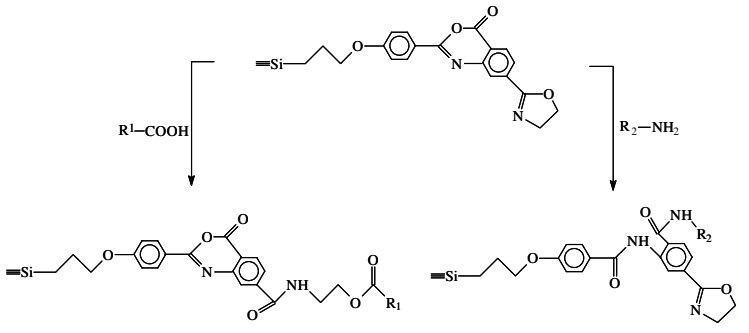
Multifunctional polysiloxanes could operate as crosslinkable coupling agents. They are also able to compatibilise heterogenous polymer blends or to form copolymers with polysiloxanes. An exemplary product is the coupling agent containing 2-oxazoline and 2-oxazine as well a hydrosilane moieties, which has been prepared by hydrosilylation of the corresponding allyl ether containing precursor with a

copoly(dimethyl, hydromethyl)siloxane, in the presence of Karstedt's catalyst [99], according to (Eq. 8.37):



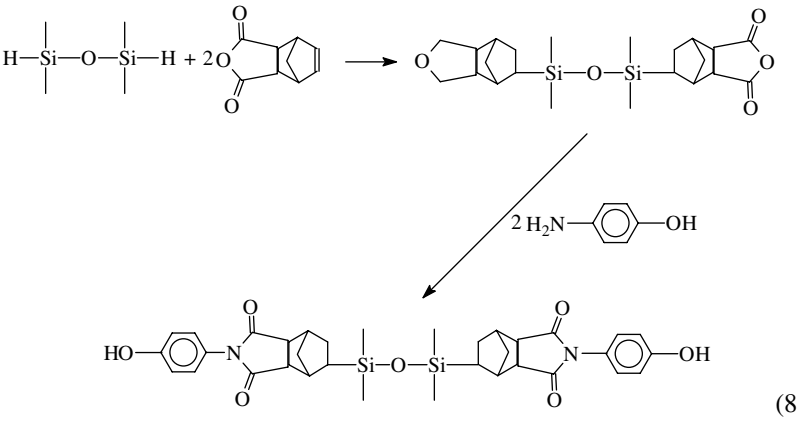
(8.37)

The use of this compound for the modification of the interfaces in a polymer blend, such as amino-terminated poly(methyl methacrylate) and carboxylic acid-terminated polystyrene has led to the coupling of these polymers and their crosslinking via the reaction of oxazoline unit with carboxylic group and oxazinone unit with amine group, according to (Eq. 8.38). The remaining hydrosilane units should be accessible to crosslinking:



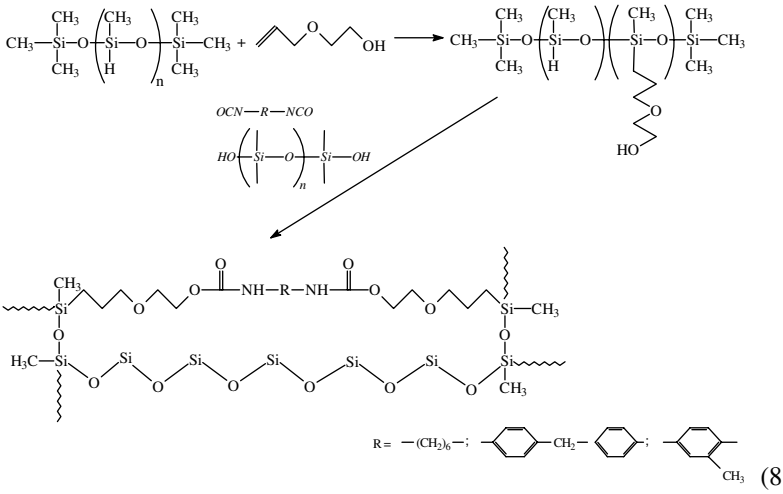
(8.38)

Hydrosilylation of nadic anhydride by tetramethyldisiloxane, followed by the reaction with 4-aminophenol leads to formation of N,N'-bis(4-hydroxyphenyl)-5,5'-(1,1,3,3-tetramethyldisiloxane)-bis norbornane –2,3-dicarboximide, useful for curing epoxy resin [100]:



(8.39)

Hydroxy terminated polysiloxanes make another group of crosslinkers, which have been synthesised by hydrosilylation of allyl alcohol, catalysed by Karstedt's catalyst, or propargyl alcohol in the presence of H_2PtCl_6] [101]. Such compounds were used for synthesis of poly(siloxane-urethane) [102, 103] and poly(ethylene oxide)-polysiloxane-chitosan copolymers [104].



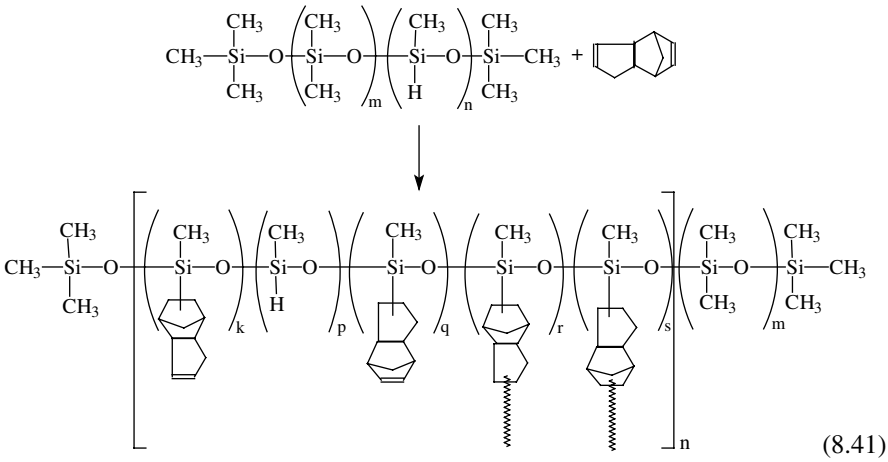
(8.40)

Hydroxy groups are able to link the soft segmented polysiloxane with the hard segments of polyurethane, giving very good membrane materials.

Moreover, chemical crosslinking or grafting of polysiloxane on chitosan is very interesting. Chitosan is a biodegradable, biocompatible and inexpensive natural polymer which is used in various biomedical applications, (such as orthopaedic, periodontal, drug delivery, tissue engineering, etc.), however, its application is limited due to the high degree of crystallinity, resulting in its rigid structure. Incorporation of an elastomeric polymer (such as polysiloxane) improves its mechanical properties [105, 106].

Polysiloxanes are also modified by aromatic fragments. The hydrosilylation of styrene, α-methylstyrene, phenylacetylene [107, 108] allyl methoxybenzene and allyl dimethoxybenzene [109], in the presence of Karstedt's catalyst and H_2PtCl_6 in THF, showed that Karstedt's catalyst is more efficient in the reactions examined.

In the hydrosilylation of tricyclodecadiene by poly(dimethyl, hydrometyl)siloxane, catalysed by H_2PtCl_6, the reaction of addition could proceed both to 1,2 and 9,10 position, moreover the product containing tricyclodecenyl and hydride group could easily enter intermolecular hydrosilylation, giving organosilicon rubber [110], according to (Eq. 8.41):



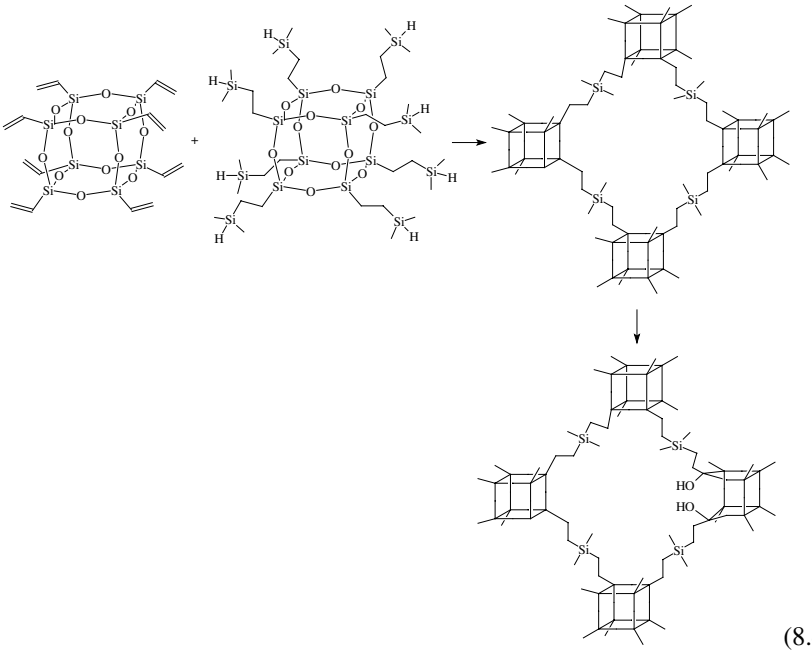
(8.41)

8.3 Silsesquioxane-based Nanocomposites

POSS nanostructured chemicals, whose molecules are from 1 to 3 nm in diameter, can be thought of as the smallest possible particles of silica. On the other hand, in contrast to silica, each POSS molecule contains organic substituents, which make

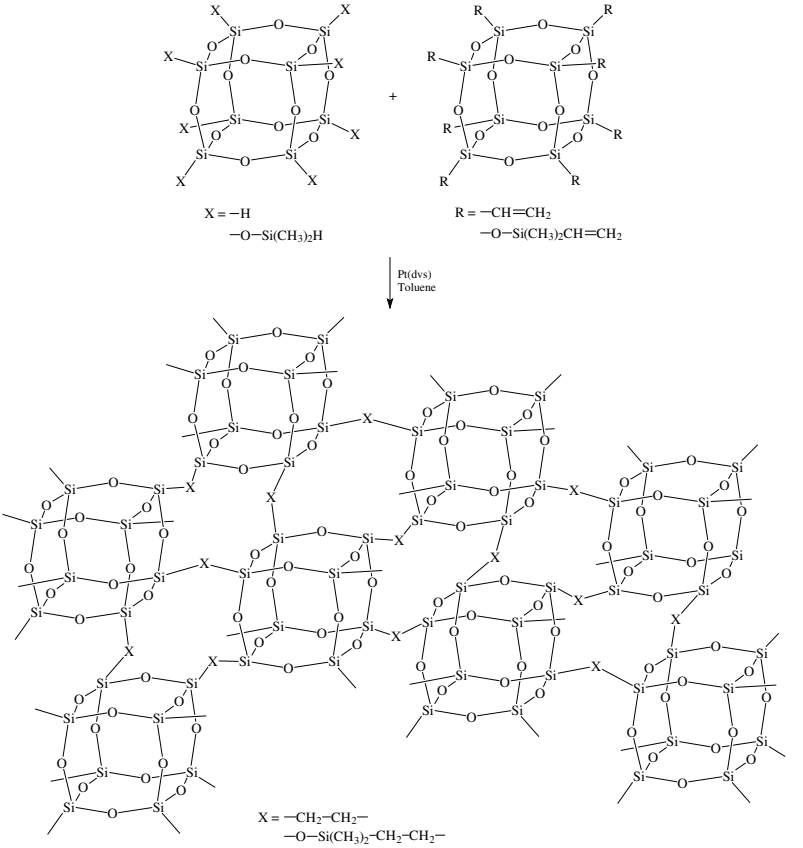
the POSS structure compatible with polymers, biological system or surfaces [111]. The availability of diverse nanocomponents which are easily made, and whose properties can be closely controlled can have a significant impact on the development of nanomaterials and nanotechnologies.

These compounds provide an excellent platform for synthesis of new inorganic-organic hybrid materials. The reaction of octavinyl-POSS with octahydrido-POSS, in the presence of a Karstedt's catalyst produces the porous network polymer, porosity of which is in the micro to meso range [56, 112]. However, such a polymer could be further functionalised which was carried out by the reaction with triflic acid or sodium hydroxide, resulting in the ring opening of a small amount of the POSS to produce silanol groups that can be functionalised by titanium complex [113].



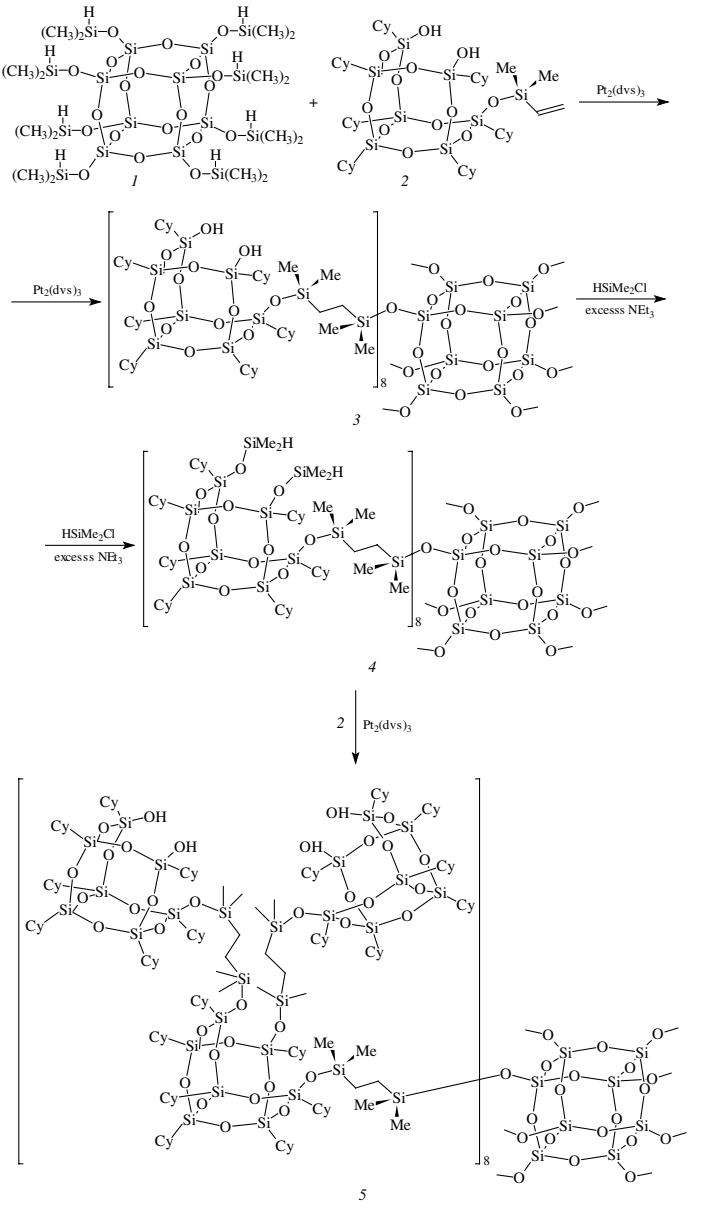
(8.42)

The most interesting reaction is the octahydrido- with octavinylsilsesquioxane (or its allyl analogue) which provides the opportunity to produce micro- and mesoporous materials [114, 115]:



(8.43)

Recently, the synthesis of novel starburst-type and dendritic giant molecules, utilising polyhedral spherosilicate (octakis(dimethylsiloxy)silsesquioxane) and silsesquioxane disilanols bearing alkenylsilyl moieties, has been reported [116] (see Eq. 8.44):

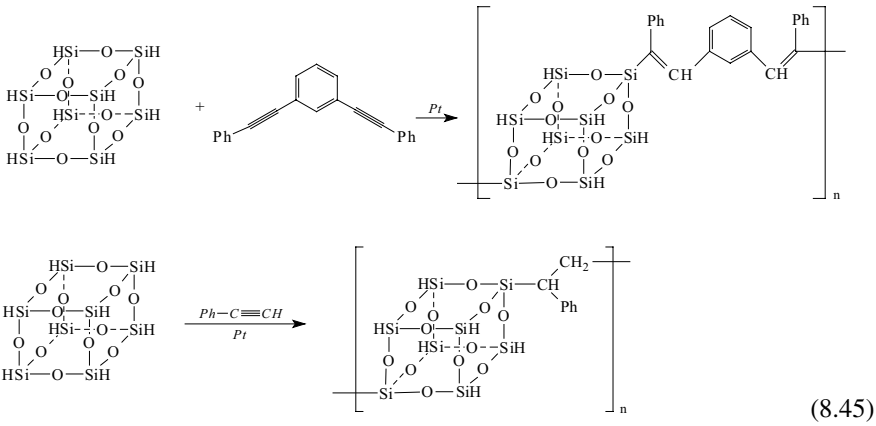


(8.44)

This is the first example of a dendrimer in which both the core and branched moieties are composed of polyhedral oligosilsesquioxanes.

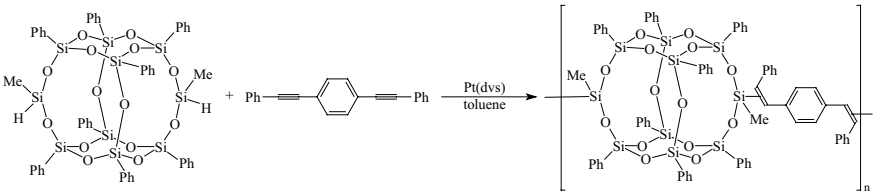
In most cases the materials made by employing silsesquioxanes as the building blocks have afforded gels or insoluble network materials, however, a few examples

of soluble resins have also been reported [117–119]. For example, such resins were obtained by hydrosilylation of divinyl (or dialkynyl) species with octahydrido POSS in the presence of Karstedt's catalyst:



(8.45)

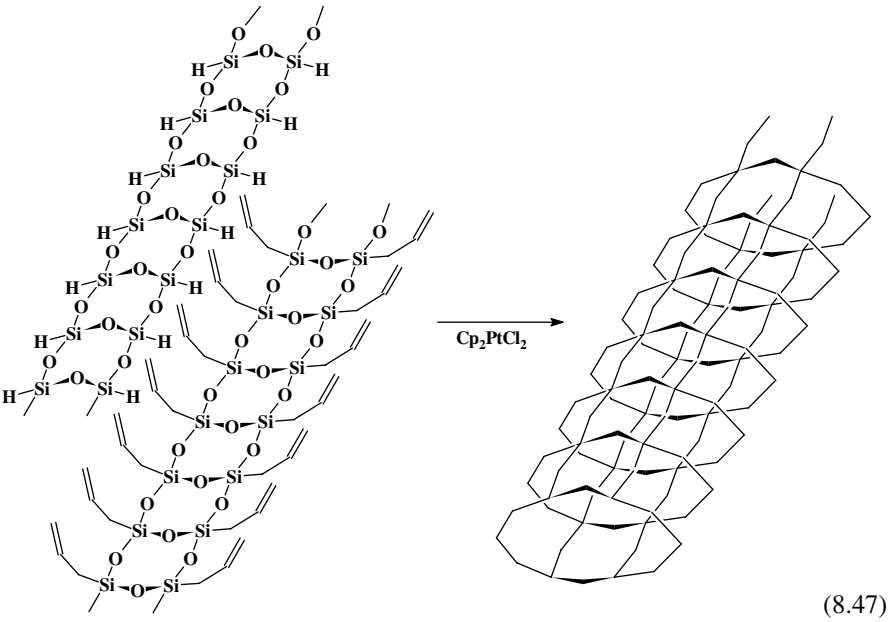
The use of a novel POSS, double-decker-shaped silsesquioxane, containing two reactive hydrosilyl group, in the hydrosilylation reaction with diynes, catalysed by Karstedt's catalyst, leads to a linear, soluble hybrid polymer [120]:



(8.46)

Ladder silsesquioxane oligomer and policarbosilane were used as the components of the silicon based interpenetrating networks, IPN. Polycarbosilane was synthesised by hydrosilylation polymerisation of bifunctional Si-H and Si-vinyl monomers, catalysed by Karstedt's catalyst [121, 122].

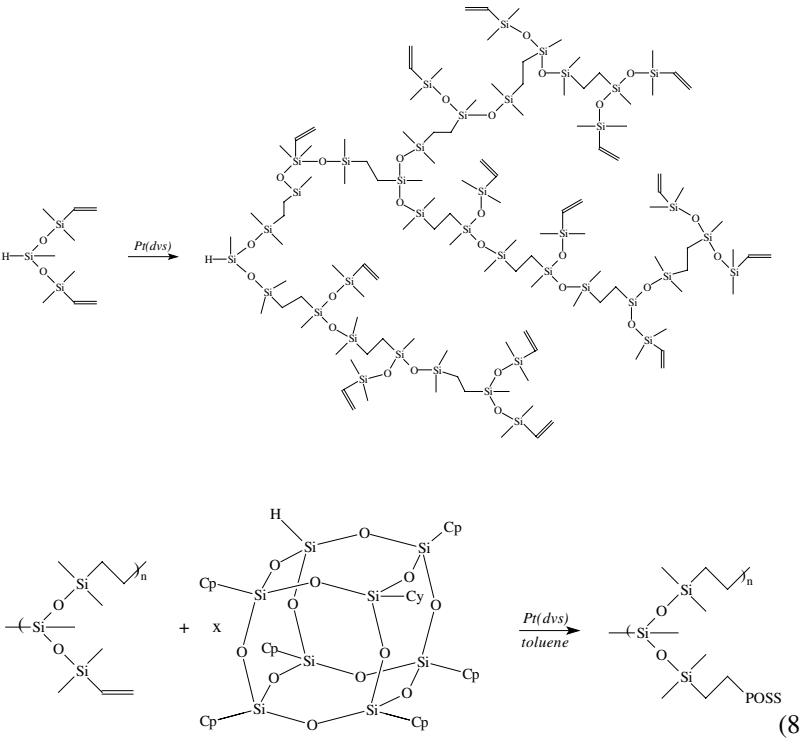
The reaction between hydrido- and allyl functional ladder-like silsesquioxanes has led to obtaining very interesting polysiloxanes containing nanoscale tubular structure [123], according to (Eq. 8.47):



(8.47)

Considerable effort was made to use the POSS cubes as building blocks, in order to prepare organic-inorganic nanocomposite materials and precursors [124, 125]. Homopolymerisation and copolymerisation with organic monomers lead to "pendant" and "triblock" architectures, respectively [126]. Incorporating such POSS cages into polymeric materials has already provided strengthening of the useful properties, such as increased glass-transition temperatures, decompositions temperatures, and mechanical strength. For example, monovinyl functional silsesquioxane, synthesised by hydrosilylation starting from T_8H, was used as a comonomer in the synthesis of copolymers with ethene and propene. This POSS incorporation was accounted for an improved thermostability with respect to polyethylene [127].

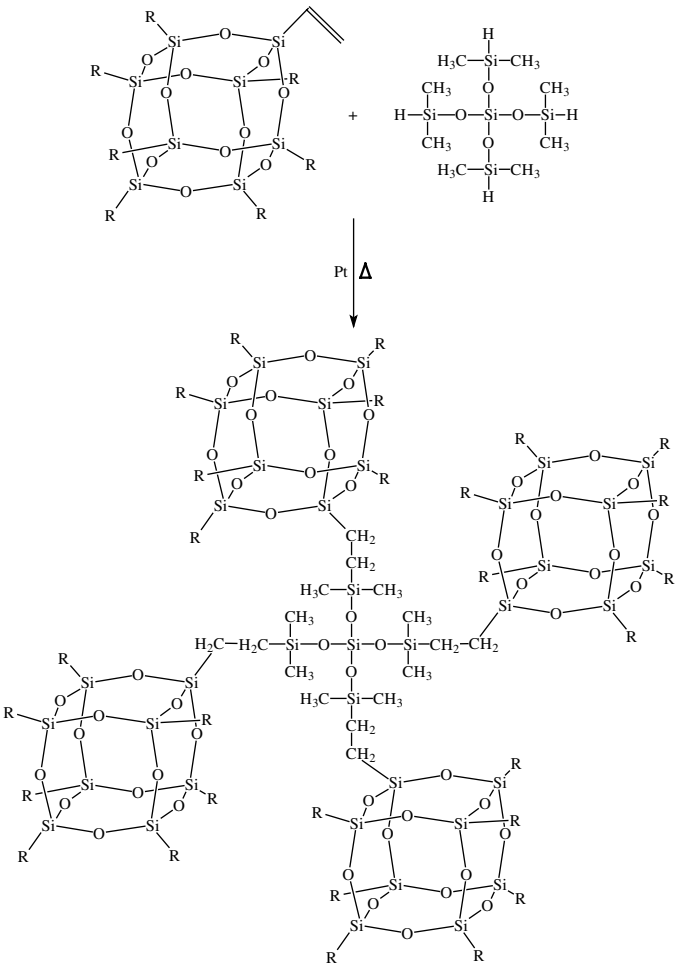
Monosubstituted POSS are also incorporated into various elastomers, like linear polysiloxanes or hyperbranched polysiloxanes. For example, hyperbranched polysiloxanes with POSS groups at the terminal position and controllable degree of substitution, are synthesised via hydrosilylation catalysed by Karstedt's catalyst [128], according to (Eq. 8.48):



(8.48)

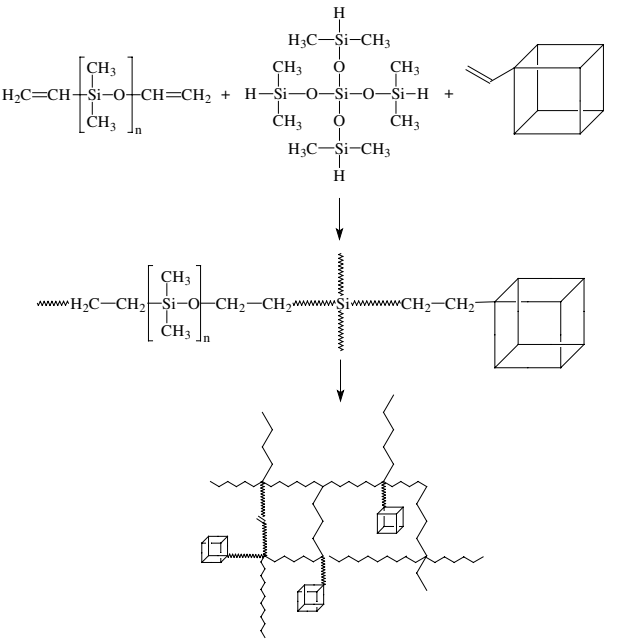
The POSS groups crystallise, and the degree of crystallinity is proportional to the content of the POSS groups.

Monovinyl substituted POSS was used in preparation of filler particles of controlled structure (of sises between those of the POSS cages themselves and much larger silica particles) which are typically used for reinforcing siloxane elastomers. The hydrosilylation of four molecules of vinyl POSS by tetrakis(dimethylsiloxy)-silane, catalysed by $[(C_2H_5)_2S]_2PtCl_2$ [129] leads to some kind of filler:



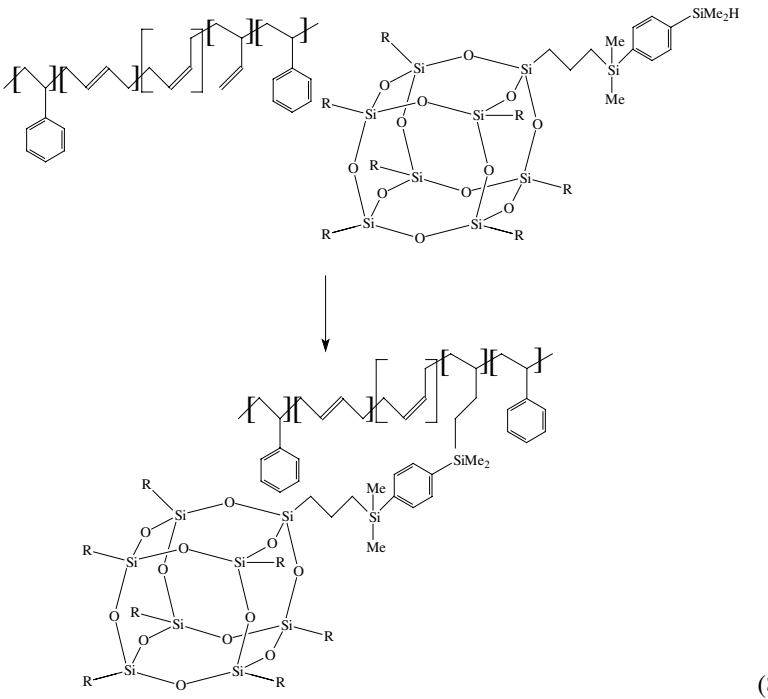
(8.49)

Blending these fillers into silanol-terminated poly(dimethylsiloxane) had little effect on mechanical properties, but bonding them to divinyl polimethylsiloxane, via hydrosilylation (according to Eq. 8.50), provided a considerable reinforcement:



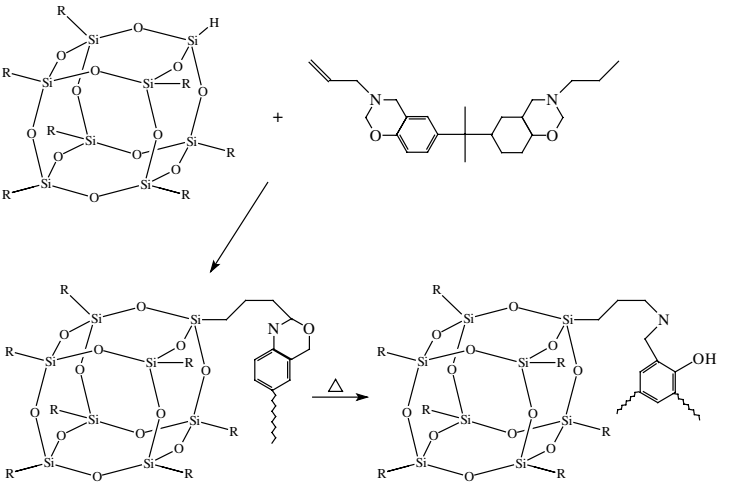
(8.50)

Monoallyl POSS was also grafted with styrene-butadiene-styrene triblock copolymer, which, as a result, influenced rheological and morphological properties of this copolymer [130]. In the first step, allyl POSS was hydrosilylated by bis(dimethylsilyl)benzene, in the presence of Karstedt's catalyst, and then the product was grafted with triblock copolymers via hydrosilylation:



(8.51)

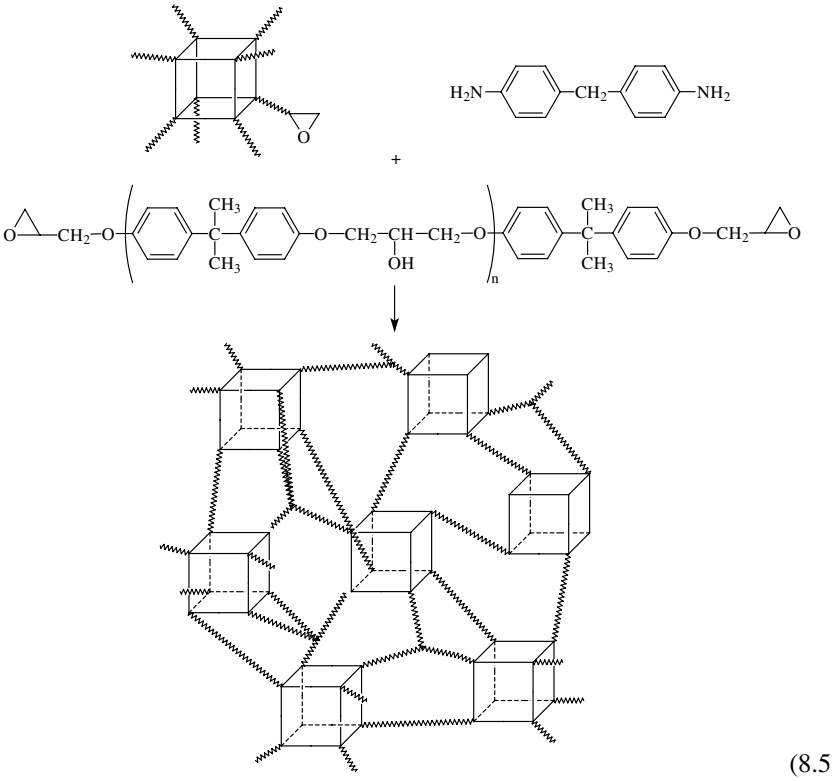
Another example of polymer reinforcing is the incorporation of monohydrido POSS into the vinyl-terminated benzoxazine monomer, which is then subjected to the ring-opening polymerisation [131]. Thermally induced reaction of the terminal vinyl group leads to hydrosilylation and chain extension (one vinyl group is able to couple with Si-H group of the POSS and then the remaining vinyl group can be polymerised) which contributes to obtaining high performance nanocomposite materials:



(8.52)

As mentioned above, among all the derivatives of silsesquioxanes the most widely spread and important for applied purposes are octafunctional silsesquioxanes, particularly spherosilicates.

Epoxy functional POSS were employed to prepare the POSS containing nanocomposites, obtained via the in situ curing reaction between diglycidyl ether of bisphenol A and diamine (e.g. 4,4-diaminodiphenylmethane) in the presence of epoxyfunctional POSS [132], according to (Eq. 8.53):



(8.53)

Methacryloxyfunctional POSS are suitable thermal and UV curable precursors to organic/inorganic nanocomposites [133, 134].

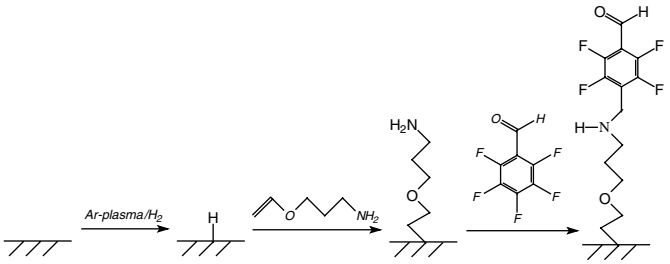
Some other functionalised silsesquioxanes containing isocyanate [135], chloroethylalkyl ether [136] or benzoxazine [137] were used for the formation of an organic-inorganic hybrid polyurethane, as a photoresistant material, and as a curing agent of polybenzoxazine networks.

8.4 Surface Functionalisation

8.4.1 Material Surface Modification

The surface modification of polymers as well as other materials, improves their hydrophilicity or hydrophobicity and other surface properties. Many modification

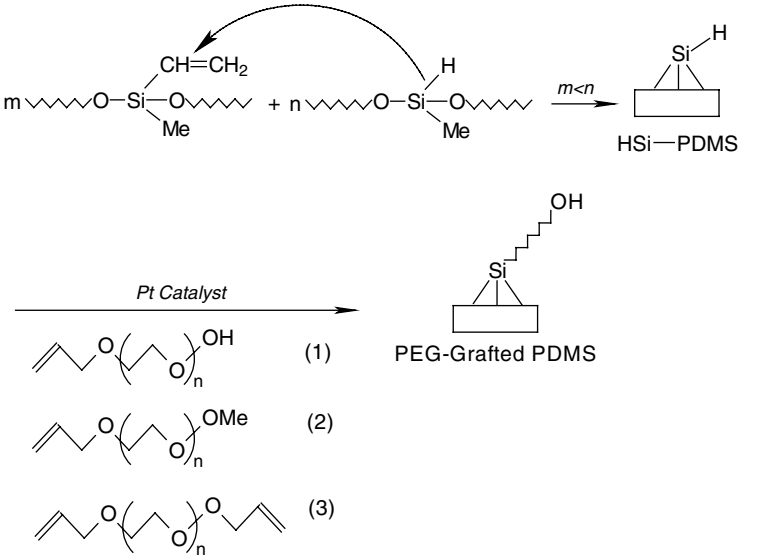
strategies have been reported and one of them is based on the hydrosilylation processes [138–142]. However, the presence of Si-H group at the outermost surface layer is necessary. The treatment of silicone elastomer with an argon plasma led to formation of the Si-H group [143]. Such modified surfaces can be further functionalised by hydrosilylation, e.g. with allyl tetrafluoroethyl ether [144]. A similar method was used for hydrosilylation grafting of aminopropyl vinyl ether to Si-H groups formed by argon plasma treatment of polysiloxane and subsequent derivatisation using pentafluorobenzaldehyde [145], according to (Eq. 8.54):



(8.54)

The replacement of pentafluorobenzaldehyde by a heparin derivative led to the formation of silicone elastomer with covalently bonded heparin which was expected to be hydrolytically stable.

Another strategy for surface activation includes vulcanising an off-ratio mixture to obtain the hydrosilane rich polydimethylsiloxane:

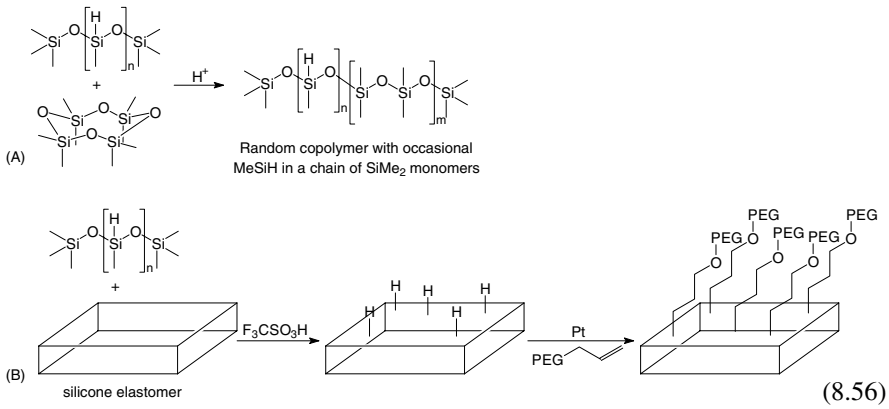


(8.55)

The excess Si-H species on the surface are employed to use the hydrosilylation reaction with allyl poly(ethylene glycol) species to form poly(ethylene glycol)

monolayer, with permanent hydrophilicity and non-fouling surface towards proteins and bacteria [146, 147].

Similarly, poly(ethylene glycol) was grafted to the surface which was functionalised with Si-H group by acid-catalysed equilibration of silicone elastomer in the presence of $(MeHSiO)_n$, [148]:

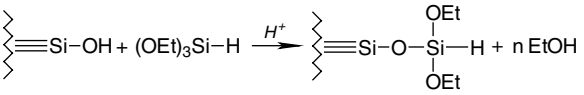


(8.56)

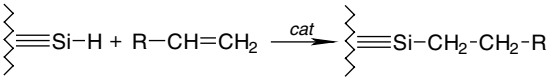
Reductions in protein adsorption of as much as 90% were noted on these surfaces.

Poly(ethylene glycol) chains were incorporated into silicones via siloxane tethers, having the general formula α-$(EtO)_3Si(CH_2)_2$-oligodimethylsiloxane-block-poly(ethylene glycol). Such macromonomers were synthesised by regioselective hydrosilylation catalysed by $[RhCl(PPh_3)_3]$ and, in the next step, their sol-gel cross-linking [149].

The monolayer of hydride on the surface can be obtained by silanisation with the use of trialkoxysilane. Such a surface is modified by hydrosilylation with alkenes producing hydrolytically stable stationary phases [150–152]:



(8.57)



(8.58)

Hydrosilylation of alkynes has also been introduced as a method of bonding organic moieties to hydride surface [153, 154]. Other examples of the reaction systems of hydridosilica-monomer were studied as a catalytic hydrosilylation of styrene [155], acrylic acid [156], divinyltetramethyldisiloxane and 2-hydroxyethyl methacrylate in the presence of Speier catalyst [157–159] and some reactive

complexes of olefins with metal ions [160]. The combined hydrosilylation and sol-gel technology allows the anchorage of many functional olefins on silica, including optically active and complexing compounds [161]. A very similar strategy was used for synthesis of fullerene containing silica glasses and polysiloxanes which have been prepared by the sol-gel of alkoxysilanes with C_{60}. Triethoxysilylated C_{60} was synthesised by the hydrosilylation of fullerene with triethoxysilane in the presence of H_2PtCl_6 [162, 163]. Fullerene has also been hydrosilylated by poly(methylhydridomethyloctylsiloxane), producing a soluble, oxidation resistant fullerene-siloxane copolymer [164]

8.4.2 Silicon Surface Modification

Relatively young (aprox. 10–12 years old) but very exciting branch of hydrosilylation chemistry is the formation of robust, Si—C bonded organic monolayers at hydrogen terminated silicon surfaces. These monolayers have become useful for a range of applications because:

the chemistry is compatible with many functional groups
the monolayers can be well-ordered
they provide access to an alternative substrate

They have been used as a platform for several immobilisation chemistries, e.g., DNA [165,166], further organic reactions [167], polymer grafting [168], solid-phase oligosynthesis [169, 170] and they have also used to cap silicon nanoparticles [170, 171].

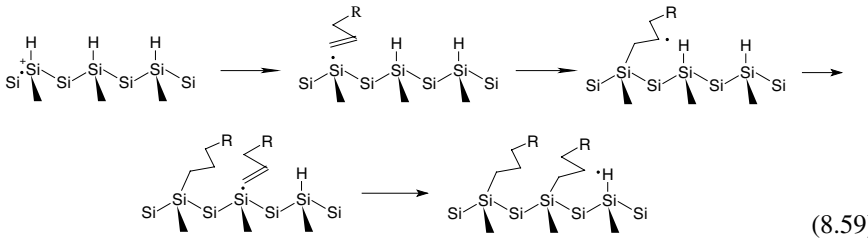
Grafting of organic layers onto silicon surface may be carried out using:

organometallic species (Grignard or lithiated compounds) onto the hydrogen or halogen terminated surfaces [172];
cathodic or anodic electrografting onto Si-H-terminated surface [173];
hydrosilylation.

The formation of Si—C bonded monolayers on silicon can proceed by either thermally [174–183], electrochemically [184, 185], or photochemically induced [186–193], exciton-mediated [194, 195], microwave assisted [196], triphenylcarbenium cation mediated [197], Lewis acid [198–203] or transition metal complexes [202, 204, 205] mediated hydrosilylation reactions.

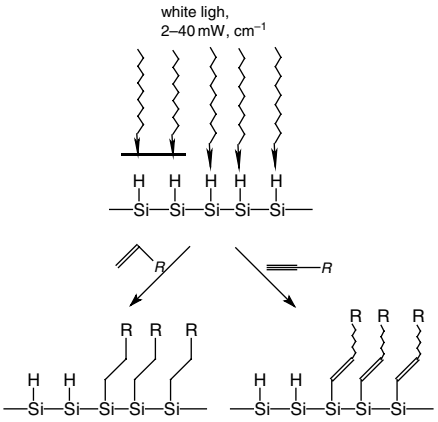
The same class of hydrosilylation reactions allows formation of organic monolayers (from 1-alkenes, 1-alkynes or functional olefins) on porous silicon [174, 206] and single-crystal wafers [170, 171, 207, 208].

Mechanistic examinations and theoretical investigations have shown that the formation of monolayers at both porous silicon surfaces and single-crystals surfaces occurs via the same radical chain process [175, 176, 209]



(8.59)

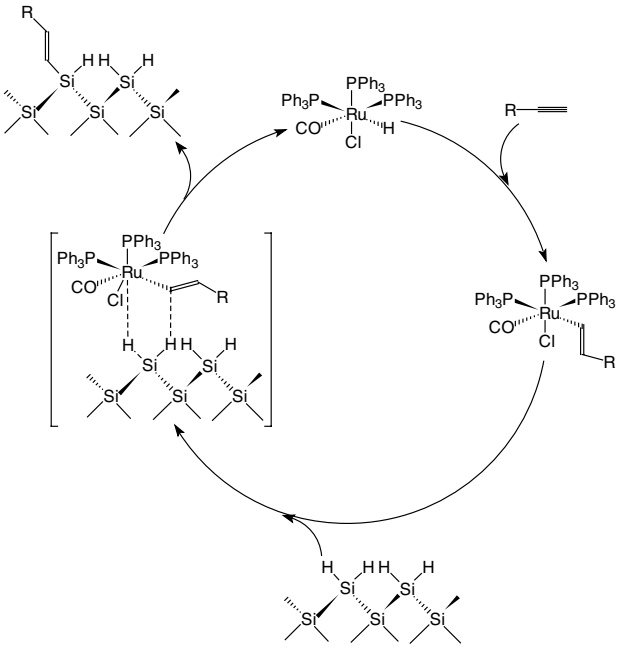
The radical initiation step occurs via abstraction of a hydrogen atom, e.g. by a trace of oxygen, or another reaction involving the majority of carriers (holes) followed by the loss of a proton. Silyl radical attacks the alkene to form both the Si—C bond and a radical center on the β-carbon atom. In the next step, this carbon radical abstracts a hydrogen atom from a neighbouring Si–H bond to propagate the chain. This example describes the thermally induced hydrosilylation, however, the same mechanism has been proposed for UV-induced hydrosilylation, which involves homolysis of the surface Si—H bond and the formation of a silicon radical after light illumination (wavelengths 350 nm or shorter) [186, 209]. The white light-promoted hydrosilylation has been reported, however, it is only effective when using porous silicon that exhibits strong, visible photoluminescence [194, 195]. An unbound exciton produced by the light absorption leads to a surface-localised supra-band gap positive charge, which can then interact with an alkene and form a silylated β-carbocation upon Si—C bond formation. The next step is the same as in the above mechanism. It is an elegant and the most economical method of light mediated hydrosilylation of alkenes and alkynes on photoluminescent porous silicon. According to Eq. 8.60, shown below through simple masking procedures regions of different chemical functionalities can be prepared



(8.60)

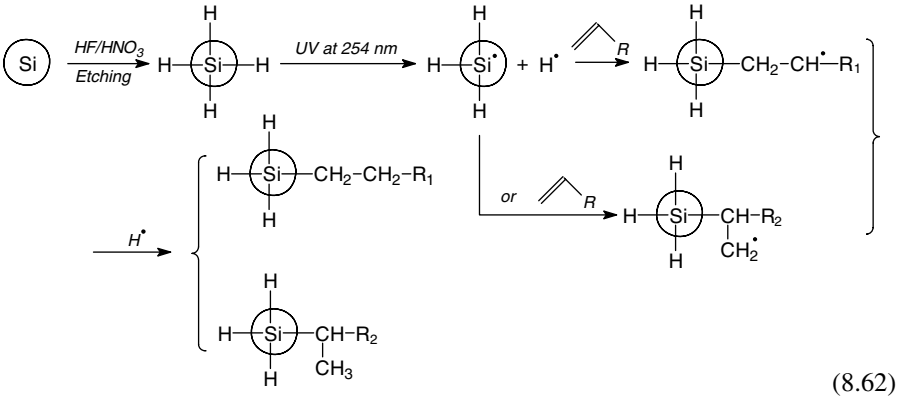
Most of the catalytic hydrosilylation reactions on silicon surface, occur in the presence of Lewis acid, mainly $EtAlCl_2$ [198–203]. The mechanism of this process is very similar to that proposed for the thermally or photo-induced reaction,

however, in this case H atom shifts from the Si to the C atom of a Lewis acid-alkene intermediate [210]. Hydrosilylation of alkynes catalysed by $EtAlCl_2$ is supposed to yield cis alkenes. On the contrary, the transition metal- catalysed hydrosilylation of terminal alkynes is an efficient way to also synthesise trans alkenylsilanes. Very recently, the grafting of aromatic alkynes onto a silicon single-crystal surface with trans configuration control has been reported [204]. Such a reaction was catalysed by $[RuHCl(CO)(PPh_3)_3]$. The mechanism proposed explains the formation of trans alkene covalently bonded to the silicon surface:



(8.61)

Photoinitiated hydrosilylation has also been used for high-coverage grafting of organic molecules onto photoluminescent silicon nanoparticles [193], according to (Eq. 8.62):



(8.62)

In the first step, H-terminated surface on silicon nanoparticles with bright photoluminescence ranging was produced using an etching procedure. Then, photoinitiated hydrosilylation was carried out with the use of various olefins, yielding α- and β-adduct. The resulting, covalently bonded monolayers were able to protect the particles from chemical attack and also allowed formation of stable dispersion of nanoparticles in a variety of solvents.

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Part III
Chemo- and Enantio-Selective Hydrosilylation of Unsaturated Carbon–Heteroatom Bonds

Chapter 9
Hydrosilylation of Unsaturated Carbon—Heteroatom Bonds

Abstract Catalytic hydrosilylation is one of the most important and convenient methods of reduction of C=O and C=N bonds. Hydrosilylation of ketones (imines) produces in single step silyl ethers (silylamines) which can be easily transformed into alcohols (amines) via an additional hydrolysis step. In this chapter, the hydrosilylation of carbonyl compounds, imines and nitriles with emphasis put on the synthetic, catalytic and mechanistic aspects is reviewed. Efficient catalysts including mainly transition metal complexes but also main group metal complexes, nucleophiles or electrophiles, free-radical initiating systems as well as metals (or supported metals) are described. In a separate section, the progress in hydrosilylation of CO_2 is summarised. Finally, the addition of Si—H to other unsaturated bonds such as C=S, S=O and N=N is shortly described.

Catalytic reduction of C=O and C=N bonds is one of the most fundamental transformations in organic chemistry. It can be realised with the use of a number of reducing agents with dihydrogen being the most frequently used. The discovery by Ojima of the high catalytic activity of Wilkinson's catalyst [$RhCl(PPh_3)_3$] in hydrosilylation of carbonyl compounds [1, 2] instigated great development in hydrosilylation of C=O and C=N bonds, which make catalytic hydrosilylation one of the most important and convenient reduction method to obtain secondary alcohols and amines.

Formally, hydrosilylation of ketones produces (in single step) silyl ethers, which are protected forms of alcohol frequently used in organic synthesis. Alcohol synthesis requires an additional hydrolysis (deprotection) step (Scheme 9.1). Hydrolysis is realized by one of the standard techniques depending on the specificity of the reaction system. Analogously, hydrosilylation of imine leads to silylamine formation which is transformed to amine via the hydrolysis step. Hydrosilylation with subsequent hydrolysis lead to reduction of carbonyl (imine) fragment of the molecule so are often referred to as the reduction by silanes. Within the reactants containing C=O or C=N bond, a specific group is formed by α,β-unsaturated derivatives. For these compounds, both 1,2- and 1,4-additions are possible. The regioselectivity of the hydrosilylation of α,β-unsaturated systems depends on the type of the catalysts and the silane. In literature, the sequence of 1,4-hydrosilylation / hydrolysis is often referred to as conjugate reduction.

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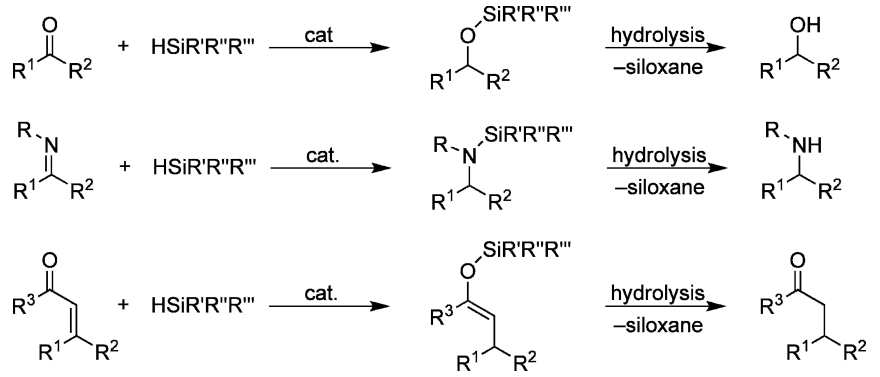


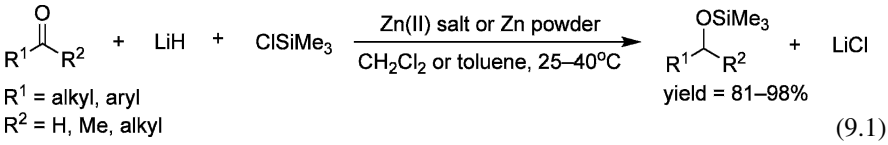
Scheme 9.1 (**a**) Hydrosilylation of ketones and subsequent hydrolysis (ketone reduction) (**b**) hydrosilylation of imines and subsequent hydrolysis (imine reduction) (**c**) 1,4-hydrosilylation of α,β-unsaturated enones and subsequent hydrolysis (conjugate reduction)

In this chapter progress of hydrosilylation of carbonyl compounds, imines, nitriles and a range of other compounds containing unsaturated carbon-heteroatom or heteroatom-heteroatom bond achieved since 1990 has been reviewed. The topic was described in a number of general review articles [3–14].

9.1 Hydrosilylation of Carbonyl Compounds

9.1.1 Late Transition Metal Complexes as Catalysts

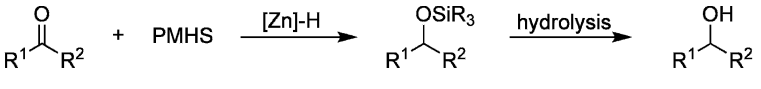
The hydrosilylation of carbonyl compound in the presence of zinc based catalytic system ($ZnCl_2$/NaH/*tert*-pentanol) was first reported by Caubere in 1982 [15]. Commercially available lithium hydride in the presence of equimolar amount of $ClSiMe_3$ undergoes the effective Zn(II) salts or zinc powder catalysed reaction with aromatic and aliphatic ketones as well as non-enolizable aldehydes to form the corresponding silyl ethers (Eq. 9.1) in 81–98% yield under mild reaction conditions [16]. The procedure offers a convenient method for reduction of carbonyl derivatives.



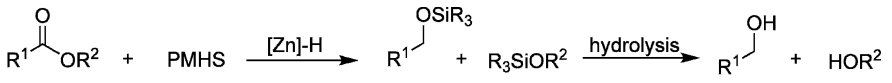
(9.1)

In contrast to the remarkable catalytic effects of Zn salts, the other metal salts such as $MgCl_2$, $BaCl_2$, $CeCl_3$, $TiCl_4$, $ZrCl_4$, WCl_6, $FeCl_2$, $FeCl_3$, $NiCl_2$, CuCl, $CdCl_2$, $AlCl_3$, $GaCl_3$, $InCl_3$, $SnCl_2$ and $SnCl_4$ were found inactive [16]. The efficient and selective hydrosilylation of aldehydes, ketones and esters to the corresponding alcohols by PMHS (polymethylhydrosiloxane) was reported to proceed in the presence of zinc hydrides, best generated by the reaction of soluble zinc carboxylates

with a hydride reducing agent such as sodium borohydride (Eqs. 9.2 and 9.3) [17].

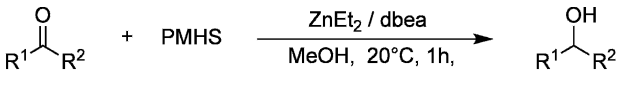


(9.2)



(9.3)

This catalytic system generally does not disproportionate PMHS. Ligated zinc hydride complexes such as $[\{ZnH(Me)NCH_2CH_2NMe_2\}_2]$ and $[(PhZnH)_2(TMEDA)]$ were found active in hydrosilylation but less effective than hydride species generated *in situ*. The protocol enables a selective reduction of aldehydes, ketones and esters. The α,β-unsaturated enones undergo selective 1,2-hydrosilylation. The hydrosilylation of chiral reagents does not change the enantiopurity. The mechanistic pathway suggested assumed the active role of soluble zinc hydride complexes in the catalytic cycle. The zinc catalysed reduction procedure is simple, highly selective for a large spectrum of carbonyl substrates, convenient, inexpensive and safe (when compared to the methods using hazardous $LiAlH_4$ reagents) [17]. However, the reaction cannot be operated in protic solvent as they are silylated by PMHS in the presence of zinc hydrides. The improved one step procedure enables an efficient chemoselective reduction of ketones with PMHS in the presence of zinc diamine catalyst – $ZnEt_2$ / *N*,*N*′-dibenzylethylenediamine (dbea) (1:1) to give the corresponding alcohols (Eq. 9.4) [18]. The protocol enables the reaction to be performed in methanol, which permits avoidance of the hydrolysis step. Molecular silanes such as H_3SiPh, H_2SiPh_2, H_2SiEt_2 can also be used but are not as convenient as PMHS.



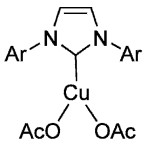
(9.4)

Hexameric $[\{CuH(PPh_3)\}_6]$ referred to as Stryker's reagent was demonstrated to be excellent for effecting stoichiometric conjugate reductions of α,β-unsaturated carbonyl compounds [19–22]. Molecular hydrogen, Bu_3SnH and various silanes can serve as stoichiometric sources of hydride, thereby allowing Stryker's reagent to be used catalytically. Stoichiometric conjugate reduction of α,β-unsaturated carbonyl compounds by copper hydride complexes obtained in the reaction of Cu(I) salt with silanes, was reported by Hosomi [23] and Mori [24,25]. Mori indicated the possibility of substoichiometric use of copper for the reduction of α,β-unsaturated ketones

with silanes [24]. Efficient 1,4-hydrosilylation of α,β-unsaturated ketones, aldehyde and ester with phenylsilane in the presence of catalytic amounts of Stryker's reagent was reported by Lipshutz [26]. Treatment of enone (or enal) with 1.5 eq. of H_3SiPh in the presence of 5 mol% (down to 0.5 mol% for higher substrate concentration) of $[\{CuH(PPh_3)\}_6]$ gave high to quantitative yields of conjugate reduction products.

N-heterocyclic carbene (NHC) copper(II) complex $[(NHC)Cu(OAc)_2]$ (Fig. 9.1) efficiently catalyses the 1,4-hydrosilylation of substituted α,β-unsaturated cyclohexenones with TMDS [27]. Two series of $[Cu(NHC)_2]X$ complexes ($X=PF_6^-$ or BF_4^-) (Fig. 9.2) were synthesised and tested in the hydrosilylation of ketones. Both the ligand and the counterion were found to affect the catalytic performance. When compared with the [CuCl(NHC)] analogues, the cationic species are more efficient under similar reaction conditions. The ^1H NMR spectroscopic studies showed the activation of $[Cu(NHC)_2]X$ complexes by NaO(*t*-Bu) to form neutral [Cu(NHC)(O-*t*-Bu)], which is a direct precursor of an NHC ligated copper hydride – the real catalyst [28].

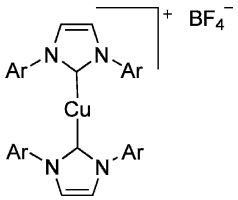
Fig. 9.1



Ar = 2,6-C_6H_3(*i*-Pr)$_2$

[(IPr)Cu(OAc)$_2$]

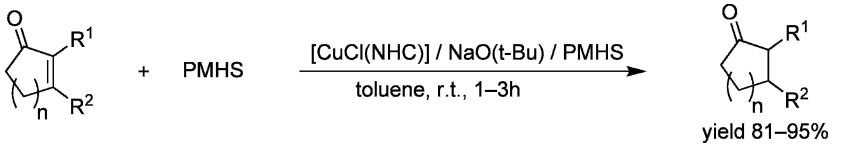
Fig. 9.2



Ar = 2,6-C_6H_3(*i*-Pr)$_2$

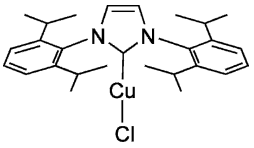
[Cu(IPr)$_2$]BF_4

N-heterocyclic carbene copper chloride [(NHC)CuCl] (Fig. 9.3) was used as precatalyst in the conjugate reduction of α,β-unsaturated carbonyl compounds (Eqs. 9.5 and 9.6) [29].

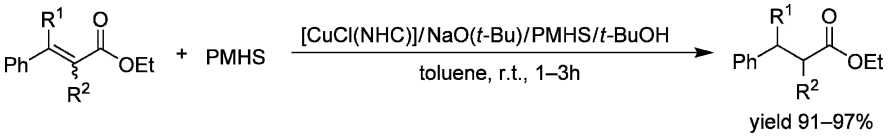


(9.5)

Fig. 9.3



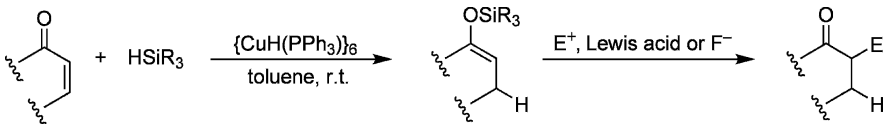
[(IPr)CuCl]



(9.6)

Cyclic substituted pentenones and hexenone were reduced with 81–95% yield. Addition of an excess of *tert*-butanol allows efficient 1,4-hydrosilylation of linear esters. (The effect of alcohol addition on copper-catalysed conjugate reduction of α,β-unsaturated lactones, lactams, and esters was reported by Buchwald [30]). Generation of active copper hydride complex was proposed to proceed via a combination of catalytic amounts of [(NHC)CuCl], NaO(*t*-Bu) and PMHS. Convenient, *in situ* generation of [(NHC)CuH] from commercially available 1,3-bis(2,6-di-*iso*propylphenyl)imidazolium salt, $CuCl_2 \cdot 2H_2O$, NaO(*t*-Bu), and PMHS was described.

A number of tandem protocols have been devised, on the basis of the intermediacy of enolate derivative. These protocols include conjugate reduction/intramolecular aldol cyclisation sequence [e.g. 31], tandem 1,4-hydrosilylation combined with a subsequent Lewis catalysed aldol reaction with aldehydes [32], 1,4-hydrosilylation/fluorine ion catalysed alkylation with organyl halides (Scheme 9.2) [32]. Copper mediated reductive aldol reactions with the use of silanes were shortly summarised [33].

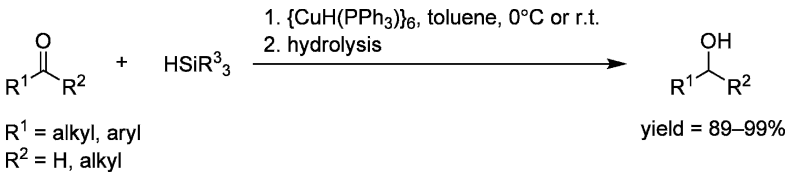


Scheme 9.2 Tandem protocol based on intermediacy of enolate derivative

Application of copper, silver and gold complexes in hydrosilylation has been recently reviewed [9]. The first copper(I)-catalysed reduction of acetophenone using diphenylsilane as the reducing agent was described by Brunner [34].

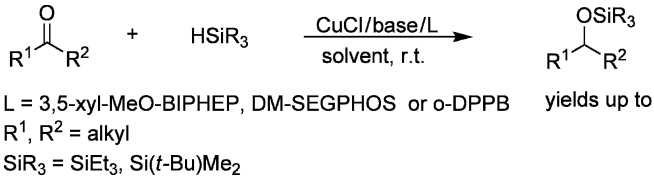
The potential of copper hydride to reduce aldehydes and ketones was mainly used for 1,4-addition processes (conjugate reduction). Only recently, the 1,2-addition has also become of synthetic value. Lipshutz demonstrated the catalytic activity

of Stryker's reagent in the hydrosilylation of aliphatic and aromatic aldehydes and ketones with different silanes to get silyl ethers or (after subsequent hydrolysis step) the corresponding alcohols with high yields ranging from 89 to 99% (Eq. 9.7) [35]. The protocol enabled selective reduction of aldehydes in the presence of ketones and selective reduction C=O double bonds in the presence of non-conjugated C=C bond. A number of silanes were found active in the reaction ($HSiMe_2Ph$, $HSiMePh_2$, $HSi(t\text{-Bu})Ph_2$, H_3SiPh, PMHS). Dramatic acceleration of the reaction rates was observed in the presence of bidentate phosphine ligands, such as DPPF [bis(diphenylphosphino)ferrocene] or racemic BINAP (for (*S*)-isomer see Chapter 10, Fig. 10.14) in amounts equal to that of copper hydride.



(9.7)

Lipshutz reported also a simple protocol for the conversion of dialkyl ketones to the corresponding silyl ethers in the presence of *in situ* generated copper hydride catalyst (Eq. 9.8) [36].



(9.8)

High efficiency was achieved by variations in the reagents and stoichiometries used to generate CuH *in situ*, as well as the nature of the ligands present. Within the mono- and diphosphine ligands screened the best convertions at S/L ratio equal to 2000 were obtained for 3,5-xyl-MeO-BIPHEP (see Chapter 10, Fig. 10.18), DM-SEGPHOS (Fig. 9.4) or o-DPPB (Fig. 9.5).

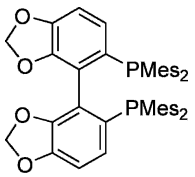
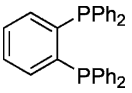


Fig. 9.4 DM-SEGPHOS

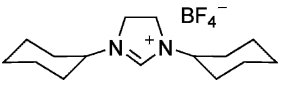
Fig. 9.5



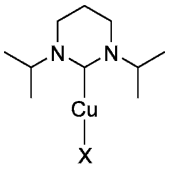
o–DPPB

Aryl alkyl, dialkyl and cyclic ketones undergo hydrosilylation with $HSiEt_3$ in the presence of *N*-heterocyclic carbene copper complexes [(NHC)CuCl] (e.g. Fig. 9.3) either generated in situ by treatment of CuCl with NaO(*t*-Bu) and respective imidazolium salt or pre-synthesised [37]. The corresponding silyl ethers were obtained with high yield (up to 99%). The reaction allows efficient conversion of hindered and functionalised ketones. Copper(I) chloride combined with the synthesised NHC precursors, especially ICy·BF_4 (Fig. 9.6), exhibit the ability to catalyse the hydrosilylation of a functionalised alkyl, cyclic, bicyclic, aromatic and heteroaromatic ketones with $HSiEt_3$ to give corresponding silyl ethers with isolated yield up to 99% [38]. Air stable and well-defined carbene–copper(II) complex (Fig. 9.1) was found an efficient precatalyst for the 1,2-reduction of carbonyl compounds with PMHS [27]. Cationic air- and moisture-stable copper complexes bearing two *N*-heterocyclic carbene ligands are highly active towards the hydrosilylation of ketones with various steric congestion, aldehydes, and esters with $HSiEt_3$ [39]. When compared with [(IPr)CuCl], the precatalyst [$(IPr)_2Cu$][BF_4] (Fig. 9.2) allows the hydrosilylation reaction to proceed under smoother reaction conditions and using a lower hydrosilane loading.

Fig. 9.6



Buchmeiser reported copper(I) NHC complexes (Figs. 9.7 and 9.8) highly active in the hydrosilylation of simple ketones or aldehydes with $HSiEt_3$ [40]. Excellent reactivity was observed, giving raise to turnover numbers (TONs) of up to 100,000. The immobilised version of monocarbene complex (Fig. 9.9) was synthesised and proved active.



a X = Cl
b X = Br

Fig. 9.7

A three-component reaction of electrophilic double bonds and aldehydes with dimethylethoxysilane (reductive aldol reaction) was catalysed by a family of copper *N*-heterocyclic carbene complexes [(NHC)Cu(dbm)] (dbm=dibenzoylmethanoate) (Fig. 9.10) (Eq. 9.9) [41]. The corresponding silyl ethers (mixtures of *syn* and *anti*

Fig. 9.8

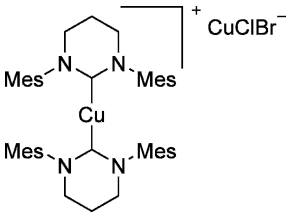


Fig. 9.9

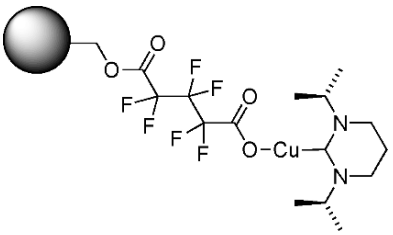
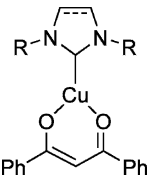
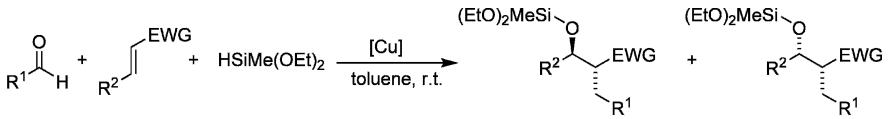


Fig. 9.10



isomers) were formed with moderate to high yield and diastereoselectivity (up to *syn* / *anti* = 74 / 26).



[Cu] see Fig. 9.10
R^1 = alkyl, aryl, R^2 = H, Me
EWG = COOMe, COMe, CN

total yield = 70–80%
syn/*anti* = 51/43–71/29

(9.9)

The ability of free AgX to mediate the hydrosilylation of acetophenone was indicated by Nishiyama [42]. In 2006, Stradiotto reported the first application of silver species as catalysts for the hydrosilylation of unsaturated organic substrates [43]. Silver triflate, used either alone or in the presence of an appropriate phosphine or NHC ligand, was shown to catalyse the chemoselective hydrosilylation of aromatic and aliphatic aldehydes to yield silyl ethers with the yield up to 98%. The 1,2-addition was observed in the Et_3P–AgOTf catalysed reaction of α,β-unsaturated aldehyde. The first examples of the hydrosilylation of aldehydes using catalytic amounts of a gold complex were reported in 2000 by Hosomi [44]. In the presence of an excess of PBu_3, [AuCl(PPh_3)] was found active in hydrosilylation of benzaldehyde and some others aryl and alkyl aldehydes (but not ketones) to give, after

hydrolysis, the corresponding alcohols with the yields up to 94%. Cinnamaldehyde was converted to the 1,2-addition product with high selectivity. Tetrahydrotiophene (tht) complex [AuCl(tht)] stabilised by PBu_3 exhibits similar activity [45]. In the presence of an excess of PBu_3, [$AuCl(Ph_3P)$] enabled the hydrosilylation of benzaldehyde with $HSiMe_2Ph$ to give 99% yield of the corresponding silyl ether. The compound [$AuCl(Me_2S)$] combined with an excess of PEt_3, PBu_3 or P(*t*-Bu)$_3$ remains active at room temperature [46]. Mechanistic examinations revealed that both PBu_3 and the aldehyde play an important role in stabilizing the gold catalyst and/or forming the catalytically active species [33]. Fluorous gold(I) compounds were prepared and used as recoverable catalysts for the hydrosilylation of aldehydes [47]. Pyridine ONN-pincer gold(III) complex (Fig. 9.11) was found to catalyse hydrosilylation of benzaldehyde and benzophenone with H_2SiPh_2 [48]. Gold particles of an average size of 4nm supported on nanoparticulated CeO_2 can selectively catalyse the hydrosilylation of aldehydes, ketones and imines (also olefins and alkynes) owing to the presence of stabilised Au(III) on the surface. This catalyst can be recycled without loss of activity and it is regio- and chemoselective. Well-defined Schiff base Au(III) complexes (e.g. Fig. 9.11) can catalyse the hydrosilylation of carbonyls without the need to introduce any phosphine groups to avoid formation of metallic gold [49].

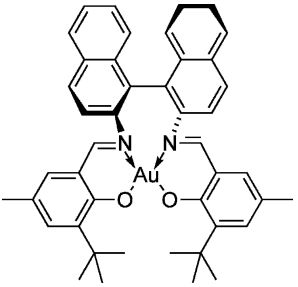
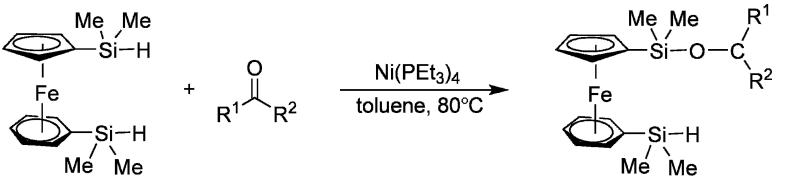


Fig. 9.11

The compound [$Ni(PEt_3)_4$] was reported to catalyse the hydrosilylation of carbonyl compounds with 1,10-bis(dimethylsilyl)ferrocene (Eq. 9.10) [50]. A series of ferrocene-based organosilicon compounds was obtained with low to moderate yields (40–75%). In reaction with isopropylaldehyde both Si—H bonds undergo addition to form bis(isopropoxy)derivative with 60% yield.

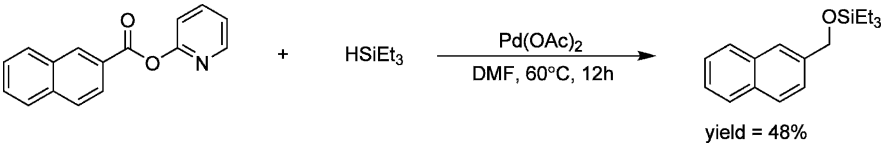


(9.10)

The compound [(Ind)$NiCl(PPh_3)$] in combination with $NaBPh_4$ was found catalytically active in the hydrosilylation of acetophenone and 2-nonanone with phenylsilane giving nearly quantitative conversions [51]. A mechanism involving the active

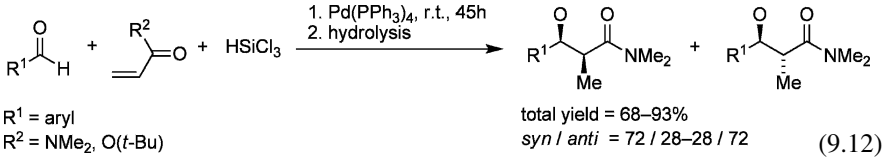
role of Ni-H species originating from the interaction of H_3SiPh and the initially generated Ni cation was proposed.

2-Pyridinyl esters undergo reduction with triethylsilanes in the presence of $Pd(OAc)_2$ / PPh_3 to form respective aldehydes [52]. In the absence of phosphine in the catalytic system overreduction takes place and formation of silyl ether was observed (Eq. 9.11)



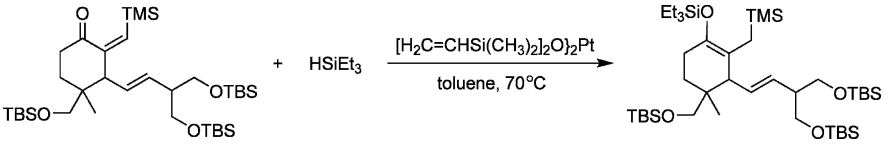
(9.11)

Aryl aldehydes undergo mild aldol reaction with α,β-unsaturated carbonyl compounds and trichlorosilane in the presence of $[Pd(PPh_3)_4]$ (Eq. 9.12) [53].



(9.12)

Platinum complex *cis*-$[PtCl_2(PhCH{=}CH_2)_2]$ combined with pyridine derivatives, PPh_3, $AsPh_3$ or $SbPh_3$ is catalytically active in the reduction of carbonyl functions (acetophenone, benzaldehyde, dialkylketones) with chlodimethylsilane to give the respective silyl ethers with moderate to high yield [54]. In the presence of the platinum Karstedt's catalyst a variety of enones undergo selective 1,4-hydrosilylation with triisopropylsilane or triphenylsilane to give silyl enol ethers in high yields (78–99%) [55]. Platinum catalysed 1,4-hydrosilylation was also used as a step in total synthesis of antiulcerogenic agent (+)-cassiol (Eq. 9.13) [56].

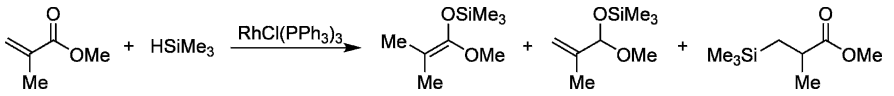


(9.13)

Substituted acetophenones $(4\text{-}C_6H_4X)COCH_3$ (X=H, Me, MeO, F, Cl, NO_2) undergo hydrosilylation with 1,1,3,3-tetramethyldisiloxane in the presence of a different platinum(II) complexes (e.g. *cis*-$[PtCl_2(Et_2SO)_2]$, (−)-*cis*-[$PtCl_2$(Me-*p*-TolSO)(Py)], and *cis*-[$PtCl_2$(EtCN)(dmso)]) [57, 58]. The yields of these reactions strongly depend on the substituent at the phenyl ring and a complete transformation was observed for X=OMe.

Activity of Wilkinson's catalyst [$RhCl(PPh_3)_3$] in hydrosilylation of carbonyl compounds was reported by Ojima already in 1972. Since that time much progress has been made in investigation of hydrosilylation and many active catalytic systems have been described. At present, much effort is directed to the search of new catalytic systems that would ensure the stereo- and in particular enantioselective run of the process. Although reaction has been known for decades, there are only few reports concerning investigation of its mechanism. The commonly accepted mechanism of rhodium catalysed hydrosilylation of ketones, involving oxidative addition of Si—H bond to rhodium(I) complex followed by coordination of ketone, its insertion to Rh—Si bond and reductive elimination of silyl ether has been proposed by Ojima [59].

Early results of the study of rhodium catalysed hydrosilylation of α,β-unsaturated esters indicated the formation of 1,4-hydrosilylation product accompanied by 1,2-hydrosilylation and vinyl addition products (Eq. 9.14) [60]. The improved protocol using hydrated rhodium trichloride as precatalyst and optimised reaction conditions enables the synthesis of dimethylketene trimethylsilyl acetal with 85% yield [61].



(9.14)

Hydrosilylation of *p*-substituted acetophenones $XC_6H_4COCH_3$ (X=H, Me, MeO, HO, F, Cl, NO_2) with 1,1,3,3-tetramethyldisiloxane occurred in the presence of [$Rh(acac)(CO)_2$], [$Rh(Ph_2PNCO)_2(CO)Cl$] or [$RhCl(Ph_3P)_3$]. The reaction leads to the selective formation of monosubstituted products and the conversion depends on the electronic properties of the substituents at phenyl ring [57, 58]. Selectivity of the hydrosilylation of 2,2,4,4-tetramethyl-1,3-cyclobutanedione in the presence of rhodium complexes depends on the silane structure. Dialkylsubstituted silanes and diethylmethylsilane in the presence of [$RhCl(PPh_3)_3$] give selectively (after hydrolysis) 3-hydroxy-2,2,4,4-tetramethylcyclobutanone. On the other hand, the reaction of the dione with amylsilane in the presence of [$RhCl_2(cod)$] / PR_3 leads to formation of diols (mixture of syn and anti isomers) of different composition depending on the phosphine ligand used [62].

Disubstituted silanes are known to undergo selective 1,2-addition to α,β-unsaturated ketones in the presence of rhodium catalyst. Recently, a series of $H_2SiPh(2\text{-}C_6H_4\text{-}R)$ (R=H, CH_2OMe, Me, Et, Pr) and $H_2SiPh(2,4,6\text{-}C_6H_2Me_3)$ were tested in hydrosilylation of cyclohexenone in the presence of the Wilkinson catalyst. It was demonstrated that regioselectivity of an addition strongly depends on nature of substituents at phenyl ring. For R=CH_2OMe a selective 1,4-addition was observed [63]. In the presence of [$\{RhCl(cod)\}_2$] / PR_3 as a catalytic system it was also demonstrated that exclusive 1,2- or 1,4-addition of $H_2SiPh[2\text{-}C_6H_4(CH_2OMe)]$ to cyclohexenone can be achieved by the proper choice of phosphine ligand. Unusual rate enhancement was observed in the [$RhCl(PPh_3)_3$]-catalysed hydrosilylation of

ketones with some bifunctional organosilanes having two Si—H bonds at an appropriate distance [64]. The rate acceleration observed was attributed to the formation of disilametallacyclic intermediates via double oxidative addition of both Si—H bonds to $[RhCl(PPh_3)_3]$. A similar effect was observed also for hydrosilylation of alkenes and alkynes [65]. Bowl-shaped phosphine ligands (Figs. 9.12 and 9.13) markedly accelerated the hydrosilylation of ketones and ketimines catalysed by rhodium monophosphine complexes compared with the effect of conventional phosphine ligands such as PPh_3 and PCy_3 [66, 67]. A series of phosphines have been tested in the hydrosilylation of ketones with $HSiMe_2Ph$ catalysed by a simple system of $[\{RhCl(C_2H_4)_2\}_2]$ / PR_3. Remarkable differences in activity observed between ligands presented in Figs. 9.12 and 9.13 (having comparable basicities and similar values of cone angle) were attributed to the different structural characteristic of the ligands. On the basis of structural comparison carried out using the HF/6-31G(d)-CONFLEX/MM3 calculations, it was proposed that the differences in depths of the bowls formed by the ligands (Figs. 9.12 and 9.13) are responsible for their different catalytic properties.

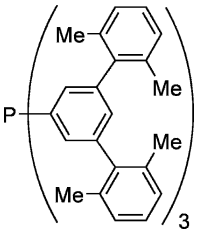
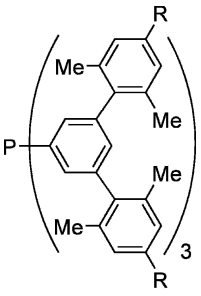


Fig. 9.12



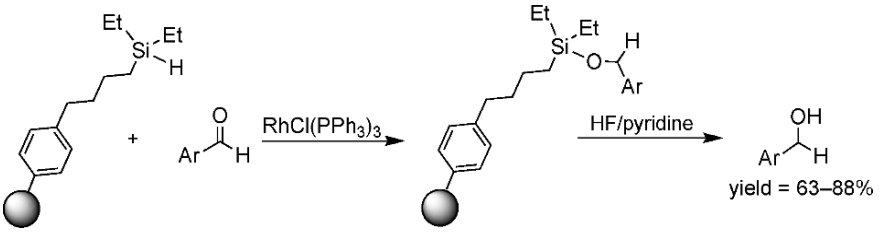
a R = Me
b R = *t*-Bu

Fig. 9.13

Gladysz introduced the Horvath's fluorous biphase chemistry concept to the field of hydrosilylation. Aliphatic fluorous phosphine analogue of Wilkinson's catalyst $[RhCl\{P[CH_2CH_2(CF_2)_nCF_3]_3\}_3]$ (n=5, 7) soluble in $CF_3C_6F_{11}$ was reported to be catalytically active in biphasic or monophasic conditions in hydrosilylation of cyclic ketones or enones with $HSiMe_2Ph$. The catalysts were efficiently recycled under fluorous–organic liquid–liquid biphasic conditions [68]. The hydrosilylation

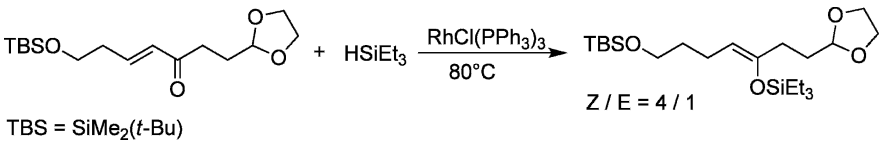
of α,β-unsaturated ketones with $HSiMe_2Ph$ under biphasic conditions in $CF_3C_6F_{11}$/toluene or monophasic conditions in $CF_3C_6F_{11}$/hexane leads to mixtures of 1,4- and 1,2-hydrosilylation products (>99–92 : <1–8) in 93–88% yields. Minor decreases in activity were observed over four subsequent cycles using recycled catalyst [69]. In an improved protocol Gladysz described the thermomorphic fluorous rhodium catalyst active in hydrosilylation of cyclohexanone with $HSiMe_2Ph$ which can be recycled by simple liquid/solid phase separation. Interaction of the fluorous domains of the catalyst with the surface of a Teflon tape was observed, which makes the catalyst easy for handling and recovery [70].

Polystyrene-diethylsilane resin reacts with adehydes in the presence of [$RhCl(PPh_3)_3$] to afford the corresponding resin bound silyl ethers in moderate yields. The silyl ethers formed can be effectively cleaved by using HF / pyridine solution in THF (Eq. 9.15) [71]. Analogous reaction with acetophenone gives 2-phenylalcohol in 50% yield.



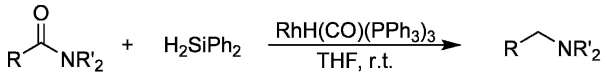
(9.15)

Selective 1,4-hydrosilylation catalysed by [$RhCl(PPh_3)_3$] was applied as a step for the synthesis of 9-α-methyl- and 9-α-cyanoisocarbacyclins, promising agents for the treatment of thrombosis, stroke and heart attack [72]. Rhodium catalysed conjugate reduction was also used as a step in the synthesis of *trans*-fused bis(pyran) derivatives from enones (Eq. 9.16) [73].



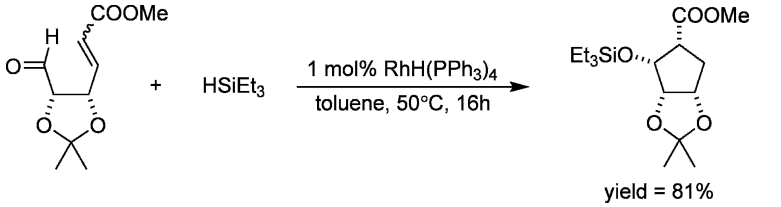
(9.16)

A wide range of tertiary amides undergo hydrosilylation with two fold excess of diphenylsilane in the presence of [$RhH(CO)(PPh_3)_3$] or some other rhodium complexes to give the corresponding tertiary amines with 64–98% yield (Eq. 9.17) [74]. Chemoselective reduction of amides having ester or epoxy functionalities was reported.



(9.17)

$[RhH(PPh_3)_4]$ was found to be an active precursor in hydrosilylation of a variety of ketones, diketones, α,β-unsaturated ketones and esters [75, 76]. Ketones were selectively reduced in the presence of isolated carbon—carbon double bond or ester functionality. Regioselectivity in the reaction of α,β-unsaturated ketones and esters is highly dependent on the silane used. Diphenylsilane was found to give 1,2-hydrosilylation, whereas dimethylphenylsilane and other trisubstituted silanes gave 1,4-addition products. On the basis of the results obtained a mechanism was proposed in which ketone coordinates to silicon rather than to rhodium. $[RhH(PPh_3)_4]$ combined with diethylamine catalysed reduction of *N*-acetylpiperidine with triethylsilane to form the corresponding amine [77]. Whitehead reported rhodium(I) hydride catalysed tandem hydrosilylation/intramolecular aldol reaction, which is a convenient way for preparation of substituted cycloalkanols [78, 79]. This strategy was successfully applied as a step (Eq. 9.18) in the synthesis of the highly potent anti-HIV carbocyclic nucleosides (−)-carbovir and (−)-abacavir [80].

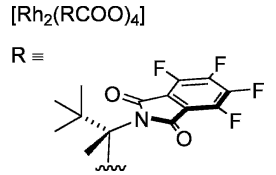


(9.18)

$[RhCl(PPh_3)_3]$ efficiently catalyses the homogeneous hydrosilylation of non-labile organoiron acyl complexes $[Cp(CO)_2Fe(COR)]$ with dihydrosilanes to produce stable siloxyalkyl derivatives [81, 82].

$[\{RhCl(cod)\}_2]$ was found to be active catalyst of the hydrosilylation of unsaturated furan and aromatic aldehydes with $HSiEt_3$ [83]. The protocol enabled 1,4- and 1,2-addition reactions giving unsaturated silyl ethers in *cis*- and *trans*-configurations. However, hydrosilylation products were accompanied by those of unwanted side reactions such as hydrogenation, migration of the alkyl group and dehydrogenative silylation. $[\{Rh(OH)(cod)\}_2]$ was found to be a highly efficient catalyst for 1,4-hydrosilylation of α,β-unsaturated carbonyl compounds. In the presence of a low catalyst loading (down to 0.005 mol%) 2-cyclohexen-1-one and a number of linear enones undergo hydrosilylation with trisubstituted silanes to give the corresponding ethers in high yield (80–99%) under mild conditions [84]. A series of dirhodium(II) catalysts such as $[Rh_2(pfb)_4]$, (pfb = perfluorobutyrate), $[Rh_2(OAc)_4]$, $[Rh_2(C_7H_{15}COO)_4]$, $[Rh_2(Ph_3CCOO)_4]$, were reported to be highly active catalyst precursors of 1,4-hydrosilylation of a series of α,β-unsaturated ketones and aldehydes with trisubstituted silanes [85]. In the presence of small metal loadings (down to 0.01 mol%) the corresponding silyl ethers were synthesised with the yield 88–97%. As expected for rhodium complexes, the reaction

Fig. 9.14



of cyclohexenone with H_2SiPh_2 led to selective formation of 1,2-addition product (91% yield). Dirhodium(II) tetrakis[*N*-tetrafluorophthaloyl-(*S*)-*tert*-leucinate], (Fig. 9.14) is an efficient catalyst for one-pot sequential 1,4-hydrosilylation/amination procedure for the enantioselective synthesis of *N*-(2-nitrophenylsulphonyl)-α-amino ketones from α,β-enones [86].

Acetaldehydes undergo selective hydrosilylation with $HSiMe_2Ph$ in the presence of cobalt acyl complex $[Co(CO)_3(PPh_3)(COMe)]$ [87]. The compounds $[Rh_4(CO)_{12}]$, $[Co_2(CO)_8]$, $[Co_2Rh_2(CO)_{12}]$, and $[Co_3Rh(CO)_{12}]$ were found catalytically active in hydrosilylation of cyclohexanone and cyclohexenone [88, 89]. In the presence of $[Rh_4(CO)_{12}]$ or $[Co_2Rh_2(CO)_{12}]$, the hydrosilylation of cyclohexanone with $HSiEt_3$ led to selective and quantitative formation of (cyclohexyloxy)triethylsilane. The selectivity of the reaction with cyclohexenone depends strongly on the silane used. The reaction with $HSiMe_2Ph$ proceeds smoothly at ambient temperature to give exclusively the 1,4-addition product. On the other hand, 1,2-addition products were formed quantitatively in reactions with H_2SiPh_2. $[Co(dpm)_2]$ (dpm = 2,2,6,6-tetramethylheptane-3,5-dionate) catalyses diastereoselective reductive intramolecular aldol and Michael reactions, which proceed via 1,4-addition of phenylsilane and formation of silyl enolates [90].

Half sandwich rhodium complex containing spherically extended π-conjugated ligand $[Rh(\eta^5\text{-}C_{60}Me_5)(CO)_2]$, stable against redox conditions catalysed hydrosilylation of acetophenone with H_2SiPh_2 under visible light irradiation [91]. Higher TON were observed than for the cyclopentadiene analogue $[Rh(\eta^5\text{-}Cp)(CO)_2]$. Bulky isocyanide ligands having *meta*-terphenyl backbone were tested in the presence of $[Rh(cod)_2]BF_4$ in hydrosilylation of cyclohexanone with $HSiMe_2Ph$ [92]. The highest activity was observed for trimethylsilyl derivative (Fig. 9.15). The complexes containing other isocyanides show the activities similar to those of the triphenylophosphine analogues.

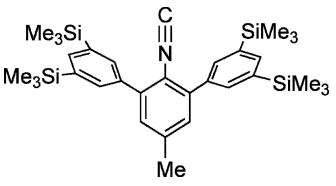
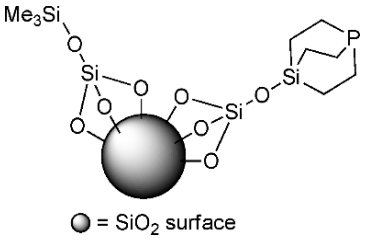


Fig. 9.15

Sawamura described immobilisation of a compact silicon-constrained monodentate alkylphosphine on a silica surface and its coordination properties (Fig. 9.16) [93]. An immobilized catalyst prepared from supported phosphine and

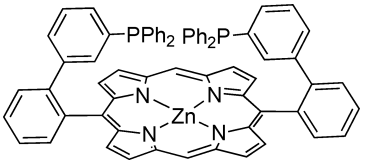
$[\{RhCl(C_2H_4)_2\}_2]$ showed high activity for the hydrosilylation of sterically hindered ketones with $HSiMe_2Ph$, $HSiEt_3$ or $HSi(t\text{-}Bu)Me_2$. The corresponding silyl ethers were synthesised in high yields (97–100%) under mild conditions.

Fig. 9.16



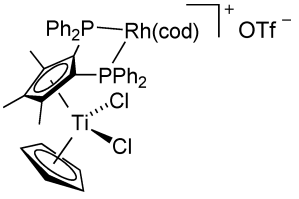
The zinc porphyrin-diphosphine complex was found to work as an effective ligand for the Rh(I)-catalysed hydrosilylation of aryl ketones with H_2SiPh_2 (Fig. 9.17). The corresponding alcohols were synthesised (after acid hydrolysis) with moderate yields (up to 82%) [94].

Fig. 9.17

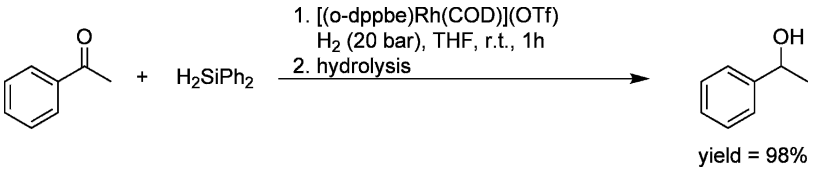


The heterobimetallic complex [(TiPHOS)Rh(cod)](OTf) (Fig. 9.18) has been tested in the hydrosilylation of aromatic ketones with diphenylsilane and found more active than the analogous rhodium complex containing chelating 1,2-bis(diphenylphosphino)benzene (o-dppbe) [95].

Fig. 9.18



The activity of rhodium complexes bearing common diphosphines [(o-dppbe)Rh(cod)](OTf) and [(dppe)Rh(cod)](OTf) (dppe = 1,2-bis(diphenylphosphino)ethane) in the hydrosilylation of various ketones with diphenylsilane was found to be several orders of magnitude higher when the reaction is performed under dihydrogen pressure than under an inert atmosphere (Eq. 9.19) [96].



(9.19)

The [{RhCl(cod)}$_2$] / (*R*)-BINAP catalysed hydrosilylation of acetophenone system H_2SiPh_2, H_2SiEt_2, H_2SiBu_2, $HSiBu_3$, $HSiPh_3$ or $HSi(4\text{-}C_6H_4CF_3)_3$ was studied by the ^{1}H NMR spectroscopy, GC/MS, and H/D exchange experiments with acetophenone-d_6. Simulation of the kinetic results, based on the Ojima mechanism [59] qualitatively fits the observed formation of silyl ethers [97]. Sterically congested bisphosphites (Fig. 9.19) were shown to be effective ligands for the Rh-catalysed hydrosilylation of ketones with diphenylsilane. In the hydrosilylation of the (−)-menthone, the 75:25 molar ratio of (+)-neomenthol (less stable)/(−)-menthol was obtained [98]. Rhodium acetylacetonate bearing ferrocene bis(phosphonite) ligand (Fig. 9.20) was used in hydrosilylation of acetophenone to give after hydrolytic work up 1-phenylethanol with 93% isolated yield [99].

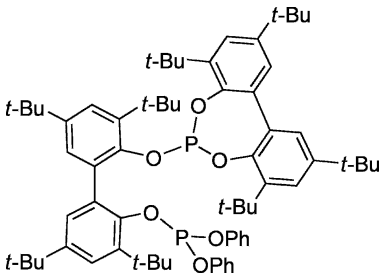


Fig. 9.19

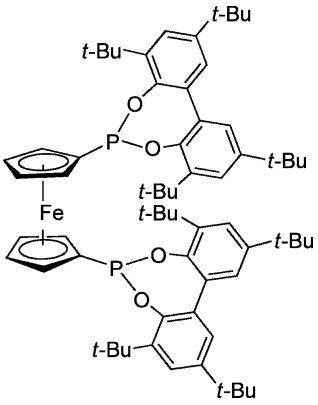
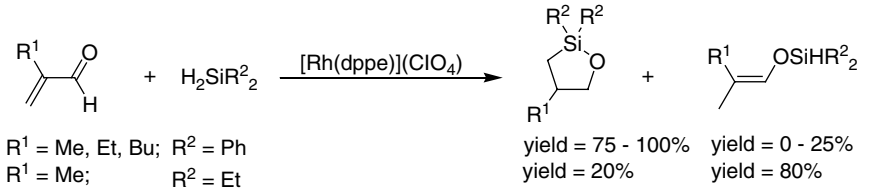
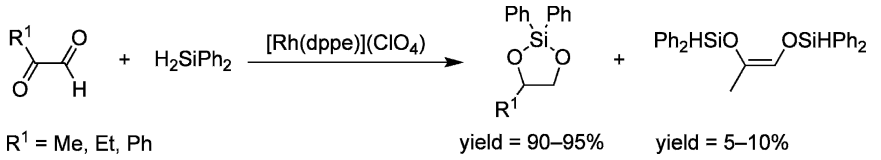


Fig. 9.20

Bosnich reported consecutive catalytic sequence in which β-ketoalcohols and α,β-unsaturated aldehydes in the presence of diphenyl- or diethylsilanes are first converted to the corresponding monohydrosilyl ethers, which are then cyclised (Eqs. 9.20, 9.21) [100].



(9.20)



(9.21)

The 1,4-hydrosilylation of α,β-unsaturated esters in the presence of rhodium DuPHOS (see chapter 10 Fig. 10.38) complex leads to silylketene acetal which undergo reaction with a variety of aldehydes to give the *syn*-aldol products in high yields and diastereoselectivity [101, 102].

Rhodium(bisoxazolinylphenyl) complex (Fig. 9.21) catalysed the hydrosilylation of a wide range of α,β-unsaturated aldehydes with diethoxymethylsilane and some other silanes [103]. Cinnamaldehyde was transformed to the corresponding product of 1,4-addition with high yield (87–98%) and selectivity (89–99%). Conjugate reduction of substituted cinnamaldehyde proceeded with lower regioselectivity.

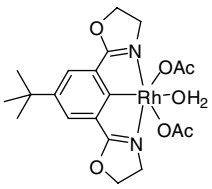
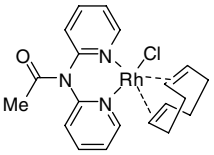


Fig. 9.21

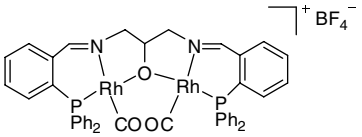
[RhCl(CH_3CONPy_2)(cod)] (Fig. 9.22) was found to be a highly active catalyst of hydrosilylation of aldehydes and ketones with $HSiEt_3$ [104]. High turn-over numbers (up to 50,000) and yields of the corresponding products in the range of 85–100% were observed for reaction performed at 70°C in the presence of NaO(*t*-Bu).

Fig. 9.22



Hydrosilylation of acetophenone with diphenylsilane in the presence of dinuclear rhodium complex (Fig. 9.23) gave a mixture of silyl ether and silyl enol ether at the ratio of 3:7 [105].

Fig. 9.23



Over the last decade, *N*-heterocyclic carbenes (NHC) have emerged as efficient ligands in transition metal catalysed reactions [106]. NHC rhodium complexes (Fig. 9.24) catalyse the hydrosilylation of acetophenone and its simple derivatives with triethylsilane to give respective silyl ethers with 63–99% yield [107]. Related dirodium complexes bridged by xylylbis(imidazolidinylidene) bidentate ligand exhibit similar activity [108]. NHC rhodium complex (Fig. 9.25) was found to be catalytically active in the hydrosilylation of ketones with diphenylsilane to give after hydrolysis the corresponding alcohols with moderate to high yields (67–93%) [109]. The iridium analogue exhibited poor activity.

Fig. 9.24

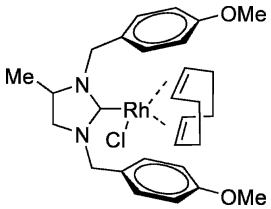
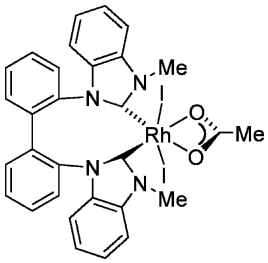
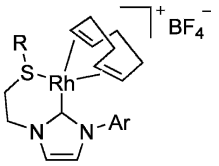


Fig. 9.25



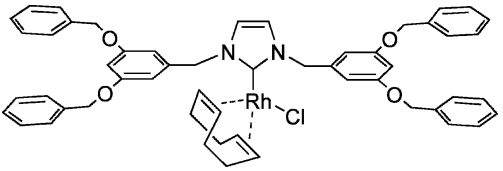
Cationic rhodium(I) complexes (Fig. 9.26) were found to be active catalyst in the hydrosilylation of acetophenone and its derivatives with diphenylsilane [110].

Fig. 9.26



a R = *t*-Bu, Ar = 2,4,6-$C_6H_2Me_3$
b R = *t*-Bu, Ar = 2,6-C_6H_3(*i*-Pr)$_2$
c R = Et, Ar = 2,4,6-$C_6H_2Me_3$

Fig. 9.27



The corresponding 2-arylalcohols were obtained (after hydrolysis) with the yield typically 90–99% in the reaction run under mild conditions. No conversion was observed for trisubstituted silanes tested ($HSiEt_3$, $HSiMeEt_2$ and $HSiCl_3$). A series of *N*-heterocyclic carbene complexes containing zeroth to the third generations of polybenzyl ether dendrimers bound to nitrogen of the NHC ligand, e.g., (Fig. 9.27) were synthesised and found catalytically active in the hydrosilylation of ketones with diphenylsilane [111]. The yields of the corresponding alcohols were found to increase with increasing dendrimer generation bound to the catalyst. The most active system catalysed the hydrosilylation of acetophenone and cyclohexanone under mild conditions to give the corresponding alcohols (after hydrolysis) with the yield 92 and 99%, respectively. Analogous complexes with *N*-heterocyclic carbenes bearing a 2,3,4,5-tetraphenylphenyl (Fig. 9.28) and higher dendritic frameworks were synthesised and found catalytically active in hydrosilylation of α,β-unsaturated ketones with H_2SiPh_2 [112]. Moderate to high yields of related products were obtained. 1,2-/1,4-addition selectivity was found to depend both on the structure of substrate and on the structure of catalyst. The dendrimer bound catalyst exhibited preference for 1,2-addition, that is the opposite regioselectivity to the one observed for conventional Rh-phosphine or Rh–NHC catalysts.

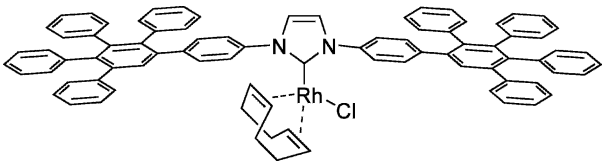
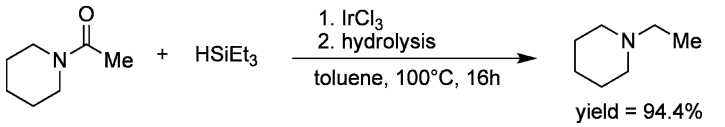


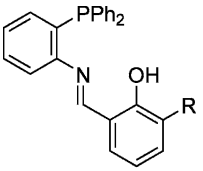
Fig. 9.28

[IrCl(CO)(PPh_3)$_2$] was found an active catalyst of the hydrosilylation of unsaturated furan and aromatic aldehydes with $HSiEt_3$ [83]. $IrCl_3$ and $K_2[IrCl_6]$/Et_2NH were active precatalyst of reduction of *N*-acetylpiperidine with triethylsilane (Eq. 9.22) [77].



(9.22)

Iridium(III) silylene cationic complex $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ exhibited moderate activity in hydrosilylation of benzo- and acetophenone with diphenylsilane [113]. Iminophosphine iridium complexes formed *in situ* from $[\{IrCl(cod)\}_2]$ and a series of iminophosphines are catalytically active in the hydrosilylation of acetophenone under mild conditions. The catalysts formed from monobasic iminophosphines (Fig. 9.29) give the highest conversions (up to 74%) [114]. The cationic Ir(I) complexes (Figs. 9.30 and 9.31) catalyse the hydroamination of 4-pentyn-1-amine to give 2-methylpyrroline and subsequent hydrosilylation leading to 1-(triethylsilyl)-2-methylpyrrolidine in a one-pot, tandem procedure with essentially quantitative yields [115].



a R = H
b R = *t*-Bu

Fig. 9.29

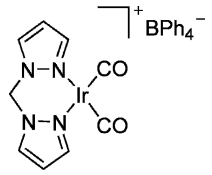


Fig. 9.30

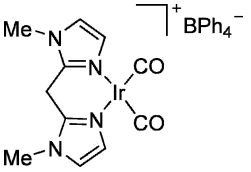
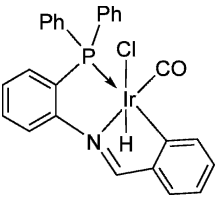
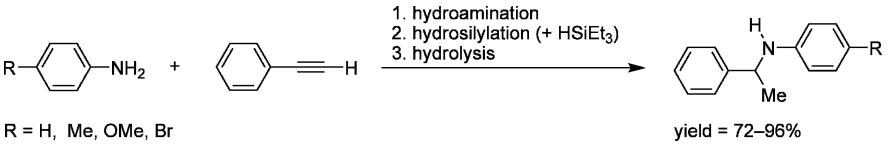


Fig. 9.31

Phosphine-imine iridium hydride complexes (Fig. 9.32) in combination with sodium tetrakis(3,5-trifluoromethylphenyl)borate are catalytically active in a similar sequence of intermolecular hydroamination of phenylacetylenes with anilines followed by hydrosilylation (Eq. 9.23). The *N*-silylated amines obtained, after the hydrolysis step afford secondary amines [116].

Fig. 9.32





(9.23)

The complexes [CpFe(CO)$_2$Me], (+) and (−)-[CpFe(CO)(X)L] as well as (+) and (−)-[(Ind)Fe(CO)(X)L] (X=CO, COMe; L=(*S*)-Ph$_2$P-N(Me)CHMePh) exhibit catalytic activity in the hydrosilylation of acetophenone with diphenylsilane [117]. An active intermediate [CpFe(CO)(SiPh$_2$H)$_2$H] was isolated from the reaction mixture and proved more active than the parent complex ([CpFe(CO)$_2$Me]) [118]. Fe(OAc)$_2$ combined with multi-nitrogen-based ligands such as *N,N,N',N'*-tetramethylethyenediamine, bis(*tert*-butyl)-bipyridine (Fig. 9.33) or pyridinebis (oxazoline) (Fig. 9.34) efficiently catalyses hydrosilylation of ketones to give (after hydrolysis step) the corresponding alcohols in moderate to high yields [119].

Fig. 9.33

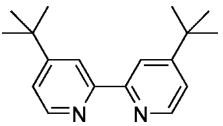
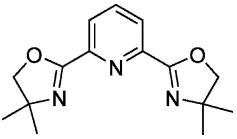
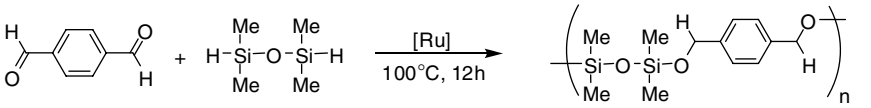


Fig. 9.34



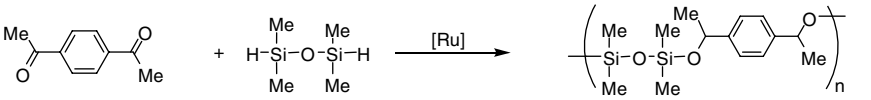
Beller reported highly chemoselective hydrosilylation of aldehydes with PMHS using Fe(OAc)$_2$ as iron precursor and tricyclohexylphosphine as ligand [120]. Aryl, heteroaryl and alkyl aldehydes were efficiently reduced to give (after hydrolysis) the corresponding primary alcohols with high yields. No sign of 1,4-reduction was detected for hydrosilylation of α,β-unsaturated (*E*)-cinnamaldehyde. Catalyst derived from iron(II) acetate Fe(OAc)$_2$ and sodium thiophene-2-carboxylate efficiently catalysed hydrosilylation of aromatic and aliphatic ketones to give the corresponding secondary alcohols in high yields (89–99%) and selectivities [121]. For α,β-unsaturated ketones, the dependence of regioselectivity on the substrate structure with a preference for 1,2-addition was observed.

In the presence of $[Ru(H)_2(CO)(PPh_3)_3]$, activated by treatment with styrene, terephthaldehyde and diacetoxy derivatives undergo polyhydrosilylation with 1,3-tetramethyldisiloxane (Eqs. 9.24, 9.25) [122].



M_w = 93400, M_n = 34100, PDI = 2.74

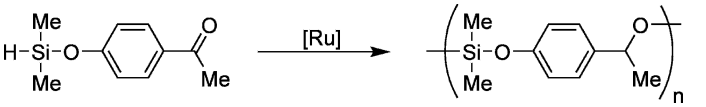
(9.24)



M_w = 86180, M_n = 24700, PDI = 3.49

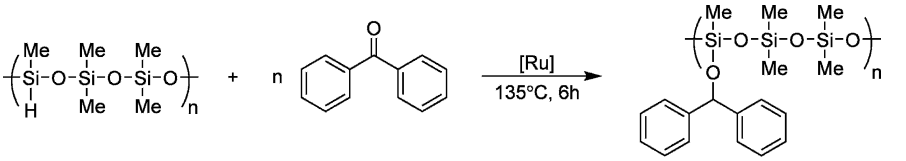
(9.25)

The same complex catalysed the hydrosilylation polymerisation of dimethylsilyloxyaryl ketones (Eq. 9.26) or aldehydes, the copolymerisation of aromatic α,ω-diketones with oligo-α,ω-dihydridodimethylsiloxanes to yield poly(silyl ethers) [123] and copolymerisation-hydrosilylation of aliphatic α,ω-diketones with α,ω-dihydridooligodimethylsiloxanes to yield symmetrical poly(silyl ether)s [124].



(9.26)

Quantitative hydrosilylation of poly(1-hydro-1,3,3,5,5-pentamethyltrisiloxane) with benzophenone was catalysed by activated $[RuH_2(CO)_2(PPh_3)_4]$ (Eq. 9.27) [125].



yield = 86%, M_w = 120 500
M_n = 64290, PDI = 1.87

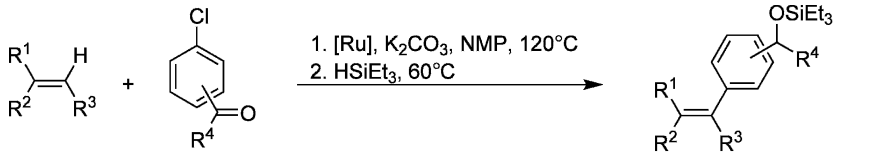
(9.27)

$[RuCl_2(CO)(PPh_3)_2]$ was reported to be moderately active in the 1,4-hydrosilylation of (*E*)-3-(2-furyl)acrolein with $HSiEt_3$ [83]. The same complex combined with EtI, ruthenium dihydride $[RuH_2(CO)(PPh_3)_3]$, $[Ru(acac)_3]$ or $[\{RuCl_2(CO)_3\}_2]$

combined with EtI and diethylamine, or $[Ru_3(CO)_{12}]$ used without additives, catalyse the reduction of linear and cyclic amides, e.g. *N*-acetylpiperidine with trisubstituted silanes to amines, with high yields and selectivities [77]. $[Os_3(CO)_{12}]$ used with Et_2NH also exhibits catalytic activity in the reaction.

First generation Grubbs catalyst $[Cl_2(PCy_3)_2Ru(=CHPh)]$ at elevated temperatures (50–80°C) exhibits catalytic activity in hydrosilylation of simple aldehydes and ketones with various silanes. The corresponding silyl ethers were obtained with the yield typically in the range 80–95% [126]. The reaction between croton aldehyde and allyldimethylsilane yielded selectively 1,4-addition products (mixture of *cis* and *trans* isomers).

$[Cl_2(PCy_3)_2Ru(=CHPh)]$ was found catalytically active in arylation of arenes or alkenes with organic electrophiles. A sequence – arylation / hydrosilylation – was demonstrated to proceed in one pot, without the need of repeated addition of precatalyst (Eq. 9.28) [127].



[Ru] = $[RuCl_2(PCy_3)_2(=CHPh)]$
R^1 = pyridyl; R^2 = H, alkyl;
R^3 = aryl, alkyl; Me, Ph
NMP = N-methylpyrrolidinone

isolated yield = 64–91%

(9.28)

$[Ru_3(CO)_{12}]$ was found catalytically active in hydrosilylation of acetophenone with $HSi(OEt)_3$ [128]. The hydrosilylation of esters catalysed by $[Ru_3(CO)_{12}]$ afforded alkyl silyl acetals in mostly moderate yields. $[\{RuCl_2(CO)_3\}_2]$ exhibits similar activity in the presence of diethylamine and ethyl iodide as co-catalysts [129]. The resulting acetals can be converted into aldehydes by acidic hydrolysis. Other transition-metal carbonyl complexes such as $[Cr(CO)_6]$, $[W(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Re_2(CO)_{10}]$, $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, $[Co_2(CO)_8]$ and $[Rh_6(CO)_{16}]$ show no or little catalytic activity in these processes.

Triruthenium cluster $[(\mu^3,\eta^2{:}\eta^3{:}\eta^5\text{-acenaphthylene})Ru_3(CO)_7]$ (Fig. 9.35) catalysed the hydrosilylation of olefins, acetylenes, ketones, and aldehydes with different silanes. The reactions of aldehydes and ketones proceed at room temperature to form the corresponding silyl ethers in good yield [130]. In the reduction of α,β-unsaturated ketones or aldehydes the regioselectivity depends on the structure of both reagents.

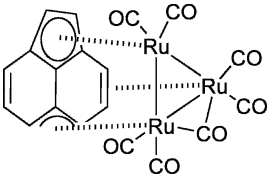
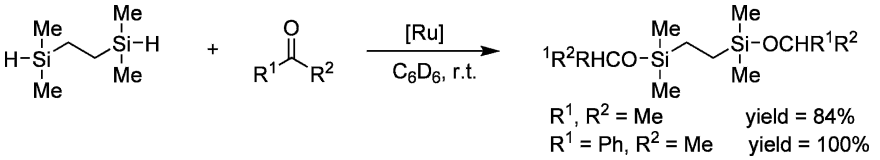


Fig. 9.35

Dihydrosilanes exhibited much higher reactivity than trialkylsilanes in the reaction. The hydrosilylation of ketones with $Me_2(H)SiCH_2CH_2Si(H)Me_2$ catalysed by (Fig. 9.35) allows conversion of both Si-H groups in the molecule (Eq. 9.29).



(9.29)

Analogous cluster $[(\mu^3,\eta^5{:}\eta^5\text{-}4,6,8\text{-trimethylazulene})Ru_3(CO)_7]$ (Fig. 9.36) catalysed hydrosilylation of acetophenone with moderate activity [131]. Diruthenium complex $[\{Ru(CO)_2(SiR_2H)\}_2(\mu\text{-dppm})(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2SiR_2)]$ (where R=4-C_6H_4Me) with Ru-H-Si interactions (Fig. 9.37), exhibited catalytic activity in hydrosilylation of various ketones and imines with diarylsilanes [132]. Trisubstituted silanes were found inactive. The α,β-unsaturated ketone undergoes selective 1,2-addition. A series of ruthenium complexes supported on different poliamide chains were obtained via polycondensation of monomeric *N*-heterocyclic hexamethylbenzene ruthenium complex (Fig. 9.38) with aromatic dianhydrides. The complexes obtained were tested in the hydrosilylation of acetophenone with triethylsilane and high yields of expected products were obtained in each case [133].

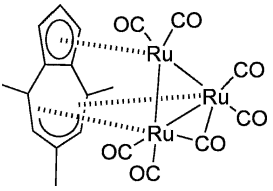


Fig. 9.36

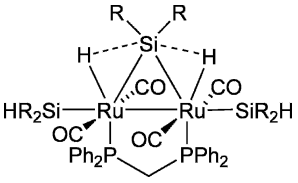


Fig. 9.37

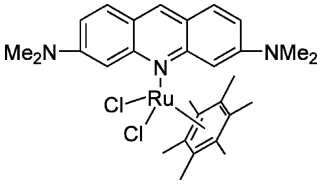
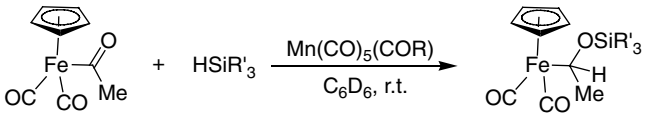


Fig. 9.38

9.1.2 Transition Metal Complexes of the Group 4-7 as Catalysts

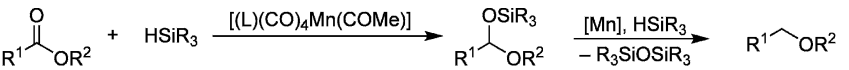
Manganese acyl complexes [L(CO)$_4$Mn(COR)] (where L=CO, R=Me, Ph; L=PPh$_3$, PEt$_3$, R=Me) are effective catalyst of hydrosilylation of C=O bond in acyl ligand of the iron complex [CpFe(CO)$_2$(COR)] with mono-, di-, and trisubstituted silanes (Eq. 9.30). [(CO)$_5$Mn(COMe)] and [(PR$_3$)(CO)$_4$Mn(COMe)] allow quantitative conversion with H_2SiPh_2. Catalytic activity was also observed for other manganese complexes such as [(CO)$_5$Mn(SiMe$_3$)], [Mn$_2$(CO)$_{10}$], [(CO)$_5$MnMe] and [(CO)$_5$MnCHPh(OSiHR$_2$)] [82, 134].



R = Me, SiR'$_3$ = SiEt$_3$ yield = 95%
R = Ph, SiR'$_3$ = SiEt$_3$ 90%
R = Ph, SiR'$_3$ = SiMe$_2$Ph 66%

(9.30)

Acetyl and benzoyl manganese compounds [(CO)$_5$Mn(COR)] undergo addition of di- and trisubstituted silanes with formation of α-siloxyalkyl complexes [135,136]. Manganese acyl complexes [(L)(CO)$_4$Mn(COMe)] [L=PPh$_3$, CO] catalyse the hydrosilylation of esters (Eq. 9.31) [137] to give silylacetals, which undergo successive reduction leading to the corresponding ethers. The reaction proceeds cleanly (yield up to 96%) for straight chain esters. Esters bearing more bulky substituents gave mixtures of the corresponding ethers and alkoxysilanes.

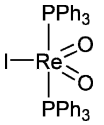


R^1 = alkyl (linear), R^2 = Me, Et, *i*-Pr yield = 85–96%
L = PPh$_3$, CO

(9.31)

Manganese carbonyl complexes catalyse the hydrosilylation of ketones with $HSiMe_2Ph$ and H_2SiPh_2 [138]. In the optimum conditions [(PPh$_3$)(CO)$_4$Mn(COMe)] is much more reactive than [RhCl(PPh$_3$)$_3$] for the hydrosilylation of acetone, acetophenone and cyclohexanone with $HSiMe_2Ph$ and enables the synthesis of the corresponding silyl ethers with yields exceeding 90%, with no evidence of competing dehydrogenative silylation. Both catalysts exhibit similar reactivity with H_2SiPh_2. The compound [(η^5-C$_{10}$H$_9$)Mn(CO)$_3$] was found to be an effective catalyst for the hydrosilylation of alkyl and aryl ketones with H_2SiPh_2. The reaction enables quantitative formation of the corresponding silyl ethers. The facile $\eta^5 \rightarrow \eta^3$ slippage in the 1-hydronaphtalene ring of the complex was demonstrated to play a decisive role in catalysis [139, 140]. Mimoun reported the catalytic activity of Mn(stearate)$_2$ activated by $NaBH_4$ in the hydrosilylation of methyl benzoate with PMHS. Quantitative conversion and 100% selectivity towards formation of the corresponding alcohols (after hydrolysis step) was observed [5]. [Mn$_2$(CO)$_{10}$]

Fig. 9.39



and $[Re_2(CO)_{10}]$ combined with diethylamine are active precatalyst of reduction of *N*-acetylpiperidine with triethylsilane (Eq. 9.22) [77]. In 2003 Toste reported the catalytic activity of the iododioxobis(triphenylphosphine)rhenium(V) complex (Fig. 9.39) in the hydrosilylation of aldehydes and ketones [141]. This important and unexpected finding opened a new class of transition metals reduction catalysts. A wide range of aromatic, heteroaromatic, and aliphatic aldehydes were transformed in the reaction with dimethylphenylsilane into the corresponding silyl ethers in 63–95% of isolated yields. Moreover, hydrosilylation was readily applied to a variety of aromatic and aliphatic ketones to give the corresponding silyl ethers or (after TBAF deprotection) alcohols with excellent yields [142]. Rhenium(V) catalytic system tolerates a wide range of functional groups including a Lewis-basic tertiary amine.

Since the Toste communication, a number of other rhenium complexes have been proved active in hydrosilylation. Abu-Omar reported high catalytic activity of monooxorhenium(V) catalyst (Fig. 9.40) [143] and cationic oxorhenium(V) salen complex (Fig. 9.41) [144, 145] in hydrosilylation of various aldehydes and ketones with organosilanes under mild conditions. A number of rhenium complexes $[Re(O)Cl_3(PPh_3)_2]$, $[Re(O)Cl_3(PCy_3)_2]$, $[Re(O)Cl_2H(PPh_3)_2]$, $[Re(NPh)Cl_3(PPh_3)_2]$, $[Re(NMes)Cl_3(PPh_3)_2]$, $[Re(NMes)Cl_3(PPh_3)(NH_2Mes)]$, $[Re(N)Cl_2(PPh_3)_2]$, $[Re(N)Cl_2(PCy_3)_2]$ were proved active in the catalytic hydrosilylation of PhCHO with $HSiEt_3$ [146]. The hydrosilylation of aliphatic and aromatic aldehydes with dimethylphenylsilane was also reported to be catalysed by other rhenium oxo compounds: $[Re_2O_7]$, $[ReMeO_3]$, $[Re(\eta^5\text{-}C_5H_5)O_3]$, $[ReO_2Cl(DMSO)_2]$, $[ReO_2Me(PhC{\equiv}CPh)$, and $[ReOCl_3(PPh_3)_2]$. Methyltrioxorhenium(VII) and oxotrichlorobis(triphenylphosphine)rhenium(V) were shown to be the most active and versatile catalysts for the hydrosilylation of aliphatic and aromatic aldehydes and ketones [147]. Two distinct mechanistic pathways were proposed for rhenium high oxidation state complexes catalysed hydrosilylation. For the reaction proceeding in the presence of *cis* dioxorhenium(V) complex (Fig. 9.39) Toste proposed the unprecedented mechanism that begins with the formation of a siloxyrhenium hydride complex, stabilised by the presence of a spectator oxo ligand (Scheme 9.3) [141, 142]. This mechanism was supported by the density functional theory (DFT) studies performed for the hydrosilylation of acetaldehyde with $HSiMe_3$ catalysed by $[ReI(O)_2(PR_3)_2]$

Fig. 9.40

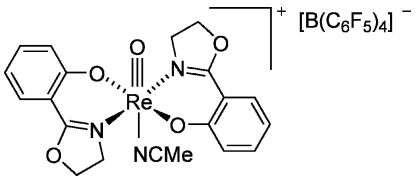
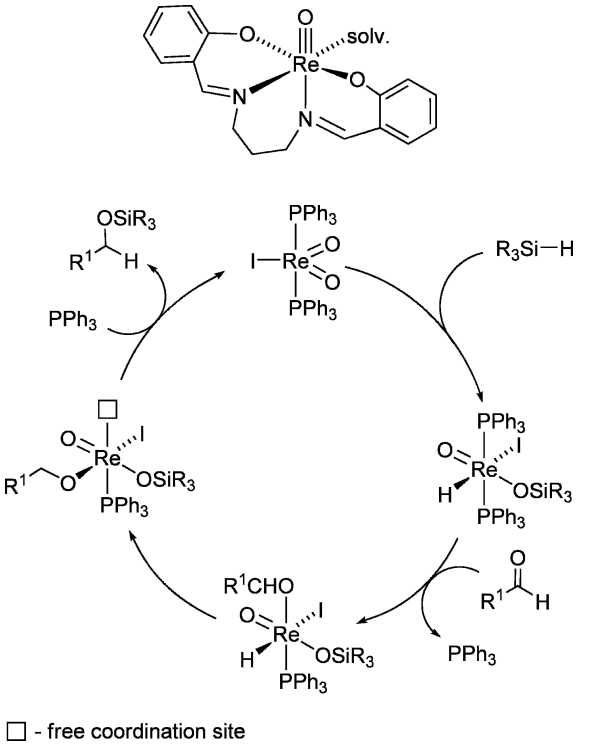


Fig. 9.41



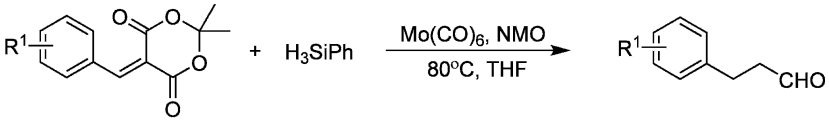
Scheme 9.3 Mechanism of hydrosilylation of carbonyl derivatives catalysed by iododioxobis(triphenylphosphine)rhenium(V)

(R=Me, Ph). According to these calculations the most favorable pathway starts with PR_3 dissociation, followed by [2+2] addition of Si—H to the Re=O bond, coordination of the aldehyde to rhenium, reduction of the coordinated aldehyde to alkoxide, rearrangement, and a final intramolecular attack of the alkoxide on the Si atom of the coordinated siloxide [148].

On the other hand, complexation of η^2-silane *cis* to the Re≡X bond followed by heterolytic cleavage at the electrophilic rhenium center was demonstrated by Amu-Omar to be the most viable catalytic pathway for the rhenium high oxidation state complexes of the type $[Re(X)Cl_n(PR_3)_2]$ (X=O, NAr, or N; n=2 or 3; and R=Ph or Cy) [146]. Reduction catalysis mechanism by high oxidation state transition metal complexes was shortly discussed by Thiel [149]. Hydrosilylation of aldehydes and ketones with dimethylphenylsilane in the presence of perrhenic acid ($[HReO_4]$) is suggested to occur via the radical mechanism (see Section 9.1.4) [150].

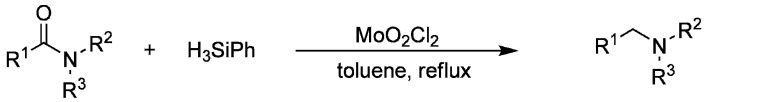
The anionic μ-hydride complexes $[HM_2(CO)_{10}]^{-}\cdot$ (M=Cr, Mo, W) catalyse hydrosilylation of simple aldehydes and ketones with triethylsilane to give silyl ethers in high yields [151]. Bis(benzene)chromium was found active in hydrosilylation of aryl ketones and aldehydes with diphenylsilane [152]. In the optimum conditions acetophenone and *p*-anisaldehyde were converted (after hydrolysis steps) to the

corresponding alcohols with 90% and 95% yield, respectively. Carbonyl molybdenum and tungsten oxadiene complexes $[M(CO)_2(oxadiene)_2]$ (where oxadiene= pulegone, pinocarvone and (*E*)-5-methyl-3-hexen-2-one) exhibit catalytic activity in the hydrosilylation of unsaturated ketones and aldehydes with H_3SiPh [153]. However, as a result of the hydrosilylation of α,β-unsaturated ketones a mixture of 1,2- and 1,4-addition products is observed. High predominance of the 1,4-addition product is observed only for the reaction of pinocarvone with phenylsilane in the presence of $[Mo(CO)_2(pinocarvone)_2]$. With α,β-unsaturated aldehydes the reaction (after hydrolysis step) produces selectively the corresponding allylic alcohols. Efficient synthesis of β-aryl aldehydes from α,β-unsaturated Meldrum's acid derivatives (Eq. 9.32) was reported employing a tandem $[Mo(CO)_6]$ catalysed hydrosilylation reaction. The mechanism of aldehyde formation was proposed to involve two hydrosilylation steps, 1,4-hydrosilylation of the starting compound and hydrosilylation of a key ketene intermediate [154].



NMO = N-methylmorpholine-N-oxide yield = 37–85% (9.32)

The communication by Toste on the catalytic activity of high valent rhenium complex in hydrosilylation [141] has inspired a search for similar systems containing other metals. Molybdenum, the neighbour of rhenium in the periodic table, forming a variety of dioxo complexes seemed to be an ideal candidate. Indeed, molybdenum-dioxo complex $[MoO_2Cl_2]$ was found to catalyse the addition of dimethylphenylsilane to aldehydes and ketones to afford the corresponding dimethylphenylsilyl ethers in moderate to high yield [155]. The dioxomolybdenum(VI) complexes $[MoO_2Cl_2]$, $[MoO_2(acac)_2]$, $[CpMoO_2Cl]$, $[MoO_2(Mes)_2]$ and the polymeric organotin-oxomolybdates $[(R_3Sn)_2MoO_4]$ [R=*n*-Bu, *t*-Bu, Me] were examined as catalysts for the hydrosilylation of aldehydes and ketones with dimethylphenylsilane. $[MoO_2Cl_2]$ was the most efficient catalyst, affording quantitative yields of the corresponding silylated ethers at room temperature [156]. The mechanism of the $[MoCl_2O_2]$ catalysed hydrosilylation of aldehydes and ketones was studied by means of the density functional theory calculations [157, 158]. $[MoO_2Cl_2]$ was proved to be an efficient catalyst for the reduction of aliphatic and aromatic esters with silanes to give the corresponding alcohols in good yields. H_3SiPh was found the most active within all silanes tested. However, the high reactivity was observed also for not expensive and convenient in handling PMHS. As $[MoO_2Cl_2]$ is completely insoluble in benzene and toluene (found to be the best reaction solvents), the reaction is most likely heterogeneous [159]. Dioxomolybdenum dichloride exhibits catalytic activity in reduction (hydrosilylation) of tertiary or secondary amides with H_3SiPh or PMHS (Eq. 9.33). The corresponding amines were synthesised in moderate to good isolated yields (40–87%). The best results were obtained for the reduction of tertiary amides with bulky *N*-substituents [160].



(9.33)

R^1 = Me, aryl; R^2 = H; R^3 = aryl, benzyl
R^1 = Me; NR^2R^3 = N-heterocycle

isolated yield = 40–87%

Solvent free hydrosilylation of ketones with $HSiEt_3$ in the presence of $[CpW(CO)_2IMes][B(C_6F_5)_4]$ leads to formation of silylethers with the yield ranging from 77 to 98%. The catalyst in this specific system remains dissolved until essentially all the liquid substrate is converted to liquid products and then precipitates [161]. Such catalyst ability was attributed to the transient formation of a liquid clathrate containing few molecules of the substrate per molecule of the otherwise solid catalyst.

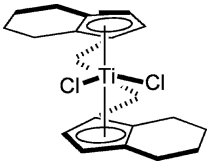
The photochemically activated $[W(CO)_6]$ was tested as a catalyst in the hydrosilylation of ketones, RMeC=O (R=Me, *i*-Pr, Pr, Ph) with diphenylsilane. The reaction leads to a mixture of silicon containing products with predominance of the expected silyl ethers [162]. In 2006 Tobita reported stoichiometric hydrosilylation reactions of acetone with neutral hydrido(hydrosilylene)tungsten complex $[Cp^*(CO)_2(H)W{=}Si(H)\{C(SiMe_3)_3\}]$ to form $[Cp^*(CO)_2(H)W{=}Si(O\text{-}i\text{-}Pr)\{C(SiMe_3)_3\}]$ as a main product [163]. The mechanisms of the stoichiometric hydrosilylation of unsaturated compounds (ketone and nitrile) with the tungsten silylene complexes have been investigated with the density functional theory method [164].

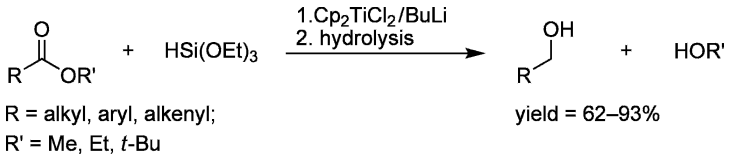
In 1988 Nagai reported the first example of titanium catalysed hydrosilylation of ketones with phenyl-, diphenyl or phenylmethylsilane [165]. In the presence of $[Cp_2TiPh_2]$ dialkylketones were transformed into the corresponding silyl ethers with the yield up to 91%. Titanocene complexes were found catalytically active in hydrosilylation of esters with diphenylsilane or triethoxysilane [166]. The treatment of titanocene dichloride (Fig. 9.42) with BuLi generates catalyst that allows selective reduction of the ester group to corresponding alcohols (Eq. 9.34), despite the presence of the potentially reactive groups like hydroxyphenyl, amino or cyclopropyl.

Fig. 9.42

Isolated di- and trisubstituted C=C double bond present in the structure of the ester remained unchanged. α,β-Unsaturated esters undergo selective 1,2-hydrosilylation. Esters containing terminal carbon-carbon double bond or epoxy group required the use of the more hindered ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium dichloride (Fig. 9.43) for successful reduction. By using this procedure a range of esters were transformed into the corresponding alcohols with moderate to high isolated yield.

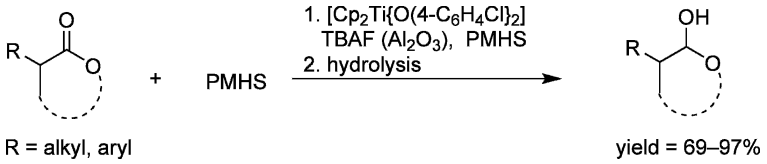
Fig. 9.43





(9.34)

The improved reaction protocol for hydrosilylation of esters involved the use of PMHS as the stoichiometric reductant and EtMgBr instead BuLi for generation of active catalyst [167]. The new protocol utilizing less hazardous chemicals was tested for a variety of esters and found similar in the scope and reactivity to the original. Important progress was made by observation of the catalytic activity of Ti(O-*i*-Pr)$_4$ [168]. In the presence of 5 mol% of titanium tetraisopropoxide esters undergo hydrosilylation with an excess of HSi(OEt)$_3$ to form (after alkaline hydrolysis) the corresponding alcohols with the yield ranging from 70 to 95%. The reaction can be carried out in the air, without solvent, and displays a high level of functional group compatibility. The modified protocol employed titanium(IV) isopropoxides or zirconium(IV) ethoxides and less expensive, non-hazardous PMHS [169]. However, to achieve high conversion equimolar amount of Ti(O-*i*-Pr)$_4$ and high excess of PMHS (10 eq) had to be used. The corresponding alcohols were formed with the yield up to 98%. In the procedure reported by Buchwald [170] efficient hydrosilylation of esters with small excess (up to 2.5 eq) of PMHS was achieved in the presence of 0.25 to 1 eq. (relative to ester used) of titanium(IV) isopropoxide. A range of esters bearing different functional groups were transformed to give (after hydrolytic work up) the corresponding alcohols with moderate to high yields. The system tolerates primary alkyl bromides and iodides, olefins, epoxides, and alkynes. On the basis of the results observed a neutral titanium hydride complex or strongly associated titanium/silane complex is assumed to be the active reducing agent.



(9.35)

Efficient hydrosilylation of five- and six-membered ring lactones with PMHS as a hydride source was reported by Buchwald (Eq. 9.35) [171]. The corresponding lactols were obtained (after hydrolytic work up) with moderate to high isolated yields (69–97%) under mild conditions. The procedure involves *in situ* generation of an active catalyst (assumed to be titanocene(III) hydride) by treatment of $Cp_2Ti(OC_6H_4C1\text{-}4)_2$ with TBAF and PMHS. Further research showed high efficiency of the catalytic systems $[Cp_2Ti(OR)_2]$/(TBAF/alumina)/PMHS and $[Cp_2TiF_2]$/PMHS [172]. Both systems exhibit similar activity and enabled synthesis of lactols in high (up to 97%) yield. Although TBAF used in the absence of the titanium complex is catalytically active in the process, the results permit excluding the dominant contribution of the fluoride catalysed reaction in the procedure proposed. Hydrosilylation of protected ribonolactone to the lactol in the presence of $[Cp_2TiF_2]$ and subsequent hydrolysis were used as a step in the total synthesis of protected ribose, which is a potential intermediate for preparing a range of nucleoside analogues [173]. Dimethylzirconocene was found active in hydrosilylation of ketones with phenylsilane [174]. The reaction leads to formation of a mixture of mono-, di- or trialkoxysilanes with the composition depending on the steric properties of ketone. For acetophenone only traces of hydrosilylation products were observed.

9.1.3 Main Group Metal-Based Catalysts

A mixture of tin(II) triflate and pyridinebisoxazoline (PYBOX) (see Chapter 10, Fig. 10.23 R=H) efficiently catalyses the hydrosilylation of ketones and ketoesters with polymethylhydrosiloxane (PMHS). The reaction performed in methanol or ethanol allows direct formation of the corresponding alcohols (without the hydrolysis step) with the yields reaching 99% [175].

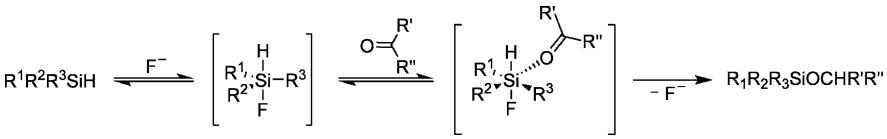
9.1.4 Nucleophilic-Electrophilic Catalysis

Lithium alkoxides were found to activate silanes by formation of hypervalent hydrosilicates. Catalytic amount of lithium methoxide was reported to catalyse the stereoselective reduction of α,β-epoxy ketones with trimethoxysilane. The reactions reveals divergent selectivity depending on the solvent used [176].

In the presence of catalytic amounts of lithium methoxide, hydroxyesters are reduced by trimethoxysilane to yield diols with 63 – 100% yield [177].

The caesium fluoride catalysed reactions of trialkylsilanes with alcohols and aromatic carbonyl compounds were first reported by Vol'pin [178] and developed by Corriu [179]. Hiyama reported the hydrosilylation of ketones and aldehydes catalysed by a homogeneous system based on TBAF or tris(diethylamino)sulphonium difluorotrimethylsilicate (TASF) [180]. The hydrosilylation catalysed by alkali metal or ammonium fluorides, hydroxides or alkoxides is generally assumed to proceed by a mechanism involving the coordination of the nucleophile to the silicon atom to

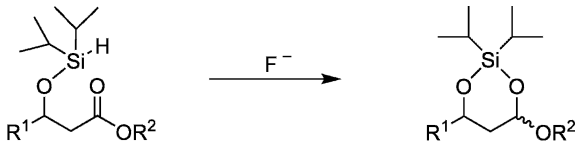
give a more reactive pentacoordinate species (Scheme 9.4). The intermediate is then attacked by the carbonyl compound giving hexacoordinate silicon intermediate (or transition state), in which the hydride transfer takes place [181].



Scheme 9.4 Mechanism of Lewis base catalysed hydrosilylation of carbonyl derivatives

Lukevics reported a protocol for the hydrosilylation of C=O bond involving the use of alkali metal fluorides (with CsF being the most effective) in combination with crown ether 18-crown-6. The protocol enabled the hydrosilylation of a number of aromatic and heteroaromatic aldehydes and ketones with dimethylphenylsilane. The use of 18-crown-6 ether increased the efficiency of CsF and allowed a reduction of aromatic carbonyl compounds in low polarity solvents such as dichloromethane. The protocol enables a quantitative reduction of acetophenone as well as reduction of thienyl, furyl and pyridyl ketones and aldehydes to the corresponding alcohols with moderate yield [182–184]. The compounds $KF/Al_2O_3{\cdot}K_2CO_3/Al_2O_3$ or KNH_2/Al_2O_3 catalyse the hydrosilylation of benzaldehyde with triethylsilane. Selective synthesis of benzyl silyl ether was observed in DMF as solvent [185]. TBAF was reported to be a highly effective catalyst for the reduction of aldehydes and cyclic ketones with PMHS [186]. High selectivity was observed in the reduction of cyclic ketones. In most cases the corresponding alcohols were formed (after decomposition of silyl ethers by treatment with another equivalent of TBAF) in high yield and a high *trans*/*cis* ratio (up to 99/1). Aldehydes were converted to alcohols up to quantitative yield. Cinnamylaldehyde undergoes 1,2-addition with the selectivity 95–99%. A similar procedure was used for the reduction of esters, carboxylic acids, ketones and aldehydes [187]. The protocol involves the use of 0.02 mol% of TBAF and enables transformation of carbocyclic esters and acids with the yield ranging form 81–95% and 67–82%, respectively. Exclusive 1,2-hydrosilylation of α,β-unsaturated esters was observed. Isolated carbon—carbon double bonds remained unaffected. Substituted acetophenones and benzaldehydes were reduced in the presence of TBAF or benzyltrimethylammonium hydroxide with high yield. Stable crystalline pentacoordinate hydridosilicates $[HSi(OR)_4]K$ undergo hydrosilylation with aldehydes, ketones and esters producing after acidic hydrolysis the corresponding alcohols in moderate to high yield [188]. In the presence of KO_2/18-crown-6 aryl aldehydes react with triethylsilane to form corresponding silyl ethers accompanied by the product of the Tishchenko reaction [189]. Chemoselectivity of the reaction was demonstrated to depend on the nature of aldehyde used and experimental conditions. Solid bases like hydroxyapatite $Ca_{10}(PO_4)_5(OH)_2$ or CaO catalyses efficiently hydrosilylation of a variety of carbonyl compounds with triethoxysilane. The α,β-unsaturated ketones and aldehydes undergo a selective 1,2-addition [190, 191]. Treatment of the silyloxy esters with catalytic amounts of TBAF in CH_2C1_2 at 0°C,

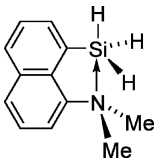
in the presence of 4A molecular sieves, results in clean and nearly quantitative conversion to alkoxysiladioxanes (mixture of isomers) (Eq. 9.36) [192, 193].



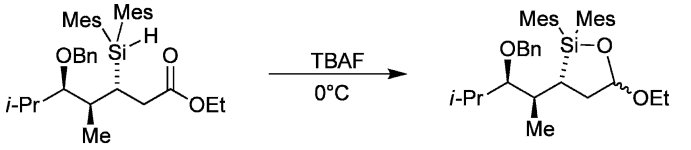
R^1 = Bu, Pr, Ph; R^2 = Me, Et — yield = 95–98% (9.36)

Corriu reported hydrosilylation of monofunctional carbonyl compounds, diketones and α-hydroxyketones with pentacoordinated substituted silane (Fig. 9.44) [194]. The structure of the silane reagent permitted avoidance of any catalytic additive. For difunctional carbonyl derivatives a diol skeleton was formed (after deprotection with $LiAH_4$) with the predominance of an *erythro* isomer.

Fig. 9.44

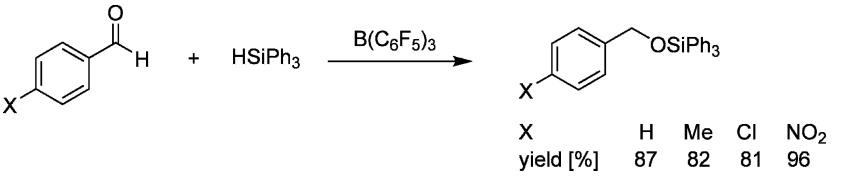


The 1-oxa-2-silacyclopentane acetals, intermediates for the formation of highly functionalised 1,3-diols, were synthesised in good yield as a mixture of acetal epimers via an intramolecular hydrosilylation of β-silyl esters catalysed by Bu_4NF (Eq. 9.37) [195].

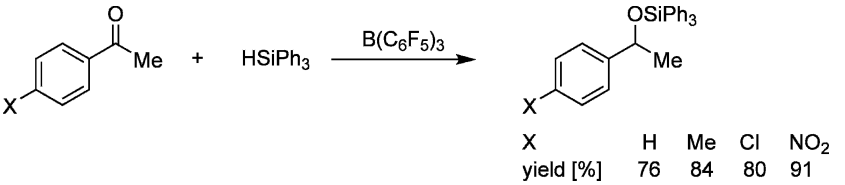


yield = 82%, 85 : 15 ds (9.37)

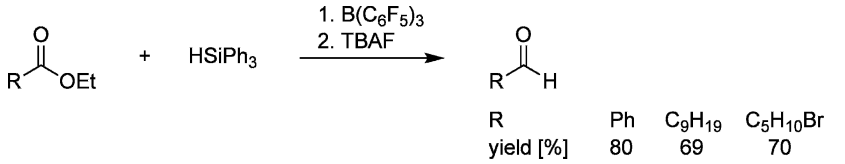
$B(C_6F_5)_3$ was found to catalyse the hydrosilylation of aromatic aldehydes, ketones or esters. The hydrosilylation of aldehydes (Eq. 9.38) and ketones (Eq. 9.39) led to the corresponding silyl ethers with the yield up to 96%. Hydrosilylation of esters (Eq. 9.40) allowed the synthesis of respected aldehydes with 45–84% yield [196, 197].



(9.38)

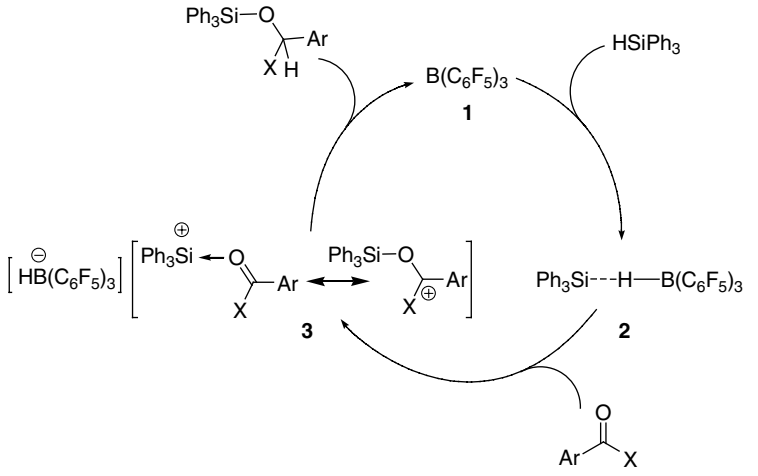


(9.39)



(9.40)

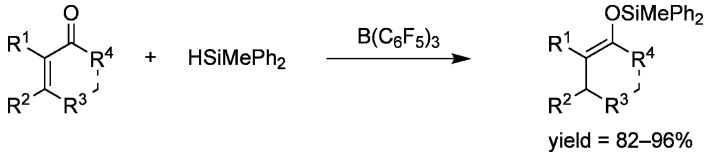
On the basis of the kinetic data collected, a mechanism was proposed (Scheme 9.5) according to which borane (**1**) activates the Si—H bond to form the borane / silane



Scheme 9.5 Mechanism of hydrosilylation of carbonyl compounds in the presence of $B(C_6F_5)_3$

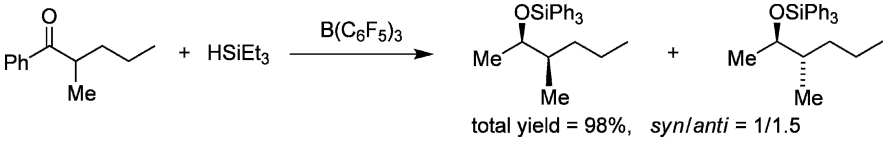
complex (**2**). Once **2** is formed, carbonyl substrate nucleophilically attacks the silicon centre with the formation of **3**. The last step of the reduction involves the addition of H^- to the carbonyl carbon, from the hydrido borate counteranion, rather than from the free silane [196, 197].

Mechanism is well in agreement with the key observation that the least basic substrates are hydrosilylated at the fastest rates and that k_{obs} is inversely proportional to carbonyl substrates concentration. $B(C_6F_5)_3$ was found an active catalyst in the 1,4-hydrosilylation of a range of a α,β-unsaturated enones with $HSiMePh_2$ (Eq. 9.41). The substrates with no steric hindrance at the β-carbon give selectively 1,4-hydrosilylation products. In other cases a competitive 1,2-addition was observed [198].



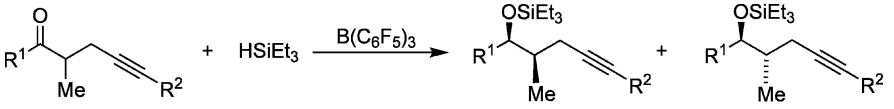
(9.41)

Activity of a number of silanes were screened in the reaction with substituted cyclohexenone. High yields (80–96%) of hydrosilylation products were obtained for all silanes tested except $HSi(i\text{-}Pr)_3$. A number of aryl alkynyl ketones were effectively and stereosectively hydrosilylated with $HSiEt_3$ under the control of σ-π chelation. Hydrosilylation of 2-methyl-1-phenylpentane with $HSiEt_3$ in the presence of catalytic amounts of $B(C_6F_5)_3$ gave *anti*-isomer (Eq. 9.42) with slight predominance over the *syn*-product.



(9.42)

In contrast, the *syn*-product was obtained stereoselectively in the reaction of 2-methyl-1-phenyl-4-yn-1-one ($syn/anti = 7/1$) (Eq. 9.43) [199, 200]. The *syn*-selectivity observed was accounted for by the σ-π chelation [200].



R^1 = Ph, R^2 = H — total yield = 90%, *syn*/*anti* = 7.0/1
R^1 = Ph, R^2 = $SiMe_3$ — total yield > 99%, *syn*/*anti* = 7.7/1
R^1 = *t*-Bu, R^2 = H — total yield > 99%, *syn*/*anti* > 30/1

(9.43)

Low generation dendrimeric molecules functionalised by (perfluoroaryl) borane were synthesised and found catalytically active in the hydrosilylation of acetophenone with $HSiEt_3$ [201].

Solid acids, such as Fe^{3+} ion-exchanged montmorillonite exhibit catalytic activity in the hydrosilylation of cyclohexanone and benzaldehyde with triethyl- and dimethylphenylsilane [190, 202]. Strongly acidic clays efficiently catalyse the reduction of aldehydes and ketones with trialkylsilanes such as $HSiEt_3$ to afford symmetrical ethers or hydrocarbons depending on properties of substituents at carbonyl groups. Bronsted acid $HClO_4$ was found to exhibit poor catalytic activity in hydrosilylation of carbonyl compounds with $HSiEt_3$ [203, 204]. It was demonstrated that hydrosilylation of carbonyl compounds with $HSiEt_3$ in the presence of Lewis acid (Et_3SiClO_4) and Bronsted acid ($HClO_4$) proceeds according to the same mechanism [204].

9.1.5 Free-Radical Initiated Hydrosilylation

Tris(trimethylsily1)silane, a versatile radical reagent undergoes the di(*tert*-butyl)peroxide initiated hydrosilylation with compounds containing the carbonyl function (diaryl or dialkyl ketones, quinines). The reactivity was found to depend significantly on the nature of the substrate [205]. Cyclohexanone undergoes hydrosilylation with $HSi(SiMe_3)_3$ in the presence of catalytic amounts of AIBN [206]. When acrylonitrile was used as a substrate selective addition to vinyl group was observed. The hydrosilylation of isopropylaldehyde with $HSi(Me_3Si)_3$ proceeds efficiently in water, in the presence of 1,1'-azobis(cyclohexanecarbonitrile) (ACCN) leading to formation of isopropyl silyl ether with 90% yield [207]. Aldehydes and ketones undergo free-radical hydrosilylation with oligosilanes initiated by AIBN to form a variety of substituted polysilanes [208]. The reaction is tolerant to a number of polar groups (-OH, $-NH_2$, -COOH) and provides a one-step procedure for introducing functional groups in side chains of polysilane. Hydrosilylation of a variety of carbonyl compounds efficiently proceeded when carbonyl compounds were treated with trimethylsilyl phenylselenide and tributylstannyl hydride in the presence of a catalytic amount of AIBN [209]. The reactions of aldehydes, ketones or α,β-diketones lead to formation of the corresponding silyl ethers in moderate yields. In the absence of carbonyl compounds, the reaction of $PhSeSiEt_3$ with Bu_3SnH produces triethylsilyl hydride. Aldehydes and ketones undergo hydrosilylation with dimethylphenylsilane catalysed by perrhenic acid, [$HReO_4$]. The reaction leads to formation of silyl ethers in good yields. Inhibition of the process by radical scavengers such as 5,5-dimethyl-4,5-dihydro-3H-pyrrole-*N*-oxide (DMPO) and Ph_2NH indicates the radical mechanism of [$HReO_4$] catalysed addition [150]. The covalent attachment of monolayers to semiconductor surfaces is of growing interest as a potential route to surface passivation or incorporation of chemical (or biochemical) functionality. Light-induced hydrosilylation of aldehydes with Si(111)-H results in formation of Si(111)-OCH_2R surface [210]. A similar

reaction was successfully achieved via thermal activation at moderate temperatures (85°C) [211].

9.1.6 Metal and Supported Metal Catalysts

Fine nickel powder obtained by reduction of nickel iodide with Na or Cd was demonstrated to be catalytically active in hydrosilylation of benzaldehyde with $HSiEt_3$ [212]. From among the other metals tested (Ti, Zr, Mo, W) only molybdenum obtained by reduction of $[MoCl_5]$ or $[MoOCl_4]$ with zinc enabled efficient formation of hydrosilylation products. Activated nickel produced by the ultrasound assisted reduction of nickel iodide with lithium catalysed the efficient and selective 1,4-addition of phenylsilanes to α,β-unsaturated ketones [213].

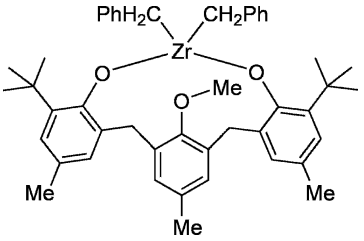
9.1.7 Hydrosilylation of CO_2

A search for the utilisation of carbon dioxide as an inexpensive and widely available raw material for chemical syntheses remains a challenge for chemists and fits well within the concept of "green chemistry". The hydrosilylation of CO_2 is a relatively poorly recognised process [214–219].

$RuCl_3 \cdot nH_2O$ catalyses the hydrosilylation of carbon dioxide with $HSi(C_6H_{13})_3$ or $HSiMe_2Ph$ in MeCN to give formoxysilanes $R_3SiOOCH$. The initial catalyst formed was identified as *trans*-$[Ru^{II}Cl(MeCN)_5][Ru^{III}Cl_4(MeCN)_2]$ [220]. Nitriles were found favourable solvents for this reaction. The catalytic activity of $[RuCl(MeCN)_5]^+[(trans)\text{-}RuCl_4(MeCN)_2]^-$ is increased by introduction of phosphine ligand. The catalyst may be recycled effectively by a thermal separation of the reaction product. By using this procedure, no loss of catalytic activity was observed over 10 runs [221]. An account of new developments in the CO_2 hydrosilylation catalysed by ruthenium nitrile complexes and a suggestion for the relevant mechanism on the basis of the experimental and DFT studies was provided by Deglmann, Hofmann and Pitter [222]. Ruthenium complexes, *mer*-$[RuX_3(MeCN)_3]$ and *cis*/*trans*-$[RuX_2(MeCN)_4]$ (where X=Br, Cl) are active precatalyst in the hydrosilylation of CO_2 with $HSiMe_2Ph$. The resulting formoxysilanes were obtained with high yield and selectivity. The general sequence of these catalysts' activity in the CO_2 hydrosilylation was found to be $RuCl_mL_n$ > $RuBr_mL_n$ and Ru(III) > Ru(II). According to DFT calculations, the key steps of the mechanism involve: transfer of the Me_3Si moiety to a coordinated halide ligand, resulting in an $LnRuH(XSiMe_3)$ intermediate, CO_2 coordination, silyl group transfer to CO_2 and reductive elimination of formoxysilane product.

Homogeneous reduction of carbon dioxide with silanes catalysed by zirconium complex (Fig. 9.45) combined with $B(C_6F_5)_3$ led to formation of methane and siloxanes [223]. By proper choice of the silane or by tuning of the [Zr]/[B] ratio, the formation of bis(silyl)acetals such as $(Et_3SiO)_2CH_2$ and $(Ph_3SiO)_2CH_2$ could be obtained with the yield 82 and 64%, respectively.

Fig. 9.45



The reduction of CO_2, by H_2SiMe_2, H_2SiEt_2 and $HSiMe_3$ in the presence of [Ir(CN)(CO)(dppe)] occurring at ambient temperatures and pressures yields methyl silyl ether and siloxanes. The mechanism was proposed to involve subsequent hydrosilylation to both C=O bonds followed by a reduction of bis(silyl)acetal with another silane molecule [224].

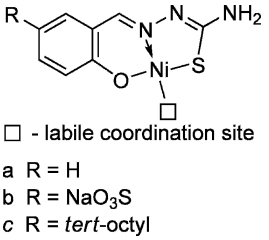
9.2 Hydrosilylation of C=N Bond

9.2.1 Transition Metal Complexes as Catalysts

A range of imines undergo hydrosilylation with PMHS in the presence of $ZnCl_2$ [225]. The corresponding amines were obtained (after hydrolysis step) with moderate yield (50–75%). The α,β-unsaturated imines undergo selective 1,2-addition. A convenient protocol for selective hydrosilylation of dialkyl imines with PMHS in the presence of $ZnEt_2$ / dbea / PMHS (dbea=*N*,*N'*-dibenzylethylenediamine) was described by Carpentier [18]. The reaction enables formation of the corresponding amines in high yields in one step procedure. The use of MeOH as a solvent permits avoidance of a hydrolysis step. Gold complex [$AuCl(PPh_3)$] in the presence of an excess of PBu_3 was found active in the hydrosilylation of *N*-phenyl benzaldimine with $HSiMe_2Ph$ [44] to give after hydrolysis the corresponding amine with 83% yield.

A series of papers reporting the hydrosilylation of a wide range of heterocyclic aldimines in the presence of transition metal complexes were published by Lukevics [226–229]. The rhodium ([$\{RhCl(cod)\}_2$]) and palladium ([$\{PdCl(allyl)\}_2$]) complexes were found the most active precatalysts of the reaction. The yields, chemo- and regioselectivities obtained depend on the specificity of the reaction system, especially on the nature of the functional groups in the imine molecules. In the presence of alkylsilanes, the cationic Ir(I) complex [Ir{bis(pyrazol-1-yl)methane}$(CO)_2$][BPh_4] (Fig. 9.31) catalyses the hydrosilylation *N*-alkyl and *N*-aryl imines leading to silylamines, which are conveniently protodesilylated with MeOH to form amines. Moderate to high conversions were achieved at room temperature [230]. *N*-phenyl imines and *N*-benzylphenylmethyl imine undergo reduction with twofold excess of triethylsilane in the presence of nickel catalyst (Fig. 9.46) formed in situ from nickel(II) acetate and the thiosemicarbazones. The reaction results in the formation (after basic hydrolysis) of secondary amines with moderate to high yield and

Fig. 9.46



□ - labile coordination site

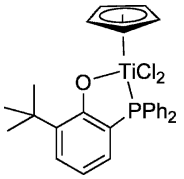
a R = H
b R = NaO_3S
c R = *tert*-octyl

is sensitive to steric properties of substituents at carbon. Low yields were observed for diphenyl- or bornan-2-yl imines [231].

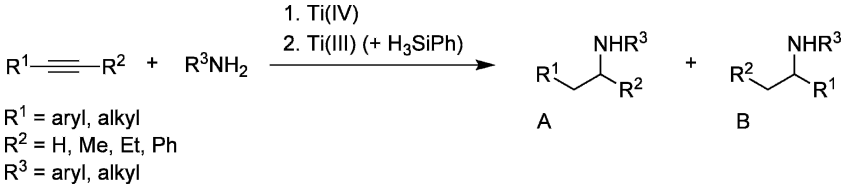
The compound [MoO_2Cl_2] was found to be a precatalyst that allows efficient reduction of *N*-aryl imines with phenylsilane or PMHS [232]. The corresponding amines were obtained with moderate to high yield (45–100%). The reaction is an example of the use of metals on their high oxidation state in catalysis of reduction processes.

Titanium complexes bearing 2-phosphinophenol ligand (Fig. 9.47) treated with BuLi and phenylsilane form the catalyst that allow a quantitative conversion of PhCH=NMe in the hydrosilylation with H_3SiPh [233].

Fig. 9.47



A number of titanocene complexes exhibit catalytic activity in the hydrosilylation of ald- and ketimines with diphenylsilane [234]. The highest conversions (up to 98%) at room temp. were observed for complex (Fig. 9.48). The sequence of [Cp_2TiMe_2] (Fig. 9.49) catalysed intermolecular hydroamination of mono- and disubstituted alkynes with primary amines and the Ti-catalysed hydrosilylation of imines with phenylsilane, was performed as efficient one-pot process (Eq. 9.44) [235].



R^1 = aryl, alkyl
R^2 = H, Me, Et, Ph
R^3 = aryl, alkyl

(9.44)

Fig. 9.48

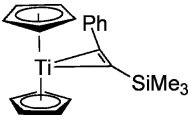
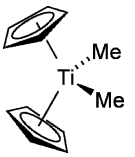
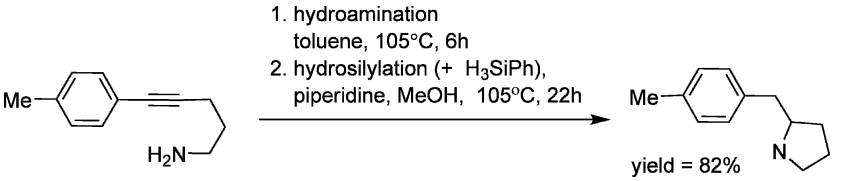


Fig. 9.49



The sequence requires *in situ* conversion of Ti(IV) complex that is catalytically active in hydroamination into the Ti(III) complex, presumed to be active in the hydrosilylation realised after hydroamination step by treatment of the reaction mixture with phenylsilane (that is also a stoichiometric hydrogen source in the reduction step), piperidine and methanol. The yield and selectivity depend on the properties of the substituents at both reagents. The highest yields (83–99%) and selectivities (A/B = 99/1) were observed for the reactions employing aryl,methyl- substituted acetylenes and 4-substituted arylamines. Intramolecular hydroamination / hydrosilylation sequence of amineacetylenes catalysed by (Fig. 9.50) allows formation of cyclic amines with the yield up to 82% (Eq. 9.45) [235].



(9.45)

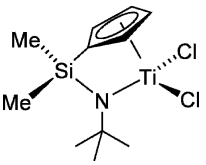
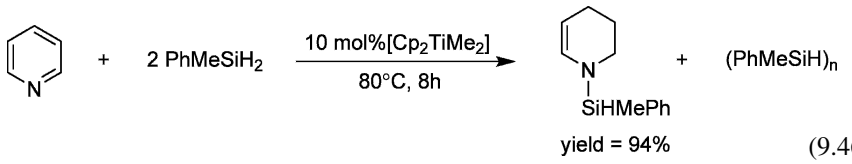


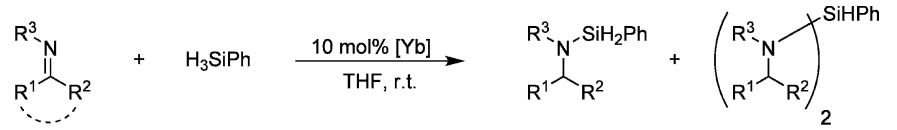
Fig. 9.50

Unprecedented homogeneous catalytic hydrosilylation of pyridines with phenyl- and phenylmethylsilane was reported by Harrod and Samuel (e.g. Eq. 9.46) [236, 237]. In the presence of $[Cp_2TiMe_2]$ and $[Cp^*CpTiMe_2]$, the corresponding products were obtained with moderate to high yields. Moderate H_2 pressure allows the synthesis of di- and terahydropyridines. Regioselectivity and the level of reduction are sensitive to the ring substitution. The initial step of the reaction was proposed to be the addition of Ti-Si species to the carbon-nitrogen bond of the pyridine to form *N*-silyldihydropyridine.



(9.46)

Ytterbium imine complex (Fig. 9.51) was reported to exhibit catalytic activity in the hydrosilylation of simple ald- and ketimines with phenylsilane (Eq. 9.47) [238, 239]. The reaction lead to the formation of a mixture of mono- and diaminosilanes.



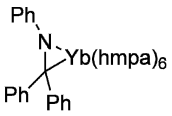
R^1 = Ph, C_7H_{15}, Pr, iPr; R^2 = H, Me; R^3 = Ph, Me, C_5H_{11} or R^1 R^2 = cyclohexyl; R^3 = C_5H_{11}

yield = 2–52%
yield = 56%

yield = 17–95%
yield = 0%

(9.47)

Fig. 9.51



hmpa - hexamethylphosphoramide

9.2.2 Main Group Metal-Based Catalysts

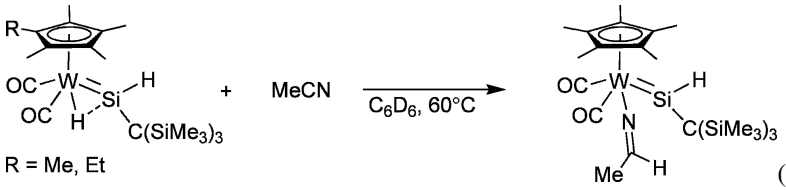
A wide range of imines undergo hydrosilylation with polymethylhydrosiloxane (PMHS) in ethanol in the presence of catalytic amount of butyltris(2-ethylhexanoate)tin [240]. The corresponding secondary amine products were obtained in mild conditions with 75–84% yield. Alkyl bromides, alkynes, epoxides, esters, nitriles, and olefins remained unaffected by using this protocol.

9.2.3 Nucleophilic-Electrophilic Catalysis

Both *N*-tosyl aldimines and ketimines were efficiently reduced to tosylamides (62–100%) in the presence of catalytic amount of lithium methoxide [177]. Benzaldimines and ketimines undergo efficient hydrosilylation with $HSiMe_2Ph$ in the presence of 5–10 mol% of $B(C_6F_5)_3$ [241]. The reaction leads to the formation of amines with the yield dependent on the substituent at nitrogen. For *N*-aryl, *N*-benzyl and *N*-sulphonyl imines the reaction proceeds smoothly at room temperature. *N*-allyl amine was obtained with moderate yield (57%) and no reaction was observed for *N*-methyl benzaldimine. The mechanism of the reaction was proposed as analogous to that proved for $B(C_6F_5)_3$ catalysed hydrosilylation of carbonyl derivatives (Scheme 9.5) and strongly supported by the spectral evidence for the intermediacy of silyliminium / hydridoborate ion pair.

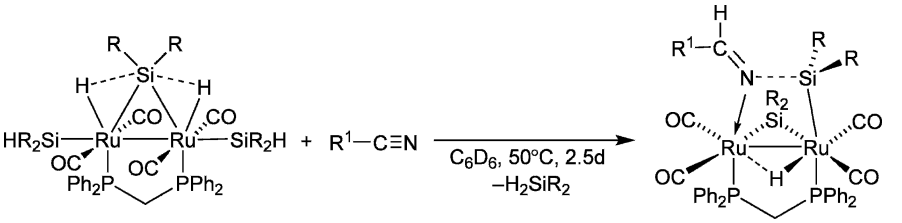
9.3 Hydrosilylation of C≡N Bond

Stoichiometric hydrosilylation of nitriles was observed in the coordination sphere of hydrido(hydrosilylene)tungsten complexes (Eq. 9.48) [163].



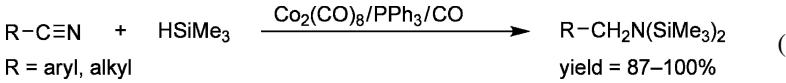
(9.48)

[{Ru(CO)$_2$(SiR$_2$H)}$_2$(μ-dppm)(μ^2-η^2:η^2-H$_2$SiR$_2$)] (where R=4-C$_6$H$_4$Me) bearing coordinated diarylsilane undergoes stoichiometric reaction with nitriles R^{1}CN (R^1=Me, Ph, *t*-Bu, CH=CH$_2$) to give silylimine complex, being a product of formal stoichiometric hydrosilylation of nitrile (Eq. 9.49) [132].



(9.49)

Efficient hydrosilylation of a wide variety of nitriles with HSiMe$_3$ was observed in the presence of [Co$_2$(CO)$_8$] [242, 243]. Aromatic nitriles with electron donating substituents generally react smoothly at 60°C to give the corresponding *N*,*N*-disilylamines in high yield (up to 91%). [Co$_2$(CO)$_8$] combined with PPh$_3$ catalyses the hydrosilylation of aliphatic nitriles leading to bis(silyl)amine derivatives with 87–100% yield (Eq. 9.50). The selectivity of the hydrosilylation of α,β-unsaturated nitriles depends on the substitution pattern of the substrate.

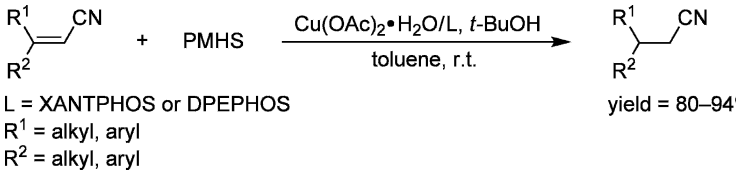


(9.50)

Rhodium dust prepared from mesitylene solvated rhodium atoms unsupported or supported on γ-Al$_2$O$_3$ is catalytically active in the hydrosilylation of aromatic nitriles with trimethyl- or trimethoxysilane. The corresponding bis(silyl)benzylamines were formed with the isolated yields up to 95% for unsupported and up to 75% for supported systems [244]. Commercially available Rh / γ-Al$_2$O$_3$ catalyst was found moderately active in the same test-reaction. The hydrosilylation of α,β-unsaturated (*E*)-cinnamonitrile led to the formation of a mixture of vinyl addition

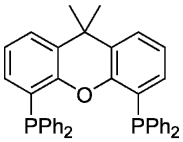
and 1,4-hydrosilylation products, whose composition was found to depend on the reaction temperature. The 1,4-addition of phenylsilanes to α,β-unsaturated nitriles proceeds efficiently and selectively in the presence of activated nickel, obtained by ultrasound promoted reduction of nickel iodide with lithium [213]. Efficient of 1,4-hydrosilylation of α,β-unsaturated nitriles with PMHS was observed in the presence of [IPrCu(OAc)$_2$] (Fig. 9.1) [15]. The reaction proceeds in the presence of *t*-BuOH at room temperature and permitted obtaining saturated nitriles with 82–94% of isolated yield.

The α,β-unsaturated nitriles were chemoselectively reduced with polymethylhydrosiloxane (PMHS) to the corresponding saturated nitriles using a copper diacetate precursor, XANTPHOS (Fig. 9.52) or DPEPHOS (Fig. 9.53) diphosphine ligands and stoichiometric amounts of *tert*-butanol as additive (Eq. 9.51) [245]. The active Cu(I)–H was generated by treatment of copper(II) acetate with organosilane.



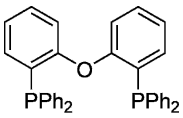
(9.51)

Fig. 9.52



XANTPHOS

Fig. 9.53

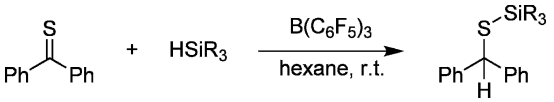


DPEPHOS

9.4 Hydrosilylation of Other Multiple Bonds

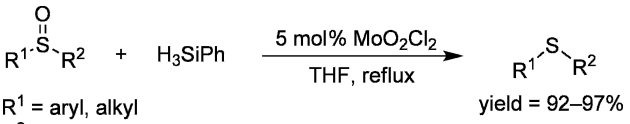
The hydrosilylation of thiobenzophenone with substituted mono- and disilanes ($HSiPh_3$, $HSiEt_3$, $HSiMePh_2$, $HSiMe_2Ph$ and $HSiMe_2SiMe_2H$) occurs quantitatively at room temperature in the presence of catalytic amounts of $B(C_6F_5)_3$ to furnish new silyl thioether compounds (Eq. 9.52) [246]. The catalyst was found to be sensitive to steric hindrance around the silane reagent. The TOF observed

ranged from $17h^{-1}$ to $30{,}000h^{-1}$. The highest value was noted for the reaction with $HSiMe_2Ph$. The method makes a clean route to formation of Si-S linkages.



(9.52)

Sulphoxides were efficiently reduced with H_3SiPh in the presence of catalytic amount of $[MoO_2Cl_2]$ (Eq. 9.53) [247]. The corresponding sulphides were synthesised in high yields. The system allows selective reduction of S=O bond in the presence of C=C or ester group. The more environmental friendly protocol proposed enables a reduction of sulphoxides with the air-stable catalyst system PMHS/$[MoO_2Cl_2(H_2O)_2]$ in water or methanol.



(9.53)

Tetrahydrodisiloxane bearing two azogroups (Eq. 9.54) and its (*Z,Z*)-derivative containing tetracoordinate silicon undergoes fluoride catalysed intramolecular hydrosilylation [248].

(9.54)

References

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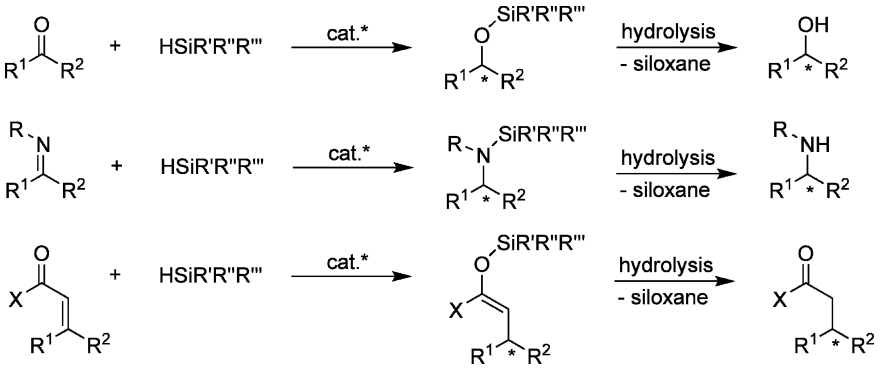
Chapter 10
Asymmetric Hydrosilylation of Unsaturated Carbon–Heteroatom Bonds

Abstract Asymmetric, catalytic hydrosilylation of prochiral ketones and imines with substituted silanes or siloxanes followed by hydrolysis provides a convenient access to chiral alcohols and amines, respectively. In this chapter, the asymmetric hydrosilylation of carbonyl compounds and imines as well as the asymmetric conjugate reduction of α,β-unsaturated enones, nitriles, sulphones and nitroalkenes are reviewed. Synthetic, catalytic and mechanistic aspects of the reactions ocurring in the presence of complexes of such transition metals as zinc, copper, rhodium, ruthenium, iridium, titanium and others are discussed. Moreover, catalysis of asymmetric hydrosilylation complexes of the main group metals, nucleophiles (including organocatalysts) and electrophiles is described.

Chiral building blocks are indispensable for the syntheses of biologically active compounds, pharmaceuticals, agrochemicals, flavours, fragrances and fine chemicals. Asymmetric, catalytic hydrosilylation of prochiral ketones and imines with substituted silanes or siloxanes followed by hydrolysis provides convenient access to chiral alcohols and amines, respectively (Scheme 10.1).



Scheme 10.1 (**a**) Asymmetric hydrosilylation of ketones; (**b**) asymmetric hydrosilylation of imines; (**c**) asymmetric 1,4-hydrosilylation (conjugate reduction) of α,β-unsaturated enones. Subsequent hydrolysis steps were indicated

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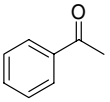
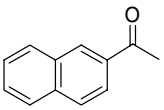
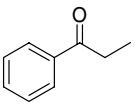
The first reports on the catalytic asymmetric hydrosilylation of carbonyl compounds appeared in the early 1970s. Platinum [1] and rhodium [2–4] complexes of chiral monodentate or bidentate phosphine ligands were found active in asymmetric reduction of acetophenone to give 1-phenylethanol with 29–43% ee. In 1973 Kagan reported the first example of catalytic enantioselective hydrosilylations reductions of imines occurring in the presence of rhodium precursor combined with non-racemic diphosphine. The corresponding amine was obtained with 50% ee [5]. Since then considerable progress have been made and highly active and enantioselective catalytic systems have been discovered. In this chapter advances in asymmetric hydrosilylation of carbon-heteroatom unsaturated bond achieved since 1990 has been detailed. This subject is covered by several reviews [6–15].

10.1 Asymmetric Hydrosilylation of C=O Bond

10.1.1 Transition Metal Complexes as Catalysts

The discovery by Mimoun from Firmenich S.A. of effective Zn-based catalyst for hydrosilylation of carbonyl derivatives with PMHS (polymethylhydrosiloxane) has been a breakthrough in asymmetric hydrosilylation, especially because it was an economic system designed for commercial use [16]. In 1999 Mimoun reported enantioselective reduction of ketones, particularly acetophenones, with PMHS in the presence of chiral zinc catalysts. The corresponding secondary alcohols were formed with high yields and enantiomeric excess reaching 88% [17]. Two developed catalytic systems involve $ZnEt_2$ (or $ZnMe_2$) combined with chiral diimine or diamine and $Zn(carboxylate)_2$ / chiral diamine, activated by $NaAlH_2(OCH_2CH_2OCH_3)_2$ (Vitride). Zinc diethylacetate or 2-ethylbutyrate are inexpensive, stable in solution and safer metal sources in comparison with organozinc compounds. Both systems permit getting similar yields and enantioselectivities. A number of chiral diimines, diamines and aminoalcohols were screened for their applicability as ligands in zinc-based catalytic system. Best catalytic performance in asymmetric hydrosilylation of acetophenone with PMHS was observed when chiral secondary diamine ligands were used (Table 10.1). The highest ee was achieved for *N,N′*-(1,2-diphenylethylene)bis(benzylamine) (Fig. 10.1) (yield = 98%, ee = 88%). Cheap and easy to prepare *N,N′*-ethylenebis(1-phenylethylamine) (ebpe) (Fig. 10.2a) allows quantitative synthesis of 1-phenylethanol (after hydrolysis step) with 75% ee. Several aryl ketones were transformed in the presence of $ZnEt_2$ / (*R*,*R*)-ebpe or $Zn(dea)_2$ / (*R*,*R*)-ebpe / Vitride at room temperature into the corresponding alcohols with enantioselectivity ranging from 64 to 81% [17]. A number of chiral diamines were tested in the zinc-catalysed enantioselective hydrosilylation of acetophenone. Diamines (Figs. 10.3–10.5) [18] and (Fig. 10.6) [19, 20], which combine chiral backbones and chiral *N,N′*-α-phenylethyl substituents, allow highly enantioselective reductions (up to 91% ee). Prochiral acetophenone derivatives and α,β-unsaturated aromatic ketones were reduced in

Table 10.1 Zinc catalysed asymmetric hydrosilylation of ketones with PMHS

Ketone	Ligand or catalyst	Time [h]	Yield [%]	ee[a] [%] (config.)	Ref.
	Fig. 10.1	18	98 (conv.)	88 (*R*)	[17]
	Fig. 10.2a	18	99 (conv.)	75 (*R*)	[17]
	Fig. 10.3	24	90	83 (*R*)	[18]
	Fig. 10.4	18	99	84 (*R*)	[18]
	Fig. 10.5	24	95	83 (*R*)	[18]
	Fig. 10.6	288	66	91 (*R*)	[19]
	Fig. 10.7	2	100	51	[22]
	Fig. 10.2a	ca 12	–	80	[17]
	$Zn(dea)_2$/Fig. 10.2a/Vitride	ca 12	–	76	[17]
	Fig. 10.3	288	72	84 (*R*)	[18]
	Fig. 10.2a	ca 12	–	77	[17]
	$Zn(dea)_2$/Fig. 10.2a/Vitride	ca 12	–	81	[17]
	Fig. 10.3	24	80	89 (*R*)	[18]
	Fig. 10.8	16	83	73 (*S*)	[24]

Reaction conditions: 2–5 mol% $ZnEt_2$; [Zn]:[L*] = 1:1; PMHS (1.2–2.0 equiv.); r.t.;
[a]determined after hydrolysis

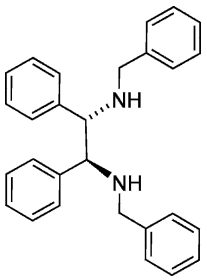
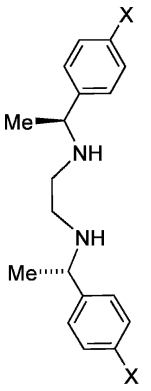


Fig. 10.1



a X = H; b X = Br
c X = Cl; d X = F

Fig. 10.2

Fig. 10.3

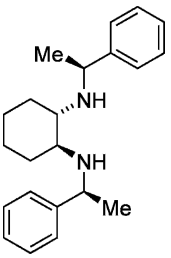


Fig. 10.4

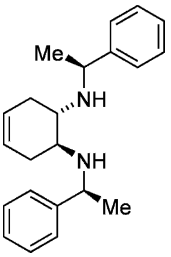


Fig. 10.5

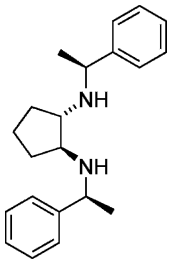
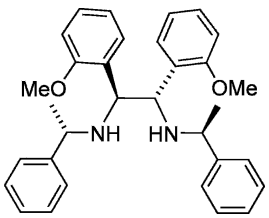
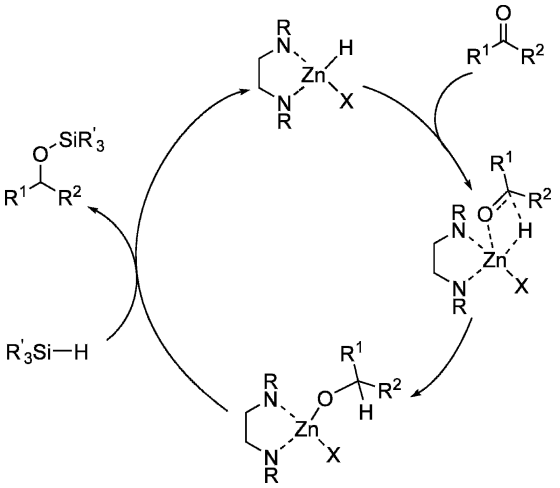


Fig. 10.6



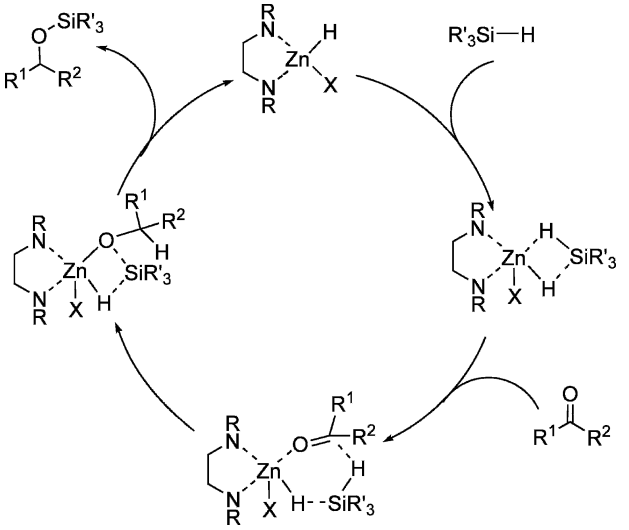
the presence of ligand (Fig. 10.5) with very high selectivity (Table 10.1) [18]. High enantioselectivity has been observed for Zn / diamine systems using PMHS [19, 20].

Three different mechanisms are considered which are compatible with the experimental data obtained (Schemes 10.2–10.4) [17]. According to mechanism presented in (Scheme 10.2), hydrogen is transferred from zinc hydride complex to coordinated ketone via a transition state involving pentavalent zinc. Such reactions were shown to occur in the presence of isolated zinc hydride complexes.



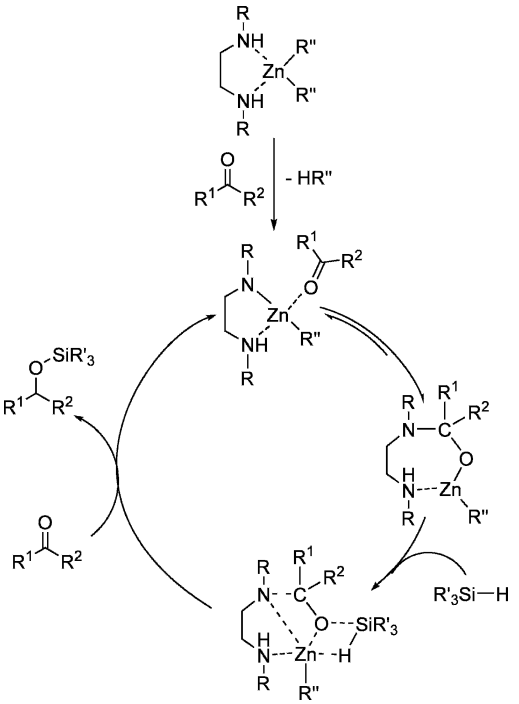
Scheme 10.2 Proposed mechanism of zinc catalysed asymmetric hydrosilylation of ketones assuming hydrogen transfer via pentavalent transition state

In alternative pathway, zinc hydride forms an adduct with silane (a reactive pentavalent silicon hydride associated to zinc Lewis acid center is formed). Then hydrogen is transferred to the carbon atom of ketone coordinated to zinc.



Scheme 10.3 Proposed mechanism of zinc catalysed asymmetric hydrosilylation of ketones assuming formation of pentavalent silicon hydride associated to zinc

In pathway illustrated in Scheme 10.4 it is assumed that diamine is not a spectator ligand but it is involved in substrate activation. According to this mechanism, the coordinated carbonyl compound is inserted to the zinc—nitrogen bond



Scheme 10.4 Proposed mechanism of zinc catalysed asymmetric hydrosilylation of ketones assuming insertion of coordinated carbonyl into Zn—N bond

of the deprotonated, coordinated secondary diamine. This pathway is supported by isolation and characterisation of dimeric complex in which ketone is inserted into Zn—N bond [17].

Zn-promoted reduction of various ketones with PMHS in protic conditions proceeds significantly faster than in toluene but at the expense of decreased enantioselectivity (down to 55%) obtained using a variety of enantiopure diamine ligands. Preliminary mechanistic investigation indicates participation of an alcohol in the *in situ* generation of the catalyst [21]. Air and moisture stable N,S-chelating zinc catalyst (Fig. 10.7) in combination with $ZnEt_2$ is highly active and moderately enantioselective in hydrosilylation of aryl alkyl ketones with PMHS (Table 10.1) [22]. Complexes generated *in situ* by the treatment of $ZnEt_2$ with chiral diamine (Fig. 10.2 a–d) and ethylene (or propylene) glycol catalyse asymmetric reduction of benzophenones substituted at the *ortho*-positions with PMHS to give (after hydrolysis) respective alcohols with high yields and enantioselectivities up to 99%. The reactions require the presence of molecular sieves and relatively high metal concentration (typically 10 mol%). Application of non-racemic BINOL ligand instead of glycol does not change the enantioselectivity [23]. Enantiomerically pure diaminobis(*tert*-thiophene) (Fig. 10.8) proved to be a valuable chiral ligand for Zn-catalysed hydrosilylations of prochiral carbonyls (ee up to 97%) (Table 10.1) [24].

Fig. 10.7

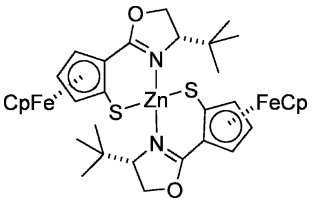
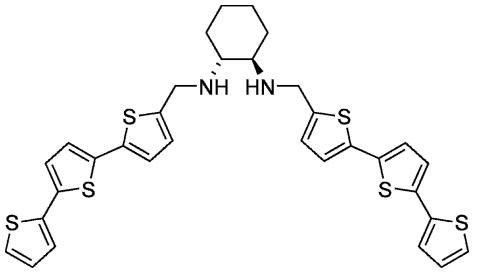
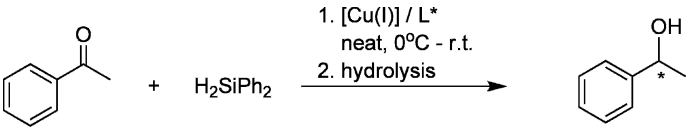


Fig. 10.8



Copper catalysed 1,4-hydrosilylation of α,β-unsaturated derivatives was developed as a consequence of the search for reduction protocols using hydrogen sources different than dihydrogen. Dihydrogen was found not to be the optimal reducing agent in copper catalysed reduction as its activation in the σ-metathesis step is slow even at elevated pressures and often leads to overreduction. Optimisation of the catalytic system involved replacement of dihydrogen by the silanes or hydrosiloxanes, especially PMHS which completely prevents overreduction by stabilizing the enol form by formation of a silyl ether. Further optimisation of the system involved the application of more stable sources of copper, variations of the base and the use of the new ligands [25]. Progress in copper catalysed hydrosilylation of carbonyl compounds and imines has been recently reviewed [25–27].

First copper(I) catalysed reduction of ketones with diphenylsilane $H_2SiPh_2$was reported by Brunner (Eq. 10.1) [28]. The catalytic system used contained the copper(I) precursor CuO(*t*-Bu) or $CuO_2CC_6H_5$ and non-racemic chelate phosphines (*S*,*S*)-DIOP (Fig. 10.9), (*S*,*S*)-NORPHOS (Fig. 10.10) or (*R*,*S*)-BPPFA (Fig. 10.11) allow enantioselective course of the reaction. However, low enantiomeric excess (up to 38.8% ee) was observed.



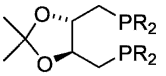
(10.1)

[Cu(I)] / L* = CuO(*t*-Bu) / (*S*,*S*)-DIOP — yield = 100%, ee = 20%

[Cu(I)] / L* = $Cu(O_2CC_6H_5)$ / (*S*,*S*)-NORPHOS — yield = 51%, ee = 38.8%

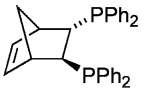
High level of efficiency and enantioselectivity was attained by the use of chiral diphosphine copper catalyst. The first examples of enantioselective reduction of α,β-unsaturated esters were reported by Buchwald (Eq. 10.2) [29].

Fig. 10.9



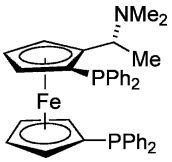
(*S*,*S*)-DIOP

Fig. 10.10

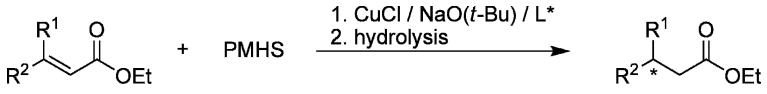


(*S*,*S*)-NORPHOS

Fig. 10.11



(*R*,*S*)-BPPFA



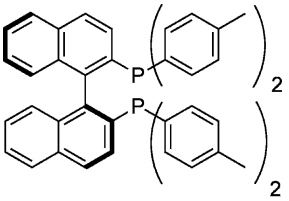
(10.2)

R^1 = Me, Et; R^2 = Ph, alkyl, alkenyl
L* = (*S*)-tol-BINAP

yield = 84–98%
ee = 80–92%

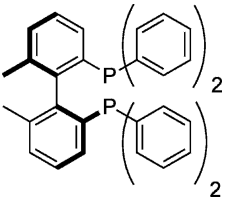
Combination of CuCl as a copper source with NaO(*t*-Bu) and (*S*)-tol-BINAP (Fig. 10.12) generated a highly enantioselective catalytic system. Important advantages of the system developed by Buchwald is *in situ* generation of CuO(*t*-Bu) (which is air sensitive), the use of cheap and commercially available polymethylsiloxane (PMHS) as hydride source and commercially available phosphine ligand.

Fig. 10.12



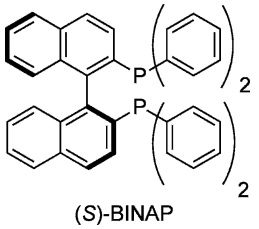
(*S*)-tol-BINAP

Fig. 10.13



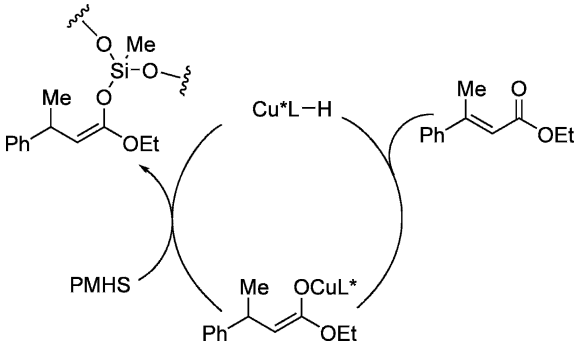
(*S*)-BIPHEMP

Fig. 10.14



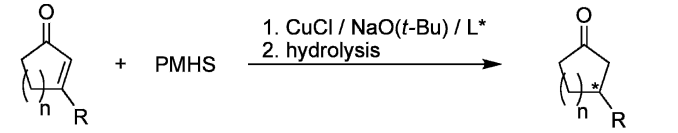
(*S*)-BINAP

Buchwald proposed the catalytic cycle in which ligated copper hydride is a real catalyst. The active hydride complex is proposed to be generated by the σ-bond metathesis between copper *tert*-butanolate and PMHS. Then the conjugate reduction takes place leading to the formation of copper enolate, that subsequently undergoes σ-bond metathesis with PMHS to form silyl enol ether and regenerate the hydride complex (Scheme 10.5) [29].



Scheme 10.5 Mechanism of copper catalysed asymmetric conjugate reduction of enones with PMHS

A similar system was used for cyclic, α,β-unsaturated ketones (Eq. 10.3) [30].



R = alkyl
L* = (*S*)-tol-BINAP

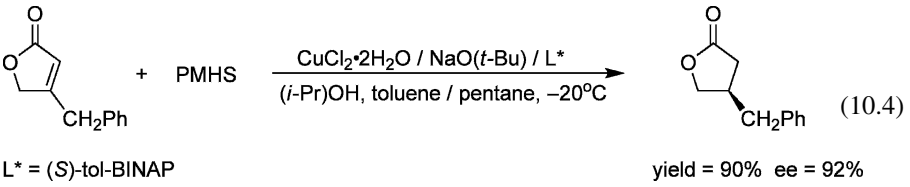
yield = 61–88%
ee = 87–98%

(10.3)

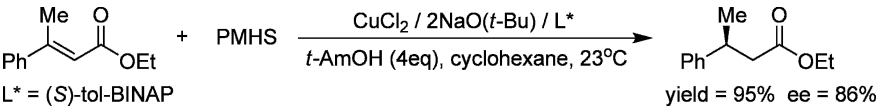
In this case besides (*S*)-tol-BINAP (Fig. 10.12) also (*S*)-BIPHEMP (Fig. 10.13) or (*S*)-BINAP (Fig. 10.14) were used as ligands. Especially high yields and selectivities were observed for cyclopentenones. With the use of cyclohexenone and cycloheptenone the reaction is less selective and 1,2-reduction has also been observed to some extent.

Good to excellent yields and enantioselectivities were obtained in conjugate reduction of α, β-unsaturated lactones (Eq. 10.4), lactams, and esters (Eq. 10.5) using

a catalyst generated *in situ* from $CuCl_2 \cdot H_2O$, NaO(*t*-Bu), tol-BINAP, and PMHS. The procedures proposed allow the catalytic enantioselective formation of five- and six-membered lactones and lactams possessing a β-stereocenter. It was found that the rate of the conjugate reduction was dramatically accelerated upon introduction of alcohol additives to the system [31].



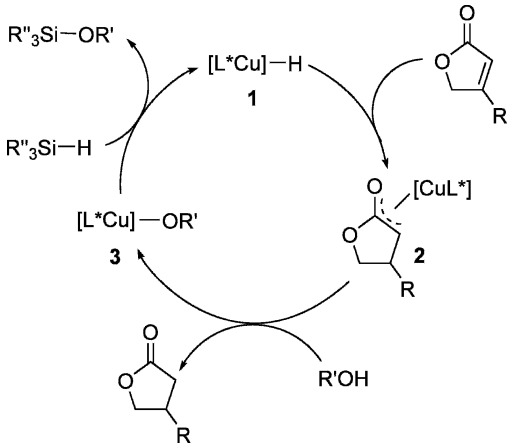
(10.4)



(10.5)

This protocol was applied in the total synthesis of eupomatilone-3 [32]. Further extension of the applicability of the reaction involved β-azaheterocyclic and α,β-unsaturated esters [33].

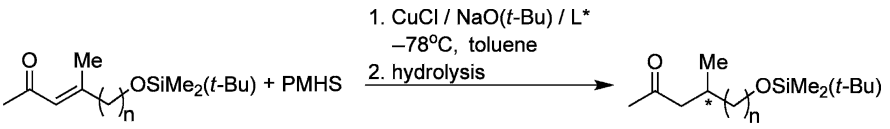
A mechanism was proposed (Scheme 10.6) suggesting the formation copper enolate (**2**) which subsequently reacts with alcohol to form saturated lactone and copper alkoxide (**3**). Complex (**3**) is proposed to undergo σ-bond metathesis with silane much faster than **2**. σ-Bond metathesis leads to formation of silyl ether and to regeneration of copper hydride (**1**) [31].



Scheme 10.6 Proposed mechanism of copper catalysed asymmetric 1,4-hydrosilylation of unsaturated lactones in the presence primary alcohol

Recently, hydrosilylation of aryl alkyl ketones, which affords chiral secondary alcohols with good yields and very high enantioselectivity (up to 99%) has been realised for BINAP combined with nanocrystalline copper(II) oxide as metal source [34].

Lipshutz reported a protocol allowing asymmetric reductions of prochiral conjugate enones with PMHS to give products with highly stereodefined centres β to acyclic ketones (Eq. 10.6) [35].



L* = (*R*,*S*)-JOSIPHOS — yield = 94% ee = 94%

L* = (*R*,*S*)-PPF-P(*t*-Bu)$_2$ — yield = 94% ee = 98%

(10.6)

The reactions proceed in the presence of copper hydride (generated *in situ* from CuCl(I), NaO(*t*-Bu) and PMHS) combined with non-racemic ferrocene-derived ligands. Such ligands (Figs. 10.15 and 10.16) were found particularly effective and allowed enantioselectivity reaching 99%. The system enabled reduction of the substrate to ligand ratio to 1650:1 and the catalyst concentration up to 1 mol% [35].

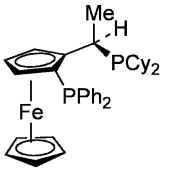


Fig. 10.15 (*R*,*S*)-JOSIPHOS

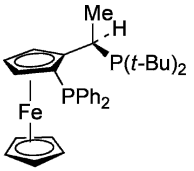
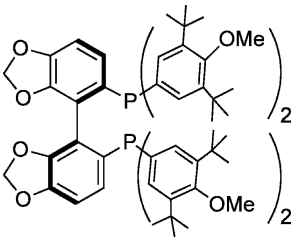


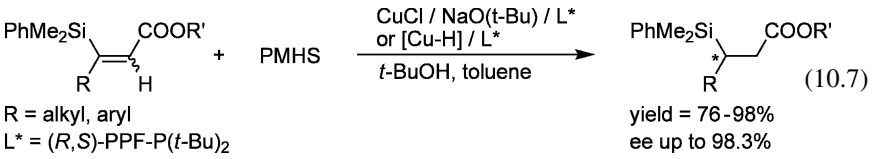
Fig. 10.16 (*R*,*S*)-PPF-P(*t*-Bu)$_2$

JOSIPHOS (Fig. 10.15) and SEGPHOS (Fig. 10.17) non-racemic bis-phosphines, when complexed with copper hydride, were found to exert high degrees of facial selectivity in 1,4-hydrosilylation of β,β-disubstituted enoates. Acyclic α,β-unsaturated esters were transformed into the corresponding esters with ee reaching 99% [36]. Non-racemic PPF-P(t-Bu)$_2$ (Fig. 10.16) was successfully used in the copper catalysed asymmetric hydrosilylation of β-silyl-α,β-unsaturated esters with PMHS (Eq. 10.7) [37].

Fig. 10.17

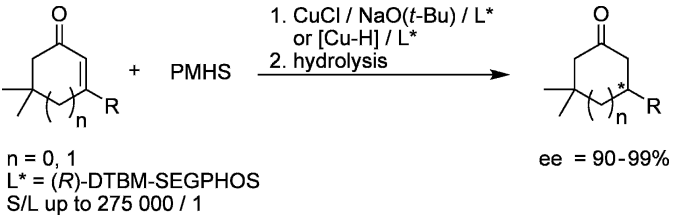


(*R*)-DTBM-SEGPHOS



(10.7)

In situ generated (*R*)-DTBM-SEGPHOS-chelated copper hydride catalyses the conjugate reductions of β-substituted cyclic enones with PMHS allowing enantioselectivity up to 99% at a large substrate to ligand ratio (Eq. 10.8) [38].



(10.8)

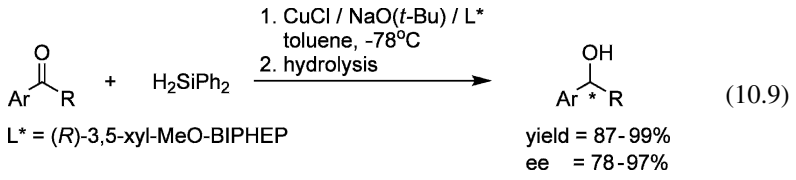
Exposure of a variety of prochiral substrates to [CuH{(*R*)-DTBM-SEGPHOS}] and PMHS under microwave or conventional heating conditions reduces the reaction times for these hydrosilylations from hours to minutes without a significant drop in enantioselectivity [39].

A stable and ready to use asymmetric hydrosilylation reagent – "Cu-H in a bottle" – the copper hydride complexed by (*R*)-DTBM-SEGPHOS (Fig. 10.17) has been prepared and proved to remain active on storage (no decrease in activity after two week storage at room temperature) [40]. High activity and enantioselectivity of this reagent was demonstrated for 1,4-hydrosilylation of cyclic α,β-unsaturated ketones, α,β-unsaturated esters and for α-hydrosilylation of simple aryl alkyl ketones. Recently, Lipshutz reported on a heterogeneous catalyst for a variety of asymmetric reductions [41]. Copper(II) immobilised on charcoal was employed as a precatalyst. In combination with NaOPh and small amounts of SEGPHOS ligand (Fig. 10.17), in the presence of a PMHS, a chiral copper(I) hydride is generated, which is very effective in the asymmetric hydrosilylation of ketones and α,β-unsaturated esters and lactones affording the corresponding products in high yields and enantioselectivities (up to 99%). There are some indications that the catalysis occurs in a heterogeneous fashion. An asymmetric hydrosilylation catalysed in the presence of copper hydride

combined with the Solvias' non-racemic JOSIPHOS-related ligand (Fig. 10.16) was successfully used to introduce each of three stereocentres placed in β-positions to carbonyl group found in the C-9 diastereomer of amphidinoketide I [42]. Experimental procedures for the efficient asymmetric 1,4-reduction of β-silylated-α,β-disubstituted enoates catalysed by CuH combined Solvias' (*R*,*S*)-PPF-P(*t*-Bu)$_2$ (Fig. 10.16) have been reported [43]. A number of sequential or tandem processes involving conjugate reduction have been developed. They include sequential conjugate reduction/alkylation [44,45], conjugate reduction/intramolecular aldol reaction (reductive aldol cyclisation) [46–48], tandem reduction/enantioselective intermolecular aldol reaction (reductive aldol reaction) [49–52] as well as conjugate reduction/Henry reaction [53]. One pot sequence: Cu-catalysed conjugate reduction and asymmetric Pd catalysed arylation has also been communicated [54].

Copper based catalysts are known as hydride delivery agents and were mainly used as stoichiometric reducing agents, from among which the most applicable was Stryker's reagent [$\{CuH(PPh_3)\}_6$]. Application of Cu(I) / PR_3 as a catalytic system for the hydrosilylation of ketones was first shown by Brunner [29]. The reaction was demonstrated to proceed under mild conditions in the presence of diphenylsilane H_2SiPh_2 and enabled quantitative transformation of acetophenone into 1-phenylethanol in a two step procedure (Scheme 10.1a). However, further research was focused mainly on the reduction of α,β-unsaturated systems. In recent years, the catalytic systems developed for conjugate reduction were applied in the 1,2-hydrosilylation of simple carbonyl compounds.

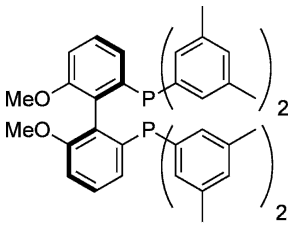
Lipshutz described the asymmetric hydrosilylation of aryl ketones mediated by *in situ* generated bidentate phosphine ligated copper hydride [55]. The procedure allowed synthesis of respective alcohols with 87–99% yield and moderate to high enantioselectivity (ee = 78–97%) under very mild conditions (Eq. 10.9). The best activities and enantioselectivities were obtained for Roche ligand 3,5-xyl-MeO-BIPHEP (Fig. 10.18) (Table 10.2). No decrease in ee was observed for the substrate to ligand ratio as low as 20000 to 1 and for the catalyst concentration of 0.5 mol%.



(10.9)

A similar protocol using CuCl / NaO(*t*-Bu) / (*R*)-BINAP as a catalytic system allows a reduction of aryl alkyl ketones with $H_2SiPhMe$ in high yields (75–99%) and enantioselectivities (ee up to 97%) [57]. A system CuCl / NaO(*t*-Bu) combined with non-racemic DTBM-SEGPHOS ligand (Fig. 10.17), leads to an especially reactive reagent capable of effecting asymmetric hydrosilylation of heteroaromatic ketones with PMHS under very mild conditions. High yields (85–97%) and enantioselectivities (ee = 90–99%) of the corresponding alcohols were obtained. The system en-

Fig. 10.18



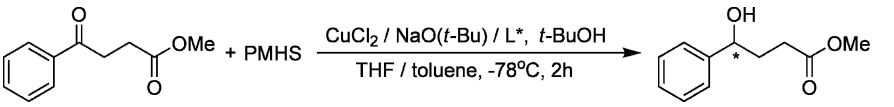
(*R*)-xyl-MeO-BIPHEP

Table 10.2 Copper catalysed asymmetric 1,2-hydrosilylation of acetophenone

Catalytic system	Silane	Temp. [°C]	Time [h]	Yield[a] [%]	Ee[b] [%] (config.)	Ref.
CuCl / NaO(*t*-Bu) / Fig. 10.18	PMHS[c]	−78	5	98	94 (*R*)	[55]
CuCl / NaO(*t*-Bu) / Fig. 10.18	PMHS[c]	−78	<1	98	94 (*R*)	[56]
CuCl / NaO(*t*-Bu) / (*R*)-BINAP	$H_2SiMePh$	−78	18	99	93 (*R*)	[57]
$Cu(OAc)_2$ / NaO(*t*-Bu) / Fig. 10.14	H_2SiPh_2	0	7	94	79 (*S*)	[58]
CuF_2 / Fig. 10.14	H_3SiPh	r.t.	16	99	79 (*S*)	[59]
CuF_2 / Fig. 10.19a	H_3SiPh	–20	24	91	89 (*S*)	[60]
$[CuF(PPh_3)\cdot 2MeOH]$ / Fig. 10.20	H_2SiPh_2	–60	1	99	93 (*R*)	[61]

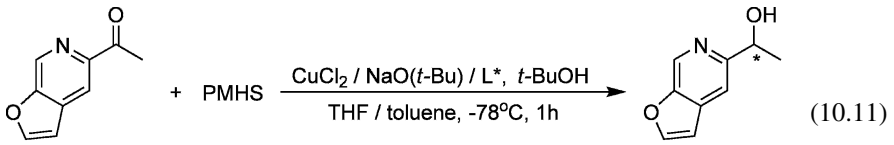
Reaction conditions: 0.5–5 mol% [Cu]; [Cu]:[L*] = 1 : 1; [C=O]:[silane] = 1:1–1:2; [a]isolated yield of alcohol; [b]determined after hydrolysis; [c][C=O]:[silane] = 1:10

ables employment of the high substrate to ligand ratios (of the order of 2000:1) [62]. (*R*)-DTBM-SEGPHOS-ligated copper hydride is shown to be a very effective catalyst in the asymmetric hydrosilylations of aryl ketones with PMHS. The optimised procedures permit the synthesis of non-racemic alcohols, which are useful precursors in the synthesis of known physiologically active compounds (Eqs 10.10 and 10.11) [63].



L* = (*R*)-DTBM-SEGPHOS yield = 92% ee = 99.4%

(10.10)

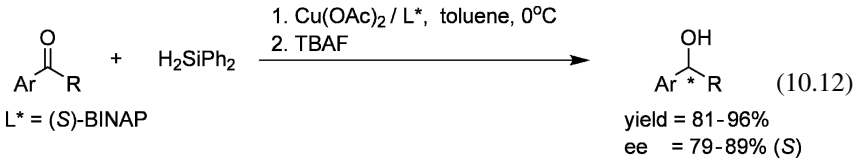


L* = (*R*)-DTBM-SEGPHOS yield = 88% ee = 97.1%

(10.11)

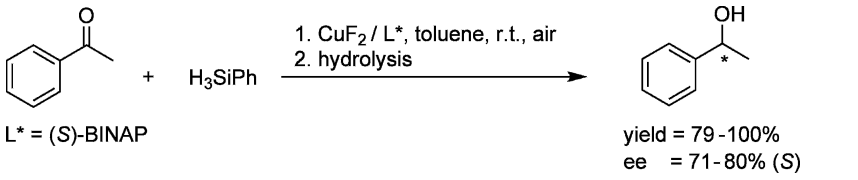
Roche's 3,5-xyl-MeO-BIPHEP (Fig. 10.18) or Takasago's DTBM-SEGPHOS (Fig. 10.17 were found especially efficient and predictable (within a large gamut of ligands) in their abilities to transfer chirality to prochiral aryl ketones [56]. The survey of the ligands screened permits suggesting structural and stereoelectronic features which impact both reactivity and chirality via association with CuH/silane complex prior to the 1,2-reduction of an aryl ketone. These features include (1) a biaryl bis-phosphine skeleton, preferably a biphenyl array; (2) aryl rather than alkyl substitution on phosphorus; and (3) a minimised dihedral angle in the biaryl bis-phosphine-ligated copper hydride. However, all efforts to identify the active species involved failed. An important feature of the copper/diphosphine catalytic system is the ligand acceleration. Remarkably high substrate-to-ligand ratios exceeding 100,000:1 have been demonstrated [56].

Yun found that CuCl / NaO(*t*-Bu) could be replaced by the copper(II) precursor such as $Cu(OAc)_2$ or $Cu(OAc)_2{\cdot}H_2O$ copper(II) acetate for generation of an active copper hydride in the presence of (*S*)-BINAP and PMHS or H_2SiPh_2. The system allows the asymmetric hydrosilylation of simple aryl ketones (Eq. 10.12) an alkoxide. The beneficial features of the protocol proposed were the possibility of using the air and moisture stable precursor which can be activated by the hydrosilylating agent itself and permitted avoidance of addition of base in the catalyst activation step [58].



(10.12)

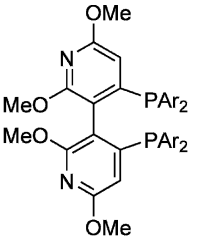
A practical and efficient method that allowed asymmetric reductions of ketones in aerobic and mild conditions was developed by Riant. The system CuF_2/ (*S*)-BINAP catalyses hydrosilylation of several aryl alkyl ketones with very high yields and moderate to high selectivity (ee = 20–92%). Dialkyl ketones and ketoesters undergo transformation with a very low enantioselectivity (Eq. 10.13) [59].



(10.13)

The combination of CuF_2, non-racemic dipyridylphosphine (Fig. 10.19 a,b) and phenylsilane as a hydride donor generates *in situ* a highly active catalyst for the hydrosilylation of a wide range of aryl alkyl ketones (Table 10.2) [60]. This system allows enantioselectivity up to 98% by using high S/L ratio (up to 100 000). The

Fig. 10.19

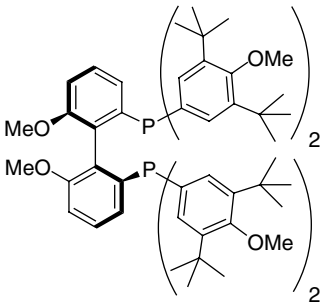


a Ar = Ph
b Ar = 3,5-$C_6H_3Me_2$

reaction proceeds under aerobic conditions at ambient temperature down to −20°C and tolerates traces of moisture.

The fluorotris(triphenylphosphine)copper(I)–bis(methanol) complex combined with chiral diphosphine catalyses the hydrosilylation of several alkyl aryl ketones with moderate to high enantioselectivity. Significant dioxygen acceleration effect was observed, that allows lowering of the catalyst concentration. With bulky Ar-MeO-BIPHEP (e.g., Fig. 10.20) ligands the enantioselectivities up to 95% were observed for the catalyst loadings as low as 0.05 mol%. The methodology proposed involves the asymmetric reduction of ketones in aerobic and mild conditions with high TON (up to 2000) and TOF (up to 1000–1500 h^{-1}) [61].

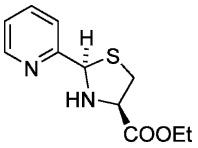
Fig. 10.20



The first generation of chiral catalyst for the asymmetric hydrosilylation of ketones was based on neutral or cationic rhodium(I) precursors in combination with chiral bidentate ligands. For the first decade after the discovery of asymmetric hydrosilylation, the search for active catalysts was limited to rhodium based systems, which are active in mild reaction conditions. However, these systems are too expensive for the large scale application. Another drawback of the rhodium catalysed reactions is the high sensitivity of activity and enantioselectivity to the silane structure. Relatively expensive di(aryl)silanes have been proved to be most efficient. Three major ligand families have been developed ensuring high performance in rhodium catalysed enantioselective reduction of ketones to secondary alcohols. These are (a) nitrogen based chelating ligands, (b) diphosphines and (c) N,P-heterobidentate ligands.

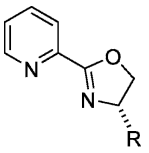
A number of highly efficient nitrogen-based chelating ligands were synthesised in the 1980s and in the early 1990s. Efficient systems involved a chiral pyridine – thiazolidine (PYTHIA) (Fig. 10.21) [62–66], pyridine-oxazoline (PYMOX) (Fig. 10.22) [67–72], pyridine-bisoxazoline (PYBOX) (Fig. 10.23) [68]; [73–77] tetradentate bipyridine-bisoxazoline (BIPYMOX) (Fig. 10.24) [78–82] or substituted phenanthroline (Fig. 10.25) [83].

Fig. 10.21



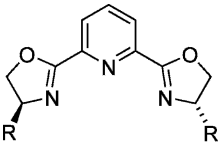
PYTHIA

Fig. 10.22



R-PYMOX

Fig. 10.23



R-PYBOX

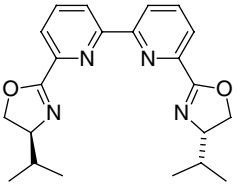


Fig. 10.24

i-Pr-BIPYMOX

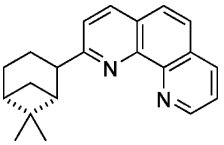


Fig. 10.25

Neutral or cationic rhodium complexes combined with these ligands catalyse the reduction of aryl alkyl ketones under mild condition with enantioselectivities exceeding 90% ee. These ligands in most cases have to be used in large excess relative to rhodium to attain high enantioselectivity. The reaction can be carried out under solvent free conditions or performed in solution. A wide gamut of solvents is available for the process (THF, diethyl ether, benzene, toluene, CH_2Cl_2 and CCl_4). Very often the reactions proceed below room temperature (down to $-78^{\circ}C$). Many nitrogen based ligands were reported in the 1990s by different research groups (Figs. 10.26–10.38). However, the selectivities obtained did not exceed 90% and often were very modest (Table 10.3).

Fig. 10.26

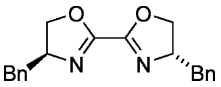
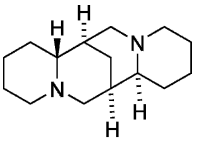


Fig. 10.27



Sparteine

Fig. 10.28

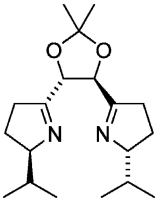


Fig. 10.29

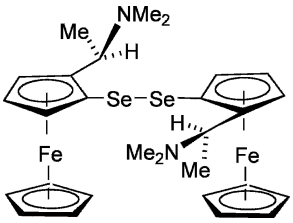


Fig. 10.30

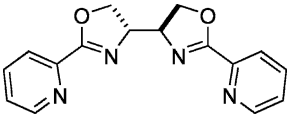


Fig. 10.31

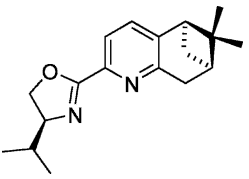


Fig. 10.32

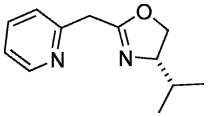


Fig. 10.33

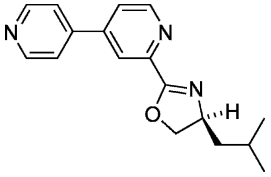


Fig. 10.34

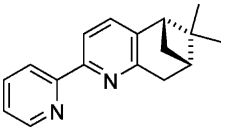


Fig. 10.35

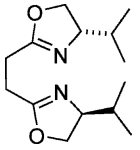


Fig. 10.36

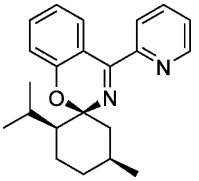


Fig. 10.37

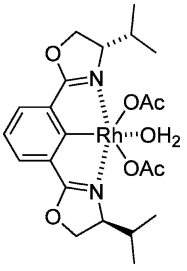
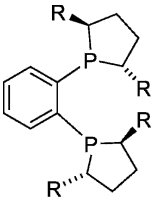


Fig. 10.38



DuPHOS

Table 10.3 Rhodium catalysed hydrosilylation of acetophenone with diphenylsilane in the presence of nitrogen-based chelating ligands

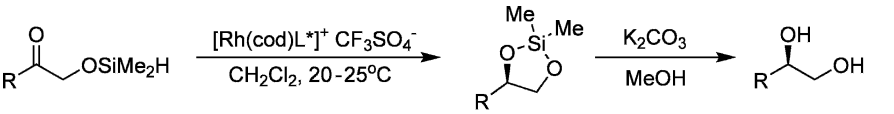
Ligand or catalyst	Temp. [°C]	Time [h]	Yield [%]	Ee[a] [%] (config.)	Ref.
Fig. 10.25	0–r.t.	18	–	75.6 (*R*)	[83]
Fig. 10.26	r.t.	–	59	84 (*S*)	[84]
$[Rh(cod)_2]BF_4$ / Fig. 10.27	25	7 days	75	37 (*S*)	[85]
$[RhCl_3L^*]$, L^* = Fig. 10.24	−40	5	98	90 (*S*)	[78]
Fig. 10.28	−5	72	90	64 (*R*)	[82]
Fig. 10.29	0	24	31	85 (*R*)	[86]
Fig. 10.30	8	30	75.5	50 (*R*)	[87]
Fig. 10.31	0–r.t.	18	90	79.6 (*S*)	[88]
Fig. 10.32	0–r.t.	48	70	42 (*R*)	[89]
Fig. 10.33	0–r.t.	18	94	73.9 (*R*)	[90]
Fig. 10.34	0–r.t.	24	88	32 (*R*)	[91]
Fig. 10.35	50	6	32	33 (*S*)	[92]
Fig. 10.36, $AgBF_4$		4 days	60	42 (*S*)	[93]

Reaction conditions: 0.5–1 mol% [Rh], catalyst precursor $[\{RhCl(cod)\}_2]$, [Pd]:$[L^*] = 1 : 4–1:5$, [C=C]:$[H_2SiPh_2] = 1 : 1.01–1:1.6$; [a]determined after hydrolysis

Several organometallic rhodium(III) (*i*-Pr)-PYBOX complexes were proved active in the hydrosilylation reaction of acetophenone to (*S*)-1-phenylethanol with high yield (up to 99%) and enantiomeric excess (up to 89%) [94]. High enantioselectivity was observed in the conjugate reduction of (*E*)-β-methylcinnamaldehyde (up to 97%) [95], phenyl-3-penten-2-one and (*E*)-4- phenyl-4-isopropyl-3-penten-2-one (95% and 98% ee, respectively) [96] and esters (up to 98% ee) [96, 97] with $HSiMe(OEt)_2$ in the presence of rhodium (*S*,*S*)-(*i*-Pr)-PHEBOX complex (Fig. 10.37). The same complex has been shown to catalyse highly *anti*-selective and enantioselective reductive aldol reaction of acrylates and aldehydes with trisubstituted silanes [98, 99] as well as the sequence – conjugate reduction of cinnamates with $HSiMePh_2$ and aldol reaction with acetone to form the corresponding intermolecular reductive aldol product in very high enantioselectivity (up to 98%) [100].

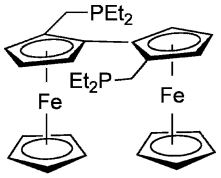
Most of the research groups in the first stage of investigation have focused on anionic or neutral rhodium source combined with *cis* chelating chiral diphosphines (e.g. DIOP). For these ligands modest asymmetric induction was observed. Synthesis and development of the DuPHOS (Fig. 10.38) ligand [101] and bidentate ferrocenylphosphines TRAP (Figs. 10.39 and 10.40) [102–105] permitted enantioselective course of the process leading to the respective products with ee exceeding 90% (Table 10.4). Rhodium(I) cationic complexes in the presence of DuPHOS

family of ligands allow intramolecular hydrosilylation of hydroxyketones (at the first stage transformed into silyl derivatives) to form after the hydrolysis step enantioenriched 1,2-diols (Eq. 10.14) with the total yield 75–93%. In the presence of iso-propylsubstituted ligand, high enantioselectivity of the corresponding products (up to 93% ee) was observed [101].



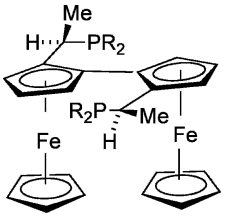
(10.14)

Fig. 10.39



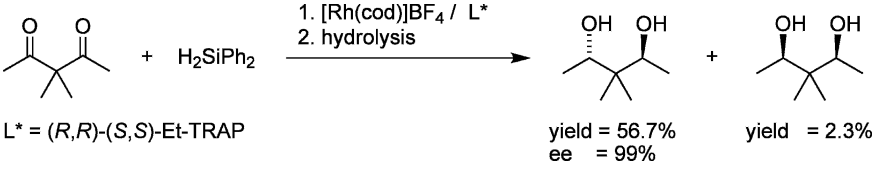
(*S*,*S*)-Et-TRAP-H

Fig. 10.40



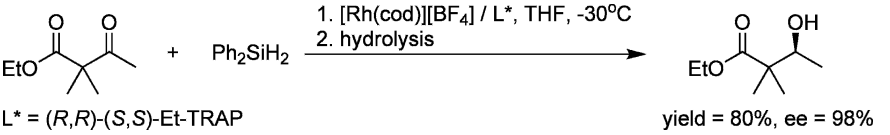
(*R*,*R*)-(*S*,*S*)-R-TRAP
a R = Bu
b R = Et

Trans-chelating chiral diphosphine (TRAP) having the wide bite angle combined with rhodium precursor [{RhCl(cod)}$_2$] allows very efficient reduction of aryl alkyl ketones, simple dialkyl and α,β-unsaturated diketones as well as α and β-ketoesters with H_2SiPh_2. The corresponding products can be obtained with high yield and ee usually exceeding 90% [102–104]. The optimum performance was obtained by tuning the alkyl substituents at phosphorus atom. Planar chiral Et-TRAP-H (Fig. 10.39) combined with [Rh(cod)$_2$][BF$_4$] catalysed the enantioselective hydrosilylation of various aryl- and alkylsubstituted ketones with H_2SiAr_2 [106, 107]. Asymmetric hydrosilylation of symmetrical diketones with diphenylsilane in the presence of catalytic amount of a rhodium complex coordinated with *trans*-chelating chiral phosphine ligand Et-TRAP gave the corresponding symmetrical diols with high enantiomeric excess (Eq. 10.15) [104, 105].



(10.15)

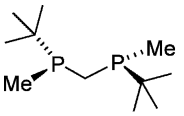
The asymmetric hydrosilylation using TRAP ligands with bulky substituents at phosphorus resulted in a much lower enantioselectivities. Et-TRAP / rhodium catalyst was also effective for asymmetric hydrosilylation of ketoesters (Eq. 10.16) (Table 10.4) [105]



(10.16)

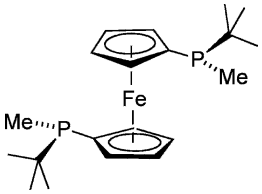
Methylene bridged P-chiral diphosphine ligand MiniPHOS (Fig. 10.41) combined with the rhodium cationic complex forms highly strained, four membered C_2-symmetric chelate which allows highly enantioselective hydrosilylation of aryl methyl ketones (Table 10.4) [108].

Fig. 10.41



(*t*-Bu)-MiniPHOS

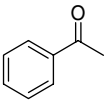
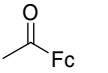
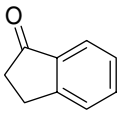
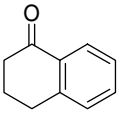
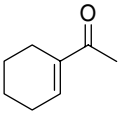
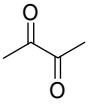
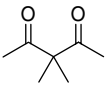
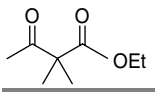
C_2-symmetric P-chiral bis(phosphine)ferrocene ligand BMPF (Fig. 10.42) in the presence of the cationic rhodium precursor allows the reduction of aryl methyl ketones with 1-naphthylphenylsilane leading to formation of the corresponding alcohols with moderate to high enantioselectivity (Table 10.4) [109].



(*S*,*S*,*S*)-BMPF

Fig. 10.42

Table 10.4 Rhodium catalysed asymmetric hydrosilylation of carbonyl compounds in the presence of highly enantioselective diphosphine ligands

Substrate	Ligand or catalyst	Temp. [°C]	Time [h]	Yield [%]	ee[a] [%] (config.)	Ref.
	Fig. 10.40a	–40	11	88	92 (*S*)	[102]
	Fig. 10.39	–40	4	89	94 (*S*)	[106]
	[Rh{(*R*,*R*)-L*}]PF_6 L* see Fig. 10.41	–40	–	86[b]	91[b]	[108]
	[Rh(nbd)$_2$]BF_4/Fig. 10.42	–20	–	96[b]	92[b] (*S*)	[109]
	Fig. 10.40a	–40	11	84	97 (*S*)	[105]
	Fig. 10.40a	–40	3	87	87 (*S*)	[105]
	Fig. 10.40a	–40	4	83	84 (*S*)	[105]
	Fig. 10.40a	–40	12	71	95 (*S*)	[102]
	Fig. 10.40b	0	30	69[c]	95 (*S*, *S*)	[104]
	Fig. 10.40b	–30	58	58[d]	99 (*S*, *S*)	[104]
	Fig. 10.40b	–30	11	69	99 (*S*)	[103]

Reaction conditions: 0.5–1 mol% [Rh], catalyst precursor: [Rh(cod)$_2$]BF_4; [Rh]:[L*] = 1:1.1, [C=O]:[H_2SiPh_2] = 1:1.25–1:1.5; [a]determined after hydrolysis; [b]1-naphthylphenylsilane was used; [c] *dl:meso* = 90:10; [d] *dl:meso* = 96:4.

In the last decade a number of new phosphorus based ligands have been synthesised and tested in rhodium catalysed hydrosilylation. However, neither improvement in activity nor in enantioselectivity was observed (Table 10.5).

Gladysz reported rhodium complex bearing chelating diphosphines that contain a rhenium stereocenter in the backbone. The catalyst (Fig. 10.49) allows reduction of phenylalkylketone with enantioselectivity up to 92% [116].

Table 10.5 Rhodium catalysed asymmetric hydrosilylation of acetophenone with diphenylsilane in the presence of selected P-based chelating ligands

Ligand	Temp. [°C]	Time [h]	Yield [%]	ee [%][a](config.)	Ref.
Fig. 10.43	0	1–4	84	37 (*S*)	[110]
Fig. 10.44	10	–	97 (conv.)	56 (*S*)	[111]
Fig. 10.45	r.t.	16	38	81 (*R*)	[112]
Fig. 10.46	0	24	46	64 (*S*)	[113]
Fig. 10.47	0–20	20	87	24.6 (*S*)	[114]
Fig. 10.48	−20	5 days	41	20	[115]

Reaction conditions: 0.25 or 1 mol% $[\{RhCl(cod)\}_2]$; H_2SiPh_2 [Rh]:[L*] = 1 : 1–1:5, [C=O]:[HSi] = 1 : 1–1:4; [a]determined after hydrolysis

Fig. 10.43

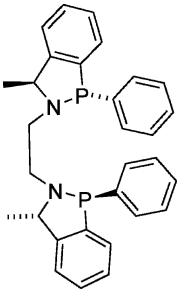
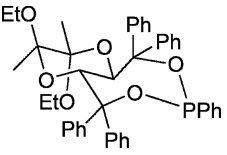


Fig. 10.44



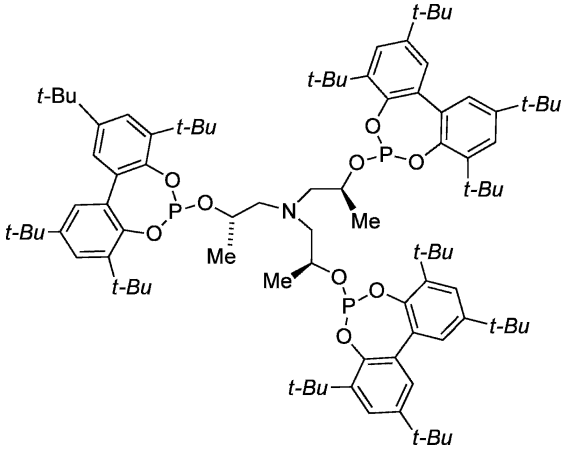


Fig. 10.45

Fig. 10.46

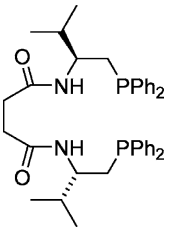


Fig. 10.47

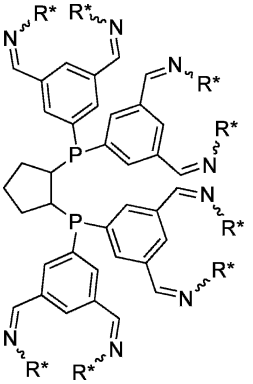


Fig. 10.48

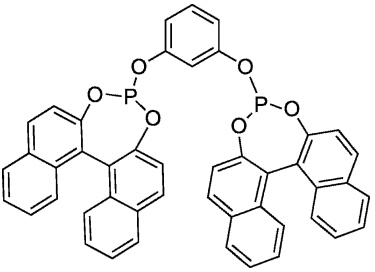
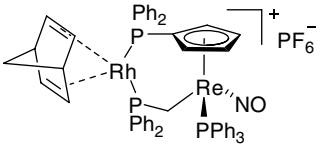


Fig. 10.49



Recently, a number of *cis*-chelating P-chiral diphosphine ligands (Figs. 10.50 and 10.51) have been applied to the rhodium-catalysed asymmetric hydrosilylation of simple ketones. The corresponding secondary alcohols were obtained in high yields with moderate to high enantiomeric excesses (up to 99%). A mechanism of the reaction was proposed assuming that the enantioselection occurs at the

Fig. 10.50

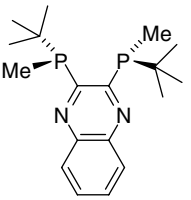
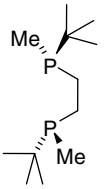


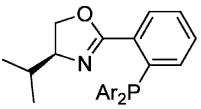
Fig. 10.51



migratory insertion step [117]. In the presence of (*R*)-BINAP or (*R*)-Cy-BINAP (2,2′-bis(dicyclohexylphosphino)-1,1′-binaphthyl) rhodium chlorocyclooctadiene dimer catalyses hydrosilylation of symmetric ketone with prochiral (1-naphthyl) phenylsilane to form chiral at silicon (*R*)-alkoxy(1-naphthyl)phenylsilane in up to 99% ee [118]. [{RhCl(cod)}$_2$] combined with (*R*)-BINAP (see Fig. 10.14 for (*S*)-isomer) catalyses reductive aldol reaction between acrylate esters, aldehydes and diethylmethylsilane with modest diastereoselectivity and good levels of enantioselectivity [119]. Analysis of the enantioselectivities and initial rates of the hydrosilylation of acetophenone with silanes catalysed by [{RhCl(cod)}$_2$] / (chiral diphosphine) indicates that the turnover limiting step is the oxidative addition of the silane to a rhodium complex. The quantitative analysis of ligand effects (QALE) concerning the stereochemistry of the reaction reveals that steric effects are non-linear i.e. there is no simple correlation between the size of the silane and the enantioselectivity of the reaction [120].

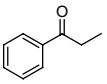
In the late 1990s a variety of chiral P,N-bidentate ligands were synthesised and tested for their efficiency in asymmetric hydrosilylation of carbonyl derivatives. Hybrid P,N-ligands combine a relatively high enantioselectivity characteristic of nitrogen-based chelating ligands with high activity of diphosphines. In 1996 Helmchen [129] and Williams [122] independently reported enantioselective reduction of simple ketones in the presence of rhodium(I) complexes of chiral phosphinooxazoline ligands (Fig. 10.52). In the optimized conditions, the hydrosilylation of acetophenone led to (*R*)-1-phenylethanol with up to 86% ee (Table 10.6) [121, 122]. A successful modification of this ligand was BPOI (Fig. 10.53) which was found to induce ee up to 94% in the reduction of aryl methyl ketones (Table 10.6) [123]. C_2-symmetric PHOS-BIOX, tetradentate ligand (Fig. 10.54) possessing chirality on the backbone was found to be an efficient ligand for the rhodium(I) catalysed asymmetric hydrosilylation of prochiral acetophenones with diphenylsilane to give secondary alcohols with ee up to 97% (Table 10.6) [124].

Fig. 10.52



a Ar = Ph
b Ar = 3,5-$C_5H_3(CF_3)_2$

Table 10.6 Rhodium catalysed asymmetric hydrosilylation of ketones in the presence of N,P-chelating ligands

Substrate	Ligand	Temp. [°C]	Time [h]	Yield [%]	Ee[a] [%]	Ref.
	Fig. 10.52a	–78	–	86	82 (*R*)	[122]
	Fig. 10.52b	–40	–	99	86 (*R*)	[121]
	Fig. 10.53	r.t.	24	84	94 (*R*)	[123]
	Fig. 10.54	–	7	98	97 (*R*)	[124]
	Fig. 10.55a	20	–	94	60 (*R*)	[125]
	Fig. 10.55b	25	–	100	91 (*R*)	[126]
	Fig. 10.56b	20	< 0.17	90	90 (*S*)	[127]
	Fig. 10.56a	20	<1	97	86 (*S*)	[127]
	Fig. 10.53	r.t.	24	91	91 (*R*)	[123]
	Fig. 10.55b	25	–	95	57 (*R*)	[126]
	Fig. 10.53	r.t.	24	97	92 (*S*)	[123]
	Fig. 10.55b	25	–	45	89 (*R*)	[126]
	Fig. 10.52a	r.t.	–	97	37	[121]
	Fig. 10.53	r.t.	24	85	87 (*R*)	[123]

Reaction conditions: 0.25 - 1mol% [{RhCl(cod)}$_2$]; H_2SiPh_2 [Rh]:[L*] = 1:1 – 1:5, [C=O]:[HSi] = 1:1 – 1:4;
[a]determined after hydrolysis

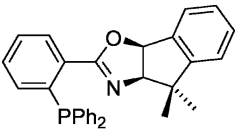


Fig. 10.53 BPOI

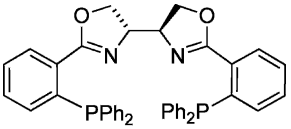
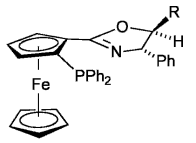


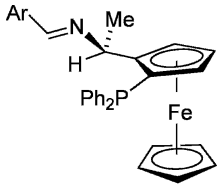
Fig. 10.54 (*S*,*S*)-PHOS - BIOX

Chiral oxazolinylferrocene-phosphine hybrid ligands, e.g., (Fig. 10.55) developed by Uemura were found very effective for the rhodium catalysed hydrosilylation of aryl methyl ketones to give the corresponding alcohols with up to 91%ee after acid hydrolysis (Table 10.6) [125, 126]. High activity and moderate enantioselectivity was observed when alkyl methyl ketones were used as substrates. Interestingly, enantioselective hydrosilylation of acetophenone with the Ir(I) / (*S,S,S*)-DIPOF system occurred highly selectively (96% ee) to give the alcohol with the opposite (*S*) configuration [126]. Similarly, ferrocenylphosphine-imines (Fig. 10.56) were demonstrated to be effective as chiral ligands for the rhodium-catalysed asymmetric hydrosilylation of acetophenone [127]. TADDOL (tetraaryldioxolanedimethanol) derived phosphonites and phosphites prepared by Seebach allow enantioselective, rhodium catalysed hydrosilylation of aryl ketones. The respective products were obtained with ee up to 87% [128]. A variety of ketones tested in the presence of phosphite (Fig. 10.57) give selectivities up to 86% ee for aryl alkyl ketones and moderate to high ee for dialkyl ketones [129]. Chiral tridentate ligand (Fig. 10.58) combined with rhodium precursor was less selective and in hydrosilylation of acetophenone formed the expected alcohol in up to 62% ee [130].



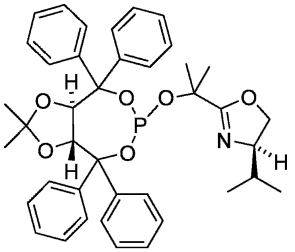
a R = H
b R = Ph (*S,S,S*)-DIPOF

Fig. 10.55



a Ar = Ph,
b Ar = 3-$C_6H_4CF_3$
c Ar = 4-$C_6H_4CF_3$

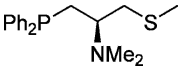
Fig. 10.56



TADDOL-POx

Fig. 10.57

Fig. 10.58



Since 2000, two systems have been developed allowing a significant progress in the field. In 2002 Fu introduced a new class of planar chiral ligands of pyridine-ferrocene structure (Fig. 10.59) [131]. In combination with neutral rhodium precursor high yields and enantioselectivities were observed in hydrosilylation of various ketones with diarylsilanes. By using this system both arylalkyl and dialkyl ketones were transformed to the corresponding alcohols of high enantiopurity (ee ranged from 81 to 99%).

Fig. 10.59

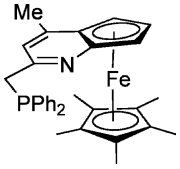
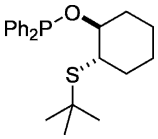
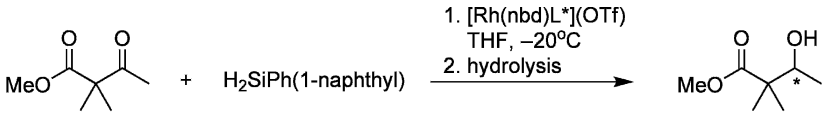


Fig. 10.60



Shortly after that Evans reported chiral mixed phosphorus/sulphur ligands coordinated to rhodium precursor, effective in enantioselective hydrosilylation of aryl methyl-, aryl alkyl-, cyclic aryl alkyl and dialkyl ketones with diarylsilanes. The optimised ligand (Fig. 10.60) permitted very high enantioselectivities (up to 99% ee) for a wide variety of ketones [132]. β-Ketoesters could also be reduced in high selectivity with this catalyst, if there is sufficient steric differentiation between the two carbonyl groups (Eq. 10.17).



L* see Fig. 10.60

yield = 94%, ee = 99%

(10.17)

High enantioselectivity (up to 95%) has also been achieved in the Rh-catalysed hydrosilylation of acetophenone, performed in the presence of ligand (Fig. 10.61) and catalytic amounts of $AgBF_4$ [133].

After 2000 many active P,N-bidentate ligands allowing selectivity reaching 90% have been tested. A series of TADDOL ligands of the general formula (Fig. 10.62) was synthesised and tested in Rh(I) catalysed asymmetric hydrosilylation of various

Fig. 10.61

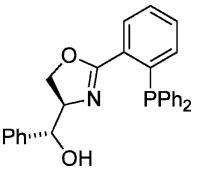


Fig. 10.62

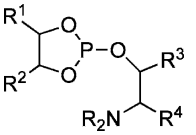
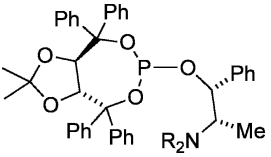


Fig. 10.63



ketones with diphenylsilane. The screening via mass spectrometry enantiomeric excess determination (MSEED) allowed selection of the ligand (Fig. 10.63) which permitted highly enantioselective run of the reaction for different ketones. In the one mmol scale hydrosilylation of acetonaphthanone with diphenylsilane the enantioselectivity reached 86% ee and 54% of isolated yield. The author has shown that minimum changes in the ligand structure can instigate dramatic changes in the enantioselectivity [134].

A family of chiral BINOL-based phosphite P,N-hybrid ligands in the presence of rhodium precursor have been tested in the hydrosilylation of acetophenone and acetylferrocene with diphenylsilane. The best enantioselectivity up to 60% was achieved for (Fig. 10.64) [135]. Thiophene phosphino-oxazolines (HETPHOX), a class of chelating P,N-ligands combined with rhodium precursor catalysed asymmetric hydrosilylation of simple ketones with diphenylsilane [136]. In the presence of ligand (Fig. 10.65) corresponding alkohols were obtained with enantioselectivity up to 88% ee.

Low-to-moderate enantioselectivities were obtained in the hydrosilylation of several aryl ketones with H_2SiPh_2 in the presence of phosphite–oxazoline ligands, the most effective of which is shown in (Fig. 10.66) [137]. Ligand (Fig. 10.67) in the presence of rhodium precursor allows the asymmetric hydrosilylation of acetophenone with diphenylsilane with 50% ee [138].

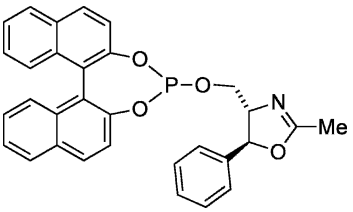


Fig. 10.64

Fig. 10.65

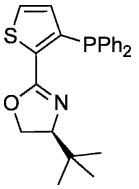


Fig. 10.66

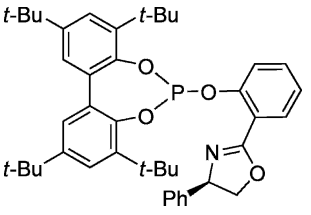
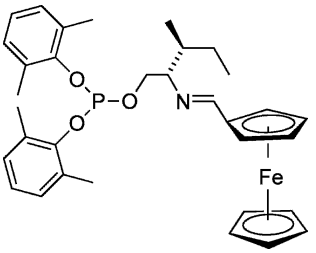


Fig. 10.67



Thioether–phosphinite ligands, prepared from inexpensive D-(+)-xylose, were tested in the Rh-catalysed hydrosilylation of ketones with diphenylsilane. High yields and enantioselectivities (up to 90% ee) were obtained in the presence of *tert*-butyl derivative (Fig. 10.68). The enantioselectivity was found to strongly depend on the steric properties of the substituent at the thioether moiety [139]. Hydrosilylation of acetophenone in the presence of another chiral P,S-hybrid ligand (Fig. 10.69) combined with a rhodium precursor allows a synthesis of 1-phenylethanol with 57% ee [140].

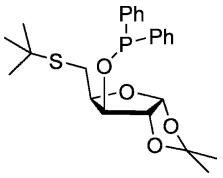


Fig. 10.68

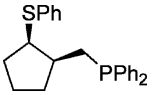
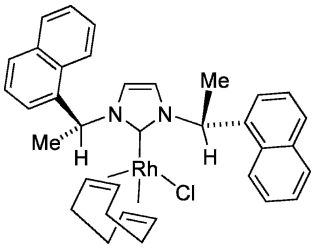


Fig. 10.69

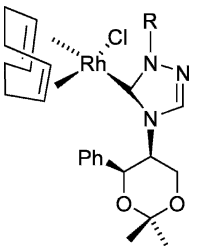
N-heterocyclic carbenes have become universal ligands in organometallic and inorganic coordination chemistry. Since the seminal work of Arduengo, this field has been dynamically developed, mainly in view of high potential of NHC complexes in homogeneous catalysis, including the asymmetric one [141]. The activity of rhodium (and ruthenium) NHC complexes in hydrosilylation of ketones was reported already in 1977 by Nile [142] and in 1984 by Lappert [143]. Rhodium complexes of chiral *N*-heterocyclic carbenes (Fig. 10.70) were applied in 1996 by Hermann for the hydrosilylation of acetophenone with diphenylsilane [144]. The enantiomeric excess achieved did not exceed 32% as simple chiral substituents at nitrogen atoms of the ligand are unable to generate significant chiral induction into the substrate. Optimization of the NHC ligand structure allowed more enantioselective transformations (ee up to 70%) [145].

Fig. 10.70



Axially chiral rhodium triazolinylidene complex (Fig. 10.71) was used for the asymmetric reduction of aryl methyl ketones with H_2SiPh_2. The corresponding alcohols were obtained with moderate to high yield. (40–60% depending on substrate) and ee up to 44% [146, 147]. Synthesis of triazolinylidene and imidazolinylidene rhodium complexes (including the immobilised ones) and their application in catalysis of asymmetric hydrosilylation were shortly reviewed [148]. Unfortunately, only poor enantioselectivities were achieved for these systems.

Fig. 10.71



Axially chiral Rh(III) complex (Fig. 10.72) allows the hydrosilylation of aryl methyl ketones with H_2SiPh_2 to give (after hydrolysis) respective alcohols with 92–98% ee [149]. The same complex and its analogue containing two saturated rings in binaphthyl substituent (Fig. 10.73) were successfully used in the asymmetric hydrosilylation of β-ketoesters (Eq. 10.18) [150]. The reduction products – 3-hydroxy-3-arylpropionic acid methyl or ethyl esters were obtained in good yields with good

Fig. 10.72

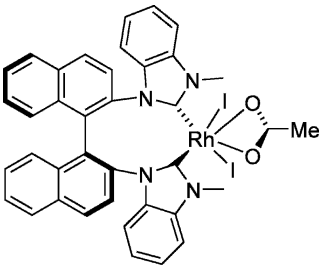
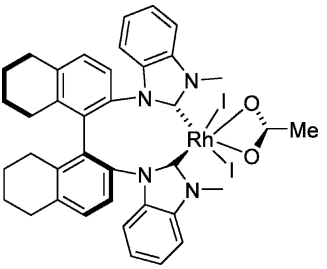
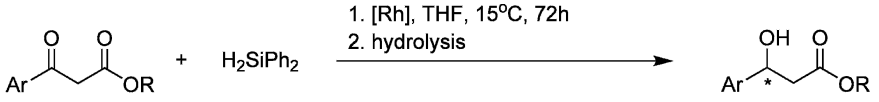


Fig. 10.73



to excellent enantioselectivities (80–99% ee). Enantiopure β-hydroxyesters are important building blocks for the synthesis of biologically active compounds and natural products.



[Rh] see Fig. 10.73
Ar = C_6H_4Me-2, C_6H_4Me-3, C_6H_4Me-4, C_6H_4OMe-2, C_6H_4Cl-4, C_6H_4Cl-2, C_6H_4Br-4
R = Me, Et

yield = 65-91%
ee = 80-99%

(10.18)

Readily accessible chiral oxazolinylcarbene rhodium complex (Fig. 10.74) activated with $AgBF_4$ efficiently catalyses the hydrosilylation of aryl alkyl ketones with H_2SiPh_2 to give corresponding alcohols with ee reaching 99%. Moderate to high enantioselectivity (up to 95%) is observed in the hydrosilylation of dialkyl ketones [151, 152]. Asymmetric hydrosilylation of acetophenone with diphenylsilane

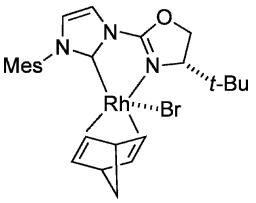
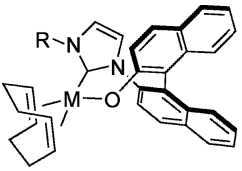


Fig. 10.74

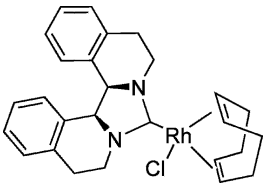
Fig. 10.75



a M = Rh, R = *i*-Pr
b M = Rh, R = CH_2Ph
c M = Ir, R = *i*-Pr
d M = Ir, R = CH_2Ph

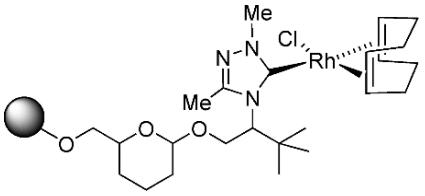
catalysed by rhodium complexes of NHC-naphthoxy ligands (Fig. 10.75a and b) gave respective silyl ether with high yield but low selectivity (up to 13% ee) [153]. Modest enantioselectivity (up to 28%) was observed in asymmetric hydrosilylation of acetophenone with diphenylsilane in the presence of complex (Fig. 10.76) [154].

Fig. 10.76



Merrified resin supported (triazolinylidene)rhodium complexes (Fig. 10.77) were tested as catalysts of the asymmetric hydrosilylation of acetophenone yielding 1-phenylethanol with enantiomeric excesses 23–24% [155].

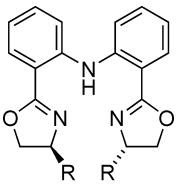
Fig. 10.77



Hydrido, phosphido bridged complex $[(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}H)(\mu\text{-}PR^*_2)(CO)_2]$ ($R^* =$ menthyl) is an enantioselective catalyst in the photochemical hydrosilylation of acetophenone with diphenylsilane to give 1-phenylethanol in up to 33% ee [156].

A combination of $Fe(OAc)_2$ with multi-nitrogen chiral ligands such as Bn-PYBOX (Fig. 10.23 for R=Bn), (*i*-Pr)-BOPA (Fig. 10.78a) and (*t*-Bu)-BOPA (Fig. 10.78b) can efficiently catalyse the hydrosilylation of ketones to give the corresponding alcohols in high yields and moderate enantioselectivity up to 79% ee [157]. The same precursor combined with Me or Et-DUPHOS (see Fig. 10.38, R= Me or Et) catalyses the enantioselective hydrosilylation of ketones with $HSi(OEt)_2Me$. In the optimised conditions high ee's of the synthesised alcohols (up to 99%) were observed. Good enantioselectivities were obtained for electronically rich and sterically hindered aryl

Fig. 10.78

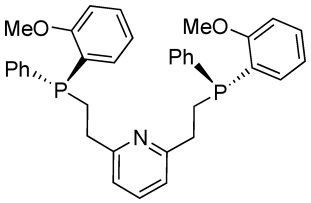


a R = *i*-Pr
b R = *t*-Bu

ketones. Diaryl and dialkyl ketones were converted into the corresponding alcohols with ee up to 79% [158].

In contrast to rhodium chemistry, the enantiomerically pure P,P-chelating ligands such as BINAP or tridentate nitrogen ligand PYBOX were either not active or not selective when tested in the ruthenium catalysed hydrosilylation of acetophenone [159]. Chiral tridentate ligand (Fig. 10.79) in combination with ruthenium precursor $[\{RuCl_2(C_6H_6)\}_2]$ catalyses asymmetric hydrosilylation of aryl methyl ketones to give after hydrolysis the respective alcohols with ee ranging from 47 to 66% (Table 10.7) [159].

Fig. 10.79

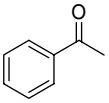
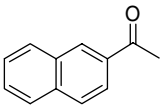
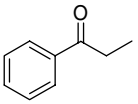
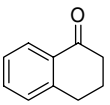
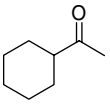


Ruthenium complexes bearing oxazolinylferrocene-phosphine ligand (Fig. 10.80a) catalyse the hydrosilylation aryl alkyl ketones with diphenylsilane to give the respective alcohols (after hydrolysis) with moderate yield and moderate to high enantioselectivity (Table 10.7) [160]. Addition of AgOTf or $Cu(OTf)_2$ to the reaction system dramatically improves the enantioselectivity. A small library of precatalysts of the type illustrated in (Fig. 10.81) was synthesised from different enantiopure P,P- and N,N-chelating ligands. Parallel screening approach permitted identification of the effective catalyst. However, only moderate enantioselectivity was observed by using the optimum precursor (Fig. 10.82) (Table 10.7) [161]. The addition of AgOTf increased the enantioselectivity which is consistent with the earlier observations reported for both Ru and Rh based catalytic systems.

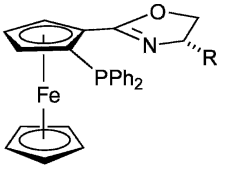
Recently, new chiral bis(paracyclophane)-substituted *N*-heterocyclic carbene ligands (Figs. 10.83–10.85) have been found efficient in the ruthenium catalysed asymmetric hydrosilylation of aryl ketones with diphenylsilane. In the presence of silver(I) triflate, under mild conditions, high activity and enantioselectivity (up to 97%) were observed (Table 10.7) [162].

Compared to rhodium, little attention has been paid to iridium-based catalytic systems. Bis(oxazoline) (Fig. 10.35) derivative combined with $[\{IrCl(cod)\}_2]$

Table 10.7 Asymmetric hydrosilylation of ketones with diphenylsilane in the presence of ruthenium complexes

Ketone	Ligand or catalyst	Temp. [°C]	Time [h]	Yield [%][a]	Ee [%][b]	Ref.
	$[\{RuCl_2(C_6H_6)\}_2]$/Fig.10.79/AgOTf	r.t.	24	97	54 (*S*)	[159]
	Fig. 10.82 AgOTf	r.t.	–	53	82	[161]
	$[RuCl_2(PPh_3)L^*]/Cu(OTf)_2$	0	24	59	95 (*R*)	[160]
	L* see Fig. 10.80a					
	$[RuCl_2(PPh_3)_3]$/Fig.10.85/AgOTf	r.t.	16	98	97 (*S*)	[162]
	$[\{RuCl_2(C_6H_6)\}_2]$/Fig.10.79 AgOTf	r.t.	24	98	66 (*S*)	[159]
	Fig. 10.82 AgOTf	r.t.	–	88	68	[161]
	$[RuCl_2(PPh_3)_3]$/Fig.10.85/AgOTf	r.t.	20	98	96	[162]
	$[RuCl_2(PPh_3)L^*]/Cu(OTf)_2$	0	40	76	97 (*R*)	[160]
	L* see Fig. 10.80a					
	$[RuCl_2(PPh_3)_3]$/Fig.10.85/AgOTf	r.t.	16	96	92	[162]
	$[\{RuCl_2(C_6H_6)\}_2]$/Fig.10.79 AgOTf	r.t.	60	91	47 (*S*)	[159]
	$[RuCl_2(PPh_3)_3]$/Fig.10.85/AgOTf	r.t.	30	90	92	[162]
	$[RuCl_2(PPh_3)L^*]$/AgOTf	0	70	52	43 (*R*)	[160]
	L*= Fig. 10.80a					
	$[RuCl_2(PPh_3)_3]$/Fig.10.85/AgOTf	r.t.	36	93	58	[162]

Reaction conditions: 1 mol% [Ru]; [Ru] : [L*] = 1:2.2–2.4; [C=O]:[H_2SiPh_2] = 1:1.6–2.5;
[a]isolated yield of alcohol; [b]determined after hydrolysis.



a R = Ph
b R = *i*-Pr

Fig. 10.80

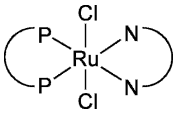


Fig. 10.81

Fig. 10.82

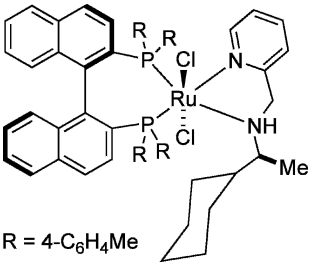


Fig. 10.83

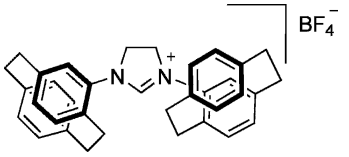


Fig. 10.84

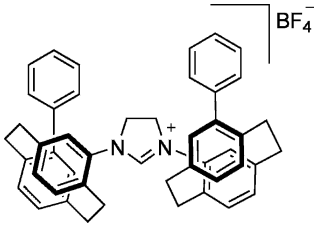
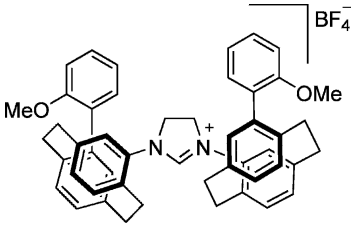
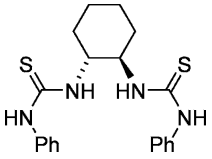


Fig. 10.85



allows the enantioselective hydrosilylation of acetophenone with ee up to 50% [92]. Iridium PYBOX catalysts convert diethylmethylsilane, methyl acrylate, and certain aldehydes to the derived reductive aldol adduct with good enantio- and diastereocontrol [163]. Asymmetric hydrosilylation of acetophenone was carried out with iridium catalysts containing chiral diamines or thiourea ligands. Dithioureas were found to be better asymmetric inducers than the corresponding diamines. In the presence of the ligand (Fig. 10.86) 74% ee was achieved in hydrosilylation of acetophenone with diphenylsilane [164].

Fig. 10.86



Synthesis of the oxazolinylferrocene-phosphine hybrid ligands (Fig. 10.55) caused a remarkable progress in the rhodium catalysed asymmetric hydrosilylation. In combination with a iridium precursor, DIPOF (Fig. 10.55) forms complexes highly active in the asymmetric hydrosilylation of simple ketones. By treatment of aryl alkyl ketone with diphenylsilane, the corresponding alcohols can be formed (after hydrolysis step) with enantiomeric excess up to 96% [125, 165]. Quantitative transformation and high enantioselectivity (ee = 96%, isomer *S*) was obtained by using [{IrCl(cod)}$_2$] / (*S,S,S*)-DIPOF in the hydrosilylation of acetophenone. Interestingly, the rhodium complex combined with the same ligand affords selectively (ee = 91%) the enantiomer of the opposite configuration. (*R,S*)-di[2-(1-dimethylaminoethyl)ferrocenyl]dichalcogenides have been tested in combination with [{IrCl(cod)}$_2$] for the hydrosilylation of acetophenone with H_2SiPh_2. Complete conversion but low enantioselectivity (up to 23%) was observed for selenium derivative (Fig. 10.29) [86, 166]. Iridium complexes bearing NHC-naphthoxy ligands (Fig. 10.75c and d) transform acetophenone and diphenylsilane to a mixture of hydrosilylation product and minor amounts of silyl enol ether. As a result of hydrolysis,1-phenylethanol is formed with enantiomeric excess up to 60% [153].

Transition metals of group 10 play marginal role as catalysts of hydrosilylation of both C=O and C=N bonds. Platinum complexes combined with chiral monodentate phosphine [1], chelating diimines [167] and ferrocenylphosphine amines [168] proved active in hydrosilylations of prochiral ketones. However, in all cases very low enantioselectivities were observed. Nickel(0) precursor combined with non-racemic DIOP ligand (Fig. 10.9) was reported to catalyse hydrosilylation of acetophenone and simple ketones with high yield and moderate enantioselectivity (up to 71% ee) [169].

One of the major breakthroughs in the field of asymmetric hydrosilylation of ketones was the discovery of titanium based chiral catalysts [170–172]. In 1994 Halterman described the application chiral C_2-symmetric titanocene dichlorides bearing various chiral backbones as precatalysts in the catalytic asymmetric hydrosilylation of aromatic ketones with triethoxysilane [171]. The metal precursor activated with BuLi was found to be very active in hydrosilylation of a range of aryl ketones. Although quantitative conversions were observed even at −78°C, the reactions proceed with low enantioselectivity. The best selectivity for acetophenone (ee = 14%) and for 2-acetylnaphthalene (ee = 40%) were obtained by using binaphthyl bridged tetrahydroindenyl titanium precursor (Fig. 10.87).

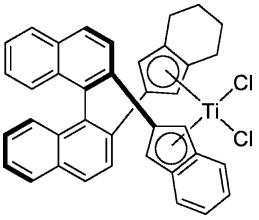
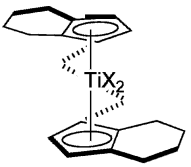


Fig. 10.87

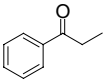
C_2-symmetric (*R*,*R*,*R*)-1,2-bis(tetrahydroindenyl)ethane (BTHIE) titanium(IV) binaphtholate (Fig. 10.88), efficient precatalyst in the asymmetric hydrogenation of imines and olefins, was applied by Buchwald in the hydrosilylation of ketones [170]. Treatment of the precursor with butyllithium and PMHS (which was also a substrate) generates active catalysts (either titanium(III) or titanium(IV) hydride) capable of enantioselective reduction of aryl methyl ketones. Ketones without α-unsaturation were reduced with poor enantioselectivity. The activity of PMHS is an advantage of a Buchwald system as PMHS is the safe, inexpensive and commercially available silane source. However, the catalytic system suffered from the low activity. To achieve complete conversion of substrates it was necessary to use high catalyst loadings and/or extended reaction time (Table 10.8) [170].

Fig. 10.88



(*R*,*R*)-isomer
X_2 = 1,1'-binaphth-2,2'-diolate

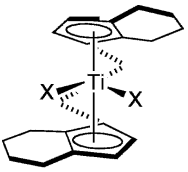
Table 10.8 Titanium catalysed asymmetric hydrosilylation of ketones

Ketone	Catalyst generating system	Temp. [°C]	Time [h]	Yield[a] [%]	Ee[b] [%] (config.)	Ref.
	Fig. 10.88 / BuLi / PMHS	r.t.	22	73	97	[170]
	Fig. 10.87 / BuLi	–78 - r.t.	13	100[c]	14[c]	[171]
	Fig. 10.89 / MeLi / $H_2SiMePh$	r.t.	300	90[d]	12[d] (*R*)	[172]
	Fig. 10.89a / BuLi / $HSi(OEt)_2Me$	–	24	100[e]	99[e] (*R*)	[173]
	Fig. 10.88 / BuLi / PMHS	r.t.	24	96	95	[170]
	Fig. 10.89b / pyrrolidine / MeOH / H_3SiPh	60	13	86	98	[174]
	Fig. 10.89a / MeLi	–	72	100[e]	48[e] (*R*)	[173]
	Fig. 10.89b / pyrrolidine / MeOH / H_3SiPh	60	17	30	53	[174]

Reaction conditions: 0.5-2 mol% [Ti]; PMHS, [C=O]:[silane] = 1:1.2 – 1:5; [a]) isolated yield of alcohol; [b]) determined for alcohol; [c]) $HSi(OEt)_3$ was used; [d]) $H_2SiMePh$ was used; [e]) $HSi(OEt)_2Me$ was used

(*S*,*S*)-Bis(tetrahydroindenyl)ethanetitanium(IV) dichloride (Fig. 10.89a) or (*S,S,S*)-[1,2-bis(tetrahydroindenyl)ethane]titanium(IV) binaphtholate (Fig. 10.88) for (*R,R,R*)-isomer) activated by treatment with MeLi were used as catalysts for the hydrosilylation of dialkyl ketones with diphenyl- or methylphenylsilane. The enantioselectivity was found to be sensitive to the bulkiness of the alkyl group and the highest value (ee = 70%) was observed for cyclopentyl ethyl ketone [172]. The change of an activating agent from MeLi to BuLi and application of PMHS, its oligomeric analogue or alkoxy substituted silanes as reducing agents resulted

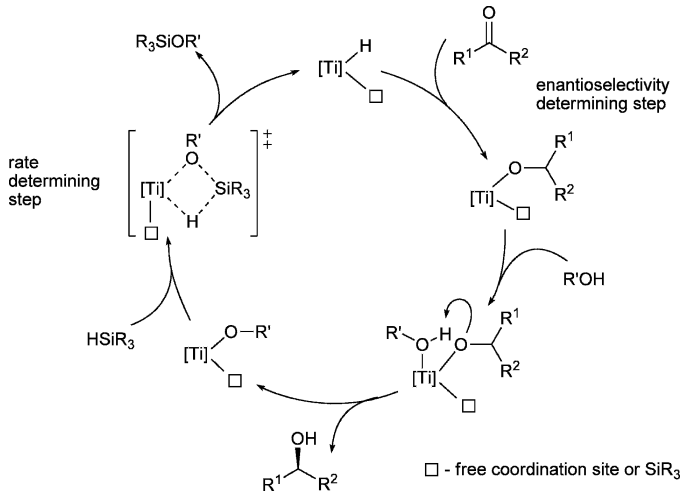
Fig. 10.89



(*S*,*S*)-isomer
a X = Cl
b X = F

in a dramatic increase in activity and enantioselectivity of the catalytic systems in asymmetric hydrosilylation of aryl alkyl ketones. In the presence of modified system acetophenone was converted quantitatively into the corresponding alcohol with enantiomeric excess up to 99%. However, the modified system remained moderately selective in hydrosilylation of dialkyl ketones [173].

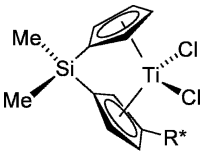
In 1999 Buchwald reported a new optimised protocol of hydrosilylation of a wide range of aryl alkyl ketones with PMHS, leading to high yield and enantioselectivity of respective alcohols while keeping low catalyst loading (Table 10.8) [174]. Generation of the active catalyst is achieved by the treatment of titanocene difluoride with H_3SiPh in the presence of pyrrolidine. The protocol involves a slow addition of primary alcohol to the reaction mixture throughout the reaction, which results in a significant increase in the reaction rate, reduction of the catalyst loading to 0.5–2 mol% and further increase in the enantiomeric excess. Moderate efficiency (ee up to 53%) was observed for dialkyl ketones. The protocol obviates the need to use organolithium reagents to activate the catalyst. A catalytic cycle was proposed to explain the observed dramatic effect of alcohol addition on the reaction rate (Scheme 10.7) [174].



Scheme 10.7 Mechanism of the titanium catalysed asymmetric hydrosilylation in the presence of alcohol

According to the mechanism proposed, the step determining the enantioselectivity is different than that determining the reaction rate. The rate determining step postulated is the σ-bond metathesis between titanium—oxygen and silicon—hydrogen bonds. The increase in the reaction rate caused by addition of alcohol is a consequence of the reduction of the size of the OR group (OR' is smaller than $OCHR^1R^2$) participating in the rate determining step. The additive is not involved in the enantioselectivity determining step, so it does not change the inherent selectivity of the process. The increase in enantioselectivity observed upon addition of alcohol is explained by an increase in the rate of the strongly selective step in relation to non-selective reduction pathways [174]. After activation with BuLi, the two diastereoisomers of $[TiCl_2(\eta^5{:}\eta^5\text{-}C_5Me_4\ SiMe_2C_5H_3R^*)]$ (Fig. 10.90) catalyse the hydrosilylation of ketones [175, 176]. Hydrosilylation of acetophenone with the (R_p)-isomer gives, after hydrolysis, (*S*)-PhCH(OH)Me in 82% ee, whereas only 16% ee of (*R*)-PhCH(OH)Me is obtained by using (S_p)-isomer of the catalyst.

Fig. 10.90



R* = menthyl
(R_p) - isomer

Asymmetric hydrosilylation of ketones with titanium catalysts is not limited to the use of titanocenes. A search for more effective and practical catalyst (especially for olefin polymerisation) provided a new ligand suitable for coordination chemistry of early transition metals. Nakai reported the use of tetraalkoxide catalyst (Fig. 10.91) [177]. The catalyst was used in the asymmetric hydrosilylation of acetophenone with trialkoxysilane. The corresponding alcohol was obtained with ee = 55%. Bottoni and Cozzi used commercially available or easy to synthesise bis(oxazoline) ligands for preparations of the new chiral titanium catalysts. Best enantioselectivities were observed for tetraphenylsubstituted bis(oxazoline) (Fig. 10.92). Bis(oxazoline) titanium complex generated *in situ* from lithium salt of bis(oxazoline) and TiF_4 enabled hydrosilylation of a number of aryl and alkyl ketones with triethoxysilane. The corresponding alcohols were obtained (after hydrolysis step) with enantioselectivities in the range 34–85%. Calculations indicated the involvement of Ti(IV) hydride in the catalytic cycle [178, 179].

Fig. 10.91

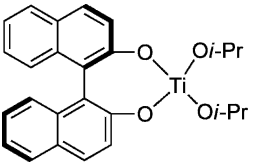
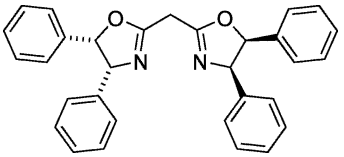


Fig. 10.92



10.1.2 Main Group Metal-Based Catalysts

Tin(II) triflate (10 mol%) combined with PYBOX is an efficient catalyst for the reduction of ketones with PMHS. The use of an enantiomerically enriched PYBOX ligand (Fig. 10.23) allows synthesis of respective alcohols with moderate enantioselectivity (up to 58% ee) [180]. The process requires the presence of alcohol, whose role is supposed to be similar to that proposed for copper and titanium based systems (compare Scheme 10.6).

10.1.3 Nucleophilic-Electrophilic Catalysis

Chiral ammonium fluorides derived from cinchona alkaloids (Figs. 10.93 and 10.94) have been demonstrated to catalyse the hydrosilylation of acetophenone and other simple aryl alkyl ketones with trimethoxysilane or tris(trimethylsiloxy)silane to give the corresponding alcohols with moderate enantioselectivity (51–78% ee) [181].

Fig. 10.93

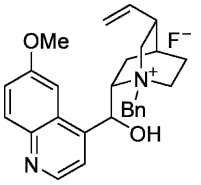
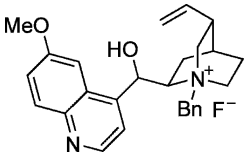


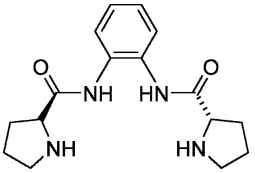
Fig. 10.94



Significant progress has been observed in the asymmetric reduction of ketones and imines with substituted silanes catalysed by well-designed chiral Lewis bases – organocatalysts. In 1988 Hosomi reported the catalytic asymmetric hydrosilylation employing a dilithium salt of phenylalaninol as a catalyst [182]. This reaction was a pioneering example of catalytic asymmetric reactions involving hypervalent silicates. Lithium 1,2-diphenyl-1,2-ethanediolate catalyses the hydrosilylation of

ketones to give alcohols with ee ranging from 12 to 82% [183]. High catalytic activity and low to moderate enantioselectivity in hydrosilylation of aromatic ketones with triethoxysilanes was reported for monolithium salt of (*R*)-binaphthol [184], lithium imidazolide and dilithium salt of histidine [185] and C_2-symmetric diimidazole ligands [186]. Spectroscopic studies of histidine salts has revealed that pentacoordinated silicon is the active intermediate when either the mono- or dianion of histidine is used. Extracoordinate chiral silane generated *in situ* from triethoxysilane and bisproline ligand (Fig. 10.95) undergoes hydrosilylation with prochiral ketones to give the corresponding products with moderate enantioselectivity (up to 64% ee) [187].

Fig. 10.95



N-Formylated pyrrolidine derivative (Fig. 10.96) is an efficient catalyst for the hydrosilylation of ketones with trichlorosilane and affords (after hydrolysis) the corresponding secondary alcohols in good yield and moderate enantioselectivity (up to 51%) [188]. Isoquinolineoxazoline (Fig. 10.97) catalyses enantioselective reduction of aromatic ketones to form the corresponding alcohols with up to 94% ee [189]. L-Pipecolinic acid derived Lewis basic *N*-formamide (Fig. 10.98) is a highly effective catalyst for the asymmetric reduction of various ketones with $HSiCl_3$ to give the corresponding alcohols with good yield (up to 99%) and enantioselectivity (up to 92%) [190]. Lewis base catalysed asymmetric reactions involving hypervalent silicate intermediates were recently reviewed [191, 192].

Fig. 10.96

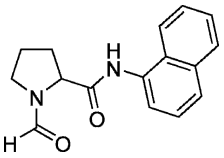


Fig. 10.97

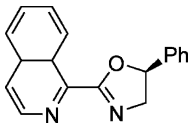
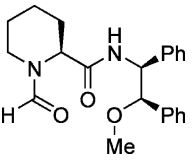


Fig. 10.98

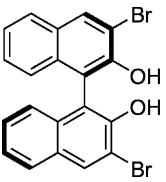


10.2 Asymmetric Hydrosilylation of C=N Bond

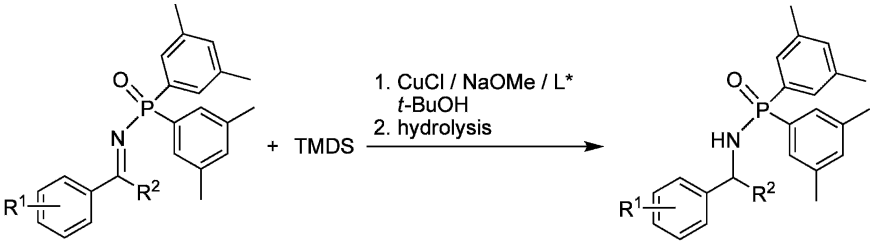
10.2.1 Transition Metal Complexes as Catalysts

$Zn(OTf)_2$ combined with binaphthol derivative (Fig. 10.99) catalyses reduction of *N*-benzylphenylethylimine with PMHS to give after hydrolysis the corresponding amine with 33% ee [193]. Highly enantioselective reduction of *N*-diphenylphosphinylimines with PMHS, TMDS or diphenylsilane was achieved by employing diethylzinc combined with chiral diamine ligand [194]. Several aryl imines were reduced with PMHS in the presence of $ZnEt_2$ / Fig. 10.1 to give the respective amines with ee typically in the range 96–98%. The reaction proceeds readily at room temperature in protic conditions. The reduction of *N*-diphenylphosphinyl phenyl methyl imine with PMHS in the presence of $ZnEt_2$ combined with enantiomerically pure diaminobis(*tert*-thiophene) (Fig. 10.8) leads to formation of the respective phosphinylamine in 97% ee [24].

Fig. 10.99



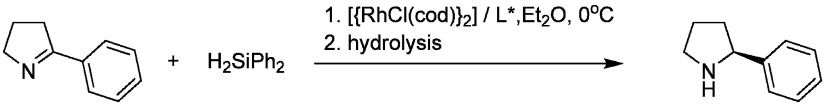
Lipshutz reported a procedure for the asymmetric hydrosilylations of *N*-diphenylphosphinyl aryl ketimines with tetramethyldisiloxane (TMDS) based on catalytic amounts of copper hydride (Eq. 10.19) [195]. The protocol is an extension of the copper-based reduction methodology developed for enones and saturated carbonyl compounds. *In situ* generated Cu-H, when coordinated by enantiopure (*R*)-DTBM-SEGPHOS (Fig. 10.17) can effectively reduce aryl imines under mild conditions. The process is economically attractive as the starting materials and catalyst are inexpensive. The reaction is highly efficient as regards both chemical yields and enantioselectivities (ee up to 99.3%). The diphenylphosphinyl derivatives can be readily hydrolysed to the amines desired without a decrease in enantiopurity.



(10.19)

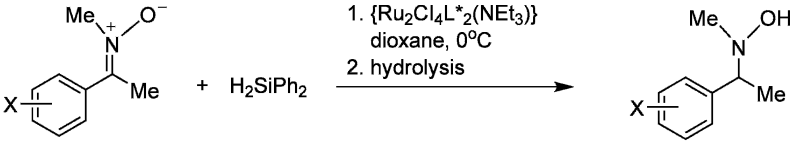
Contrary to the copper-based hydrosilylations of carbonyl systems, a dramatic impact of silane structure on the levels of induction was observed. Replacing PMHS by tetramethyldisiloxane significantly increased the ee values observed for imine reduction products. A decisive step for effective conversion is a successive addition of *t*-BuOH throughout the reaction.

Although a number of efficient catalytic systems for rhodium-based asymmetric reduction of carbonyl derivatives are known, almost no information is available on successful reduction of imines in the presence of rhodium catalyst. In the 1980s, Brunner reported rhodium catalysed hydrosilylation of alkyl aryl ketoximes with diphenylsilane in the presence of (−)-DIOP as non-racemic ligand. The respective amines were formed with enantioselectivities up to 36% [196, 197]. Chiral oxazolinylferrocenylphosphines (Fig. 10.80), effective ligands for the Ir(I)- and Ru(II)-catalysed asymmetric hydrosilylation of imines were tested in the presence of rhodium complex. However, compared with the iridium and ruthenium systems, the rhodium one showed relatively low catalytic activity and enantioselectivity (Eq. 10.20) [198].



(10.20)

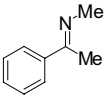
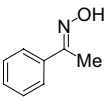
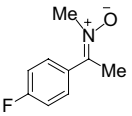
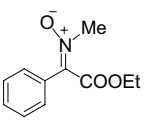
Ruthenium(II) diphosphine complex $[Ru_2Cl_4L_2(NEt_3)]$, where L = (*S*)-tol-BINAP (Fig. 10.12) catalyses hydrosilylation of nitrones with diphenylsilanes (Eq. 10.21) [199].



(10.21)

The corresponding enantioenriched *N,N*-disubstituted hydroxylamines were formed with moderate to high yields and enantiomeric excess up to 91% (Table 10.9). The observed enantioselectivity depends on the silane used and increases in the following order: diphenylsilane > diethylsilane > l-naphthylphenylsilane > methylphenylsilane >> phenylsilane [199]. Oxazolinylferrocenylphosphine substituted ruthenium complex $[RuCl_2(PPh_3)L^*]$ (L^* = Fig. 10.80a) exhibits activity in the asymmetric hydrosilylations of cyclic imines (Table 10.9) [160, 198]. Addition of AgOTf (an activating agent used in Ru(II) / oxazolinylferrocenylphosphine catalysed reduction of ketones) completely ceased the reaction. The complex $[RuCl_2(PPh_3)L^*]$ (where L^* = Fig. 10.80a or Fig. 10.80b) catalyses the asymmetric hydrosilylation of ketoximes with H_2SiPh_2 [200]. The reaction results in formation of the corresponding primary amines (after acid hydrolysis) with high enantioselectivities (up to 89% ee) but with low to moderate yields (Table 10.9).

Table 10.9 Ruthenium catalysed asymmetric hydrosilylation of C = N bond with diphenylsilane

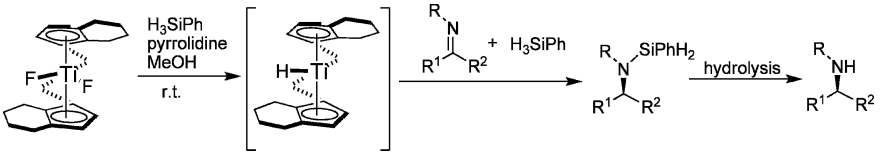
Substrate	Catalyst	Temp. [°C]	Time [h]	Yield[a] [%]	Ee[a] [%] (config.)	Ref.
	$[RuCl_2(PPh_3)L^*]$ L* see Fig. 10.80a	0	40	60	88 (*S*)	[198]
	$[RuCl_2(PPh_3)L^*]$ L* see Fig. 10.80a	0	90	51	73 (*S*)	[198]
	$[RuCl_2(PPh_3)L^*]$ L* see Fig. 10.80b, AgOTf,	r.t.	40	21	89 (*R*)	[200]
	$[Ru_2Cl_4L^*_2(NEt_3)]$ L* see Fig. 10.12	0	2	63	86 (*S*)	[199]
	$[Ru_2Cl_4L^*_2(NEt_3)]$ L* see Fig. 10.12	0	2	24	91 (*S*)	[199]

Reaction conditions: 1mol% [Ru]; [C=N]:[silane] = 1:2– 1:4; [a]) determined after hydrolysis

Chiral oxazolinylferrocenylphosphine (Fig. 10.80) successfully used in the rhodium and iridium based asymmetric hydrosilylation of simple ketones was found an effective ligand in the iridium catalysed asymmetric hydrosilylation of cyclic (five-membered ring) and *N*-methyl imines with H_2SiPh_2 [198]. The corresponding amines were obtained (after hydrolysis step) with high enantioselectivities (up to 89% ee). Interestingly, when oxazolinylphenylphosphine, which does not have

planar chirality due to the ferrocenyl substituent, was used as a ligand almost the same enantioselectivity was observed.

Difluoro[1,2-bis(η^5,η^5-tetrahydroindenyl)ethane]titanium(IV) (Fig. 10.89b) activated by interaction with H_3SiPh in the presence of pyrrolidine and MeOH was demonstrated to be a very efficient catalyst of the hydrosilylation of a range of N-methyl and cyclic imines with H_3SiPh (Scheme 10.8) [201].

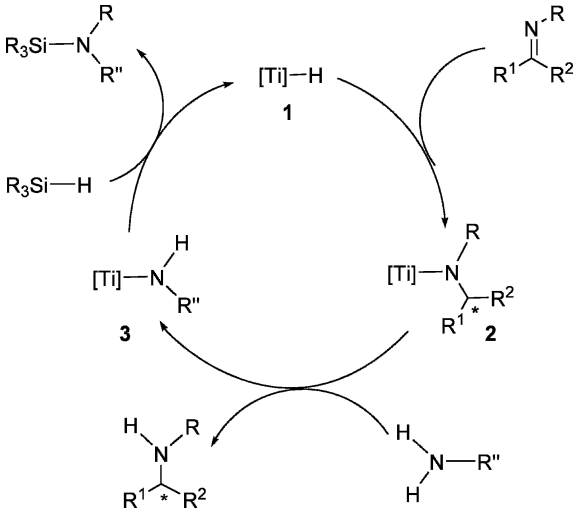


Scheme 10.8 Hydrosilylation of imines in the presence of difluoro[1,2-bis(η^5,η^5-tetrahydroindenyl)ethane]titanium(IV)

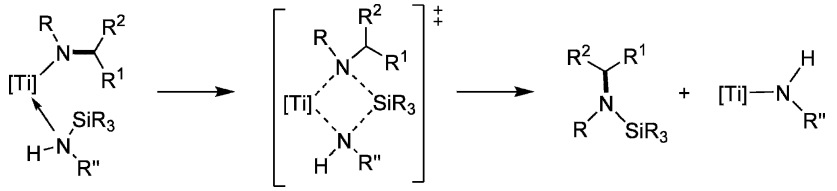
The methodology permits a synthesis of the corresponding amines (after hydrolysis step) with high yield (80–97%) and very high enantioselectivity (86–99% ee) by using small catalyst loadings (down to 0.02 mol%). Although the mechanism of generation of catalytically active species is not clear, it is assumed that Ti(III) hydride is the real catalyst of the process [201]. The titanium-based hydrosilylation protocol was successfully applied for the synthesis of piperidine alkaloids (*S*)-coniine and (*2R,6R*)-*trans*-Solenopsin A [202] as well as for kinetic resolution of the N-methyl imines of 3-substituted indanones and 4-substituted tetralones [203].

In 1998 Buchwald reported a protocol which enabled the efficient asymmetric hydrosilylation of a wide array of *N*-benzyl and *N*-aryl imines with PMHS [204]. The key modification of the reaction system was the use of primary amine as additive. Addition of amine (isopropylamine and hexylamine were proved to give best results) gave rise to an increase in the overall activity of the catalytic system and achieved enantioselectivity. The procedure permits the synthesis of the corresponding aryl alkyl amines with 92–97% yield and enantioselectivities ranging from 92 to 99% ee [204]. High sensitivity of the catalytic system to the steric bulk of the substituent at nitrogen was observed. The replacement of the methyl substituent by a benzyl one leads to a considerable decrease in the activity and selectivity. Although no detailed mechanistic studies were undertaken, a reasonable mechanism explaining the observed effect of amine addition was proposed (Scheme 10.9) [204].

According to the mechanism proposed, the chirality transfer step is the insertion of imine into the Ti—H bond (by analogy to the imine asymmetric hydrogenation mechanism [205]). In the next step titanium amido complex (**2**) reacts with a primary amine to form a less crowded complex (**3**). Finally, the reaction of **3** with silane produces silylated amine and regenerates the titanium hydride complex (**1**) [204].



Scheme 10.9 Proposed mechanism of titanium catalysed asymmetric hydrosilylation of imines in the presence of primary amine



Scheme 10.10 Mechanism of promoting effect of primary amine addition on titanium catalysed asymmetric hydrosilylation of imines (alternative explanation)

According to an alternative mechanism (Scheme 10.10), the primary amine can be silylated to an *N*-silylamine. These species might facilitate cleavage of the Ti—N bond by coordination to the titanium centre followed by σ-bond metathesis.

The Buchwald catalytic system was successfully used for the synthesis of a wide range of *N*-aryl dialkylamines [206]. The asymmetric hydrosilylation of *N*-aryl imines derived from non-aromatic ketones with PMHS has been successfully performed to give chiral amines with high enantioselectivities. *N*-Aryl dialkylimines could be reduced with moderate to high yield (70–99%) and enantiomeric excess 88–99%. In contrast, aryl-substituted *N*-aryl imines undergo non-selective reduction. The new protocol was applied as a step in total synthesis NPSR-568 – an active compound for the treatment of hyperparathyroidism [207]. Recently Lipshutz reported a heterogeneous catalyst active in reductions of imines [41]. Copper(II) immobilised on charcoal in combination with NaOPh and small amounts of (*R*)-DTBM-SEGPHOS (Fig. 10.17) or BIPHEP ligand (Fig. 10.18), in the presence of a

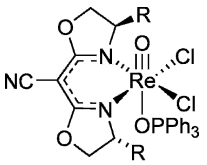
PMHS is very effective in asymmetric hydrosilylation of imines and allow formation of the corresponding amines in high yields and enantioselectivities (up to 88% ee).

10.2.2 Miscellaneous Metal-Based Catalysts

The use of high-throughput techniques has allowed rapid identification of the catalytic activity of $Sn(OTf)_2$, and $In(OTf)_3$ combined with binaphthol derivative (Fig. 10.99). Reduction of *N*-benzylphenylethylimine with PMHS leads (after hydrolysis) to the corresponding amine with enantiomeric excess 60 and 36%, respectively. $Cd(chb)_2$ / *i*-Pr-PYBOX system (chb = cyclohexanebutyrate) is also found active in the reaction giving 60% yield and 33% ee [193].

Re(V)-oxo complex with monoanionic bidentate ligands (Fig. 10.100) catalyses the enantioselective reduction of various N-phosphinyl imines with very high enantioselectivity, exceeding 99% ee [208].

Fig. 10.100



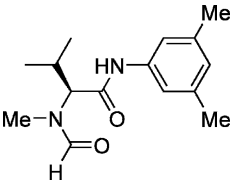
R = 4-C_6H_4(*t*-Bu)

10.2.3 Nucleophilic-Electrophilic Catalysis

Similarly as for the hydrosilylation of C=O bond, the lithium salts of some organic derivatives have been noted to catalyse hydrosilylation of imines. The optically active lithium alkoxides catalyse the asymmetric hydrosilylation of *N*-tosyl or *N*-*p*-nitrobenzenesulphonyl imines with trimethoxysilane to form respective amines in moderate enantioselectivity (up to 72% ee) [209].

Recently, the synthesis of chiral secondary amines via the metal-free asymmetric organocatalytic hydrosilylation of imines received much attention, as it permitted avoidance of a number of problems characteristic of transition metal catalysed processes [210, 211]. Chiral amides have been recognised as efficient Lewis basis organocatalysts for the asymmetric reduction of imines. The *N*-formylpyrrolidine derivatives have been found to activate trichlorosilane for direct reduction of imines to amines. Non-racemic *N*-formylproline derivatives activate trichlorosilane and induce asymmetric addition to imines to give enantiomerically enriched amines in moderate (up to 66%). Reaction is not affected by the presence of carbonyl groups [212]. *N*-methyl L-valine derivative (Fig. 10.101) catalyses asymmetric hydrosilylation of *N*-phenyl aryl imines with trichlorosilane to form the corresponding amines with up to 92% ee. The structure-reactivity investigation suggests the hydrogen bonding and arene-arene interactions between the catalyst and the incoming imine as the main factors determining enantioselectivity [213, 214].

Fig. 10.101



Introduction of a fluorous tag to the catalyst structure (Fig. 10.102) simplifies the isolation procedure, without the loss of enantioselectivity [215]. The reduction of α-chloroimines with $HSiCl_3$ in the presence of the L-valine-derived formamide (Fig. 10.103) (5 mol%), produced the corresponding vicinal α-chloroamines in good yields and high enantioselectivity (96% ee). Reaction was applied as a step in the synthesis of 1,2-diaryl aziridines [216]. Recent examples of hydrosilylation of *N*-aryl or *N*-benzylimines performed in the presence of organocatalysts were collected in Table 10.10.

Fig. 10.102

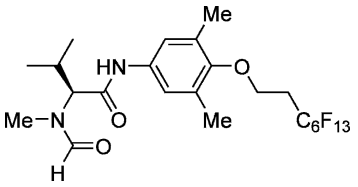


Fig. 10.103

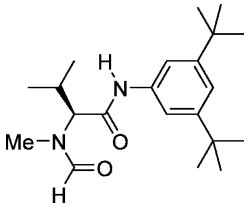


Table 10.10 Asymmetric hydrosilylation of *N*-aryl or *N*-benzyl aryl alkyl imines in the presence of organocatalysts

Catalyst	Temp. [°C]	Time [h]	Yield [%]	Ee [%]	Ref.
Fig. 10.104	0–r.t.	4	24–90	67–80	[217]
Fig. 10.105	0	60	74–95	68–86	[218]
Fig. 10.106	−20	24	51–67	85–87	[189]
Fig. 10.107	−10	24	80–93	76–93	[219]
Fig. 10.108	0	16	75–98	87–96	[220]
Fig. 10.109	−20	24	85–98	83–93	[190]
Fig. 10.110	−20	48	63–99	82–97	[221]
Fig. 10.111	−20	24–48	73–98[a]	86–93[a]	[222]

Reaction conditions: organocatalyst 10 mol% (relative to imine), [C=N]:[silane] = 1:1.5–1:2.1; [a]organocatalyst 20 mol%

Fig. 10.104

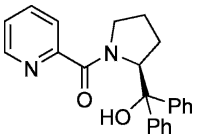


Fig. 10.105

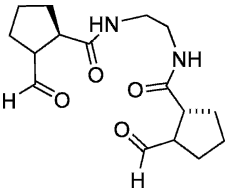


Fig. 10.106

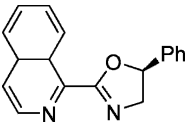


Fig. 10.107

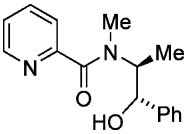


Fig. 10.108

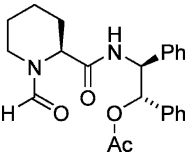


Fig. 10.109

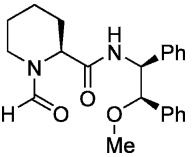


Fig. 10.110

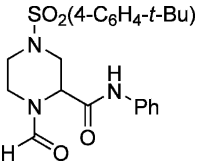
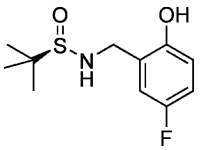
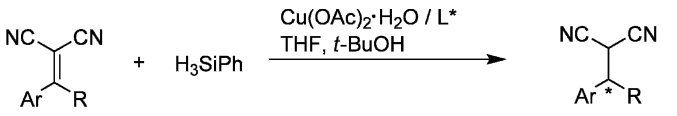


Fig. 10.111



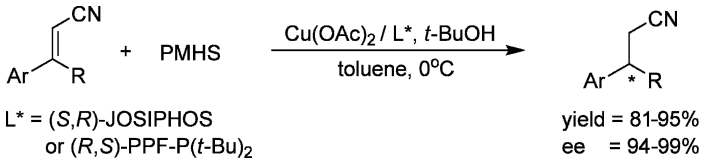
10.3 Asymmetric Conjugate Reduction of Nitriles, Nitroalkenes and Sulphones

A copper hydride complex, generated *in situ* from CuO(*t*-Bu), (*S*)-BINAP, and H_3SiPh, allows the asymmetric reduction of the α,β-unsaturated dinitriles with phenylsilane to give products with moderate to high yield and enantioselectivity. In addition to CuO(t-Bu), some air and moisture stable Cu salts such as $Cu(OAc)_2$ were also effective as catalyst precursors (Eq. 10.22) [223].



(10.22)

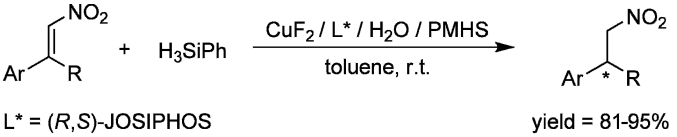
Air stable precursors $Cu(OAc)_2$ combined with readily available, commercial bisphosphine ligand JOSIPHOS (Fig. 10.15) or (*R*,*S*)-PPF-P(t-Bu)$_2$ (Fig. 10.16) catalyse the highly enantioselective reduction of α,β-unsaturated nitriles with PMHS (Eq. 10.23) [224, 225].



(10.23)

The same catalytic system allows reduction of a range of 3-aryl-3-pyridylacrylonitriles with high levels of enantioselectivity (86–96% ee) [226].

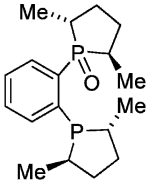
Ferrocenyldiphosphine JOSIPHOS (Fig. 10.15) and (*S*)-tol-BINAP (Fig. 10.12) combined with CuO(*t*-Bu) were successfully used by Carreira for the catalytic enantioselective conjugate reduction of β,β-disubstituted nitroalkenes with PMHS / H_3SiPh mixture providing access to optically active nitroamines with enantiomeric excess 66–94% [227]. The same reaction was reported to take place in the presence of a catalytic system containing commercially available CuF_2 and non-racemic JOSIPHOS as a ligand (Eq. 10.24) [228].



(10.24)

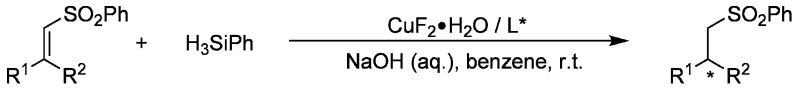
Hydrosilylation of β,β-disubstituted vinyl sulphones with phenylsilane, diphenylsilane or PMHS proceeds in the presence of catalyst generated *in situ* from hydrated copper fluoride and bis(phosphine) monoxide ligand (Fig. 10.112). [229].

Fig. 10.112



Me-DUPHOS (O)

The reaction runs efficiently in the presence of basic additives such as KOH or NaOH and provides alkyl sulphones with high yields and excellent enantiomeric excesses (up to 99%) (Eq. 10.25) [230].



L* = (*R*,*R*)-(*R*,*R*)-Me-DUPHOS (O)

yield = 61-97%
ee = 70-99%

(10.25)

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