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Modern Organoaluminum Reagents

Preparation, Structure, Reactivity and Use

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Modern Organoaluminum Reagents

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Volume Editors: Simon Woodward · Samuel Dagorne

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Aims and Scope

The series *Topics in Organometallic Chemistry* presents critical overviews of research results in organometallic chemistry. As our understanding of organometallic structures, properties and mechanisms grows, new paths are opened for the design of organometallic compounds and reactions tailored to the needs of such diverse areas as organic synthesis, medical research, biology and materials science. Thus the scope of coverage includes a broad range of topics of pure and applied organometallic chemistry, where new breakthroughs are being made that are of significance to a larger scientific audience.

The individual volumes of *Topics in Organometallic Chemistry* are thematic. Review articles are generally invited by the volume editors.

In references *Topics in Organometallic Chemistry* is abbreviated Top Organomet Chem and is cited as a journal. From volume 29 onwards this series is listed with ISI/Web of Knowledge and in coming years it will acquire an impact factor.

Preface

It is strange, given that aluminum is the most populous metal in the earth's crust and that $AlMe_3$ is the world's largest tonnage organometallic, that books specifically dedicated to the chemistry of alanes and their organometallic reactions are so scarce.

First prepared in the period 1859–1865, Al-R chemistry has consistently been only afforded, what might be described as "a Cinderella role" in overviews, occasional book chapters, and other reviews. In the last two decades, the Editors can only think of two other major volumes dedicated aluminum organometallics – while literary offerings to her many "p and d block sisters" abound. It is therefore hardly surprising that when through the auspices of the *Topics in Organometallic Chemistry* Editorial Board the opportunity to prepare a specific volume on alane chemistry arose, leading scientists in this community jumped at the opportunity to join the project. In fact, remarkably, not a single original author declined our invitation – there was in fact a slight oversubscription of potential contributors. As Editors we are wildly grateful to these authors: for their time, their enthusiasm, and their dedication to this volume – you have done a fantastic job as the following 200+ pages attest to!

On the basis that, rather like organoaluminums, all prefaces simply do their job (and then pass largely unnoticed), let us move swiftly on to the main course of this volume: a comprehensive study of the "state-of-play" in organoaluminum chemistry at the start of the twenty-first century, some 150 years after these compounds were first prepared.

Nottingham — Simon Woodward
Strasbourg — Samuel Dagorne
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Simple Trivalent Organoaluminum Species: Perspectives on Structure, Bonding, and Reactivity

Janusz Lewiński and Andrew E.H. Wheatley

Abstract This chapter deals with the most significant developments in Al(III) organoaluminum chemistry since 2000. The most prominent synthetic and structural features along with reactivity trends are discussed for organoaluminum compounds featuring simple σ-bonded substituents and the corresponding 4- and 5-coordinate complexes formed in the presence of Lewis base. The structural effects of including ligands with group 15 and 16 donors are discussed in terms of the formation of heteroatom bridges and the ubiquitous formation of cyclic motifs. The structural implications of using bidentate, chelating ligands are also introduced, including the propensity of these for stabilizing cationic Al(III) species. The current and potential utility of such species in areas such as catalysis and material science is also highlighted with, whenever appropriate, structure/reactivity correlations.

Keywords Catalysis, Coordination chemistry, Material science, Organoaluminum, Reactivity, Structure

Contents

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Abbreviations

3,5-*t*Bu$_2$pz	3,5-Di-tert-butylpyrazolyl
Ar-Dimpy	2,6-(ArNCR)$_2$C$_5$H$_3$N]
BHT	2,6-Di-*tert*-butyl-4-methylphenolate
bpy	2,2′-Bipyridyl
BINOL	1,1′-Bi-2-naphthol
Cy	Cyclohexyl
ε-CL	ε-Caprolactone
DAB	Diazabutadiene
Dipp	2,6-*i*Pr$_2$-C$_6$H$_3$
Dipp-BIAN	1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene
DMF	Dimethylformamide
EDBP	2,2′-Ethylidenebis(4,6-di-*tert*-butylphenoxide)
elacH	*rac*-Ethyl lactate
EPR	Electron paramagnetic resonance
Et	Ethyl
FLP	Frustrated Lewis pair
H-dpt	1,3-Diphenyltriazene
H-hacet	2′-Hydroxyacetophenone
*i*Bu	Isobutyl
IMes	1,3-Dimesitylimidazol-2-ylidene
Impy	2,6-Bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine
*i*Pr	Isopropyl
*i*Pr$_2$-ATI	*N*,*N*′-Diisopropylaminotroponiminate
LA	Lactide
Me	Methyl
Mes	2,4,6-Me$_3$-C$_6$H$_3$H$_2$
Mes*	2,4,6-*t*Bu$_3$-C$_6$H$_2$

mesal	Methyl salycilate anion
MPV	Meerwein–Ponndorf–Verley
NHC	N-Heterocyclic carbene
NMR	Nuclear magnetic resonance
OPP	Oppenauer
Ph	Phenyl
py-O	Pyridine oxide
py	Pyridine
py-Me	γ-Picoline
pz	Pyrazolyl
ROP	Ring-opening polymerization
salen	(*N*,*N*′-Alkyl/aryl)bis-salicylideneimine
salophen	O-Phenylenediamine-bridged
tbp	Trigonal bipyramidal
*t*Bu	*tert*-Butyl
Tf	Triflate
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1 Introduction

This chapter seeks to update the recent literature concerning organometallic compounds of Al(III) [1–19]. Heterobimetallic systems are essentially excluded from the present contribution, even where there is no inter-metal interaction and the aluminum is in the +III oxidation state. Some of these aspects are discussed in detail in [286]. Whilst this eliminates the extensive subsection of heterometallic aluminum compounds known as "ate complexes," these have been reviewed elsewhere [20].

The present contribution is structured around three main classes of organoaluminum species.

- Organoaluminum compounds featuring simple σ-bonded aliphatic or aryl substituents [21, 22]. By virtue of the polarity in the metal–carbon bond, these groups render the metal highly reactive to both moisture and oxygen and discussion will focus on the synthetic procedures and precautions necessary to prevent decomposition as well as on the ability to harness insertion reactions for benefit. Focus will then shift to the effects of introducing Lewis base and the observation of 4- and 5-coordinate complexes.
- Compounds with group 16 donor ligands. These will be discussed with an emphasis placed on how the steric and, to a lesser extent, electronic properties of alkoxide and aryloxide ligands [23–25] can influence the stability of the metal center and the possibility of aggregation. The dramatic structural effects of heteroatom inclusion will be considered in detail, with aggregation now being enabled through the formation of heteroatom bridges and the ubiquitous formation of dimeric motifs based on Al_2X_2 diamond cores. The focus will then shift

to aluminum hydroxide [26, 27] and oxide [28] chemistry, including the products yielded when organoaluminum compounds undergo scavenging reactions in the presence of oxygen [29] or moisture [30].

The ability to manipulate aggregation chemistry by utilizing potentially chelating bi- and multifunctional ligands will be developed, focusing firstly on non-delocalized systems and moving thereafter to ligands in which the donor centers communicate. The structural implications and resulting synthetic applications of *O*,*O*- and *N*,*O*- (including = (*N*,*N*′-alkyl/aryl)bis-salicylideneimine [31]) chelated compounds will be discussed in detail [32–35]. Lastly, aluminum carboxylates will be covered.

– Organoaluminum compounds with group 15 donor ligands. Emphasis will be on aluminum amides [36], with imides [37] and azides [38, 39] having been reviewed recently. Organolaluminum compounds containing higher group 15 donors will not be covered but have been reviewed lately [40–44]. As with group 16 stabilized systems, the effects of bidentate ligands will be examined for *N*,*N*′-chelated systems, including discussion of their affinity for stabilizing cationic Al(III) species [45–47].

This article aims to provide a critical review of literature that broadly covers the period 2000–present, though as an aide to the general reader, formative research will be included as appropriate. Present and potential applications in organometallic reactivity, synthesis, and catalysis will be discussed [48–58], though the design and use of organolaluminum compounds as polymerization catalysts/co-catalysts [46, 59–69] falls outside the remit of this review and is dealt with in [287].

2 Aluminum Trialkyls: Structures and Complexes with Lewis Bases

Homoleptic aluminum alkyl compounds are among the most common organometallic reagents used in organic and organometallic synthesis. It is not surprising that much effort has been devoted to characterizing the structures of these compounds, both in solution and in the solid state. The lower homologs of tri-alkylaluminum compounds are well known to form dimeric $R_2Al(\mu\text{-}R)_2AlR_2$ species with symmetrical alkyl bridges that involve the overlap of the hybrid orbital of the bridging carbon atom with two metal orbitals, an archetype of 3-center-2-electron bonding. It is pertinent to note that the long history of studies on the nature of the bridge bonding in Al_2Me_6 (**1**, Fig. 1) is well documented [70], and the central importance of these studies to an understanding of metal–alkyl bonding in general is well recognized. Replacing alkyl by aryl or other unsaturated organic ligands gives rise to new electronic and geometric options for secondary bonding. Triphenylaluminum follows the example of $AlMe_3$ in forming dimeric $Ph_2Al(\mu\text{-}Ph)_2AlPh_2$ moieties with symmetrical phenyl bridges [71], whereas the corresponding benzyl compound, $Al(CH_2Ph)_3$ (**2**, Fig. 1), is monomeric in the solid state [72]. In the latter

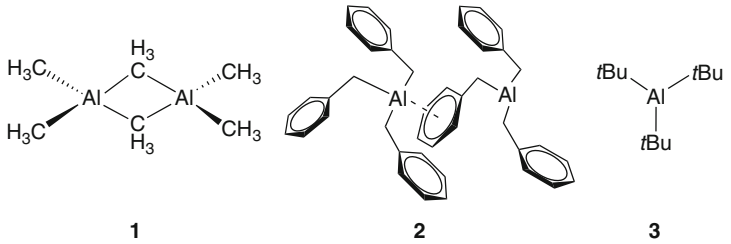


Fig. 1 Representative examples of simple AlR_3 species

case, the metal is displaced 0.475 Å above the plane described by the three methylene carbon atoms and more detailed examination of the intermolecular interactions clearly indicated that this distortion from planarity toward a tetrahedral arrangement results from there being a strong interaction of the aromatic π-face of the benzyl groups with the metal (the shortest intermolecular Al···C distance is 2.453 Å). This example demonstrates that a proper disposition of aromatic rings can lead to cooperative π-electron interactions with the vacant *p* orbital on aluminum and that this stabilization mode can effectively compete with 3-center-2-electron bonding. Increasing the bulk of the alkyl substituent reduces its capacity to form alkyl bridges through 3-center-2-electron bonding: thus, a compound such as Al*t*Bu$_3$ (**3**, Fig. 1) is monomeric in the gas phase, solution, and the solid state [73, 74].

Organoaluminum compounds exhibit a significant tendency to maximize their coordination number through the formation of adducts with a wide range of neutral donor ligands or by self-association to give aggregates containing tetrahedral or higher coordinated aluminum centers. Homoleptic aluminum alkyls readily form Lewis acid–base complexes, in which the aluminum is four-coordinate. The formation of exclusively four-coordinate $R_3Al(L)$ adducts has been observed regardless of potential ligand denticity, and there is only one exception known to this. When $AlMe_3$ reacts with an excessive amount of a sulfur-based crown ether, [12]aneS_4, a five-coordinate adduct $Me_3Al(L)_2$ (**4**, Fig. 2) results [75]. In this unique adduct the aluminum atom resides in a trigonal bipyramidal environment, the aluminum and carbon atoms of the $AlMe_3$ unit are coplanar reflecting the presence of the five-coordinate aluminum center. The Al–S bonds differ strongly in length (2.718(3) vs. 3.052(3) Å) though the latter distance remains significantly below the sum of the van der Waals radii, which fall in the range of 3.50–3.80 Å [76, 77].

In line with the observation of five-coordinate aluminum (above) is the crystal structure of a homoleptic sulfur-substituted alkylaluminum compound, $Al(CH_2SMe)_3$ (**5**, Fig. 2) [78]. In the solid state, molecules of **5** self-organize into a polymeric structure in which the aluminum atoms possess a trigonal bipyramidal arrangement with the coordination polyhedron defined by three carbon and two sulfur atoms; two of the three CH_2SMe ligands act as bridging ligands (μ-η^2; 1κC:2κS), and the third is terminally bound, η^1; κC. The two Al–S bond lengths (2.618(4) and 2.770(4) Å) are significantly shorter than that observed in **4**, which is manifested in noticeable differences in the average Al–C bonds length for **5** and **4** (2.033 Å and 1.949 Å,

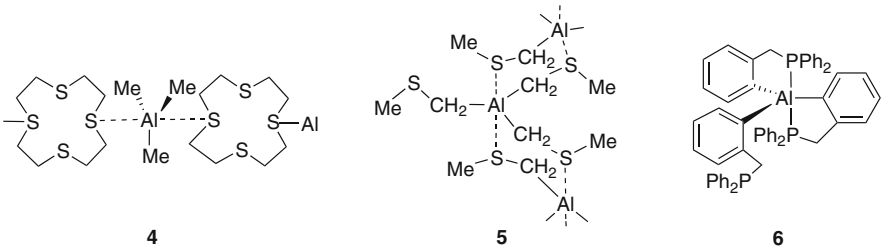


Fig. 2 Examples of five-coordinate species featuring AlC_3 centers

respectively). Pentacoordination in triorganoaluminum compounds is otherwise met only when two or more of the organic groups carries a suitably placed functional group that can coordinate intramolecularly. An example of this is the phosphorus-substituted alkylaluminum compound, $Al[(2\text{-}Ph_2PCH_2)C_6H_4]_3$ (**6**, Fig. 2), which forms a discrete five-coordinate complex with two ligands actually chelating, while the third phosphorus site does not bind the metal [79]. Similar structures featuring five-coordinate AlC_3 centers were reported for alkylaluminum complexes supported by bis(amino)aryl or bis(imino)aryl NCN-pincer ligands [80, 81]. In these complexes, the monoanionic NCN pincer ligands coordinate to the central metal in a tridentate fashion. The geometry around the Al atom can be described as distorted tbp with three carbon atoms in the equator and two nitrogen atoms in the apical positions.

For the five-coordinate aluminum complexes of tbp geometry mentioned above one could describe the bonding in terms of electron-rich hypervalent systems [82, 83] in which the interaction of a vacant 2*p* orbital of the central aluminum atom with two lone-pair electrons of the apical ligands takes place. The interaction leads to the formation of a linear three-center four-electron (3c-4e) hypervalent bonding system; thus, they may be called hypervalent compounds. Sometimes, an alternative type of five-coordinate complex has been suggested, whereby a vacant sp^3-hybridized aluminum atom overlaps with two lone electron pairs of donor centers in a bidentate Lewis base. Up to now, however, there is no evidence that AlR_3 compounds are able to form this type of five-coordinate complex. In this regard, it is worth noting that a related adduct was structurally characterized involving $InMe_3$ and *N*,*N*′,*N*″-triisopropyl-1,3,5-triazacyclohexane (*N*,*N*,*N*). In the molecular structure of $Me_3In(N,N,N)$ (**7**, Fig. 3) the indium atom resides above the six-membered ring and accepts three lone pairs [84]. In contrast, systems incorporating $AlMe_3$ and nitrogen-, oxygen- or sulfur-based macrocyclic ligands have always resulted in the isolation of classical four-coordinate complexes, such as compound **8** (Fig. 3) [85, 86].

Aluminum trialkyls are highly reactive with a variety of simple molecules including oxygen and water (vide infra), and alkenes. For example, the addition of $AlEt_3$ to ethylene is the key reaction in the development of Ziegler chemistry [87]. Investigations of this reactivity have led to the development of commercially important alkylaluminum reagents and catalysts, and these are discussed in the subsequent subsections. A newly emerging area in organoaluminum chemistry involving compounds with an AlC_3 core concerns so-called frustrated Lewis pairs

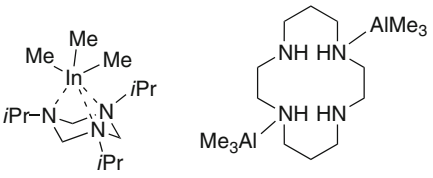
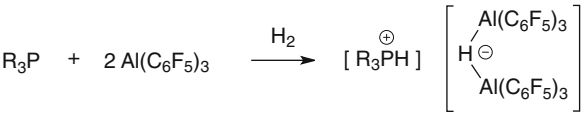


Fig. 3 Molecular structures of complexes **7** and **8**

(FLPs) [88]. Organometallic complexes of the type $[R_mAlCH_2ER'_n]_x$ with heteroatoms in positions geminal to the metal (R, R′ = organic groups; E = N, P, S, O) [89] have shown potential as new reagents for synthetic applications [90]. Organoaluminum FLPs bearing donor and acceptor sites in close proximity are of considerable interest for the dipolar activation of small molecules, such as H_2 [91] and CO_2 (Eqs. 1 and 2) [92, 93]. Such entities were also shown to promote the C–H activation of alkenes [94] or alkynes [95, 96]. In the near future one can expect a number of new spectacular discoveries and unique transformations involving FLPs, i.e., the combination of main group Lewis acids and bases that are sterically hindered toward the formation of Lewis adducts, including the development of various aluminum-based FLPs to produce catalysts for the activation of small molecules or the reduction of unsaturated hydrocarbons.



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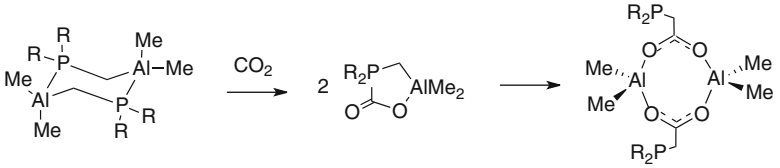

(2)

3 Organoaluminum Alkoxides and Aryloxides

The chemistry of aluminum alkoxides has progressed significantly in the last fifty years due to advances in their synthetic methodology and in the understanding of the role ligands and coligands play in stabilizing the compounds and ensuring solubility. The elimination–condensation reaction sequence (Eq. 3) which occurs between an alkylaluminum compound and a Brønsted acid is undoubtedly the cornerstone of much of organoaluminum chemistry [97].

$$AlR_3 + nHL = R_{3-n}Al(L)_n + nHR \tag{3}$$

In general this reaction is very facile and is proposed to occur *via* an intermediate Lewis acid–base complex, i.e., $AlR_3(HL)$. Such alkylaluminum complexes with oxygen-based Brønsted acids (e.g., H_2O, HOR, and HO_2CR) are very unstable

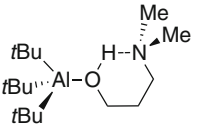

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Fig. 4 A rare example of a well-defined R_3Al-HOR adduct

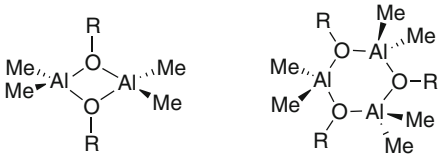
and this precludes their isolation. Nevertheless, stable alcohol coordination complexes of trialkyaluminums have been isolated through the application of intramolecular hydrogen bonding to an amine. For example, reaction of Al*t*Bu$_3$ with $HOCH_2CH_2CH_2NMe_2$ allowed the isolation and structural characterization of the Lewis acid–base complex, *t*Bu$_3$Al[O(H)$CH_2CH_2CH_2NMe_2$] (**9**, Fig. 4), which undergoes alkane elimination above 45°C to yield [*t*Bu$_2$Al(μ-$OCH_2CH_2CH_2NMe_2$)]$_2$, as observed by ^{1}H NMR spectroscopy [98]. As noted by the authors, based upon the relative basicity of alcohols and tertiary amines, co-ordination of the $HOCH_2CH_2CH_2NMe_2$ ligand could be expected to occur *via* the nitrogen, and the observed complexation through the oxygen is presumably as a consequence of the strong hydrogen-bond interaction "tying-up" the amine's lone pair.

3.1 Derivatives of Alcohols and Phenols

The controlled addition of alcohol or phenol to an alkylaluminum compound represents a general and broadly applicable method by which to prepare organoaluminum alkoxides or aryloxides. The marked tendency of these type of compounds to oligomerise through the formation of strong aluminum–oxygen bridges is well documented [99, 100]. In the absence of overwhelming steric bulk, simple dimethylaluminum alkoxides, [$Me_2Al(\mu\text{-}OR)]_n$, exist in dimeric **10** and trimeric **11** forms (Fig. 5). For example, based on molecular weight studies [101, 102] and as subsequently confirmed by electron diffraction [103], "Me_2AlOMe" was demonstrated to be trimeric, adopting a non-planar six-membered $A1_3O_3$ ring structure, while the moiety "Me_2AlOPh" was shown to exhibit a dimer/trimer equilibrium [104]. Dimethylaluminum alkoxides with straight-chain hydrocarbon substituents may be both di- and tri-meric in solution; interestingly, they are trimeric when synthesized at low temperatures, but rearrange to dimers at elevated temperatures [105].

It is only with sufficiently sterically bulky ligands, such as 2,6-di-tertbutyl-4-methylphenolate (BHT), that monomeric Al species are formed: $Me_2Al(BHT)$ and $MeAl(BHT)_2$ (**12** and **13**, Fig. 6) [106, 107]. The isolation of these monomeric compounds is undoubtedly attributable to the steric hindrance of the aryloxide precluding dimerization via bridging by the aryloxide moieties. For these compounds, the short Al–O distances and large Al–O–C bond angles observed in the solid state were proposed to arise from π-interaction between the vacant *p* orbital on aluminum and the lone pairs on the aryloxide oxygens (structure **14**, Fig. 6).

Fig. 5 Dimeric and trimeric structures for compounds of the type $[Me_2Al(\mu\text{-}OR)]_n$



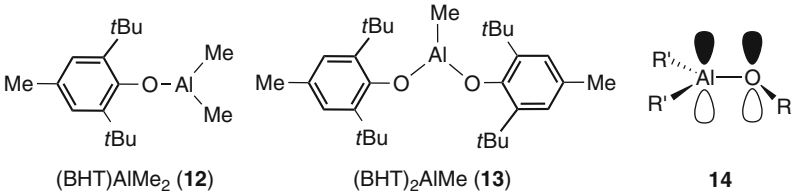


Fig. 6 Molecular structure of $Me_2Al(BHT)$ and $MeAl(BHT)_2$ and the geometrical conformation for Al-O_{Ar} π-bonding interactions

Although such a bonding scheme is compatible with the commonly accepted concept (i.e., the presence of any form of π-bonding to a group 13 element would require a trigonal planar coordinatively unsaturated metal center), the relative importance of π-donation from the aryloxide to aluminum in this group of compounds has not achieved a consensus [106–109].

Despite steric hindrance, all monomeric aryloxide compounds reported to date have readily formed Lewis acid–base complexes, in which the aluminum is four-coordinate [106, 109, 110]. For their intrinsic attractive features, sterically hindered three-coordinate aluminum aryloxides have been developed and subsequently used as Lewis acid catalysts for stereo-, regio-, and chemo-selective carbon–carbon bond-forming reactions [111]. Compared with classical Lewis acids, these aluminum reagents coordinate strongly with various oxygen-containing substrates, and this coordination is affected by the steric environment of their ligands.

In the last decade a range of Al(III) aryloxides derived from bis(phenols) have been extensively investigated, and only a brief summary of salient structural and reactivity chemistry is presented here [64, 112]. Specifically, a number of aluminum complexes supported by 2,2′-ethylidenebis(4,6-di-*tert*-butylphenoxide) (EDBP) or related bulky aryloxide ligands have been prepared and tested as initiators for the bulk polymerization of cyclic esters [64]. Generally, RAl(bisphenoxide) compounds form dimeric structures with the aryloxide ligands acting as oxygen bridges, while the corresponding (RO)Al(bisphenoxide) species associate through alkoxide bridges. Interestingly, reaction of a [MeAl(EDBP)] with ε-caprolactone (ε-CL) resulted in the isolation of the first well-defined aluminum-(ε-CL) adduct, MeAl(EDBP)(ε-CL) (**15**, Fig. 7) [113]. Single-crystal X-ray analysis of **15** demonstrated that the lactone molecule is coordinated by the carbonyl oxygen atom with the aluminum center (the Al–O bond length is 1.876(3) Å) being in the

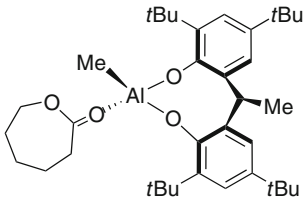


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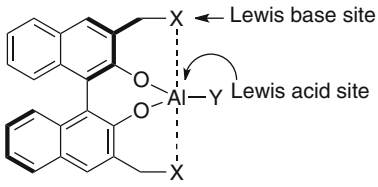
Fig. 7 Molecular structure of MeAl(EDBP)(ε-CL): the first well-defined aluminum-(ε-CL) adduct



16

Fig. 8 General structure for BINOL-Al-type bifunctional complexes

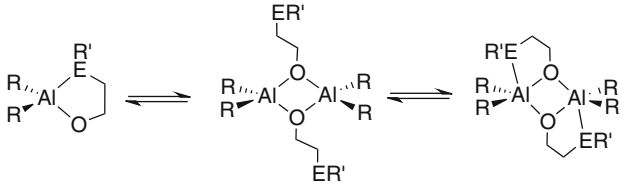
nodal plane of the C=O bond, and the complex adopts a *syn* conformation. The IR spectrum of **15** exhibited only one band for the carbonyl group stretching frequency at 1,640 cm^{-1}. The decrease in the carbonyl stretching frequency by 88 cm^{-1} in comparison with that in free ε-CL (1,728 cm^{-1}) is consistent with the strong coordination of the carbonyl group to the metal center [113]. Yet compound **15** is inactive in ε-CL polymerization, thus showing that Lewis acid activation of the monomer may not be the only factor decisive in ε-CL polymerization mediated by Al species.

1,1′-Bi-2-naphthol (BINOL) derived bifunctional chiral Al(III) complexes of type **16** (Fig. 8) constitute another important family of aluminum aryloxides and have been particularly prevalent in recent years. BINOL–Al complexes have been tremendously developed as bifunctional catalysts for a broad range of asymmetric catalytic reactions [112, 114, 115]. Such catalysts could attach both electrophilic and nucleophilic substrates to the chiral catalyst in the transition state, and thus could lead to strong stereodiscrimination and catalyze the reaction with high enantioselectivity and reactivity. Intramolecular tethering of the donor function X (Fig. 8) to the metal center provides efficient stabilization of these bifunctional catalysts in the resting state.

Undoubtedly, further studies will stimulate chemists to develop new ligand types, and thus to advance both fundamental and applied directions for this field of bifunctional catalysts.

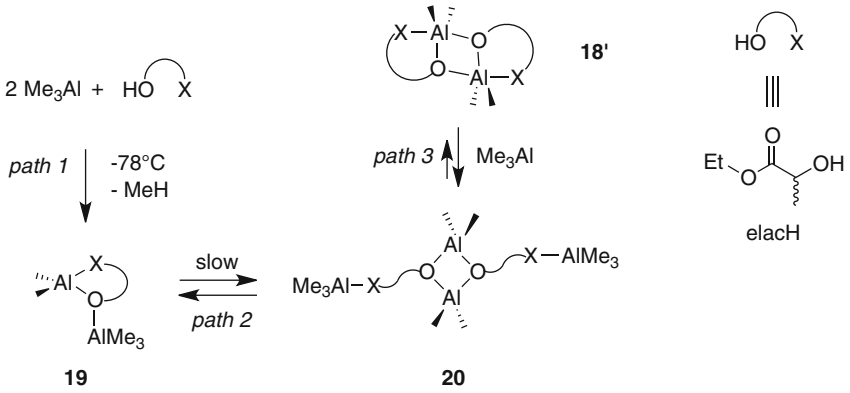
3.2 *Derivatives of Alcohols with Donor Termini*

In contrast to sterically hindered aluminum aryloxides, simple aluminum alkoxides derived from monofunctional alcohols do not form stable adducts when reacted with Lewis bases. However, a rather intriguing group of compounds are organoaluminum derivatives of alcohols with neutral Lewis base termini. These contain both anionic and neutral ancillary donor groups, and may, for instance, be of the type $[O(CH_2)_nER'_x]^-$ (n = 2, 3; ER'_x = OR′, SR′, NR'_2). The reaction of AlR_3 compounds with the corresponding $HO(CH_2)_nER'_x$ alcohol leads to the formation of dimeric dialkylaluminum $R_2Al(\mu\text{-}O,ER')$ species. Well-defined monoalkylaluminum $RAl(O,ER')_2$ species are very rare, and there are only two examples of such bis-chelated alkylaluminum species to have been structurally authenticated, both being supported by monoanionic aminoalkoxide ligands [116, 117]. Dialkylaluminum compounds bearing ether- or amine-alkoxide ligands have been extensively investigated over the last three decades by virtue of their fundamental and practical importance [118–126]. In the solid state they have shown a tendency to form $[R_2Al(\mu\text{-}O,ER')]_2$-type adducts (**18**, Eq. 4) containing the planar $Al_2(\mu\text{-}O)_2$ ring with disparate Al–O bond distances and five-coordinate aluminum centers that tend to adopt a tbp geometry. The commonly observed disparity in the Al–O distances within the central $Al_2(\mu\text{-}O)_2$ ring nicely reflects the presence of pentacoordinated aluminum centers, which dictates that each bridging oxygen atom is in the equatorial position with respect to one aluminum atom and in the axial position with respect to the other. In such complexes, the Al–*ER′* distances were found to be within the wide range 1.85–3.25 Å, with the longest of these interactions approaching the van der Waals surface [123]. This type of complex appears to represent a very useful model for analysis of borderline distances and angular distributions of secondary interactions. Such Al derivatives may also provide insights into the trajectory for the incoming ligand at the metal's fifth coordination site and the mapping out of the minimum-energy pathways in associative reactions. On that matter, results in this area have evidenced a strongly preferred trajectory for the approach of a ligand to the fifth coordinate site [123].



16 **17** **18** (4)

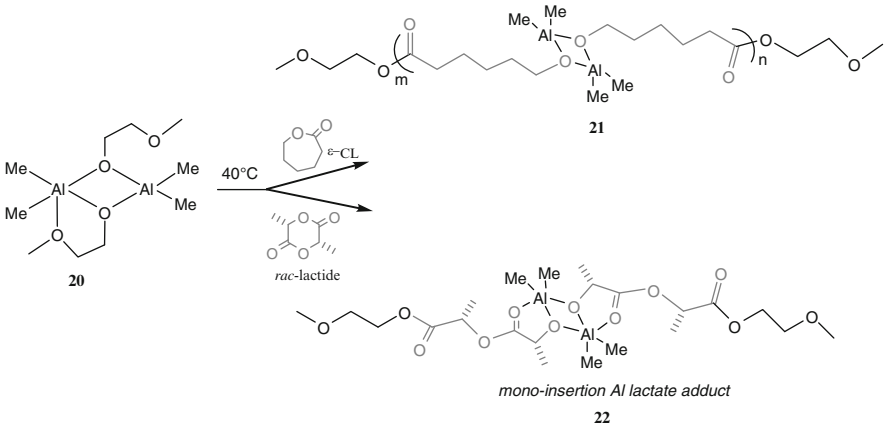
In solution $[R_2Al(\mu\text{-}O,ER')]_2$ compounds exhibit a considerably greater structural variety than in the solid state, depending on the nature of the bifunctional ligand. The observation of equilibria between four-coordinate monomeric chelate **16** and dimeric **17** compounds (Eq. 4) and the five-coordinate dimer **18** was shown to be due to the fluxional behavior of hemilabile monoanionic *O,ER′*-ligands.



Scheme 1 Various reaction pathways and products upon reacting ethyl lactate with $AlMe_3$

The latter equilibrium involves a dissociation/recoordination sequence of the weakly bound neutral donor group *ER′* [119–121]. Factors that control the coordination about aluminum and the degree of association include: (1) the steric bulk of the Al*R* and *ER′* substituents, (2) the basicity of the *ER′* group versus that of the anionic donor center, and (3) the ring size of the Al chelate formed upon coordination of *ER′* group to the metal center. The dynamic behavior of $[R_2Al(\mu\text{-}O,ER')]_2$-type adducts in solution has been extensively analyzed using variable temperature NMR studies [119, 120, 122, 123, 125], from which dissociation energies of the Al–*ER′* intramolecular bond could be estimated (from 2.3 to 13.2 kJ mol^{-1}). These values are significantly lower than those observed for their four-coordinate analogues, $R_3Al(ER')$ (64–125 kJ mol^{-1}) [118]. Intriguingly, variable temperature X-ray diffraction experiments with a series of $[R_2Al(\mu\text{-}O,ER')]_2$ compounds demonstrated that the Al–*ER′* interactions are weak enough to undergo a thermal expansion effect likely caused by thermal excitation of these presumably weak bonds [124]. Thus, taking to account the observed Al–*ER′* distances and the corresponding bond dissociation energies, the discussed interactions could be classified as typical hypervalent interactions [82, 83] for the shorter bond distances and secondary [127] (vs non-covalent interactions) for the longer distances. Moreover, effective competition between secondary donor–acceptor bonds and hydrogen bonds in group 13 complexes has also been demonstrated [128].

The complexity of the solution chemistry exhibited by this family of aluminum alkoxides has been further evidenced by thorough studies of the reaction between *rac*-ethyl lactate (elacH) (a hydroxyl ester organic compound) and $AlMe_3$ (Scheme 1) [125]. For example, the reaction of elacH with one equiv. of $AlMe_3$ resulted in the quantitative formation of the homochiral racemic mixture (*R*,*R*)- and (*S*,*S*)-$[Me_2Al(elac)]_2$ (**18′**) and thus proceeded in a highly stereoselective fashion. In contrast, the reaction of elacH with two equiv. of $AlMe_3$ at low temperature afforded the dinuclear complex **19** (Scheme 1, *path 1*). Yet, carrying out this reaction at room temperature affords a mixture of **19** and **20**. Moreover, the initial and quantitative formation of the tetranuclear adduct **20** was observed upon

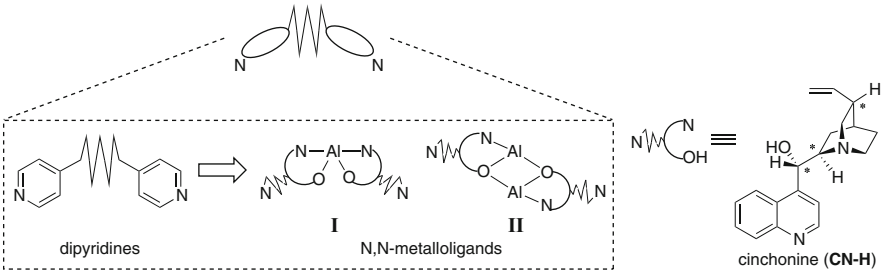


Scheme 2 Reactivity of ε-CL and *rac*-LA with the dimeric dialkylaluminum alkoxide **21**

addition of $AlMe_3$ to dimeric complex **18′** (Scheme 1, *path 3*). Thus, depending on reaction conditions, different types of species may be generated upon reacting simple alkylaluminum reagents with donor-functionalized alcohols.

A well-defined dimeric dialkylaluminum alkoxide with pendant donor sites, $[Me_2Al(\mu\text{-}OCH_2CH_2OMe)]_2$ (**21**, Scheme 2), was used as a model complex mimicking intermediate species in the initiation and propagation steps of the ring-opening polymerization (ROP) of cyclic esters [129]. These studies proved the anticipated significance of the fifth coordination site on the aluminum center in steps relevant to ROP. The crucial role of chelation effects, whether in the starting initiator **21** or in the mono-inserted product (i.e., formed from an initial monomer insertion into the Al–OR bond of species **21**), was elucidated. For species such as **21**, the initiation process was found to proceed in a similar manner for ε-CL and lactide (LA) since both incoming monomers experience an identical Al chelate species. However, a significant chelation effect was observed in the propagation step, resulting in species **21** being devoid of LA polymerization activity, yet promoting that of ε-CL with a reasonable activity (structure of the propagating species: **22**, Scheme 2). Such a difference of reactivity between ε-CL and LA arises from the structural differences of the mono-insertion species generated upon reaction of **21** with these two cyclic esters (**23** for *rac*-LA insertion, Scheme 2). Thus, compound **23** was found to be unreactive toward subsequent *rac*-LA insertion (under the studied conditions), which may be ascribed to the stability of the formed Al lactate chelate. Compound **23** constitutes the first instance in which a mono-insertion metal-lactate intermediate (of relevance to ROP catalysis of LA) has been characterized.

Practical applications of organoaluminum derivatives of alcohols with -NR_2 donor termini have begun to be exploited in recent years. Thus, $[R_2Al(\mu\text{-}O,ER')]_2$ compounds have proven to be useful reagents for C–C bond formation [130, 131, 288]. More recently, new chiral Al(III) complexes derived from readily accessible Cinchona alkaloids have been used as unprecedented building blocks for the

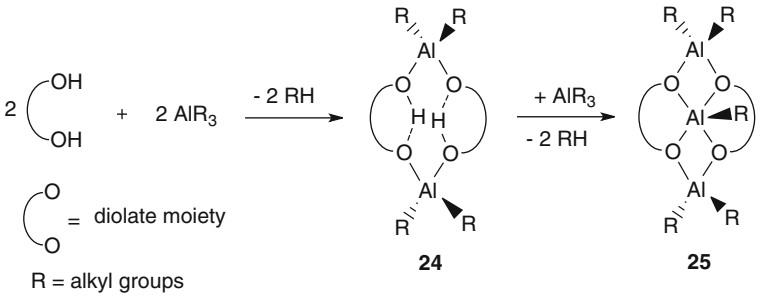


Scheme 3 The development of novel Al-incorporating *N*-ditopic linkers

design and preparation of novel chiral metal–organic frameworks (MOFs) [117, 126, 132]. Intriguingly, both the dinuclear aluminum–cinchonine $[R_2Al(\mu\text{-}O,NR')]_2$ complexes (**II**, Scheme 3) as well as the bis-chelate aluminum complexes $[XAl(O,NR')_2]$ (X = Me or Cl and O,NR' = deprotonated cinchonine, **I**, Scheme 3) have been effectively utilized for the generation of unique chiral nanotubular architectures through non-covalent interaction-driven self-assembly. These novel and flexible microporous inorganic–organic materials feature unique structural properties and are prone to enantioselective sorption of small organic molecules and gas separation. The type **I** and **II** dimeric aluminum complexes (Scheme 3) bearing a cinchonine backbone as chiral *N*,*N*-ditopic metalloligands were also employed for the generation of homochiral heterometallic coordination polymers with ZnX_2 species as nodes [117]. Thus, this novel strategy appears to represent an efficient method for providing semi-rigid mononuclear and dinuclear chiral *N*,*N*-ditopic metalloligands with tunable angles between the *N*-donor centers. Undoubtedly, developing versatile strategies for facile generation of chiral bipyridine-type linkers appears to be a key challenge for advancing the field of homochiral MOFs.

3.3 Derivatives of Diols

Although less common than the ubiquitous organoaluminum compounds supported by monoanionic alkoxide ligands, there are nevertheless still many examples of aluminum complexes incorporating diol-type ligands. The syntheses, structures, and reactivities of these derivatives have been thoroughly reviewed [133]. Their structural diversity, ranging from dinuclear (**24**), trinuclear (**25**) complexes (Scheme 4) to amorphous polymeric compounds, has been established. Both the reaction course and the structural outcome strongly depend on steric hindrance and on the nature of the diolate backbone [133–137]. Dinuclear complexes possessing two unreacted hydroxyl groups and featuring two intra-molecular hydrogen bonds were only assessable with bulky AlR_3 reagents [136, 137]. For example, the reaction of butane-1,4-diol with one equivalent of Al*t*Bu$_3$ results in the formation of the dimeric product $[\{tBu_4Al_2(O(CH_2)_4OH)_2\}]$ [137].



Scheme 4 Di- and trinuclear organoaluminum diolate species

3.4 Complexes Supported by Bidentate Ligands with a Delocalized Bond System

Considerable efforts have been devoted to the synthesis and reactivity studies of alkylaluminum complexes supported by π-delocalized monoanionic *O*,*O*′- and *O*,*N*-bidentate ligands because of their potential usefulness in polar monomer polymerization catalysis or as precursors to cationic organoaluminum reagents. Species of general formula $R_2Al(O,X)$ (where *O*,*X* is a bidentate and monoanionic oxygen–oxygen or oxygen–nitrogen ligand) have received particular attention. For instance, the equimolar reaction of R_3Al with *β*-hydroxy carbonyl compounds or salicylideneiminates form the corresponding $R_2Al(O,X)$ complexes: these were found to be monomeric in solution, while they tend to aggregate in the solid state with the formation of $R_2Al(O,X)]_2$-type dimeric adducts where both Al centers are five-coordinate [138–140]. In these dimers, the simultaneous weakening of the internal axial Al–(μ-O) bond and strengthening of the external axial Al–O bond is related to the *O*,*X*-chelating ligand π-conjugation. For instance, the methyl salicylate dimethylaluminum derivative, $[Me_2Al(OC_6H_4\text{-}2\text{-}CO_2Me)]$ (**26**, Fig. 9), exhibits a slightly longer Al–(μ-O) bond length (2.082(2) Å) than the external axial Al–O bond (2.003(2) Å). Thus, the Al–O bridging bond linking two monomeric units is the weakest Al–O bond and undergoes cleavage upon dissolution of the solid in organic solvents [139].

Interestingly, solid-state structure investigations on methyl thiosalicylate dialkylaluminum compounds uncovered close intermolecular S···C(π) contacts (with an average S···C distance of 3.382 Å significantly below the sum of the corresponding van der Waals radii [76, 77]) between the Al–S thiolate units and the ester component (**28**, Fig. 9) that can effectively compete with the putative sulfur–aluminum hypercoordinate bond (**27**, Fig. 9) [141]. The latter results provide the first evidence for the competition of intermolecular n→π* interactions, involving the thiolate sulfur atom and the electrophilic ester carbon atom, with the hypercoordinate bond in metal complexes: it opens up an interesting area for further studies.

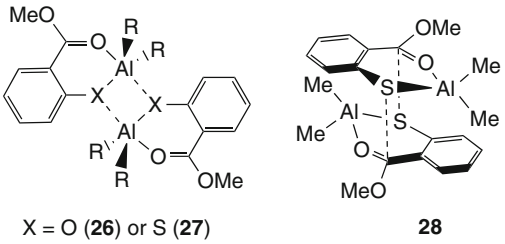


Fig. 9 Salicylate and thiosalicylate alkylaluminum species

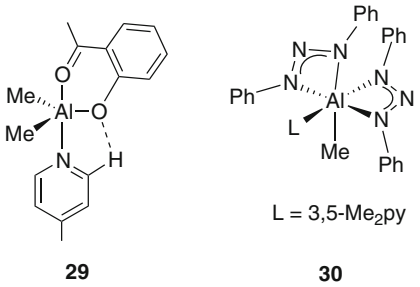


Fig. 10 Molecular structures of the penta- and hexa-coordinate Al complexes $Me_2Al(hacet)$•py-Me and $MeAl(dpt)_2(3,5\text{-}Me_2py)$

The observed tendency toward the formation of five-coordinate $[R_2Al(\mu\text{-}O,X)]_2$ adducts indicates that the metal center in monomeric $R_2Al(O,X)$ molecules may accommodate an extra ligand. Nevertheless, such complexes usually disproportionate upon addition of a Lewis base to afford monomeric five-coordinate $RAl(O,X)_2$ complexes. To date, only one example of a $R_2Al(O,X)$ adduct with a donor ligand has been isolated and structurally authenticated [142]. The reaction of $Me_2Al(hacet)$ (hacet = deprotonated 2′-hydroxyacetophenone) with γ-picoline (py-Me) allowed the isolation of the Lewis acid–base adduct $Me_2Al(hacet)$·py-Me (**29**, Fig. 10). The formation of stable adducts was not observed when weaker Lewis bases such as Et_2O or THF were used. The five-coordinate aluminum atom in **29** adopts a distorted tbp geometry, with the equatorial positions occupied by the two carbon atoms and the aryloxide oxygen, while the carbonyl oxygen atom and the pyridine nitrogen are axially located (O–Al–N = 172.67(6)°). Unlike the apical Al–O bond (2.066(2) Å), the equatorial Al–O distance (1.797(2) Å) is substantially shorter than the corresponding Al–O bond distances in the dimeric species **26**. Detailed analysis of the molecular structure of this unique adduct revealed that the presence of an intramolecular C–H···O hydrogen bond, the *trans* influence of the axial substituents, and electronic along with electronic and conformational changes within the *O*,*O*′-chelating ligand all play a role in the stability of **29**. The structural *trans*-influence of the axial substituents was also clearly observed in five-coordinate $[R_2Al(O,O')]_2$ compounds [138] and $MeAl(dpt)_2(3,5\text{-}Me_2py)$

(H-dpt = 1,3-diphenyltriazene) (**30**, Fig. 10), the first monomeric six-coordinate organoaluminum compound [143]. Thus, specific geometrical parameters in the solid-state structures of **25** and **30** also enable us to describe the bonding for these five- and six-coordinate complexes as that of an electron-rich hypervalent system. For skeptics who doubt such a description one can recommend the following statement of R. Hoffmann and co-workers: "*Some people do not like the term hypervalent. We view it as a historically and heuristically useful categorization of bonding in electron-rich systems, and will use the term interchangeably with electron–rich multi–center bonding.*" [82]. It seems likely that for five-coordinate $RAl(O,X)_2$ complexes with a decreased number of Al–C bonds, such as $MeAl[O{=}C(Me)C_6H_4\text{-}2\text{-}NH]_2$ [144], ionic character prevails over hypervalency in qualitatively describing the of their electronic structure.

3.5 Schiff Base Complexes and Related Structures

In aluminum Schiff base complexes, the various coordination properties and diversity permitted by multidentate Schiff bases and related dianionic ligands such as salen (ethylenediamine-bridged) and salophen (*o*-phenylenediamine-bridged) allows for tuning of the metal coordination environment via the use of variously substituted chelating ligands. This provides a useful range of steric and electronic properties through which a fine-tuning of the structure/reactivity interplay may be achieved. Aluminum complexes with this type of ligand have been shown to catalyze a wide variety of organic reactions and polymerization processes. The synthesis, structure, and reactivity of these complexes have been the subject of several reviews [32, 145]. Monoanionic bidentate *N*,*O*-salicylaldiminato ligands act as strongly coordinating chelate ligands and, in this regard, they resemble the symmetrical acetylacetonato ligand as well as related *β*-diketonates. For example, dialkylaluminum complexes supported by the monoanionic *N*-phenylsalicylideneiminato ligand exist as monomeric tetrahedral $R_2Al(O,N)$ complexes (**31**, Fig. 11) in solution and the solid state; they, however, disproportionate to the five-coordinate $RAl(O,N)_2$ complexes in the presence of a Lewis base [139]. Potentially tridentate salicylaldiminato ligands bearing a pendant *O*- or *N*-donor arm attached to the nitrogen imine form monomeric five-coordinate dialkyl [*N*,*O*-salicylaldiminato]aluminum complexes (**32**, Fig. 11) with *N*- or *O*-donor termini; the use of alkyl-substituted phenolate units significantly increases the solubility of the resulting complexes in common aryl and alkyl solvents [146].

Aluminum complexes with salen-type and related N_2O_2-tetradendate ligands (**33**, Fig. 11) are relatively stable and do not dissociate readily. Alkylaluminum complexes supported by tetradendate Schiff base ligands are conveniently prepared by combining the salen ligand with AlR_3. Combination of the resulting alkyl complexes with an alcohol readily proceeds via an alkane elimination reaction to typically yield the corresponding monomeric Al alkoxide derivatives. Nevertheless, in some instances, the formation of alkoxide-bridged (salen)Al–OR species has

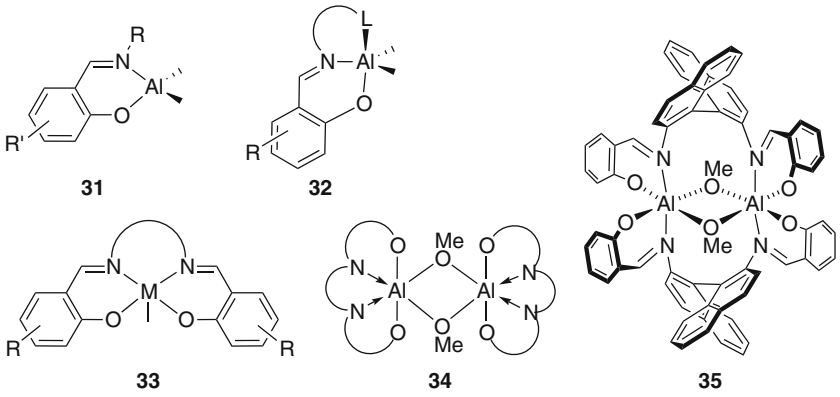


Fig. 11 Structural diversity in organoaluminum species supported by Schiff bases

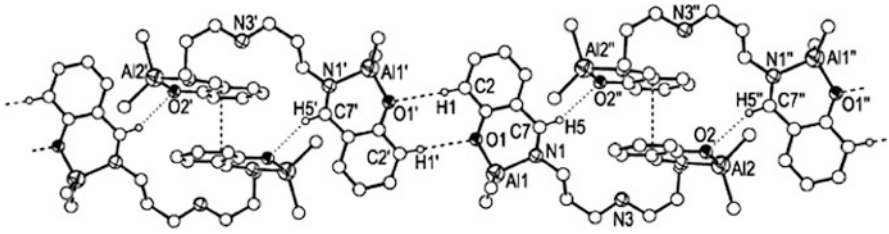
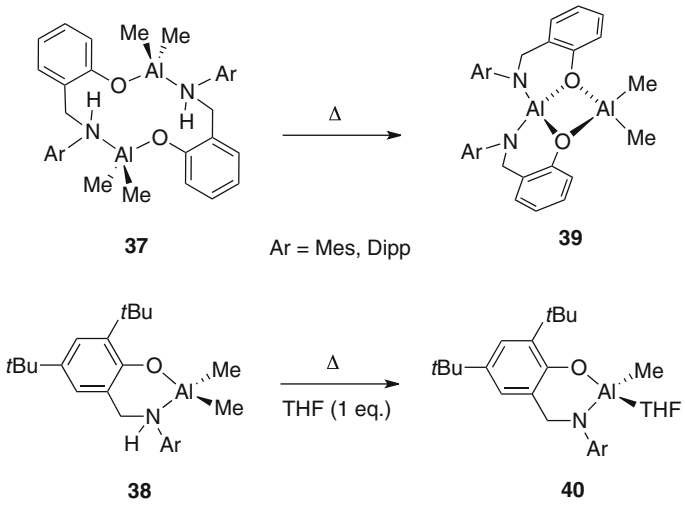


Fig. 12 Crystal structure of amino-bis(*N*-propylenesalicylideneiminato)]-tetramethyldialuminum (**36**). Reprinted from Lewiński et al. Coord Chem Rev (2005) 249:1185

been observed (**34** and **35**, Fig. 11) [147, 148]. The monomeric complexes comprise a five-coordinate Al center adopting either a tbp or a square pyramidal geometry depending on the bis-imine ligand backbone. Thus, whereas the ethyl and *o*-aryl backbones were observed to promote a square pyramidal geometry at Al, more flexible salen ligands usually favor an Al metal center in a tbp geometry [32].

Thus far, the vast majority of investigations on aluminum complexes supported by Schiff base ligands have focused on the first coordination sphere of the metal. Yet the ligand frameworks may contain various donor and acceptor sites capable of undergoing internal hydrogen bonding to an adjacent metal-bound ligand or to an incoming substrate. Not surprisingly, intra- and intermolecular non-covalent interactions of the type $C–H_{imino}\cdots O$, $C–H_{aryl}\cdots O$, $C–H_{aliph}\cdots O$, $C–H\cdots\pi$ hydrogen bonds, and π-stacking are frequently observed, but these non-covalent interactions are rarely reported and, for the most part, ignored [145]. The role of such non-covalent interactions in the self-organization of organoaluminum complexes is nicely demonstrated, for example, by the supramolecular structure of [amino-bis (*N*-propylenesalicylideneiminato)]-tetramethyldialuminum **36** (Fig. 12). Detailed analysis of intermolecular contacts in the crystal structure of **36** revealed a complex supramolecular structure in which the two molecules are related by a symmetry



Scheme 5 Synthesis and structural diversity in organoaluminum supported by dianionic aminophenolate ligands

center and held together by two C–H···O bonds formed by the imino hydrogens and aryloxyde oxygen atoms; this results in the formation of a hydrogen-bonded molecular chain. In addition, π–π stacking interactions between the salicylideneiminate ligands of neighboring molecules (distance of about 3.5 Å) play a substantial role in the molecular organization of this system [145].

Hydrogen bonding and other types of non-covalent interactions may also be of importance in controlling processes that take place at metal sites as well as in the rapidly developing fields of crystal engineering and material chemistry. It seems likely that cooperation between the coordination center and non-coordinating active-site residues very often plays an important (though frequently unrevealed) role in molecular recognition and activation processes involving Schiff base catalysts. Moreover, such Schiff base Al entities promise to be of fundamental importance in the design of well-organized solid-state materials with specific properties. Undoubtedly, apart from the wide application of Schiff base metal complexes in various fields of chemistry, the exploitation of non-covalent interactions exhibited by this group of compounds represents an emerging area of research.

Surprisingly, the chemistry of organoaluminum complexes supported by aminophenolate ligands remains an essentially undeveloped field. A number of alkylaluminum species supported by variously substituted mono- and dianionic aminophenolate bidentate ligands have been reported in the past few years [35, 149–151]. The structural variety observed in these species is clearly related to the bonding versatility of the aminophenolate moiety, as reflected by the diverse bonding modes that it may adopt. For example, the low temperature reaction of $AlMe_3$ with the sterically unhindered aminophenol ligand 2-$CH_2NH(Ar)C_6H_4OH$ (Ar = Mes) readily affords the corresponding dimeric species [μ-η^1,η^1-*N*,*O*-{2-$CH_2NH(Ar)$-C_6H_4O}]$_2Al_2Me_4$ (**37**, Scheme 5), consisting of a twelve-membered aluminacycle

with two monoanionic aminophenolate units. In contrast, the reaction of the bulky aminophenol pro-ligand 2-CH_2NH(Ar)-4,6-*t*Bu_2-C_6H_2OH with $AlMe_3$ yields the monomeric dimethylaluminum aminophenolate chelate complex η^2-*N*,*O*-{2-CH_2NH(Ar)-4,6-*t*Bu_2-C_6H_2O}$AlMe_2$ (**38**). Upon heating, compounds **37** or **38** are quantitatively converted to the dinuclear aluminum complex Al[η^2-*N*;μ,η^2-*O*-{2-CH_2N(Ar)-C_6H_4O}]$AlMe_2$ (**39**) and the corresponding methyl(amido)aluminum complex η^2-*N*,*O*-{2-CH_2N(Ar)-4,6-*t*Bu_2-C_6H_2O}Al(Me)(THF) (**40**), respectively. The isolation of **40** opens new opportunities for the design of novel Lewis acids of the type RAl(*O*,*N*).

4 Organoaluminum Carboxylates

Aluminum carboxylates are attracting increasing attention by virtue of their usefulness as precursors in material science [152] and also for their biological relevance [153, 154]. The first crystallographic evidence for organoaluminum carboxylate structure, namely that of the $[MeCO_2(AlMe_3)_2]^-$ anion (**41**, Fig. 13) [155], was presented in 1977. More recently, dialkylaluminum monocarboxylates of the type $[R_2Al(\mu\text{-}O_2CR')]_2$ (**42**, Fig. 13), which are dimers featuring a central eight-membered $Al_2O_4C_2$ ring in a chair-like conformation, have been characterized in the solid state [156]. A series of alkylaluminum polynuclear species derived from bifunctional carboxylic acids have also been isolated and structurally authenticated (**43**, Fig. 13) [157–163]. A preference for *anti* coordination of the organoaluminum units (with respect to the carboxylate moiety) was identified [158]. For example, the reaction of two equiv. of AlR_3 (R = Me, Et) with aromatic bifunctional carboxylic acids, such as salicylic, anthranilic and phthalic acid, produced the corresponding tetraaluminum compound of type **43** [157–159, 161].

Particularly intriguing results were obtained upon reacting phthalic acid with an excess of $AlMe_3$, with a subsequent addition of 1,2-bis(4-pyridyl)ethane (Scheme 6) [164]. Hence, the reaction with three equivalents of $AlMe_3$ affords the hexanuclear Al species **44**. The latter may be described as two tetramethylalumoxane moieties being entrapped by the alkylaluminumphthalate monomeric subunit, while the 1,2-bis(4-pyridyl)ethane ligand links the two alumoxane Al centers to afford a 22-membered macrocyclic ring system. Interestingly, carrying out the same reaction but using four equiv. of $AlMe_3$ afforded the crystalline Lewis acid–base tetramethylaluminoxane-bipyridine adduct **45** and the cyclic ester **45′** in good yield. This simple method to access aluminoxanes and carboxyaluminoxanes opens new opportunities to probe more in-depth chemistry of these important classes of compounds. In addition, the fact that aluminoxanes can act as secondary building units in the construction of extended macrocyclic assemblies or functional coordination networks should be of interest in catalysis and material science.

Notably, the reactions of $AlMe_3$ with diphenylglycolic acid and the amino acid 2,2-diphenylglycine, were found to lead to the remarkable 16-membered macrocyclic structures **46** and **47** that contain six aluminum centers, and the

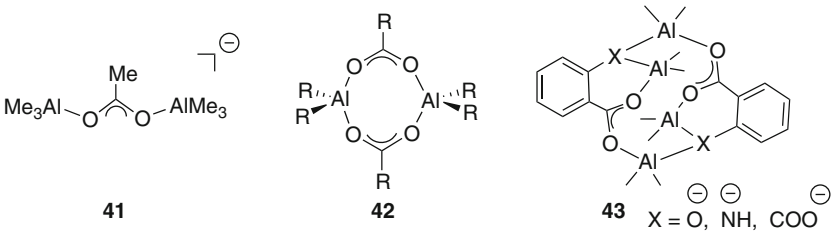
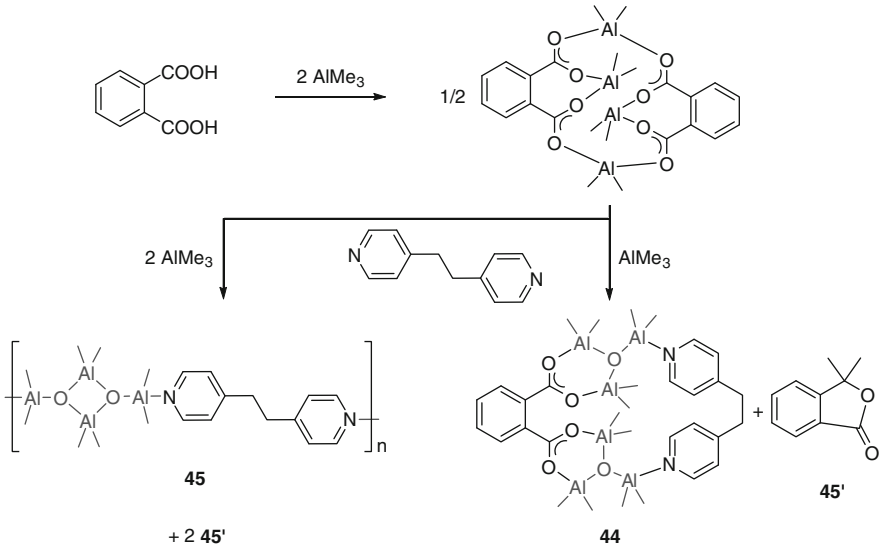


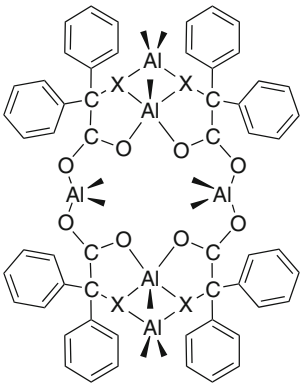
Fig. 13 Structural motifs in carboxylate organoaluminum carboxylate species



Scheme 6 Preparation and reactivity of phthalic acid derived organoaluminum carboxylates

non-symmetrical 32-membered ring complex **48** incorporating twelve aluminum centers (Fig. 14) [162].

Structurally characterized organoaluminum carboxylate complexes typically exhibit bridging carboxylate ligands and the first molecularly well-defined Lewis acid–base adducts containing a non-bridging and Al-chelating carboxylate ligand, $[Cl_2Al\text{-}(\lambda_2\text{-}O_2CPh)(py\text{-}Me)_2]$ (**49**, Fig. 15), was only recently reported [165]. Compound **49** was isolated in a nearly quantitative yield from the reaction of dichloroaluminum benzoate with γ-picoline. This unique adduct consists of a six-coordinate aluminum center in a distorted octahedral configuration symmetrically η^2-*O*,*O*-chelated by a carboxylate ion (O–Al–O = 66.4(1)° and O–C–O = 115.8 (3)°). The Al–O bond length (1.975(1) Å) in compound **49** is significantly longer than that observed for the four-coordinate dimer $[Cl_2Al(\mu\text{-}O_2CPh)]_2$, ($Al\text{–}O_{avg}$ = 1.766 Å) [165].



46 (X = NH), **47** (X = O)

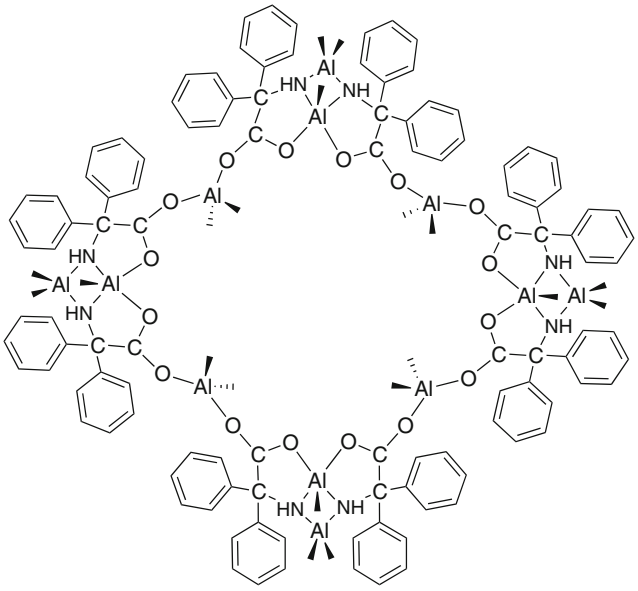


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Fig. 14 Polynuclear aluminum carboxylate complexes

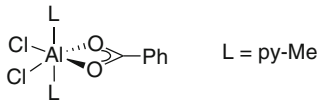

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Fig. 15 A mononuclear Al complex with a η^2-*O*,*O*-chelating carboxylate ligand

5 Organoaluminum Hydroxides

The controlled hydrolysis of alkyl- and arylaluminum compounds has been attracting attention for some years now and, as such, has been the subject of several reviews [27, 30]. Spectroscopic investigations have long-since shown that the hydrolysis of AlR_3 proceeds via the initial formation of an aqua adduct that subsequently eliminates RH (Eqs. 5 and 6) [166]. Recent NMR studies carried out at various temperatures on the hydrolysis of bulky homoleptic organoaluminums reinforced this view. Thus, for instance, the formation of the intermediate $\{(Mes_3Al{\cdot}OH_2){\cdot}n\text{THF}\}$ was proposed to precede that of the isolable Al hydroxide dimer $(Mes_2AlOH{\cdot}\text{THF})_2$ that contains a four-membered Al_2O_2 ring and in which both bridging hydroxide groups are hydrogen-bonded to a THF molecule [167]. The hydrolysis of simple alanes is well known to yield a variety of trimeric aluminum hydroxide structures, such as the cyclic trimer $(t\text{Bu}_2\text{AlOH})_3$ (**50**, Fig. 16) reported by Barron. The latter could be synthesized via a low temperature hydrolysis of $Al t\text{Bu}_3$ and each hydroxide group was shown to act as an inter-metal bridge upon exposure of **50** to THF or MeCN, yielding the incompletely solvated species **50**·2S (S = THF or MeCN) [168]. These studies extended to cover the effects of temperature and moisture on the structures of the derived organoaluminum systems and led, for instance, to the identification of novel aluminum oxide cage compounds (vide infra).

$$AlR_3 + H_2O \rightarrow R_3Al(H_2O) \tag{5}$$

$$R_3Al(H_2O) \rightarrow R_2AlOH + RH \tag{6}$$

Despite its being quite well established for some decades, the coordination chemistry of β-diketiminato ligands remains a subject of constant interest [34] and recent developments in this area include the novel aluminum-nitrogen compounds discussed below. Recent work has seen this class of ligand being used to support a series of organoaluminum hydroxides of the type LAlR(OH), where L = ArNC(R′)CHC(Me)NAr (R′ = Me, Ar = Mes, Dipp = 2,6-$i\text{PrC}_6\text{H}_3$; R′ = *t*Bu, Ar = Dipp) and the Al hydroxides (**51** and **52**, Fig. 17) were prepared by hydrolyzing the corresponding dichloride precursors $LAlCl_2$ in the presence of HCl (used as a scavenger). The crystalline Al hydroxides revealed mono- and dimeric motifs depending upon the sterics of the β-diketiminato ligand. Hence, with Ar = Dipp, the formation of the monomeric Al hydroxide **51** was observed (Fig. 17). In contrast, for Ar = Mes, the dimer **52** (featuring an Al_2O_2 core metallocycle) was isolated [169].

To conclude on aluminum hydroxides, it is noteworthy that deprotonation by an organometallic base of the Al–OH moiety has been developed to access the corresponding heterobimetallic Al–O–M-bonded analogues (M = a main group, a transition or a lanthanide metal center) [170]. Such discrete heterometallic species

Fig. 16 Molecular structure of the cyclic trimer **50**

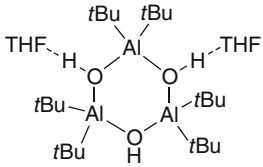

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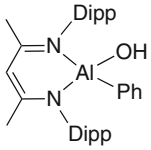
Fig. 17 Monomeric and dimeric Al hydroxide species



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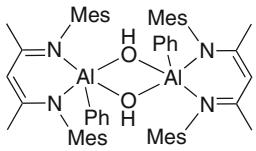

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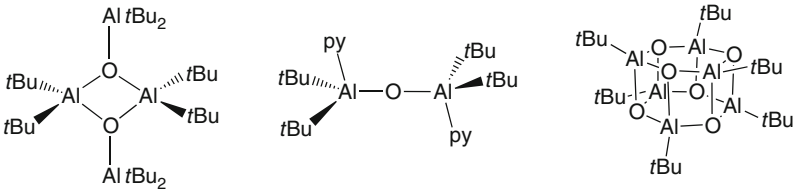
were shown to be of interest as olefin polymerization catalysts (see Chapter 4, "Organoaluminum species in homogeneous polymerization catalysis").

6 Organoaluminum Oxides

Aluminoxanes are of great importance as highly active catalysts or co-catalysts for the polymerization of a wide range of organic monomers. Initial studies on these systems go back to the end of the 1950s [171, 172]. Renewed interest in alkylaluminoxanes was generated in the 1980s, following a major breakthrough by Kaminsky and co-workers who showed that aluminoxanes may be used as potent and effective co-catalysts in olefin polymerization [173]. Most commonly, aluminoxanes of general formula $(R_2AlOAlR_2)_n$ or $(RAlO)_n$ are formed by the controlled hydrolysis of alkylaluminum compounds [174]. Despite the numerous studies carried out so far, there is a relative paucity of structural data for such compounds. The exact composition and structure of aluminoxanes with low-alkyl substituents remains to be clearly established: the presence of multiple equilibria and rapid exchange reactions in such systems have thus far prevented clear-cut assessments of their exact molecular structures. Reported characterizations for simple systems are limited to the anionic species $[Al_7O_6Me_{16}]^-$ [175] and $[(Me_2AlOAlMe_3)_2]_2^-$ [176]. The first thorough and meaningful studies toward the structural elucidation of aluminoxane species were reported by Barron and co-workers in 1993 [168] and involved the controlled hydrolysis of sterically demanding *tert*-butylaluminum derivatives. Based on their earlier findings on aluminum hydroxide trimers (see preceding section), these authors demonstrated that such Al hydroxide species may further react in a controlled manner (via alkane elimination)



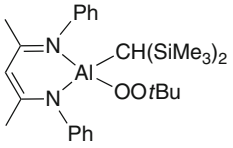
53 **54** **55**

Fig. 18 Three structural motifs in aluminoxane chemistry

to form aluminoxane-type derivatives (Eq. 7). These investigations led to the structural characterization of the first tetraalkylaluminoxane, $(t\text{Bu}_2\text{AlOAl}t\text{Bu}_2)_2$ (**53**, Fig. 18), a dimer in the solid state with two μ-OAltBu$_2$ moieties [168]. Reaction of the Al hydroxide trimer **50** (vide supra, Fig. 16) with an excess of py resulted in formation of the aluminoxane $\{t\text{Bu}_2\text{Al(py)}\}_2(\mu\text{-O})$ (**54**, Fig. 18), a reaction thought to proceed via deprotonation of a hydroxide group in **50** by pyridine [177]. A series of cage clusters based on the tBuAlO fragment were also prepared including hexameric (**55**, Fig. 18), heptameric, nonameric, and dodedameric aluminoxanes [168, 178]. The intimate relationship between aluminoxane and aluminum hydroxide chemistry has also been explored with the characterization of dual oxide-hydroxide cages such as $\text{Al}_4\{\text{C(SiMe}_3)_3\}_4(\mu\text{-O})_2(\mu\text{-OH})_4$ [179] and $\text{Al}_6t\text{Bu}_6(\mu_3\text{-O})_4(\mu\text{-OH})_4$ [180]. The anhydrous formation of aluminoxanes may also be achieved using various oxygen-containing organic and inorganic oxygen sources. Thus, aluminoxane species have been prepared by reacting an excess of AlMe_3 with carboxylic acids [157, 164, 181]. Also, the oxidation reaction of the Al(II) compound $[\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Al}]_2$ with DMSO was found to yield the aluminoxane $[\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Al}]_2(\mu\text{-O})$ [182]. The simplest model of monosubstituted organoaluminoxanes of formula $(\text{RAlO})_n$, e.g., the cyclic tetrameric aluminoxane $(\text{Mes*AlO})_4$ (Mes* = 2,4,6-$t\text{Bu}_3$-C_6H_2), was synthesized via reaction of $(\text{Mes*AlH}_2)_2$ with $(\text{Me}_2\text{SiO})_3$ [183], while the reaction of magnesium or manganese alkoxides with AlMe_3 provided access to the methylaluminoxane $[\text{Al}_3(\mu_3\text{-O})\text{Me}_6]^+$ unit capped by the corresponding Mg(II) or Mn(II) anionic moieties [184, 185].

$$[\text{R}_2\text{Al}(\mu\text{-OH})]_n \rightarrow (\text{RAlO})_n + n\,\text{RH} \tag{7}$$

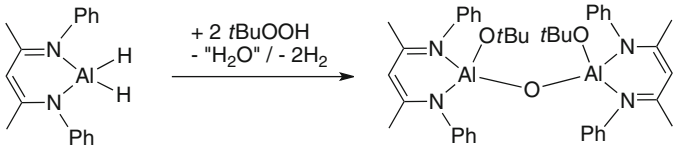
A facet of aluminoxane formation that recently attracted attention involves the use of sterically encumbering β-diketiminates as supporting ligands for the inorganic moiety. For example, diphenyl-β-diketiminatoaluminum hydrido species PhN(AlHR)C(Me)CHC(Me)NPh (R = H, CH_2SiMe_3, CH_2tBu) were reacted with tBuOOH to afford dialuminoxanes **56**–**58** (Eqs. 8 and 9) rather than the expected peroxo derivatives [186]. Hence, in each reagent one Al–H bond was sacrificed, with the peroxide acting as an oxidant to insert an oxygen atom into the strongly reducing metal hydride bond. The resulting aluminum hydroxide may then be deprotonated to yield the final product [186]. Notably, the use of the more sterically demanding β-diketiminato Al species PhN[AlH{$\text{CH(SiMe}_3)_2$}]C(Me)CHC(Me)NPh



59

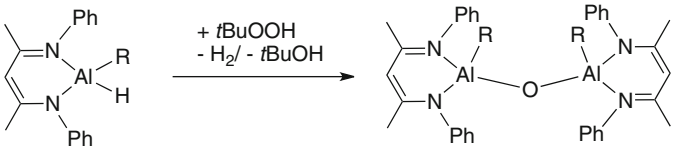
Fig. 19 A monomeric aluminum peroxide species

(containing a bulky $AlCH(SiMe_3)_2$ group) afforded peroxide **59** (Fig. 19), which was persistent enough to be isolated [187].



(8)

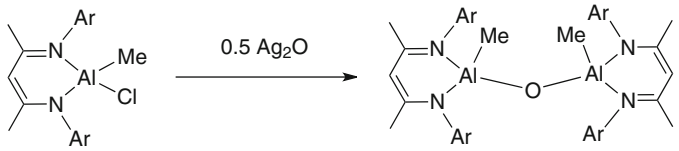
56



(9)

57 R = CH_2SiMe_3
58 R = CH_2tBu

Controlled hydrolysis of the Al dihydride $ArN(AlH_2)C(Me)CHC(Me)NAr$ provided access to the dialuminoxane hydride $\{ArN(AlH)C(Me)CHC(Me)NAr\}_2(\mu\text{-}O)$ (**60**, Eq. 10) [188]. In a similar vein, the Al methyl chloro compound $ArN(AlMeCl)C(Me)CHC(Me)NAr$ (Ar = 2,6-$Me_2C_6H_3$) was observed to undergo a controlled hydrolysis in the presence of an equimolar amount of water and an HCl scavenger to produce a β-diketiminato aluminoxane of type **60**, alongside the hydroxide-bridged dimer of $ArN\{Al(OH)Cl\}C(Me)CHC(Me)NAr$ (see previous section). Notably, as an extension of the earlier work by Uhl [182], an anhydrous route to type-**60** compounds was achieved upon treatment of $ArN(AlMeCl)C(Me)CHC(Me)NAr$ with Ag_2O (Eq. 10) [188].

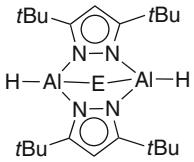


Ar = 2,6-$Me_2C_6H_3$

(10)

60

Interestingly, the dimeric Al species $[Al_2H_4(3,5\text{-}tBu_2pz)_2]$ has been shown to abstract an oxygen atom from dioxane, yielding tetranuclear $[Al_4H_4(\mu_3\text{-}O)_2(\mu\text{-}3,5\text{-}$



E = S (**61**), Se (**62**), Te (**63**)

Fig. 20 Dinuclear aluminum chalcogenide species

tBu$_2$pz)$_4$], while treatment of the parent pyrazolate complex in toluene with other chalcogen elements (i.e., S, Se and Te) afforded the corresponding chalcogenide compounds of the type [(η^1-3,5-tBu$_2$pz(μ-AlH))$_2$E] (E = S, Se or Te, **61–63**, Fig. 20) with a butterfly-type cluster core [189]. In contrast, controlled hydrolysis of the same precursor but in THF yielded [Al$_3$H$_3$(μ$_3$-O)(μ-3,5-tBu$_2$pz)$_2$(3,5-tBu$_2$pz)$_2$] [190].

The continuous interest in hydrolytic and anhydrous methods to access aluminoxanes has significantly expanded the library of organoaluminum hydroxides and oxides. Further exploration and thorough studies in this area will undoubtedly provide access to novel aluminoxanes of potential applications in the field of catalysis and material science.

7 Organoaluminum Amides, Imides, and Related Compounds

The reaction of aluminum alkyls with amines certainly lies among the landmark reactions of organoaluminum chemistry. In such a reaction, the mechanism of hydrogen activation has been the subject of several studies with partly contradictory results. Most commonly, this reaction has been proposed to proceed via a concerted intramolecular elimination, possibly via a planar four-centered transition state (**III**, Fig. 21) [191]. However, in direct contrast to this view, Beachley et al. demonstrated that a Lewis acid–base adduct R$_3$Al(H$_2$NR′) readily forms, the important step for the elimination–condensation reaction being a prior dissociation of the adduct (**IV**, Fig. 21) [192]. A more recent alternative mechanism proposes that base-free AlR$_3$ may undergo an intermolecular elimination–condensation reaction with the pre-formed adduct complex R$_3$Al(H$_2$NR′) [98].

7.1 Organoaluminum Amides

Two of the mechanisms for aluminum amide formation assume the formation of an alane–amine adduct and, from a structural point of view, such Lewis pairs have been extensively studied. For instance, the treatment of AlMe$_3$ with Ph(tBuCH$_2$)NH in hexane at room temperature yielded a monomeric adduct Ph(tBuCH$_2$)NH(AlMe$_3$)

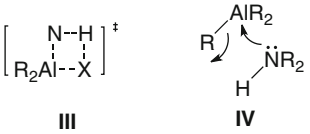
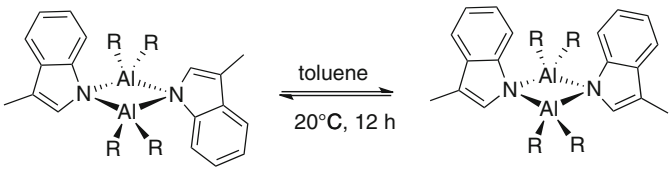


Fig. 21 Proposed pathways for organoaluminum amide formation from an alkyl aluminum and an amine

prior to the thermolytic formation of Ph(*t*BuCH$_2$)NAlMe$_2$, which is found to be dimeric in the solid state [193]. The inclusion of extra Lewis basic heteroatoms within the amide fragment [194, 195] or the use of chelating diamines to access aluminum bisamide products [196, 197] was shown to disfavor the formation of aggregates. However, in the absence of such factors, a dimeric structure is usually retained in solution. Thus, NMR studies on organoaluminum amides such as **64**, generated through the *N*-metallation of 3-methylindole by AlR$_3$ (R = Me, Et, *i*Bu), yielded evidence that the Al amido **64** exists in solution as an equilibrium mixture of *syn* and *anti* isomers (Eq. 11) [198].



(11)

anti-**64** *syn*-**64**

More recently, the coordination and structural patterns of Al(III)-hydrazine derived species have been investigated. Whereas the adduct *t*BuNHNH$_2$(Al*t*Bu$_3$) (**65**, Fig. 22) is monomeric in the solid state, it dimerizes upon heating (to 155°C) to form the aluminum hydrazide species *t*Bu$_2$AlNHNH*t*Bu (**66**), featuring a central four-membered (AlN)$_2$ metallocycle (Fig. 22). Thereafter further reactivity is observed upon heating of **66** (to 190°C): under such conditions, the formation of the drum-like hexamer of imidoalane *t*BuAlNH **67** was observed. Interestingly, the isolation and characterization of species **68**, a likely intermediate prior to the formation of **67**, could be achieved. In contrast, the less sterically congested aluminum hydrazide Me$_2$AlNH$_2$NH*t*Bu (**65′**) decomposed at room temperature into the remarkable norbornane-like precursor **69**, that underwent thermal conversion to the tetrameric aluminum hydrazinediide **70**. The structure of the latter is analogous to that of the standard cubic (AlN)$_4$ motif commonly observed in aluminum amide chemistry, notwithstanding the "insertion" of nitrogen into four of the twelve Al–N cube edges [199].

The simple Al(III) amido precursor Al(NMe$_2$)$_3$ has recently found utility as a catalyst of dehydrocoupling reactions, thereby opening the way to hydrogen production from amine-boranes using main group metal catalysts. The work arose from a longstanding interest in the use of p-block dimethylamides as redox active materials. An important factor for the dehydrocoupling reaction to proceed relies on the ability of aluminum to resist reduction. Preliminary studies utilized the reaction of Al(NMe$_2$)$_3$ with Me$_2$NHBH$_3$ to produce an initial intermediate adduct

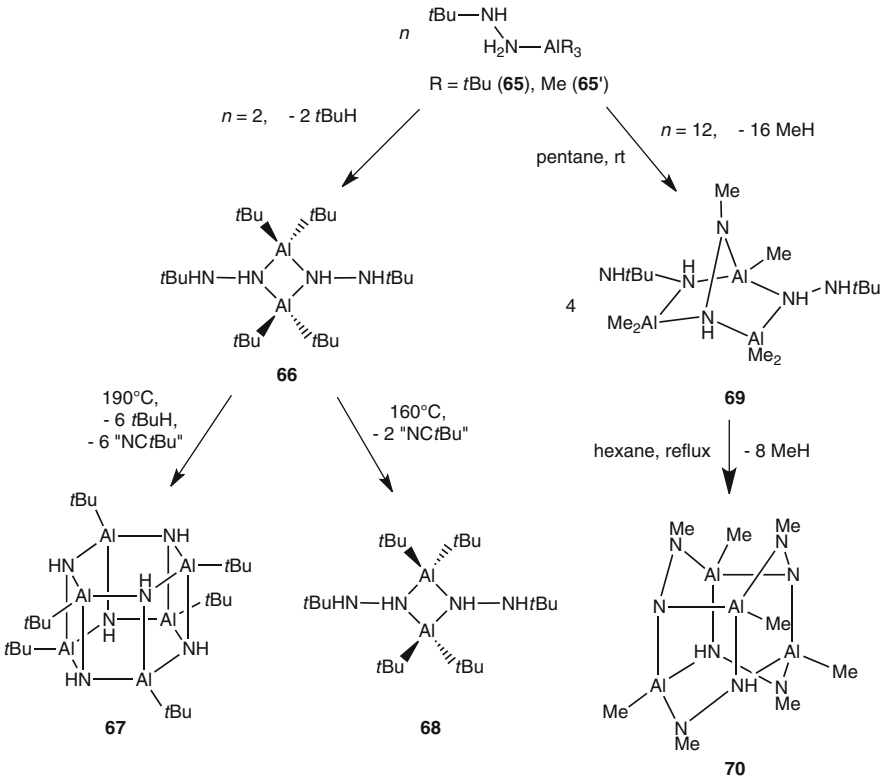
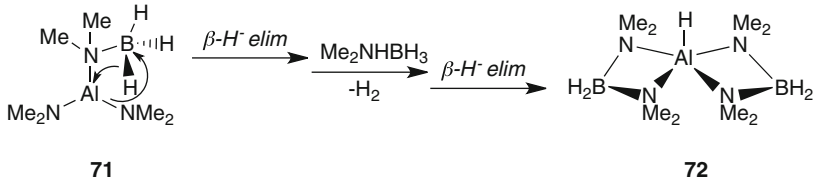


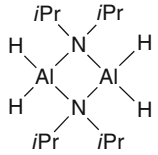
Fig. 22 Structural diversity in organoaluminum hydrazide species



Scheme 7 Catalytic dehydrocoupling of $(Me_2NH)BH_3$ with $Al(NMe_2)_3$

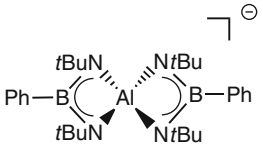
that rapidly decomposed with the production of H_2 along with the formation of the spirocyclic Al(III) hydride $\{(Me_2N)_2BH_2\}_2AlH$ (**72**, Scheme 7) and $(Me_2N)_2BH$. The presumed active catalyst, adduct **71** initially formed by reaction of Me_2NHBH_3 with $Al(NMe_2)_3$, is thought to undergo a β-hydride elimination to generate the dinuclear Al hydride $(Me_2N)HAl(\mu\text{-}NMe_2)_2BH_2$. The latter, upon reaction with Me_2NHBH_3, releases H_2 and eventually yields compound **72** [200]. More recently, it has been proposed that β-hydrogen transfer from B to Al in adduct **71** might yield an aluminum dihydride amido species, susceptible to acting as a dehydrocoupling

Fig. 23 A catalyst for the dehydrocoupling reaction of $Al(NiPr_2)_3$ and Me_2NHBH_3



73

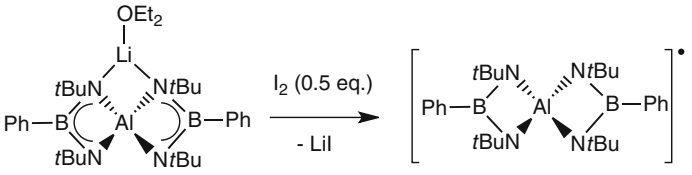
Fig. 24 An aluminum boramidinate anion



74

catalyst (and also accounting for the observed $(Me_2N)_2BH$). Such a proposal was successfully validated since the Al dihydride **73** (Fig. 23) was found to catalyze the dehydrocoupling reaction of $Al(NiPr_2)_3$ and Me_2NHBH_3 [201].

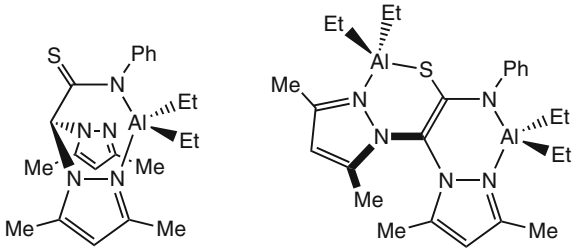
Remaining with spirocyclic chemistry, the use of the boramidinate dianion, isoelectronic with extensively studied amidinate anions, has recently witnessed renewed attention as, among other studies, this class of dianions was shown to be suitable for the synthesis spirocyclic group 13 species, such as the Al anion **74** (Fig. 24). Oxidation studies of Al(III)-containing boramidinate lithium salts led to the observation of strongly colored solutions, leading to speculation that radical anions of the type $[RB(NR')_2]^{\bullet -}$ were being formed [202]. More recently, these paramagnetic chelating ligands have been stabilized through the synthesis of spirocyclic group 13 neutral radicals, such as the dark red $[\{PhB(\mu\text{-}NtBu)_2\}_2Al]^{\bullet}$ radical (**75**, Eq. 12), stable for days in solution and weeks in the solid state under an inert atmosphere [203].



(12)

75

The aggregation of aluminum amides may be prevented for steric reasons. Recent studies on organoaluminum-bearing thioacetamido heteroscorpionate ligands constitute a representative illustration of such a trend. While the equimolar reaction of $AlEt_3$ with the corresponding pro-ligand resulted in the coordination of aluminum by one of two pyrazolyl rings to form monomer **76** (Fig. 25), the use of two equiv. of $AlEt_3$ afforded the dinuclear Al complex **77**. Remarkably, species **77** has been crystallized as a self-assembled single-stranded chiral helicate through the formation of CH-π interactions [204]. Along with those resulting from the self-assembly of Al-based cinchona alkaloid sub-units for the construction of

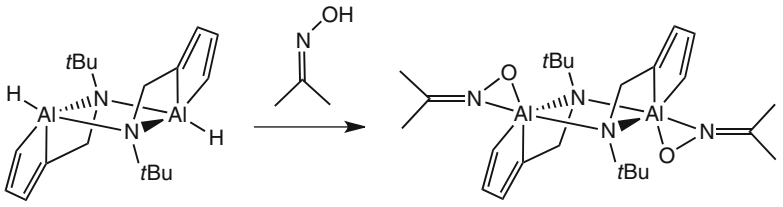


76 77

Fig. 25 Organoaluminum species bearing a thioacetamido pyrazolyl ligand

homochiral networks [132], such a material represents a rare Al-incorporating helical polymer.

The agglomeration of organoaluminum amides is well established [205] and the structure and reactivity of one such dimeric aggregate has recently been studied. Reaction of $AlH_3(NMe_3)$, generated in situ from $LiAlH_4$ and $NMe_3{\cdot}HCl$, with $C_4H_3NH(2\text{-}CH_2NHtBu)$ allowed access to the $\mu\text{-}\eta^1{:}\eta^5$-pyrrolyl dimer $[C_4H_3N(2\text{-}CH_2NtBu)AlH]_2$ (**78**, Eq. 13). Subsequent treatment of **78** with either acetone oxime or acetone yielded $[C_4H_3N(2\text{-}CH_2NtBu)Al\{\kappa O,\kappa N\text{-}(ON{=}CMe_2)\}]_2$ (**79**, Eq. 13) or the Al isopropoxide derivative $[C_4H_3N(2\text{-}CH_2NtBu)AlOCHMe_2]_2$, respectively [206]. Moreover, based on the relative strength of Al–O and Al–N bonds, the nucleophilic addition of aluminum amides to carbonyls (Eq. 14) has been harnessed to produce α-diimines from dione substrates [207].

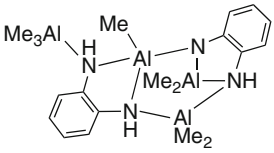


78 79 (13)

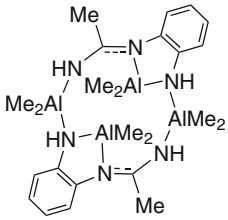
$$^1/_n\,[R_2AlN(H)Ar]_n + \text{O=C} \longrightarrow [R_2AlOH] + \text{Ar-N=C} \qquad (14)$$

The insertion of *t*BuCN into $H_3Al(NMe_3)$ has led to the isolation of an $Al_4C_4N_4$ cage structure, which may be described as one where the carbon atoms have formally inserted into the four Al–N bonds of an Al_4N_4 cubane-type motif. The latter $Al_4C_4N_4$ cage structure is apparently retained in solution according to preliminary spectroscopic studies [208]. In contrast, the presence of potentially bridging pyrazolato ligands precluded cage formation: instead, the bridging compound $(\mu\text{-}AlH_2)_2(\mu\text{-}CH_2NtBu)(\eta^1\text{-}\eta^1\text{-}tBu_2pz)_2$ was observed.

Ring expansion reactions involving Al amido compounds have recently been performed via insertion of acetonitrile into preexisting Al–N ring structures. Thus,



80



81

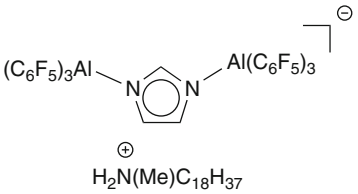
Fig. 26 Molecular structures of the aluminum amido complexes **80** and **81**

the asymmetric dinuclear adduct $(Me_2Al)AlMe\{C_6H_4(NH)_2\}_2(AlMe_3)$ (**80**, Fig. 26), arising from a 2:1 reaction between $AlMe_3$ and 1,2-diaminobenzene, was found to react with acetonitrile to afford the ring-expanded product **81**, a twelve-membered metallocyclic dimer [209]. The conversion of **80** to **81** was proposed to take place through acetonitrile insertion into Al–N bonds in a fashion akin to that previously documented for hydrazine reactivity [210].

Due to their potential usefulness in various fundamental and more applied studies, weakly coordinating anions represent a burgeoning field of chemistry. In particular, the search for weakly coordinating borate anions via tuning of the electronic and steric properties has lately been thoroughly investigated. However, the emergence of a second strategy – that enhancing the negative charge delocalization by linking borates – led to the synthesis of $[(C_6F_5)_3M–L–M(C_6F_5)_3]^-$ (M = B, Al; L = CN) [211, 212]. The development of a novel family of B- and Al-containing imidazolate anions such as **82** (Fig. 27) has also been reported [213].

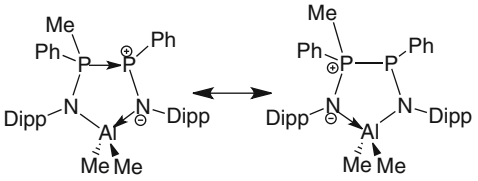
Other recent work on *N*,*N*′-chelating ligands has focused on ligand backbone modifications to access acyclic structures of the type NP(III)NCN, consisting of a zwitterionic backbone that incorporates a phosphenium center stabilized by an imidophosphine unit. The acyclic precursor DippN(H)P(Ph)N(Cy)C(*t*Bu)=NCy (Cy = cyclohexyl), readily generated upon addition of the amidinate salt Li[N(Cy)C(*t*Bu)=NCy] to PhClP(NHDipp), reacted with $AlMe_3$ to yield DippN($AlMe_2$)P(Ph)P(Me)(Ph)NDipp (**83**, Fig. 28) [214]. It is presumed that the formation of the *N*,*N*′-chelating ligand DippN(Ph)P(Ph)P(Me)(Ph)NDipp$^-$ occurs through a nucleophilic $AlMe_3$-methylation, thus creating a four-coordinate, chiral P-center. Furthermore, the formation of **83** is accompanied by that of CyN($AlMe_2$)C(*t*Bu)NCy, as experimentally observed. The new chelating ligand in **83** may be viewed in terms of resonance structures with either a phosphine–phosphonium complex or a phosphine-stabilized phosphenium cation. The structural chemistry of Al complexes supported by the related ligand $Ph_2PN(iPr)P(Ph)N(iPr)H$ has also been recently described; the latter reacted with excess AlR_3 (R = Me, Et) to produce *N*,*P*-chelated organoaluminum species $Ph_2PN(iPr)P(Ph)(AlR_3)N(iPr)AlR_2$, which were found to convert to $iPrN(AlR_2)P(Ph)P(Ph)_2$ N(*i*Pr) upon heating [215, 216].

The chemistry of boratophosphazene $N(PCl_2NMe)_2BCl_2$ has been primarily investigated so as to gain insight into the factors governing and influencing ring-opening processes in ring-containing inorganics. This has led to reactivity studies with halide acceptors (e.g., $AlCl_3$) with the isolation and characterization of a planar



82

Fig. 27 A weakly coordinating imidazolate bis-aluminate anion

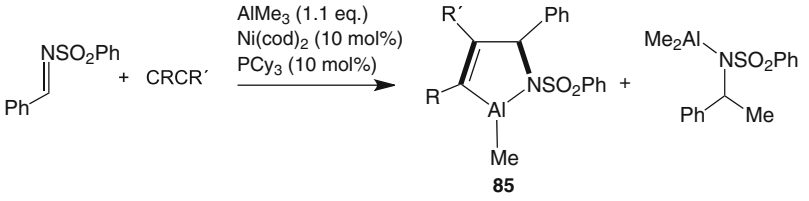


83

Fig. 28 A *N*,*N*′-chelated organoaluminum species with a phosphine-phosphonium/phosphine-stabilized phosphonium moiety

borazine–phosphazene hybrid cation [217]. A group 13 heterophosphazene has more recently been prepared upon combining $N(PCl_2NMe)_2BCl_2$ with an excess of $AlMe_3$ [218]. The resulting aluminatophosphazene $N(PCl_2NMe)_2AlClMe$ (**84**) adopts a boat conformation with the aluminum center significantly out of the ring plane and it exhibits an elongated Al–Cl bond. Based on the latter observation, compound **84** was reacted with $AgBF_4$ for chlorine abstraction. However, this yielded, rather expectedly, a reverse skeletal substitution of Al for B with the isolation of the fluorinated boratophosphazene $N(PCl_2NMe)_2BF_2$.

The oxidative cyclization of two π systems using a low valent transition metal has long promised a route towards the construction of C–C bonds. In this area, for instance, Ni(0)-catalyzed [2+2+2] alkyne-imine cycloaddition reactions affording 1,2-dihydroptridines are known [219]. These three-component alkyne/imine/organometallic entity reactions are thought to proceed via the formation of azanickelacycle intermediates, whose reactivity toward $AlMe_3$ was investigated. This led, however, to the unexpected formation of five-membered azaaluminacyclopentene **85** via a nickel/aluminum double transmetallation (R, R′ = Ph) (Eq. 15). This was followed by the successful demonstration that nickel was actually suitable for the catalysis of the three-component cyclocondensation of imines, various alkynes, and $AlMe_3$ [220].



85 (15)

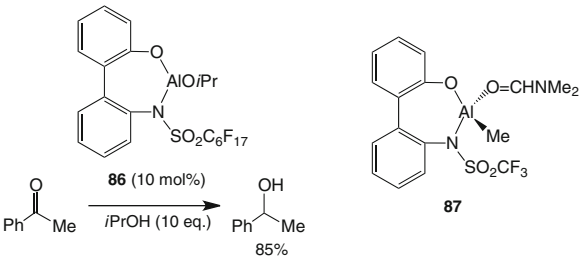
7.2 Organoaluminum Imides

Unknown ten years ago, discrete Al imido monomers supported by sterically demanding β-diketiminato ligands have been synthesized and characterized [221]. Such Al(III) imido monomers were found to be accessible via reaction of β-diketiminato Al(I) precursors with appropriate azide substrates [222]. For further details and insightful discussions on the reactivity of Al(I) and Al(I)-derived compounds with organic substrates, the reader may refer to [289].

8 Use of Organoaluminum Species Supported by Chelating Ligands: Selected Examples

8.1 Organoaluminum Species Bearing N- and/or O-Type Ligands

N,*O*-chelating ligands have been the subject of intense study in the past as catalysts for the mediation of organic transformations, largely by virtue of the versatile salen ligand system (vide supra). More recent advances in *N*,*O*-ligand chemistry have brought forth a new catalyst for the Meerwein–Ponndorf–Verley (MPV) reaction. This is a mild technique that delivers a reversible hydride transfer via a six-membered transition state and which benefits from the use of inexpensive and relatively safe reagents. However, the need for harsh reaction conditions or aggressive mixed alkoxide catalysts has proved to be a hindrance. This has led workers to experiment with catalytic procedures using bidentate ligands, though problems have remained. More recently still, difficulties, in particular with the reduction of aromatic ketones, have been overcome by the development of a readily accessible and highly active MPV catalyst based on an appropriately substituted aluminum phenoxide. Thus, the reduction of ketones by *i*PrOH (10 equiv.) was achieved in high yield using an aluminum isopropoxide derived from 2-hydroxy-2′-(perfluorooctanesulfonylamino)biphenyl (10 mol%) (**86**, Scheme 8). The nature of the catalyst was probed using the complex between Dimethylformamide (DMF) and catalyst precursor (**87**, Scheme 8), with crystallography proving the expected seven-membered cyclic structure in which the influence of the perfluoroalkyl group is electronic rather than steric [223]. More recently, a role has been developed for catalyst **86** in the reverse of the MPV reduction – the rather mild Oppenauer (OPP) oxidation of alcohols. Hence, for example, a near quantitative yield of the enone carvone was achieved from carveol using 2 mol% of **86** and *t*BuCHO as hydride acceptor [224]. Of potential importance in this work was the demonstration that **87** facilitated the ready oxidation of terpenoids and steroids by acetone.



Scheme 8 A MPV reaction catalyzed by the Al complex **86**

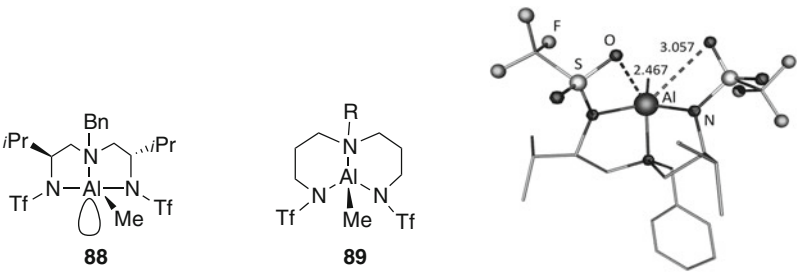
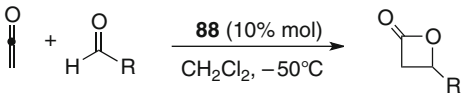


Fig. 29 Ligand-imposed geometry differences at the Al center in species **88** and **89** and the XRD-determined molecular structure of **88** (the XRD data were retrieved from the Cambridge Structural Database, version 5.33, November 2011 [227]).

More recent work on the 1,2-rearrangement of variously substituted α-siloxy aldehydes has represented an avenue for extending the catalytic chemistry of close relatives of **86** [290].

There has been unremitting interest in the development of various reaction systems initiated by Al(III) complexes based on sterically encumbered dianionic ligands bearing various Lewis base moieties at properly designed positions. In this area, a series of optically active Al(III) triamine complexes, such as complex **88** (Fig. 29), have been reported as Lewis acid catalysts for the mediation of various asymmetric transformations, including ketene-aldehyde cycloaddition reactions (Eq. 16; for more detail on these transformations, see Chapter 6 "Reactions triggered by Lewis acidic organoaluminum species") [225, 226].



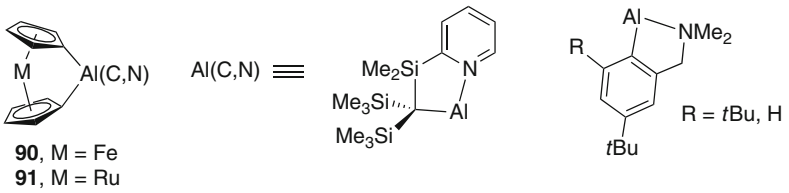
(16)

The authors examined various *N*,*N*′,*N*″-amine ligands to evaluate catalyst efficiency as a function of the triamine ligand's backbone and terminal amine functionality. For instance, these studies demonstrated that compound **88** was catalytically active in contrast to the related compound **89** (differing only in the chelate size), which was found to be completely inactive as a cycloaddition

catalyst. To explain the observed disparity dsp^3 Al ion hybridization in **88** was invoked as providing "a low-lying metal-centered LUMO," thus disposing the Al (III) center ideally to accommodate a fifth ligand and complete the tbp coordination geometry [226]. However, more detailed analysis of the geometric parameters of **88** (retrieved from the Cambridge Structural Database, version 5.33, November 2011 [227]) clearly indicates that the geometry around the Al atom is best described as a distorted tbp that has one carbon atom and two outer nitrogen atoms of the amine ligands in the equatorial positions and one nitrogen atom occupying one of the apical positions. In the second apical position, the presence of rather long Al···O contacts (2.467 and 3.057 Å) reflect weak interactions between the metal center and the tosyl donor functions, thereby suggesting a quite Lewis acidic metal center. The increased reactivity of four-coordinate tbp complex **88** (vs. its tetrahedral analogue **89**) arises from a destabilizing ligand-imposed geometry distortion at Al. Thus, compound **88** can be described as a classical alkylaluminium complex consisting of a pseudo five-coordinated Al center with intramolecular stabilization of the resting state provided by the tosyl groups, and there is therefore *no need* to invoke the dsp^3 Al center hybridization. It seems likely that for Al(III) triamine complexes with more flexible ligand backbones, as is in the case in **89**, these intramolecular interactions in the apical positions are sufficiently strong that they inhibit coordination of the metal by approaching substrate (**89** did not form a Lewis acid–base adduct with DMF [226]). Undoubtedly, these series of Al(III) triamine complexes nicely demonstrate how subtle changes in the environment of the metal center can strongly affect the Lewis acidity of the catalytic center.

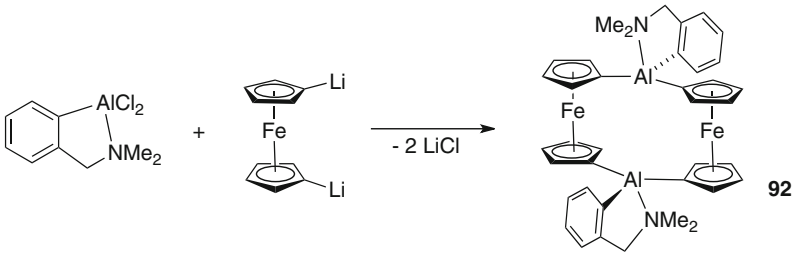
8.2 Organoaluminum Species Bearing C,N-Type Ligands

Although they have been less thoroughly investigated than their *N*,*N*′ and *N*,*O* bidentate analogues, Al(III) compounds supported by *C*,*N*-type chelating ligands have been described over the past few years [228, 229]. In this area, recently developed *C*,*N*-type Al [1]-metallocenophanes that exhibit significant ring strain (**90** and **91**, Fig. 30), which may be used as precursors for the synthesis of organoaluminum-containing metallopolymers, certainly illustrate how simple yet well-designed organoaluminum species may be the precursors to novel materials [230, 231]. Such Al [1]-metallocenophanes may be prepared via common salt metathesis routes between a dilithio metallocene precursor and a dichloroaluminum species of the type (*C*,*N*)$AlCl_2$ [232]. It is noteworthy that the use of a sterically bulky chelating *C*,*N* ligand (i.e., an *ortho*-*t*Bu-substituted phenylide amino ligand) appears crucial to access the desired ring-strained ferrocenophane entities. Indeed, carrying out such a synthesis using a dichloroaluminum precursor supported by a less hindering phenylide amino ligand led to the formation of Al-containing [1,1]-metallocenophane **92** (Eq. 17) [233].



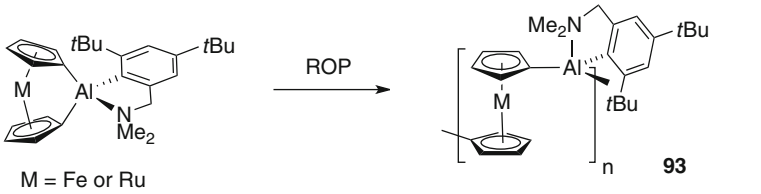
90, M = Fe
91, M = Ru

Fig. 30 Structure of [1]-metallocenophanes containing an organoaluminum moiety



(17)

Structural interest in them notwithstanding, ring-strained [1]-metallocenophane compounds **90** and **91** are highly reactive in ring-open polymerization, albeit in an uncontrolled manner, to yield the corresponding metallopolymers **93** (with M_w ranging from 8 to 106 kDa) with a random tacticity (Eq. 18). Although the mechanism of these ROPs remains to be addressed, it seems probable that residual dilithiometallocene acts an anionic ROP initiator.

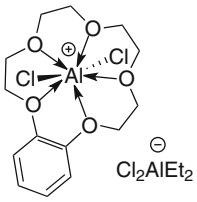


M = Fe or Ru

(18)

9 Cationic Organoaluminum Compounds

Though their applications as polymerization catalysts fall outside the remit of the present chapter, a general discussion of the advent of cationic aluminum complexes supported by various ligands is warranted [46]. Over the last two decades cationic aluminum complexes have been very intensively investigated and promise enhanced substrate coordination and activation by virtue of their increased electrophilicity. Early systematic works focused on the use of crown ethers and the synthesis of complexes $[Cl_2Al(benzo\text{-}15\text{-}crown\text{-}5)][Me_2AlCl_2]$ and



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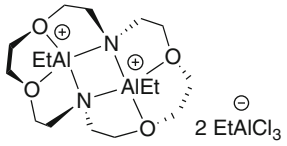
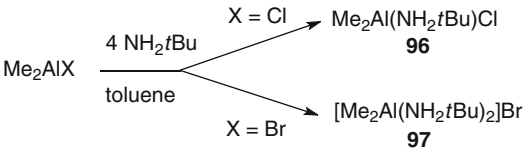


95

Fig. 31 Cationic aluminum species chelated by crown ether-type ligands



Scheme 9 Access to amine-stabilized dimethylaluminum cations via a halide displacement reaction

$[(EtAl)_2$(diaza-18-crown-6)$][EtAlCl_3]$ (**94** and **95**, Fig. 31) [234, 235]. These featured cations that incorporated seven- and penta-coordinate Al centers, respectively.

The first structurally authenticated dialkylaluminum cation supported by a monodentate ligand, $[Me_2Al(NH_2tBu)_2]Br$ (**97**, Scheme 9), was synthesized by the addition of an excess of *tert*-butylamine to dimethylaluminum bromide in toluene [236]. Interestingly, the analogous reaction involving dimethylaluminum chloride resulted in the formation of ordinary Lewis acid-base adduct $Me_2Al(NH_2tBu)Cl$ instead (**96**, Scheme 9). These simple organoaluminum cations were too reactive and labile to be used broadly in applications.

9.1 N,N′-Ligated Organoaluminum Cations

Preliminary attempts to generate free AlR_2^+ cations by reacting AlR_3 with a strong Lewis acid such as $[Ph_3C][B(C_6F_5)_4]$ afforded a mixture of the neutral species $AlR_{3-x}(C_6F_5)_x$ and $R_xB(C_6F_5)_{3-x}$, the formation of which most likely arose from the decomposition of the putative transient species $[AlR_2][B(C_6F_5)_4]$ through $C_6F_5^-$ ligand transfer from the boron center to the AlR_2^+ fragment [237]. Only in the late 1990s did Jordan et al. first report the synthesis of stable three-coordinate aluminum cations of the type $(LX)AlR^+$, where LX^- was a bulky monoanionic π-delocalized *N, N′*-bidentate ligand of the aminotroponiminate or diketiminate type (**98**, Eq. 19) [238].

98 (19)

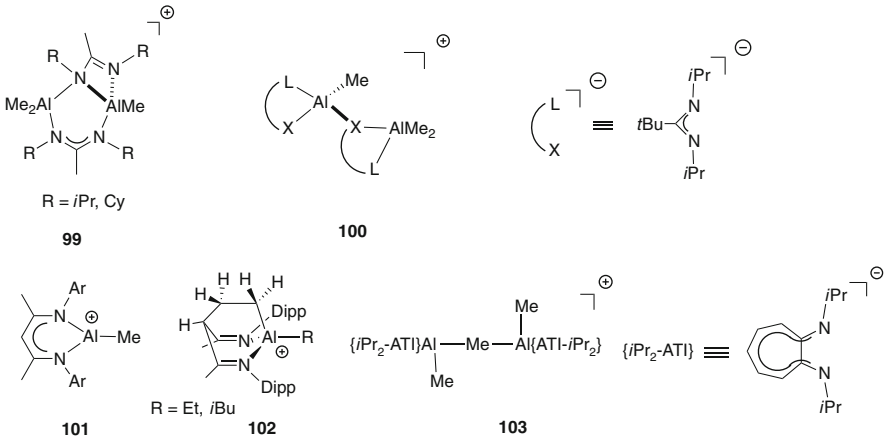


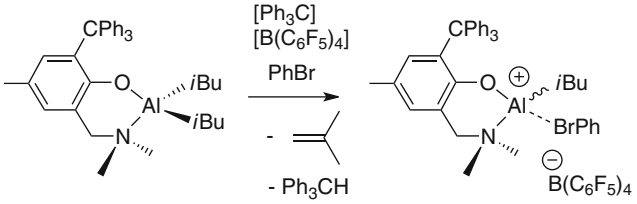
Fig. 32 Structural diversity in *N*,*N*′-supported organoaluminum cations

A range of neutral dialkylaluminum chelate complexes containing *N*,*N*′-bidentate spectator ligands have recently been used to generate three or four-coordinate cationic alkylaluminum complexes through reaction with $[CPh_3][BPh_4]$, $[HNMe_2Ph]$ $[B(C_6F_5)_4]$, or $B(C_6F_5)_3$ as the alkyl abstracting reagent. A thorough investigation of the structure and reactivity of cationic aluminum amidinate species demonstrated that the molecular structures of these entities are strongly influenced by the steric properties of the amidinate ligand and the reactivity of the counter anion [238–241]. For example, the reaction of amidinate complexes $\{RC(NR')_2\}AlMe_2$ (R = Me or *t*Bu, R′ = *i*Pr or Cy) with $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ has yielded amidinate-bridged dinuclear species (**99** and **100**, Fig. 32). The reactions described above yielded dinuclear species because the initially generated $\{RC(NR')_2\}RAl^+$ cation was trapped by the starting $\{RC(NR')_2\}AlMe_2$ complex. The difficulty in generating stable mononuclear $\{RC(NR')_2\}AlR^+$ species is considered to be due to the small bite angle of the amidinate ligand (N–Al–N angles *ca*. 70° in $\{RC(NR')_2\}AlR_2$ complexes) [238, 239]. Stable 3-coordinate $\{HC(CMeNAr)_2\}AlR^+$ cations (**101**, Fig. 32) were obtained by alkyl abstraction reactions from *N*,*N*′-diaryldiketiminate complexes $\{HC(CMeNDipp)_2\}AlMe_2$, which presents a larger ligand bite angle (N–Al–N angle *ca*. 96°) and bulky *N*-aryl substituents [240, 241]. The latter cationic species have been reacted with ethylene by reversible cycloaddition across the Al-diketiminate ring to yield products of type **102** (Fig. 32). Subsequent to this, cationic aluminum alkyl complexes incorporating the *N*,*N*′-diisopropylaminotropoiminate ligand $[iPr_2\text{-ATI}]^-$ were reported. Hence, for example, the reaction of *N*,*N*′-diisopropylaminotroponiminate complexes $(iPr_2\text{-ATI})AlMe_2$ with 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ at ambient temperature in benzene has yielded the dinuclear Me-bridged species $[\{(iPr_2\text{-ATI})AlMe\}_2(\mu\text{-Me})][B(C_6F_5)_4]$ (**103**, Fig. 32) [242]. No further reaction occurred when $(iPr_2\text{-ATI})AlMe_2$ was mixed with excess $[Ph_3C][B(C_6F_5)_4]$ in benzene at ambient temperature for several days. Compound **103** was stable at room temperature as a benzene or toluene liquid clathrate but decomposed in CH_2Cl_2. In contrast to the behavior of **103**, complexes containing higher primary alkyl groups

reacted with one equiv. $[Ph_3C][B(C_6F_5)_4]$ in aromatic solvents at 25°C by net β-H abstraction to give base-free $[(iPr_2\text{-ATI})AlR][B(C_6F_5)_4]$ salts (R > Me) and the corresponding olefin [242]. Note that the three-coordinate Al methyl cations supported by a chiral or an achiral bisoxazolinato bidentate ligand appeared thermally unstable and readily degraded to unknown species [243]. Cationic $\{HC(CMeNAr)_2\}AlR^+$ and $[(iPr_2\text{-ATI})AlR]^+$ species readily coordinated Lewis bases to form robust 4-coordinate $\{HC(CMeNAr)_2\}Al(R)(L)^+$ adducts. The higher alkyl $(iPr_2\text{-ATI})Al(CH_2CHRR')^+$ cationic species (RR′ = H_2, HMe, Me_2) reacted with acetone, *t*Bu-acetylene, and ethylene to yield $(iPr_2\text{-ATI})Al(OiPr)^+$, $(iPr_2\text{-ATI})Al(CH{=}CHtBu)^+$, and $(iPr_2\text{-ATI})AlEt^+$, respectively, with evolution of the corresponding $CH_2{=}CRR'$ olefin [242].

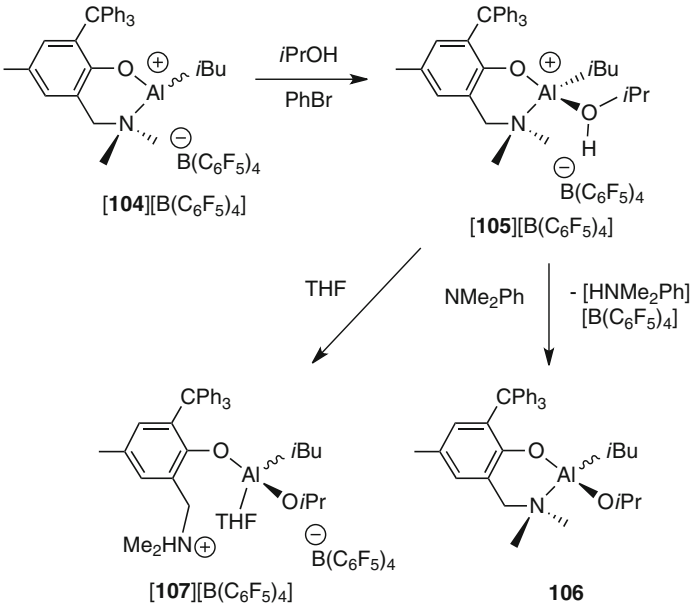
9.2 *N,O-Ligated Organoaluminum Cations*

Numerous cationic alkylaluminum complexes supported by *N,O*-type bidentate ligands have recently been reported [149, 150, 244]. The potential chemical richness of this class of species is well demonstrated in the cases of cationic alkyl- and alkoxidoaluminum complexes incorporating the sterically bulky bidentate aminophenolate ligand 6-(CH_2NMe_2)-2-CPh_3-4-Me-$C_6H_2O^-$ [149]. These complexes are derived from the ionization of neutral dialkylaluminum complexes (*O,N*)AlR_2 (R = Me, *i*Bu). Reaction of the diisobutyaluminum complex with $[Ph_3C][B(C_6F_5)_4]$ (C_6D_5Br, room temp, 10 min) has afforded quantitative formation of the robust Al-based cation $[\{6\text{-}(CH_2NMe_2)\text{-}2\text{-}CPh_3\text{-}4\text{-}Me\text{-}C_6H_2O\}Al(iBu)(PhBr)]^+$ (**104**, Eq. 20) as a fully dissociated $[B(C_6F_5)_4]^-$ salt. In the case of cation **104**, the significant steric crowding around the Al center provided by the CPh_3 and the *i*Bu group most likely accounts for the observed stability.



[**104**][$B(C_6F_5)_4$] (20)

The reaction of [**104**][$B(C_6F_5)_4$] with one equivalent of ε-CL (C_6D_5Br, room temp, 10 min) has quantitatively yielded the corresponding cationic Al-(ε-CL) adduct $[\{6\text{-}(CH_2NMe_2)\text{-}2\text{-}CPh_3\text{-}4\text{-}Me\text{-}C_6H_2O\}Al(iBu)(\varepsilon\text{-CL})]^+$ as a fully dissociated $[B(C_6F_5)_4]^-$ salt. The molecular structure of the latter cation incorporating a ε-CL ligand η^1-coordinated to the Al center represents the second structurally characterized Al-(ε-CL) complex. The reaction of [**104**][$B(C_6F_5)_4$] with one equivalent of *i*PrOH (C_6D_5Br, room temp) quantitatively yielded the corresponding cationic Al-alcohol adduct $[\{6\text{-}(CH_2NMe_2)\text{-}2\text{-}CPh_3\text{-}4\text{-}Me\text{-}C_6H_2O\}Al(iBu)(HOiPr)]^+$ (**105**) as a dissociated $[B(C_6F_5)_4]^-$ salt instead of the anticipated low-coordinate alkoxy Al-based



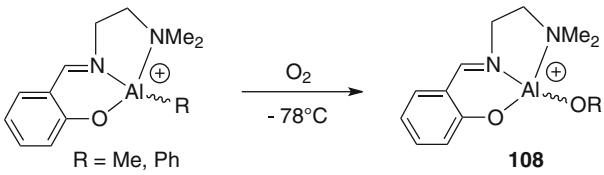
Scheme 10 Formation and reactivity of a cationic Al-alcohol organoaluminum adduct

cation (Scheme 10). The observation of a kinetically stable Al-alcohol complex such as **105** is unusual, as such adducts, which have been proposed as intermediates in the alcoholysis of organoaluminum complexes by ROH, have not generally been observed [98]. Although a few related neutral Al complexes have been reported [98], cation **105** constitutes the first example of a stable Lewis acid–base adduct between a cationic alkylaluminum complex and a simple alcohol ROH. The salt [**105**][$B(C_6F_5)_4$] has been seen to readily react with one equivalent of NMe_2Ph (C_6D_5Br, room temp, 10 min) to quantitatively form a 1:1 mixture of the neutral monoalkoxyaluminum complex [{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(O*i*Pr)(*i*Bu)] (**106**) and the ammonium salt [$NHMe_2Ph$][$B(C_6F_5)_4$] (Scheme 10). Reaction of cation **105** with THF afforded a different outcome, with an intramolecular proton transfer being observed; it reacts quickly with one equivalent of THF (C_6D_5Br, room temp, 10 min) to form the alkyl(ammonium)aluminum complex [η^1-{6-(CH_2NHMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(*i*Bu)(O*i*Pr)(THF)]$^+$ (**107**) as a fully dissociated [$B(C_6F_5)_4$]$^-$ salt (Scheme 10).

9.3 *Organoaluminum Cations Supported by Tridentate Chelating Ligands*

Whereas three-coordinate cationic alkylaluminum species have proved to be more reactive than their higher coordinate counterparts, such entities often exhibit a limited stability along with an increased tendency to form aggregates. This has

significantly hampered the scope of their potential applications in catalysis. There has, therefore, been a discernible shift in interest towards more stable, albeit less reactive, four-coordinate alkylaluminum cations supported by *N*,*N*′,*N*″-, [245, 246], *O*,*N*,*N*′-[146] and *O*,*N*,*O*-type tridentate ligands [247, 248]. This family of four-coordinate Al alkyl cations may be generated in a straightforward manner through ionization of the neutral dialkylaluminum precursors $(X,Y,L)AlR_2$ by an R^- abstracting agent. On one occasion, an Al alkoxide cation supported by an *O*,*N*,*N*′-type ligand (**108**, Eq. 21) was shown to be readily accessible through reaction of the corresponding Al alkyl cation with O_2 [247]. Notably, cation **108** was found to mediate the ROP of ε-CL in a fairly well-controlled manner.



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10 Organoaluminum Complexes Incorporating Redox-Active Ligands

Using stable, low-valent aluminum analogues of carbene synthons, Roesky and others have reported various two-electron oxidation reactions involving the transformation of Al(I) to Al(III) [222, 249, 250] (see also Chapter 3: "Low valent organoaluminum (+I, +II) species"). These results have illustrated the difficulty of using aluminum species for facile and tunable redox chemistry. An alternative strategy that can potentially be employed is based on the use of aluminum complexes bearing ligands that can exist in multiple oxidation states when coordinated to a metal ion: such ligands are typically referred to as non-innocent or redox-active [251]. However, the development of potentially redox-active aluminum(III) complexes has generally proceeded rather slowly and the majority of paramagnetic and potentially redox-active aluminum(III) complexes thus far reported have been restricted to those containing *N*-donor ligands (Fig. 33).

The first redox-active and paramagnetic complex of Al(III) to be reported was $Al(bpy)_3$ (bpy = 2,2′-bipyridyl) and was prepared by the reduction of $AlCl_3$ with Li(bpy) [252]. Based on magnetic measurements, the product species was proposed to be best described as containing an Al^{3+} cation, with the unpaired electrons being extensively delocalized on the bpy ligands. More recently, related radical anion complexes of tris(1,3-diphenyltriazenido)aluminum have been isolated and structurally characterized [253]. $Na_x[Al(dpt)_3]$ complexes were prepared by the stoichiometric reduction of $Al(dpt)_3$ by Na in THF (Eq. 22).

$$Al(dpt)_3 + xNa \rightarrow Na_x[Al(dpt)_3] \quad x = 1, 2, 3 \tag{22}$$

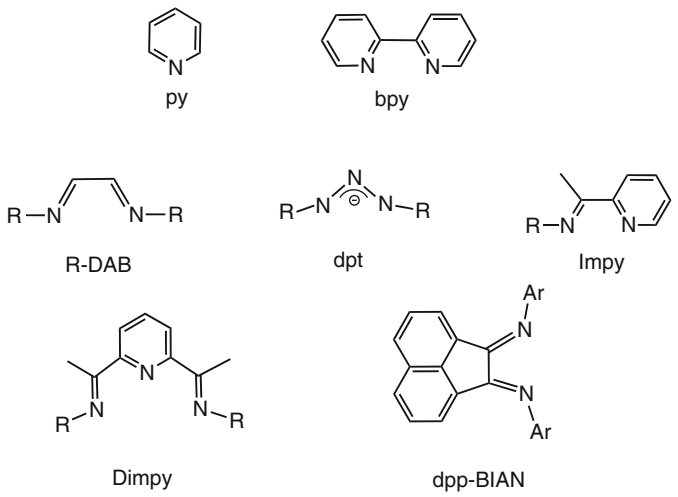
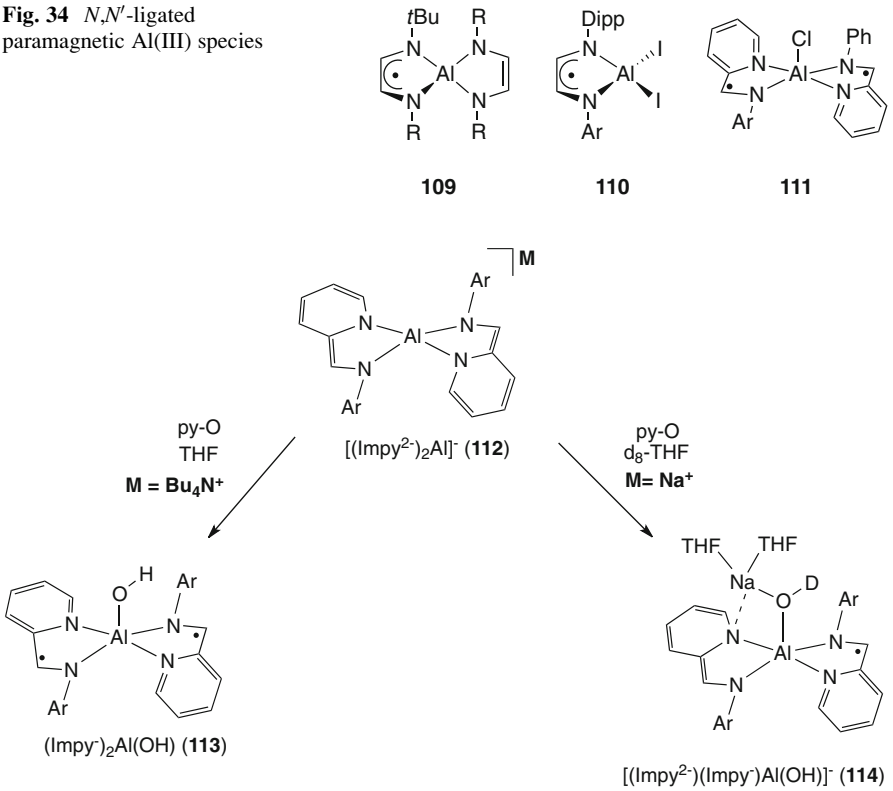


Fig. 33 Some potentially redox-active *N*-donor ligands

The first structurally authenticated paramagnetic aluminum complex, [Al(*t*Bu-DAB)(*t*Bu-DAB$^{\bullet}$)] (**109**, Fig. 34), was prepared either by co-condensing aluminum vapor with 1,4-di-*t*-butyl-1,4-diazabutadiene (*t*Bu-DAB) or by treating *t*Bu-DAB with a $LiAlH_4$ powder [254]. XPS (solid), EPR (solution) measurements, single crystal X-ray structural determination [254] along with theoretical calculations [255] supported the formal presence of Al(III) centers with the spin density of the unpaired electron being located in one of the two DAB-Al rings. The analogous paramagnetic heteroleptic diazabutadienealuminum complex [(Dipp-DAB$^{\bullet}$)AlI_2] (**110**, Fig. 34) was prepared by reacting Dipp-DAB with a 1/2 AlI_3/Al mixture in toluene. The EPR spectrum of **110** agreed with the unpaired spin density being primarily ligand-centered [256].

Very recently, a series of paramagnetic four- and five-coordinate aluminum complexes of the type $Impy_2Al$ and $Impy_2AlX$ [Impy = 2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene) phenylamine, X = monodentate ligand] containing neutral, monoanionic, and dianionic iminopyridine ligands have been structurally and electronically characterized [257]. Using $AlCl_3$ as a starting point, control over the number of Al–Cl ligands in each member of this series of complexes was achieved upon limiting the number of equivalents of Na (used as reducing agent). For example, a dark green aluminum(III) complex, $(Impy^{-})_2AlCl$ (**111**, Fig. 34), which bears two one-electron-reduced Impy ligands, was prepared upon combining $AlCl_3$ with 2 equiv. of Impy and 2 equiv. of sodium in 1,2-dimethoxyethane. Variable-temperature magnetic susceptibility and EPR spectroscopy measurements indicated that the diradical character of the ligand-based triplet in **111** was stabilized by a strong antiferromagnetic exchange coupling mediated by the Al (III) center. Thus, the latter results demonstrated that redox non-innocent ligands can be effectively employed to impart a rich redox reactivity and open-shell electronic structure to the non-redox active and strongly Lewis acidic aluminum (III) center.



Scheme 11 Oxidation of a homoleptic *N*,*N*′-supported Al(III) anion with pyridine oxide

The oxidation of the four-coordinate Al anion $[(Impy^{2-})_2Al]^-$ (**112**, Scheme 11) with pyridine oxide (py-O) has also been investigated [258]. The reaction of the NBu_4^+ salt of **112** with py-O afforded the neutral monomeric Al–OH product $(Impy^-)_2Al(OH)$ (**113**, Scheme 11), formulated as a triplet biradical on the basis of magnetic susceptibility measurements. In contrast, the Na^+ salt of **112** reacted with py-O in dry d_8-THF to produce the Al(III) compound **114** (Scheme 11), confirmed to be in a doublet spin state with spectroscopic data. Interestingly, the coordination of one of the pyridine nitrogens by the Na^+ cation in **114** was proposed to stabilize the corresponding the Impy dianion ligand towards subsequent oxidation chemistry. It is also noteworthy that all available data suggested that the formation of **114** proceeded with a C–H activation in the THF molecules bound to the Na^+ cation.

Contemporaneously, studies on paramagnetic organoaluminum compounds have been gradually developed. Early investigations resulted in the isolation of paramagnetic dialkyl Al(III) complexes of pyridine, pyrazine and bipyridine radical anions (**115**–**117**, respectively, Fig. 35) [259–264]. It has also long been recognized that conjugated imines can behave as non-innocent ligands, readily engaging in a variety of alkyl transfer reactions to either the C- or the N-atoms of the ligand

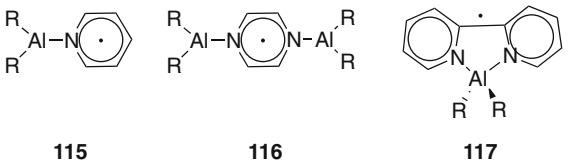
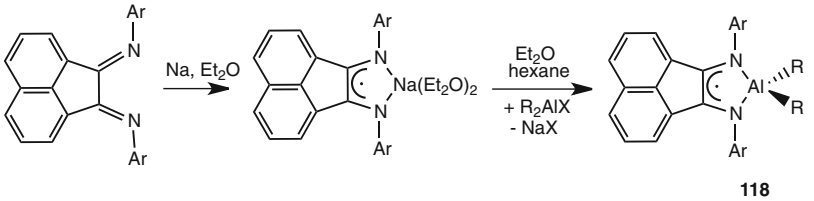


Fig. 35 Pyridine, pyrazine, and bipyridine organoaluminum(III) radical anions

115 **116** **117**

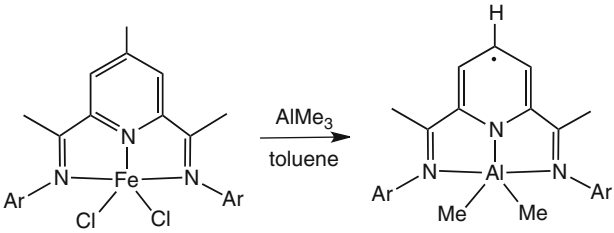


118

Scheme 12 Synthesis of paramagnetic BIAN-supported Al(III) species

skeleton, and the formation of persistent organoaluminum radical complexes [246, 265–269].

The first examples of structurally characterized alkylaluminum derivatives incorporating paramagnetic radical-anionic ligands were only reported in 2006 [267]. Thus, a series of alkylaluminum complexes of general formula [(Dipp-BIAN)AlR_2] (**118**, Scheme 12) (Dipp-BIAN = 1,2-bis[(2,6-diisopropylphenyl) imino]acenaphthene) was isolated from the metathetical reaction of the salt species [Dipp-BIAN]Na with various dialkylaluminum halides R_2AlX (R = Me, X = Cl; R = Et, X = Br; R = *i*Bu, X = Cl). Since then, the paramagnetic organoaluminum species (Ar-Dimpy)$AlMe_2$] [where Ar-Dimpy = 2,6-$(ArNCR)_2C_5H_3N$] (**119**, Eq. 23) have been prepared via reaction of (Ar-Dimpy)$FeCl_2$ with $AlMe_3$ [268]. Complexes **118** and **119** are paramagnetic due to the presence of an unpaired electron located within the diimine and 2,6-bis(imino)pyridine ligand systems, respectively.



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Surprisingly, redox chemistry involving Al(III) species supported by quinones and other O-donor non-innocent ligands remains in its infancy since early studies on the reaction of alkylaluminum dichlorides with 1,4-quinones for the production of aryl ethers via a radical-radical coupling process [270–272].

While redox chemistry of metal complexes typically takes place at the metal center, the use of metal species bearing so-called redox non-innocent ligands may promote a metal/ligand cooperation in a synergistic manner. Therefore such complexes offer interesting prospects for uncovering unprecedented stoichiometric

and catalytic transformations and future studies in the area will advance both fundamental and applied directions.

11 The Oxygenation of Alkylaluminum Compounds

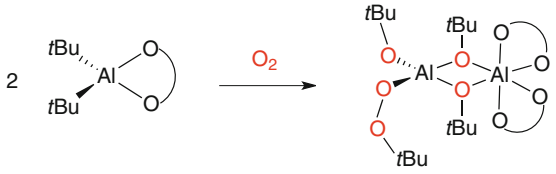
The insertion of dioxygen into a metal-carbon bond constitutes one of the oldest reactions in organometallic chemistry. The common wisdom states that the oxygenation reactions of homoleptic organometallic complexes are uncontrollably fast due to their postulated radical chain-reaction mechanism. The exact reaction mechanism is yet to be unambiguously described and debate about the details of the process is ongoing [273–276]. The preparation and handling of most organometallic compounds, in particular alkylaluminum species, is typically carried out under anaerobic conditions and dioxygen-free reaction media to avoid side reactions. At the same time, it remains a significant challenge to bring oxygenation reactions under control in order to allow the design and implementation of O_2-based reaction systems. The widely accepted free radical chain-reaction mechanism for these oxygenation reactions, as described in the vast majority of textbooks, assumes an initiation by adventitious alkyl radicals followed by a cascade of fast reactions with little opportunity for the detection of intermediates. It is only over the past few years that detailed insights into mechanistic aspects of the reaction between main group metal alkyls and O_2 have appeared in the literature. These have challenged the long-held assertion that a radical mechanism is dominant [275, 276].

Despite the well-known oxygen sensitivity of organoaluminum complexes, there are relatively few examples in the literature of alkylaluminum groups reacting with molecular oxygen. Early studies in the area reported that the reaction of alkylaluminums with dioxygen afforded complicated mixtures of aluminum alkoxides [277, 278]. More recently, the oxygenation of Al*t*Bu$_3$ was shown to result in the formation of the well-defined aluminum alkoxide [*t*Bu$_2$AlO*t*Bu]$_2$ [275]. In the latter reaction, an alkylperoxyaluminum compound proved to be highly unstable because of the high reactivity of the RO–O–Al moiety. Nevertheless, the reaction of O_2 with the four-coordinate chelate complex Et$_2$Al(mesal) (mesal = methyl salycilate anion) allowed the isolation of the alkylperoxyaluminum compound *t*BuOO(*t*BuO)Al(μ-O*t*Bu)$_2$Al(mesal)$_2$ (**120**, Scheme 13) [279].

The above studies showed that four-coordinate Al alkyl complexes could readily be oxidized to alkoxide compounds via alkyl peroxide intermediates. To date, apart from **120**, only two examples of alkylperoxyaluminum compounds have been isolated and structurally characterized. However, these compounds were synthesized by the direct reaction of organic peroxides (instead of O_2) with organoaluminum precursors [187, 280].

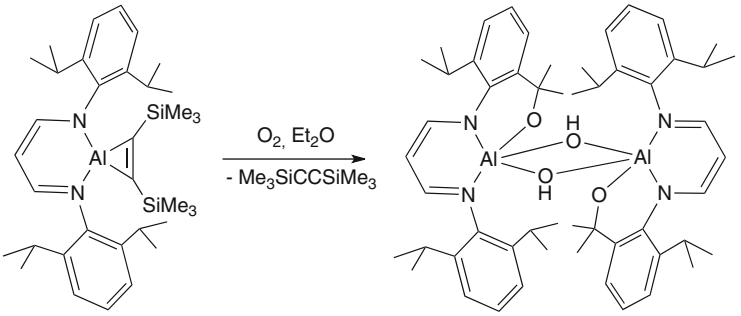
Overall, the isolation and full characterization of products derived from the oxygenation of organoaluminum complexes has proved very rare. In one example, the reaction of the tetranuclear cluster [Al$_4$(μ$_3$-8-quinolylimide)$_2$Me$_8$ with molecular oxygen selectively afforded the monoalkoxide cluster [A1$_4$(μ$_3$-8-

Scheme 13 Synthesis of a well-defined alkylperoxyaluminum compound



120

quinolylimide)$_2$Me$_7$(μ-OMe)], found to be resistant toward further oxygenation [281]. Intriguingly, the reaction of LAl[η^2-C$_2$(SiMe$_3$)$_2$] (L = HC[(CMe)(NDipp)]$_2$) with O$_2$ has been shown to yield the aluminum hydroxide species **121** (Eq. 24) with the concomitant elimination of bis-(trimethylsilyl)acetylene via an intramolecular C–H activation. It seems reasonable that species **121** forms via an initial insertion of O$_2$ into one of the Al–C bonds to yield an aluminum alkylperoxide intermediate that undergoes a homolytic O–O bond cleavage and a subsequent α-hydrogen abstraction from the CH of one of the *i*Pr groups [282].



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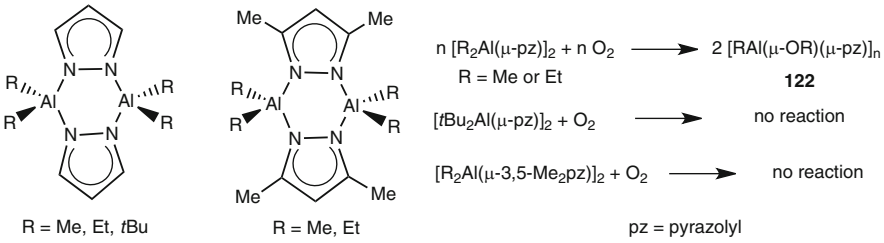
The mechanism of dioxygen activation by several types of four-coordinate aluminum alkyl has been explored. The reaction of properly designed dialkylaluminum pyrazolyl derivatives with O$_2$ demonstrated the possibility of a dioxygen attack on the Al metal center followed by insertion into an Al–C bond to generate an Al–OOR moiety. It is now recognized that this reaction sequence is key to the activation of four-coordinate organoaluminum complexes by dioxygen [273]. Recent investigations have also concluded that the initial approach of molecular oxygen to the metal center is conditioned by specific geometrical requirements. For R$_2$Al(*X*,*X*′) complexes (where *X*,*X*′ = *N*,*N*′ or *O*,*O*′ chelating ligand), O$_2$ is thought to approach via one of the two CCX planes. Evidence supporting this assertion has been provided both by structural studies on various four-coordinate alkylaluminums and the observation of a divergent behavior of these compounds towards dioxygen (Scheme 14 and Fig. 36). Thus, aluminopyrazoles bearing an essentially planar central Al$_2$N$_4$ ring were observed to be O$_2$-resistant (under 1 atm)



Scheme 14 Reactivity of dinuclear pyrazolyl organoaluminum complexes with dioxygen

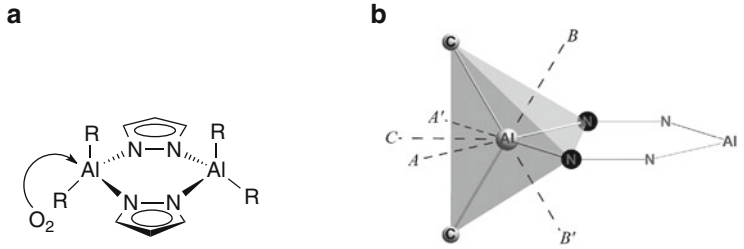


Fig. 36 Geometric requirements for the effective oxygenation of dinuclear pyrazolyl Al complexes. Reprinted from Lewiński et al. (2000) Chem Eur J 6:3215

at room temperature. In contrast, dialkylaluminum analogues and diethylaluminum bis(1-pyrazolyl)borate species, both classes of species incorporating an Al metal center eclipsed with respect to the plane defined by the four nitrogen atoms, reacted smoothly with O_2 to form the corresponding alkyl(alkoxy)aluminum complexes (**122**, Scheme 14). These results convincingly showed that O_2 can only effectively access the Al center through the trigonal CCN faces: i.e., pathway A or A′ (Fig. 36b). Other approaches, such pathways B, B′ and C (Fig. 36b), were observed not to be effective for the oxygenation reaction to occur. Strikingly, in the case of the borate aluminum complex $Et_2B(\mu\text{-}pz)_2AlEt_2$ (pz = pyrazolyl), only one Al–Et group readily reacted with O_2 (while the B–Et bonds remained intact), allowing the isolation of the dimeric five-coordinate ethyl(ethoxide)aluminum compound $[Et_2B(\mu\text{-}pz)_2Al(\mu\text{-}OEt)Et]_2$.

Despite the above developments, the reactivity of organoaluminum compounds toward dioxygen remains to be explored. In particular, the potential of such reactions so as to access aluminum alkylperoxides and alkoxides of potential utility certainly deserves to be exploited. There is a significant challenge to bring oxygenation reactions under control in order to allow the design and implementation of O_2-based reaction systems. Achievements to date mark out a course for future discoveries, including the functionalization of aliphatic C–H bonds in association with O–O bond activation.

12 Perspective and Future Outlook

The simplest triorganoaluminums have long been used to generate commercially important alkylaluminum reagents and catalysts. The richness of this chemistry in itself promises important future developments. However, it is the newly emerging field of frustrated Lewis pairs (FLPs), i.e., systems that incorporate a sterically bulky main group Lewis acid and base hindering classical formation of the classical Lewis adduct formation, that promises the most exciting new developments in catalysis and small molecule activation [91, 93, 94]. The interaction of organoaluminum compounds with dioxygen remains an area little explored thus far and, likewise, the potential of such reactions for synthesizing useful aluminum alkylperoxides and alkoxides is to be undeveloped. The better control of oxygenation reactions in order to allow the design and implementation of O_2-based reaction systems certainly constitutes a significant challenge. Achievements to date mark out a course for future discoveries, including the functionalization of aliphatic C–H bonds in association with O–O bond activation [280].

Although the field of aluminoxanes has witnessed remarkable advances over the past twenty years, accessing such species both via hydrolytic and anhydrous methods remains the subject of ongoing efforts so as to expand the library of organoaluminum hydroxides and oxides of potential interest in catalysis and material science. Recent intriguing results have been obtained by treating a phthalic acid/$AlMe_3$ mixture with 1,2-bis(4-pyridyl)ethane [164], with a reaction outcome highly dependent on stoichiometry. Thus, the reaction has been shown to yield tetramethylalumoxane moieties entrapped by the alkylaluminumphthalate monomer and linked by the 1,2-bis(4-pyridyl)ethane ligand or, varying the reaction stoichiometry, a crystalline Lewis acid–base tetramethylalumoxane-bipyridine adduct along with a cyclic ester side-product (Scheme 6). This facile route to aluminoxanes and carboxyaluminoxanes opens significant new opportunities. Moreover, the ability of aluminoxanes to act as secondary building units for macrocycles or coordination networks will be increasingly relevant to catalysis and material science. In a similar vein, diphenylglycolic acid/$AlMe_3$ and the amino acid 2,2-diphenylglycine have also been observed to yield remarkable Al_6 or Al_{12} macrocyclic structures [164]. Here again, reaction stoichiometry determined the structure of the formed macrocyclic product.

As for organoaluminum species containing Al-bonded heteroatoms, research into alkoxides and aryloxides is well established. Nevertheless, the advent of BINOL-derived bifunctional chiral Al(III) complexes has already enabled the design and synthesis of a broad range of asymmetric catalysts. Bifunctional catalysts of this type – susceptible to interact both with electrophiles and nucleophiles and so to potentially achieve spectacular stereodiscrimination – will undoubtedly lead to interesting future developments.

The use of chelating ligands for coordination to Al(III) is extensive, with the majority of investigation having focused on *N*- and *O*-donor systems. Recently though, exciting advances were made in the use of *N*,*N*′,*N*″-amine chelating ligands

designed to impose a tbp geometry at a four-coordinate Al center, rendering such species more reactive than classical tetrahedral Al complexes [225, 226]. Such Al (III) triamine complexes represent nicely how small changes in the environment of the metal center can strongly affect the Lewis acidity of a catalyst and this should encourage the development of new ligand types.

The properties of metal complexes obviously depend for the most part on the interactions of the metal center with its surrounding ligands. However, synergistic cooperation between metal and ligand-based non-coordinating active-site residues prone to be involved in multiple non-covalent interactions, particularly in hypervalent organoaluminum complexes, likely play an important role in molecular recognition and activation processes involving Al(III)-based catalysts. However, this type of cooperation has hitherto remained frequently unrevealed or underestimated. Interesting contrasts have been observed between Al–O and Al–S bonded species. Thus, for example, unlike the associative behavior of salicylate alkylaluminums, methyl thiosalicylate dialkylaluminum compounds featured short intermolecular S···C(π) contacts between the Al–S thiolate unit and the ester component that are thought to compete with sulfur-aluminum hypercoordinate bonding [141]. These data introduce the area of intermolecular n$\rightarrow\pi^*$ interactions that can compete with hypercoordinate bonding. Therefore, continued interest in both the exploitation of non-covalent interactions exhibited by various groups of organoaluminum complexes and the development of reaction systems initiated by Al(III) complexes supported by multidentate ligands bearing non-covalent active-site residues at properly designed positions can be expected in the near future.

The reactivity of Al(III) complexes has typically been centered around the metal. However, the use of redox non-innocent ligands has allowed the observation of synergistic cooperation between metal and ligand. That said, the development of redox-active aluminum(III) complexes has proceeded slowly, with research largely based on the use of *N*-donor ligands [252–258]. The same has so far proved true of paramagnetic Al(III) complexes, with the most recent advances in the area being the structural authentication of alkylaluminum derivatives incorporating paramagnetic radical-anionic ligands [266, 267]. Surprisingly, comparable redox chemistry involving O-donor ligands remains to be substantially developed, though initial work in this area has demonstrated the successful reaction of alkylaluminum dichlorides with 1,4-quinones via a radical-radical coupling process [270–272]. Overall, the use of complexes bearing redox non-innocent ligands plainly offers numerous possibilities to uncover new stoichiometric and catalytic transformations.

Finally, Arduengo's report on the first main group element *N*-heterocyclic carbene (NHC) complex, [AlH_3(IMes)] (IMes = 1,3-dimesitylimidazol-2-ylidene) [283], initiated a two decade period of sustained interest in the chemistry of Al-based NHC complexes, albeit progress in this field has been slow. Nevertheless, a recent report on the development of chiral Al-based NHC complexes as catalysts for enantioselective allylic alkylation reactions [284] and the isolation of the stable Al(II) adduct [$(NHC)_2Al_2H_4$)], in which the elusive parent dialane Al_2H_4 is stabilized by two NHC ligands [285], illustrates the potential of Al-NHC organometallic species in both application-oriented research and fundamental science.

Given the rapidly growing collection of available NHC metal complexes, it seems reasonable to expect noteworthy developments in the field of Al-NHC species over the next few years.

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Organoaluminum Complexes with Bonds to s-Block, p-Block, d-Block, and f-Block Metal Centers

Stephan Schulz

Abstract This chapter summarizes the recent developments in organoaluminum compounds containing at least one direct bond between aluminum and a s-block, p-block, d-block, or f-block metal center. General synthetic pathways to access such species are described along with their structural and bonding properties.

Keywords σ-Donor · Aluminum · Lewis acid · Lewis base · Molecular intermetallics

Contents

Abbreviations

BDE	Bond dissociation energy
Cp	Cyclopentadienyl

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Cp*	Pentamethylcyclopentadienyl
Dcpe	1,2-Bis(dicyclohexylphosphanyl)ethane
DFT	Density functional theory
Dipp	2,6-Di-*iso*-propylphenyl
Dmap	4-Dimethylaminopyridine
dpp-BIAN	1,2-Bis[(2,6-diisopropylphenyl)imino]-acenaphthene
Dvds	1,3-Divinyl-1,1,3,3-tetramethyldisiloxane
MOCVD	Metal organic chemical vapor deposition
Nacnac	β-Diketiminato
Tmeda	Tetramethylethylenediamine
Tmp	Tetramethylpiperidine
Tmpda	Tetramethylpropylenediamine

1 Introduction

Intermetallic complexes have a long standing history in organometallic chemistry not only due to their fascinating structural diversity but also due to their interesting chemical properties. For instance, olefin polymerization reactions using titanium and aluminum complexes as reported by Ziegler and Natta claimed the presence of complexes containing a direct Al–Ti bond. Even though "$[Cp_2TiAlEt_2]_2$," a model compound in the Ziegler–Natta olefin polymerization process, was later on shown to form no direct metal–metal bond, the interest in such complexes remained. Since these early studies, homo- and hetero-bimetallic complexes found widespread technological applications in organic synthesis, polymerization catalysis, and were also shown to be very promising *single source precursors* for the deposition of thin films via metal organic chemical vapor deposition (MOCVD) processes. These intermetallic materials (alloys) are also of technical interest since their electrical properties range from metallic to semiconducting (see, for instance, III/V and III/VI materials).

This chapter summarizes the synthesis and structures of intermetallic organoaluminum complexes exhibiting at least one direct bond between aluminum and either main group metals, transition metals, lanthanides, or actinides. Homometallic aluminum complexes in lower oxidation states I $(AlR)_x$ and II (Al_2R_4) containing direct Al–Al bonds as well as metalloid cluster complexes are excluded from the present chapter and will be reviewed in Chap. 3 (Low valent organoaluminium (+I, +II) species). In contrast, the synthesis, structure, and bonding properties of donor–acceptor complexes of alanediyls RAl with group 13 organometallics R'_3 M (M = Al, Ga, In) are described in the present contribution.

2 Organoaluminum Complexes with s-Block Metals

Organoaluminum complexes bound to s-group metal centers have been predicted to be stable compounds by computational calculations [1], but alanediyl complexes of alkaline metals and earth alkaline metals remain unknown to date. In contrast,

several gallane complexes have been prepared and structurally characterized [2–6]. Interestingly, dpp-BIAN complexes (dpp-BIAN = 1,2-bis[(2,6-diisopropylphenyl) imino]-acenaphthene) of aluminum and gallium exhibit different coordination modes to alkali metals. While the Ga derivatives form direct Ga–metal bonds [2, 3], the aluminum analogues contain an alkaline metal binding to the π-electronic system of the dpp-BIAN ligand rather than to the Al center [7].

3 Organoaluminum Complexes with p-Block Metals

Heterobimetallic organoaluminum complexes with p-block metals, i.e., group 13 (Ga, In), group 15 (Sb, Bi), and group 16 metals (Te), have been prepared to a large extent. The interest of such complexes does not only lie on their fundamental interest, i.e., the possible formation of Al–E (E = p-block elements) complexes containing multiple bonds [8], but also lie on their potential usefulness in material science. Complexes of group 15 and group 16 metals, for instance, were shown to be promising *single source precursors* for the gas phase deposition of thin films as well as for solution-based synthetic routes to access (nanosized) semiconducting materials such as AlSb and Al_2Te_3.

3.1 Organoaluminum Complexes with Group 13 Metals (Ga, In, Tl)

Homo- and heterobimetallic organoaluminum complexes containing a direct Al–M bond (M = Al, Ga, In) have attracted considerable attention within the last decade due to their interesting bonding properties. They are typically formed by reaction of strong Lewis acidic group 13 complexes $M'R_3$ with subvalent group 13 metal diyls RM (R = Cp*, nacnac, terphenyl), with the metal center M being in a + I formal oxidation state. Alanediyls RAl and their heavier congeners RM (M = Ga, In) exhibit a singlet electronic ground state with a larger singlet–triplet energy gap for heavier M centers. Group 13 diyls therefore behave as two-electron σ-donors, but also exhibit π-accepting properties as observed in isolobal fragments such as CO, phosphanes PR_3 and singlet carbenes CR_2. The extent of σ-donation and π-acceptance largely depends on the nature of the metal and on the organic group R, even though there is no simple correlation between the nature of the group 13 elements (M and M′), the substituents R, R′, and the stability of the complexes RM–$M'R_3'$. However, the Lewis basicity (σ-donor capacity) of group 13 diyls was found to be higher with increasing π-donor strength of the organic substituent R [9, 10]. As a consequence, strong π-donor ligands such as amido (NR_2) groups and the Cp* substituent enhance the stability of group 13–group 13 donor–acceptor complexes of the type RM–$M'R'_3$ [11]. Simultaneously, the π-acceptor properties of the MR fragment is diminished according to the partial population of the vacant

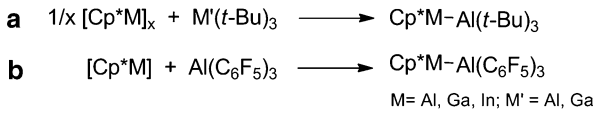

Fig. 1 Synthesis of homo- and heteronuclear group 13-diyl complexes with group 13 Lewis acidic organometallics

p-orbitals of the group 13 metal center through π-donation by the Cp* substituents. Due to the lack of any back-bonding in intermetallic group 13 element complexes with direct bond to a main group metal, only the σ-donor properties of MR are of interest. In addition, computational calculations demonstrated that the metal–metal bond energies in the corresponding group 13-transition metal complexes also primarily rely on the σ-donor properties of the group 13 diyls as well as on electrostatic contributions [12, 13].

3.1.1 Synthesis

Lewis basic group 13 diyls were found to form stable adducts with group 13 Lewis acids. In particular, heteronuclear complexes containing the strong Lewis acid $B(C_6F_5)_3$, such as Cp*M–$B(C_6F_5)_3$ (M = Al [14], Ga [15, 16]), NacnacM–$B(C_6F_5)_3$ (Nacnac = β-diketiminato, M = Al [17], Ga [16]), and R′M–$B(C_6F_5)_3$ (M = Ga, In; R′ = terphenyl) [18, 19], have been prepared and structurally characterized. The nature of the central M–B bond in these complexes was investigated by computational calculations [12, 20, 21]. In addition, the homoleptic complexes Cp*Al–$Al(C_6F_5)_3$ [22] (Fig. 1), Cp*Al–Al(*t*-Bu)$_3$ [23], Cp*Ga–Ga(*t*-Bu)$_3$ [15, 23], and Cp*Ga–Ga(Cp*)X_2 (X = Cl, I) [15] have also been synthesized. These complexes may alternatively be described as valence isomers of the corresponding divalent compounds R_2M–MR_2. The nature of the supporting ligands subtly, yet clearly, influences the stability of the resulting complexes as demonstrated by computational calculations [22, 24].

Heteronuclear group 13 bimetallic complexes were formed either by reaction of alanediyls with group 13 Lewis acids (Cp*Al–Ga(*t*-Bu)$_3$ [23]) or that of heavier group 13 diyls congeners with Lewis acidic alanes (Cp*Ga–$Al(C_6F_5)_3$ [25], Cp*Ga–Al(*t*-Bu)$_3$ [23], and Cp*In–Al(*t*-Bu)$_3$ [23]) (Fig. 1).

3.1.2 Solid State Structures

Selected bond distances and angles for the group 13 complexes discussed above are provided in Table 1. In all these derivatives, the Cp* ligand in Cp*Al–MR_3 and Cp*M–AlR_3 (M = Al, Ga, In) adopts a η^5 binding mode to the group 13 metal and the Cp*$_{centr}$–M–M units slightly deviate from linearity. The M–Cp*$_{centr}$ bond distances of the diyl adducts are significantly shorter than those in the group 13 diyl precursors Cp*M, as was previously observed for heteronuclear complexes of the type Cp*Al–BR_3 [31]. Such a shortening results from the transformation of

Table 1 Selected bond lengths (Å) and angles (°) for homo- and heterobimetallic group 13 complexes

Adduct	Al–M	M–Cp*$_{centr}$	Cp*–Al–M	Reference
Cp*Al	–	2.015[a]/2.063[b]	–	[26, 27]
Cp*Ga	–	2.081[a]/2.081[b]	–	[28, 29]
Cp*In	–	2.302[a]/2.288[b]	–	[30]
Cp*Al–B(C_6F_5)$_3$	2.169(3)	1.802(3)	172.9	[14]
NacnacAl–B(C_6F_5)$_3$	2.183(5)	–	–	[17]
Cp*Al–B(C_6F_5)$C_{12}F_8$	2.1147(15)	1.782	160.95	[31]
Cp*Al–B(Me)$C_{12}F_8$	2.149(7)	1.817/1.814	162.76	[31]
Cp*Al–B(Ph)$C_{12}H_8$	2.1347(13)	1.809	164.12	[31]
Cp*Al–Al(*t*-Bu)$_3$	2.689(2)	1.858	175.0	[23]
Cp*Ga–Al(*t*-Bu)$_3$	2.629(2)	1.913	174.2	[23]
Cp*In–Al(*t*-Bu)$_3$	2.843(2)	2.173	170.0	[23]
Cp*Al–Ga(*t*-Bu)$_3$	2.620(2)	1.861	175.5	[23]
Cp*Al–Al(C_6F_5)$_3$	2.591(2)	1.810	170.1	[22]
Cp*Ga–Al(C_6F_5)$_3$	2.515(11)	1.810	170.6	[25]

[a]As determined by single crystal X-ray diffraction for [Cp*Al]$_4$, [Cp*Ga]$_6$ and [Cp*In]$_6$
[b]As determined by electron diffraction (gas phase) for the monomeric compounds Cp*M

the partially antibonding *electron lone pair* of the diyl Cp*M unit into a donor–acceptor bond upon coordination with MR_3, along with the development of positive (donor-centered) and negative charges (acceptor-centered) at the group 13 metal centers [9].

The intermetallic Al–Al and Ga–Al bond lengths in Cp*M-Al(*t*-Bu)$_3$ are shorter than the In–Al bond length in Cp*In–Al(*t*-Bu)$_3$ due to the increased atomic radius of In vs. that of Al and Ga, respectively (Figs. 2 and 3). Moreover, these intermetallic distances are significantly longer than those in Cp*M–Al(C_6F_5)$_3$ (M = Al, Ga), clearly reflecting the different electronic and steric properties of the R substituents in AlR_3. The shortening of the M–M bond distance when going from Cp*Al–AlR_3 to Cp*Ga–AlR_3 (R = *t*-Bu, C_6F_5) presumably results from stronger electrostatic repulsion in the Al–Al derivative. Thus, upon complexation, the positive charge at the metal atom M(I) increases, with the Al metal donor featuring a larger positive charge compared to the Ga (metal donor) analogue [9]. Interestingly, structural data for NacnacAl–B(C_6F_5)$_3$ (Nacnac = β-diketiminato, M = Al) [17] agree with the presence of an Al–B donor–acceptor interaction, as expected, along with weak Al···F interactions arising from close intramolecular contacts between one *ortho*-fluorine atom and the Al atom. Therefore, in such a complex, the Janus-type electronic properties of the Al center, a metal center behaving both as a Lewis acid and a Lewis base, is clearly evidenced.

The Lewis basicity of group 13 diyls Cp*M (M = Al, Ga) was investigated by comparing the deviation from planarity of the BC_3 skeleton in Cp*M–B(C_6F_5)$_3$ complexes following a simple model described by Haaland et al. [32, 33]. According to this structural parameter, Cp*Al is slightly more Lewis basic than Cp*Ga, as may be anticipated. Indeed, the basicity of analogously substituted Lewis bases typically decreases upon going down a given group in the Periodic Table. In fact,

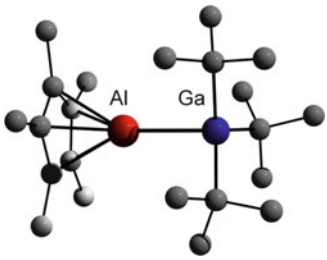

Fig. 2 Solid state structure of Cp*Al-Ga(t-Bu)$_3$

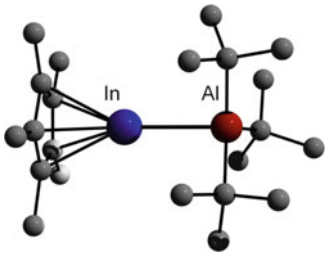

Fig. 3 Solid state structure of Cp*In-Al(t-Bu)$_3$

Cp*Al was found to be nearly as Lewis basic as PPh_3. Analogous trends were observed in complexes of the type Cp*M–Al(t-Bu)$_3$ and Cp*M–Ga(t-Bu)$_3$ (M = Al, Ga, In) [23].

3.2 *Organoaluminum Complexes with Group 15 Metals (Sb, Bi)*

Compounds containing group 13/15 bonds have a long standing history in main group organometallic chemistry. Apart from their academic interest, such entities are also of interest as novel *single source precursors* for semiconducting III/V material films and nanoparticles via gas phase deposition (MOCVD process) [34–37].

Known for decades, the general reactivity patterns in group 13/15 chemistry have been studied by Wiberg and May. For instance, the reaction of AlH_3 and NH_3 initially yields a Lewis acid–base adduct $H_3Al–NH_3$, which then further reacts at elevated temperatures with elimination of H_2 to afford the stepwise and successive formation of aminoalane $[H_2AlNH_2]_x$, iminoalane $[HAlNH]_x$, and aluminum nitride AlN as the final product [38] (Fig. 4).

Since these early studies, numerous compounds of the desired types have been prepared. However, the reaction pathway depicted in Fig. 4 only applies to the synthesis of organoaluminum complexes containing the lighter group 15 elements (N, P, and As). In contrast, access to organoaluminum species of the heavier group 15 elements, such as Sb and Bi, was nearly unknown up to 10 years ago. Nevertheless, ready access to such derivatives has been achieved over the past decade through the exploration and development of novel synthetic strategies.

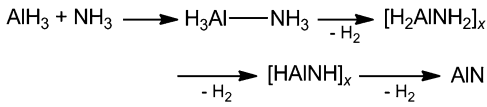

Fig. 4 Reaction of AlH_3 and NH_3 with stepwise elimination of H_2

3.2.1 Lewis Acid–Base Adducts

The reaction between a Lewis acid group 13 species of the type R_3M and a group 15 Lewis base of the type ER'_3 typically yields the corresponding Lewis acid–base adduct R_3M–ER'_3. This reaction, of fundamental interest in main group chemistry, has recently received an increased attention due to the potential use of amine-borane adducts as a hydrogen storage material [39] and to the unusual reactivity of so-called "Frustrated Lewis pairs" [40–42].

The structural properties and general coordination geometries of alane-amine and alane-phosphine adducts have long been studied in the solid state, in solution and in the gas phase [43]. In contrast, the corresponding stibine and bismuthine adducts have only been thoroughly investigated over the past few years [44]. Prior to these studies, the alane-stibine adduct, Br_3Al–$SbBr_3$, a molecular adduct in the gas phase [45] but ionic in the solid state ($[SbBr_2][AlBr_4]$) [46], had been synthesized and structurally characterized. Yet, with an enthalpy of formation of 4.3 ± 0.6 kJ mol^{-1} [47], Br_3Al–$SbBr_3$ is considered as a weakly bound Lewis acid–base adduct.

The low stability of the alane-stibine and -bismuthine adducts results from the reduced Lewis basicity of stibines and bismuthines due to the increasing s-character of the *electron lone pair* on the group 15 element [48]. However, the Lewis basicity of ER_3' can be increased via the use of alkyl substituents with a strong electron-donor inductive effect. In addition, sterically demanding substituents, such as *i*-Pr and *t*-Bu, directly affect the Lewis basicity of stibines and bismuthines. Indeed, steric hindrance results in larger C–E–C bond angles thereby decreasing the s-character of the *electron lone pair* and increasing its p-character.

Stable stibine-alane adducts are available by reaction of trialkylstibines SbR'_3 with dialkylchloroalanes R_2AlCl [49] and trialkylalanes AlR_3 [49–53], respectively. Also, the first bismuthine-alane [54, 55], distibine-alane [53, 55–57], and dibismuthine-alane adducts [58] were prepared by reaction of AlR_3 with BiR'_3, $Sb_2R'_4$, and Bi_2Et_4, respectively, and subsequently structurally characterized (Fig. 5). In most of these adducts, the acid–base interaction in the gas phase and in solution is rather weak. Dissociation enthalpies of *t*-Bu_3Al–$E(i\text{-}Pr)_3$ adducts (E = P 12.2 kcal/mol, As 9.9 kcal/mol, Sb 7.8 kcal/mol, Bi 6.9 kcal/mol) [59], as determined by NMR in solution, steadily decrease, as expected, when going to heavier group 15 elements. Such a decrease in bond strength clearly reflects a lower Lewis basicity for heavier group 15 elements.

Table 2 summarizes important structural parameters for alane-stibine and -bismuthine adducts R_3Al–ER'_3, while Table 3 features those for distibines and dibismuthines precursors R_2E–ER'_2 (E = Sb, Bi) and the corresponding alane adducts.

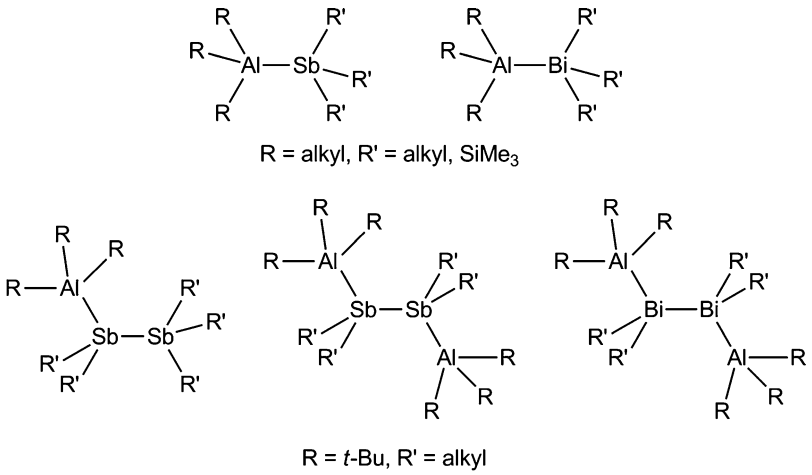

Fig. 5 Coordination modes observed for alane-stibine, distibine, -bismuthine, and dibismuthine adducts

Table 2 Selected bond lengths (Å) and angles (°) for alane-stibine and alane-bismuthine adducts

Adduct	M–E	Al–R (av)	ΣX–E–X	ΣR–Al–R	Reference
$R_3Al–Sb(SiMe_3)_3$					
R = Et	2.841(1)	1.984	310.8	347.3	[49]
R = *i*-Bu	2.848(1)	1.995	312.2	350.5	[50]
$R_2AlCl–Sb((SiMe_3)_3$					
R = *t*-Bu[a]	2.821(1); 2.798(1)	1.991; 1.994	3.126; 3.091	3.396; 3.415	[49]
$R_3Al–SbR'_3$					
R = Me; R′ = *t*-Bu	2.834(1)	1.967	319.1	347.2	[51]
R = Et; R′ = *t*-Bu	2.873(1)	1.981	317.8	343.7	[51]
R = *t*-Bu; R′ = Me	2.843(1)	2.020	295.6	349.9	[52]
R = *t*-Bu; R′ = Et	2.845(1)	2.027	301.5	346.9	[51]
R = *t*-Bu; R′ = *i*-Pr	2.927(1)	2.030	294.1	348.7	[51]
R = *t*-Bu; R′ = *i*-Bu	2.903(2)	2.019	302.4	347.2	[53]
$R_3Al–Bi((SiMe_3)_3$					
R = Et	2.921(2)	1.978	305.7	350.8	[54]
$R_3Al–BiR'_3$					
R = *t*-Bu; R′ = Et	2.940(1)	2.011	288.3	351.5	[55]
R = *t*-Bu; R′ = *i*-Pr	3.088(1)	2.018	286.5	350.4	[54]

[a]Two molecules within the asymmetric unit

In alane-stibine and alane-bismuthine adducts $R_3Al–ER'_3$, both metal centers generally adopt a distorted tetrahedral coordination geometry with the organic substituents R and R′ oriented in a staggered conformation relative to one another. The Al–E bond lengths (E = Sb 2.798(1)−2.927(1) Å; Bi 2.940(1), 3.088(1) Å), strongly dependent on the steric bulk of the organic substituents, are significantly elongated compared to the calculated single bond covalent radii

Table 3 Selected bond lengths (Å) and angles (°) for alane-distibine and alane-dibismuthine adducts

Adduct	E–E	Al–E	Al–C (av.)	E–C (av.)	ΣY–E–X[a]	ΣC–Al–C	Reference
E_2R_4							
E = Sb, R = Me	2.862; 2.830(1), 2.838(1)	–	–	2.15(2); 2.156	285.4; 289.4	–	[60, 61]
E = Sb, R = Et	2.8381(5)	–	–	2.170	288.4; 287.6	–	[56]
E = Bi, R = Et	2.9827(7)			2.291	281.8		[56]
[*t*-Bu_3Al][E_2R_4]							
E = Sb, R = *i*-Pr	2.855(1)	3.003(2)	2.029	2.196	300.9; 288.2	347.4	[55]
[*t*-Bu_3Al]$_2$[E_2R_4]							
E = Sb, R = Me	2.811(1)	2.919(1)	2.020	2.146	295.1	351.1	[57]
E = Sb, R = Et	2.838(1)	3.001(1)	2.024	2.167	292.9	350.2	[57]
E = Sb, R = *n*-Pr	2.839(1)	2.964(1)	2.022	2.156	292.2	350.1	[53]
E = Bi, R = Et	2.983(1)	3.084(2)	2.016	2.283	287.7	352.7	[58]

[a]$\Sigma Y–E–X = E–E–X_{1,2} + X_1–E–X_2$ (degree of pyramidalization)
[b] Structural data of the *trans* form

(Σr_{cov}(AlSb): 2.66 Å; Σr_{cov}(AlBi): 2.77 Å) [62]. In contrast, $Br_3Al–SbBr_3$ exhibits a significantly shorter Al–Sb bond length (2.522 Å), less than the sum of the Al and Sb covalent radii.

The longest Al–E bond lengths have been observed for the severely crowded *t*-$Bu_3Al–E(i\text{-}Pr)_3$ adducts. The Al–Bi bond lengths are much longer when compared to the Al–Sb bond lengths, a result of the larger atomic radius of Bi. However, the observed difference in *t*-$Bu_3Al–E(i\text{-}Pr)_3$ (E = Sb 2.927(1); Bi 3.088(1) Å) exceeds that of their covalent radii (Sb: 1.40, Bi: 1.51 Å) (Figs. 6 and 7).

Tetraalkyldistibines and -dibismuthines typically bind in a bidentated fashion when reacted with AlR_3 Lewis acids, yielding adducts of the type [R_3Al]$_2$[E_2R_4] (E = Sb [53, 55, 57], Bi [58], Fig. 8). Only the sterically crowded *i*-Pr_4Sb_2 was found to afford the monodentated complex [*t*-Bu_3Al][$Sb_2(i\text{-}Pr)_4$] (Fig. 9) [55]. These complexes represent the only distibine and dibismuthine complexes of main group metals. These results are strongly related to the already discussed weak Lewis basicity of ER_3 derivatives, and reflect the expressed tendency of tetraalkyldistibines and -dibismuthines to undergo disproportionation reactions with subsequent formation of the respective metal (Sb, Bi) and the corresponding trialkylstibine and -bismuthine R_3E, respectively [63].

The bulky *t*-Bu_3Al groups in the bidentate complexes [R_3Al]$_2$[E_2R_4] are, as expected, *trans* to one another for steric reasons. The Al–E bond lengths are

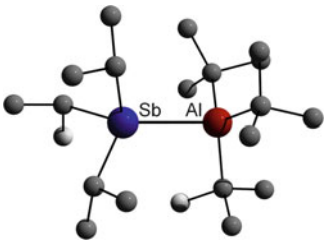

Fig. 6 Solid state structure of t-Bu_3Al–$Sb(i\text{-}Pr)_3$

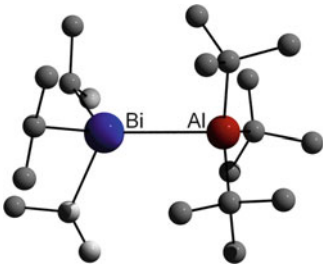

Fig. 7 Solid state structure of t-Bu_3Al–$Bi(i\text{-}Pr)_3$

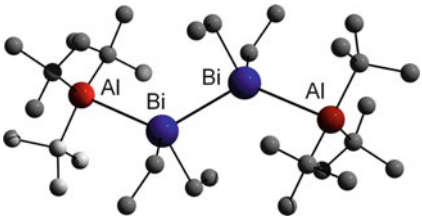

Fig. 8 Solid state structure of $[t\text{-}Bu_3Al]_2[Bi_2Et_4]$

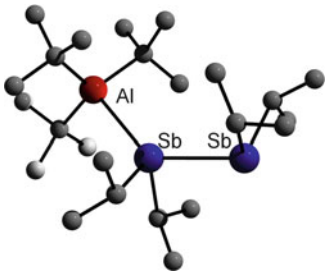

Fig. 9 Solid state structure of $[t\text{-}Bu_3Al][Sb_2(i\text{-}Pr)_4]$

comparable to those observed in simple trialkylstibine and bismuthine adducts R_3Al–ER'_3, and the central Sb–Sb and Bi–Bi bond distances are nearly identical to those in distibines and dibismuthines. These structural parameters agree with no E–E bond weakening upon adduct formation, which is consistent with rather weak Lewis acid–base interactions. The sum of the C–Al–C bond angles in t-Bu_3Al, as estimated from gas phase (electron diffraction, 355.37°) [64] and solid state structural data (355.1°, 355.9°; 355.5°) [65, 66], is comparable to that in

[*t*-$Bu_3Al]_2[E_2R_4]$ (352.7° for the dibismuthine adduct [*t*-$Bu_3Al]_2[B_2Et_4]$), further substantiating a weak Lewis acid–base bonding. Moreover, the sum of the C–Sb–C and C–Sb–Sb bond angles is larger in the distibine adducts [*t*-$Bu_3Al]_2[Sb_2R_4]$ vs. those in R_4Sb_2, which points out a partial rehybridization of the Sb centers as expected upon complexation. (The p-character of the electron lone pair is expected to increase and the s-character of the Sb–C and Sb–Sb bonding electron pairs to increase upon complexation, resulting in a widening of the C–Sb–C and C–Sb–Sb bond angles.) In addition, the C–Bi–X (X = C, Bi) bond angular sum in dibismuthine adducts [*t*-$Bu_3M]_2[Bi_2Et_4]$ lies a bit above that observed in analogously substituted distibine adducts [*t*-$Bu_3M]_2[Sb_2Et_4]$. This may be rationalized by a slightly higher p-character for the Bi–C and Bi–Bi bonding electron pairs and an increased s-character for the dative Bi–M bonding electron pairs. Therefore, Bi_2Et_4 has to be considered as a weaker Lewis base than Sb_2Et_4.

3.2.2 Heterocyclic Complexes $[R_2AlER'_2]_x$

Numerous amido-, phosphido-, and arsenide-alanes of the general type $[R_2AlER'_2]_x$ (x = 1, 2, 3) have been prepared following general and well-established synthetic routes via hydrogen elimination, alkane elimination, salt metathesis, or dehalosilylation reactions (Fig. 10).

The synthetic routes highlighted in Fig. 10, successfully applied to the synthesis of the corresponding Al–P and Al–As heterocycles as well as Ga–Sb and In–Sb heterocycles [71–79], were nevertheless shown to be inappropriate for the synthesis of aluminum heterocycles of the heavier group 15 homologues (Sb and Bi). This finding most likely results from the less acidic properties of the E–H group (E = Sb, Bi) along with the well-documented propensity of stibides and bismuthides toward reduction and subsequent formation of elemental Sb and Bi, respectively. Moreover, R_2AlCl and $Sb(SiMe_3)_3$ (R = Et, *t*-Bu) were observed not to undergo dehalosilylation as might be anticipated. Instead, the formation of the corresponding Lewis acid–base adducts was observed. In contrast, the reaction of Me_2AlCl with $Sb(SiMe_3)_3$ yielded $[Me(Cl)AlSb(SiMe_3)_2]_3$, resulting from the elimination of Me_4Si rather than Me_3SiCl. The different reactivity pattern observed for chloroalanes vs. chlorogallanes and indanes primarily arises from two key characteristics:

1. The Al–Cl bond is stronger than the Ga–Cl and In–Cl bonds [Al–Cl bond ($D°_{298}$, kJ mol^{-1}: Al–Cl 511 ± 1; Ga–Cl 481 ± 13; In–Cl 439 ± 8)] [80], disfavoring the elimination of Me_3SiCl.
2. Chloroalanes are stronger Lewis acids than their respectives chlorogallanes and -indanes, which favors the formation of Lewis acid–base adducts.

Therefore, novel reaction types had to be developed for the synthesis of heterocyclic complexes $[R_2AlER'_2]_x$ (x = 1, 2, 3). On that matter, the dehydrosilylation reaction revealed to be an extremely powerful tool [49, 67–70, 81]. Thus, dehydrosilylation reactions (Me_3SiH elimination) can be performed at low

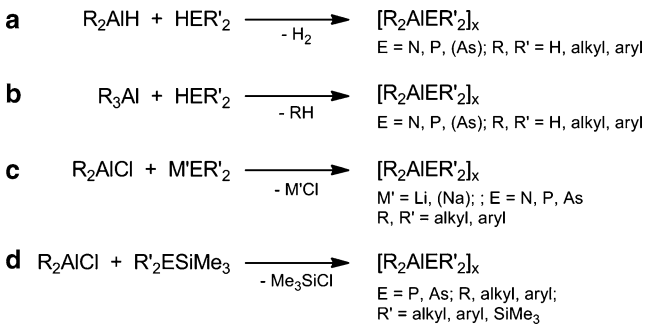

Fig. 10 Hydrogen elimination, alkane elimination, salt metathesis, and dehalosilylation reactions

Table 4 Selected bond lengths (Å) and angles (°) for heterocyclic stibidoalanes and bismuthidoalanes of the general type $[R_2AlER'_2]_x$

Heterocycle	M–E	Al–E–Al	E–Al–E	Reference
$[Me_2AlSb(SiMe_3)_2]_3$	2.703(1)–2.736(1)	118.5(1)–128.2(1)	103.5(1)–106.5(1)	[49]
$[Et_2AlSb(SiMe_3)_2]_2$	2.723(1), 2.729(1)	91.7(1)	88.3(1)	[67]
$[i\text{-}Bu_2AlSb(SiMe_3)_2]_2$	2.743(1), 2.746(1)	93.7(1)	86.3(1)	[67]
$[t\text{-}Bu_2AlSb(SiMe_3)_2]_2$	2.748(1), 2.748(1)	96.1(1)	83.9(1)	[68]
$(Me_2Al)_3(Sbt\text{–}Bu_2)_2Sb(SiMe_3)_2$	2.719(2)–2.780(2)	115.4(1)–128.4(1)	103.1(1)–106.9(1)	[69]
$[Me_2AlSb(t\text{-}Bu)_2]_3$	2.719(1)–2.784(1)	115.3(1)–128.9(1)	102.8(1)–108.2(1)	[69]
$[t\text{-}Bu_2AlSbEt_2]_2$	2.781(1), 2.786(1)	94.1(1), 94.3(1)	85.8(1)	
$[Me_2AlBi(SiMe_3)_2]_3$	2.755(3)–2.793(3)	121.7(1)–130.5(1)	101.0(1)–104.1(1)	[70]
$[t\text{-}Bu_2AlBi(SiMe_3)_2]_2$	2.840(2)	95.9(1)	84.1(1)	[68]

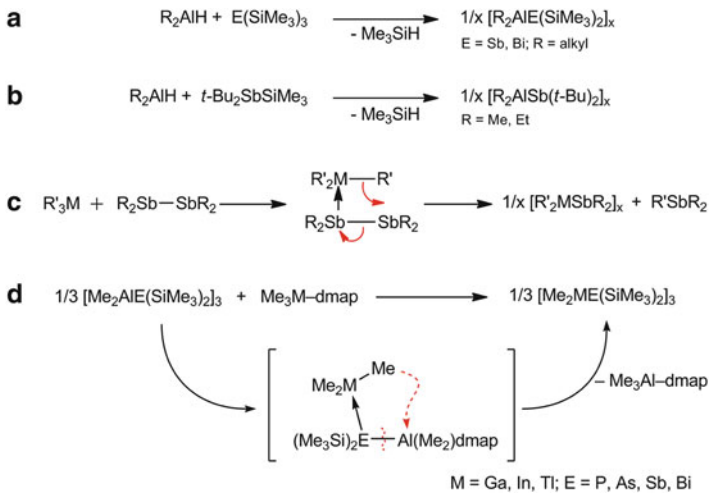

Fig. 11 Dehydrosilylation reaction, distibine cleavage reaction, and metathesis reactions

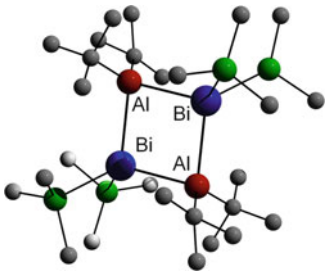

Fig. 12 Solid state structure of $[t\text{-}Bu_2AlBi(SiMe_3)_2]_2$

temperatures (0–50°C), allowing the isolation of the as-described heterocycles (frequently very temperature-labile) in very high yields (Fig. 11a, b). It is noteworthy that these preparations can be performed in the absence of any organic solvent, facilitating the isolation of the resulting heterocycles.

Albeit not structurally characterized, $(Cp^*Al)_3Sb_2$ was prepared by reaction of $[Cp^*Al]_4$ with $[t\text{-}BuSb]_4$ [82]. Also, heterocyclic aluminum-, gallium-, and indium-stibides $[R_2MSbR'_2]_x$ were produced via a novel distibine cleavage reaction ([53, 55, 57, 83]; Schulz S, Kuczkowski A et al. unpublished results) (Fig. 11c). On the other hand, a specific metathesis reaction using base-stabilized monomeric Al-pentelides of the type dmap–$AlMe_2E(SiMe_3)_2$ (E = P, As, Sb, Bi; dmap = 4-dimethylaminopyridine) allowed access to the corresponding heterocyclic gallium-, indium-, and thallium-pentelides of the general type $[Me_2MER'_2]_x$ (M = Ga, In, Tl; E = P, As, Sb, Bi) [84–86] (for most recent reviews on group 13/15 chemistry of the heavier homologues of group 15 see [87, 88]) (Fig. 11d).

Stibidoalanes $[R_2AlSbR'_2]_x$ (R = alkyl, R′ = alkyl, $SiMe_3$) and bismuthidoalanes $[R_2AlBi(SiMe_3)_2]_x$ (R = alkyl) (Fig. 12 and 13) adopt either dimeric or trimeric structures in the solid state, depending on the steric bulk of the organic substituents (Table 4). Analogous findings were previously observed for the lighter group 15 homologues. Sterically demanding substituents favor the formation of four-membered heterocycles, whereas smaller organic substituents yield six-membered heterocycles. Obviously, the nature of the formed heterocycle depends on ring strain and entropy effects. Thus, the formation of six-membered rings relate to the larger Al–E–Al and E–Al–E bond angles that results while entropy effects favor the formation of four-membered rings. Large substituents tend to increase the C–Al–C and C/Si–E–C/Si bond angles; hence the E–Al–E and Al–E–Al angles should be rather small. Thus, in such a case, four-membered rings are more stable than their six-membered ring analogues [89]. In addition, the central group 13 and group 15 elements of analogously substituted heterocycles clearly influence the ring size. The influence of the group 15 element can be seen when comparing Me-substituted heterocycles $[Me_2AlE(SiMe_3)_2]_x$. The phosphido- and arsenidoalanes form four-membered heterocycles, whereas the stibido- and bismuthidoalanes adopt six-membered ring structures. The influence of the group 13 elements is observable in Et-substituted heterocycles $[Et_2MSb(SiMe_3)_2]_x$. Thus, compounds $[Et_2AlSb(SiMe_3)_2]_2$ and $[Et_2GaSb(SiMe_3)_2]_2$ form four-membered rings, whereas $[Et_2InSb(SiMe_3)_2]_3$ adopts a six-membered ring structure (Table 5).

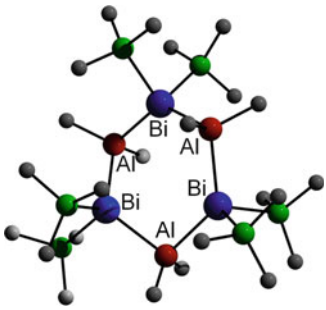

Fig. 13 Solid state structure of $[Me_2AlBi(SiMe_3)_2]_3$

The six-membered heterocycles typically form nonplanar rings in the solid state with distorted twist-boat conformations, in which the Al and Sb/Bi atoms are arranged in distorted tetrahedral environments. The Al–E bond lengths (E = Sb 2.70–2.78 Å, Bi 2.75–2.84 Å) are significantly shorter than those observed in the Lewis acid–base adducts $R_3Al–ER'_3$ and $[t\text{-}Bu_3Al]_x[E_2R_4]$, respectively, but agree with the calculated single bond covalent radii (Σr_{cov}(AlSb): 2.66 Å; Σr_{cov}(AlBi): 2.77 Å) [62]. As may be expected, the exocyclic C–Al–C bond angles strongly depend upon the steric hindrance of the *t*-Bu groups. Sterically demanding substituents thus lead to an opening of the C–Al–C bond angle, in turn decreasing the endocyclic E–Al–E bond angles and increasing the Al–E–Al bond angles.

3.2.3 Monomeric Complexes dmap-Al(R_2)ER'_2 and Intermetallic Complexes dmap–Al(R_2)ER'_2-M′R''_n

While several heterocyclic stibidoalanes or bismuthidoalanes have been prepared and structurally characterized (vide supra), monomeric derivatives $R_2Al\text{-}ER'_2$ are unknown. In contrast, *base-stabilized* complexes of the general type dmap–Al(R_2)ER'_2 were prepared by reaction of the heterocycles $[R_2AlE(SiMe_3)_2]_x$ with strong Lewis bases such as dmap (Fig. 14c) [90–93]. In addition, base-stabilized phosphanyl- and arsanylalanes $Me_3N–Al(H_2)ER_2$ (E = P, As) are available by a metathetical reaction between the base-stabilized alane $Me_3N–Al(H_2)Cl$ and $LiER_2$ (E = P, As; R = Mes = 2,4,6-$Me_3C_6H_2$) (Fig. 14b) [94] and by a dehalosilylation reaction between $H_3Al{\cdot}NMe_3$ and $E(SiMe_3)_3$ (E = P, As) (Fig. 14a) [95].

Base-stabilized monomeric compounds feature the shortest Al–E bond lengths observed to date, a likely consequence of the lower coordination number of the group 15 metal center (Table 6). Following an analogous trend earlier mentioned, the degree of pyramidalization of substituted alanes dmap–Al(R_2)E($SiMe_3$)$_2$ (E = P to Bi; R = Me, Et) (Fig. 15) steadily decreases when going to heavier group 15 elements. Similar structural parameters were observed for group 15 triorganyls such as EH_3, EPh_3, and EMe_3. The decreasing bond angles mainly result from an increased s-character of the *electron lone pair* on the group 15 element.

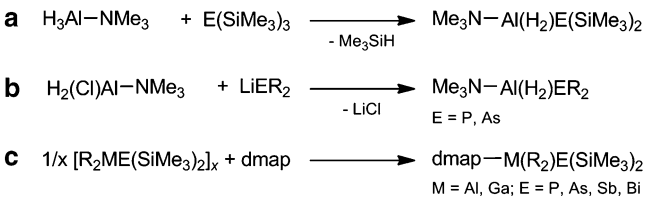

Fig. 14 Synthesis of base-stabilized monomers

Table 5 Average bond lengths (Å) and angles (°) for analogously substituted M–E heterocycles of the general type $[R_2ME(SiMe_3)_2]_x$

M	E	x	M–E	E–M–E	M–E–M	C–M–C	Si–E–Si	Reference
$[Me_2ME(SiMe_3)_2]_x$								
Al	P	2	2.457	89.4	90.6	113.4	108.3	[87, 88]
	As	2	2.536	88.3	91.7	115.0	108.1	[87, 88]
	Sb	3	2.718	104.9	124.0	117.9	101.7	[87, 88]
	Bi	3	2.774	102.3	126.8	119.2	100.5	[87, 88]
Ga	P	2	2.450	88.2	91.8	114.4	108.0	[87, 88]
	As	2	2.530	87.0	93.0	116.8	107.7	[87, 88]
	Sb	3	2.691	105.2	123.6	118.1	101.6	[87, 88]
	Bi	3	2.762	102.0	127.0	120.1	100.3	[81]
In	P	2	2.630	86.7	93.3	116.9	109.8	[87, 88]
	As	2	2.701	85.5	94.5	118.8	109.4	[87, 88]
	Sb	3	2.853	104.1	124.3	120.5	103.0	[87, 88]
	Bi	3	2.915	101.1	127.1	123.0	101.3	[85]
Tl	P	2	2.692	84.5	95.5	122.3	109.0	[85]
	As	2	2.762	93.3	96.7	124.6	108.5	[85]
	Sb	3	2.906	101.7	126.3	127.2	102.3	[86]
$[Et_2ME(SiMe_3)_2]_x$								
Al	P	2	2.457	90.2	89.8	114.6	108.0	[87, 88]
	As	2	2.565	89.6	90.4	115.1	109.3	[87, 88]
	Sb	2	2.726	91.7	88.3	114.5	107.3	[87, 88]
Ga	P	2	2.458	91.4	88.6	113.9	107.8	[87, 88]
	As	2	2.544	92.2	87.8	114.2	107.5	[87, 88]
	Sb	2	2.723	92.7	87.3	114.2	106.9	[87, 88]
In	P	2	2.646	92.5	87.5	114.2	109.1	[87, 88]
	As	2	2.712	93.6	86.4	114.6	108.5	[87, 88]
	Sb	3	2.873	125.1	104.4	116.8	101.2	[87, 88]

The use of strong σ-donor ligands (Lewis bases) has recently been demonstrated to be extremely profitable for the stabilization of unprecedented main group element compounds. Based on the work of Robinson et al., who reported on the synthesis and structure of the carbene-stabilized disilicon complex L–Si=Si–L (L = $C[N(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)CH]_2$) [96], several elusive compounds including the parent complexes L–HB=BH–L, L–P–P–L and others [97–99], long considered not to be isolable, have been structurally characterized. Moreover, Scheer et al.

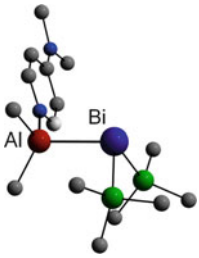

Fig. 15 Solid state structure of dmap–Al(Me_2)Bi($SiMe_3$)$_2$

Table 6 Selected bond lengths (Å) and angles (°) of dmap-stabilized monomers dmap–M(Me_2)E($SiMe_3$)$_2$ (M = Al, Ga)

Monomer	M–E	M–N	M–R (av.)	ΣX–E–X	Reference
dmap–Al(Me_2)P($SiMe_3$)$_2$	2.379(1)	1.984(2)	1.975	309.1	[87, 88]
dmap–Al(Me_2)As($SiMe_3$)$_2$	2.472(2)	1.975(4)	1.968	304.1	[87, 88]
dmap–Al(Et_2)As($SiMe_3$)$_2$	2.473(1)	1.988(3)	1.977	306.6	[87, 88]
dmap–Al(Me_2)Sb($SiMe_3$)$_2$	2.691(1)	1.978(2)	1.970	302.4	[87, 88]
dmap–Al(Et_2)Sb($SiMe_3$)$_2$	2.680(1)	1.980(2)	1.980	298.9	[87, 88]
dmap–Al(Et_2)Sb(*t*-Bu)$_2$	2.708(4)	1.989(2)	1.989	306.8	[93]
dmap–Al(Me_2)Bi($SiMe_3$)$_2$	2.755(2)	1.972(4)	1.972	296.8	[87, 88]
dmap–Al(Et_2)Bi($SiMe_3$)$_2$	2.750(2)	1.978(5)	1.988	293.4	[87, 88]
dmap–Ga(Me_2)P($SiMe_3$)$_2$	2.372(1)	2.080(2)	1.985	305.3	[87, 88]
dmap–Ga(Me_2)As($SiMe_3$)$_2$	2.455(1)	2.082(2)	1.982	300.2	[87, 88]
dmap–Ga(Et_2)Sb($SiMe_3$)$_2$	2.648(1)	2.066(2)	1.994	298.0	[87, 88]

demonstrated that the coordination of both a Lewis base and a transition metal complex stabilizes highly unstable compounds such as monomeric phosphanylalanes and -gallanes. Thus, compounds Me_3N–M(H_2)PH_2–W(CO)$_5$ (M = Al, Ga) were produced by a H_2 elimination reaction between W(CO)$_5PH_3$ and Me_3N–MH_3 [100]. According to theoretical calculations, coordination of NMe_3 (108 kJ/mol) and W(CO)$_5$ (154 kJ/mol) to H_2AlPH_2 stabilizes the monomeric unit by 262 kJ/mol, which is favored over the dimerization of phosphanylalane H_2AlPH_2 (74 kJ/mol).

Comparable compounds of the type dmap–M(Me_2)E($SiMe_3$)$_2$–M′(CO)$_n$ (M = Al, Ga; E = P, As, Sb; M′ = Ni, Fe, Cr) are generally accessible by reaction of the base-stabilized monomers dmap–M(Me_2)E($SiMe_3$)$_2$ with transition metal carbonyls such as Ni(CO)$_4$, Fe_2(CO)$_9$, and (Me_3N)Cr(CO)$_5$ [101, 102].

For such species, the carbonyl resonances in the ^{13}C-NMR spectra agree with the dmap–M(Me_2)E($SiMe_3$)$_2$ moiety being only a weak π-acceptor; hence the phosphorus–transition metal interaction is essentially a P–M′ σ-dative bond. According to the synergistic σ-donor/π-acceptor bonding concept, these findings point toward a slightly higher σ-donor/π-acceptor ratio when going down to heavier group 15 elements, as reported by Bodner et al. for over 100 transition metal complexes of the general type R_3E–M′L$_n$ (E = P, As, Sb) [103]. The observed trends were confirmed by single crystal X-ray diffraction studies, showing an

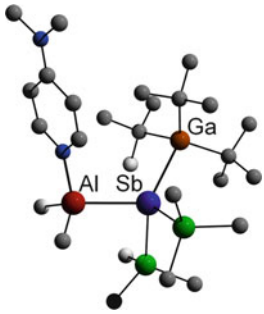

Fig. 16 Solid state structure of dmap–Al(Me_2)$Sb(SiMe_3)_2$–Ga(*t*-Bu)$_3$

Table 7 Selected bond lengths (Å) and angles (°) of complexes of the type base–M(R_2)ER'_2–M′R″$_n$

Complex	M–E	E–M′	M–N	ΣX–E–Y	Reference
dmap–Al(Me_2)P($SiMe_3$)$_2$–$GaMe_3$	2.428(1)	2.528(1)	1.963(2)	313.5	[84]
dmap–Al(Me_2)Sb($SiMe_3$)$_2$–Al(*t*-Bu)$_3$	2.725(1)	2.869(1)	1.968(3)	298.3	[84]
dmap–Al(Me_2)Sb($SiMe_3$)$_2$–Ga(*t*-Bu)$_3$	2.726(3)	2.889(1)	1.961(7)	298.2	[84]
Me_3N–Al(CH_2SiMe_3)$_2$$PPh_2$–$Cr(CO)_5$	2.485(1)	2.482(1)	2.049(3)	308.3	[104]
Me_3N–Al(H_2)PH_2–$W(CO)_5$	2.367(1)	2.549(1)	2.036(3)		[100]
Me_3N–Ga(H_2)PH_2–$W(CO)_5$	2.349(2)	2.537(2)	2.039(7)		[100]
dmap–Al(Me_2)P($SiMe_3$)$_2$–$Ni(CO)_3$	2.400(2)	2.319(2)	1.961(5)	326.0	[101]
dmap–Al(Me_2)P($SiMe_3$)$_2$–$Fe(CO)_4$	2.432(1)	2.377(1)	1.961(2)	318.9	[101]
dmap–Al(Me_2)P($SiMe_3$)$_2$–$Cr(CO)_5$	2.428(1)	2.528(1)	1.963(2)	313.5	[101]
dmap–Al(Me_2)As($SiMe_3$)$_2$–$Ni(CO)_3$	2.479(1)	2.419(1)	1.966(2)	317.7	[102]
dmap–Al(Me_2)As($SiMe_3$)$_2$–$Cr(CO)_5$	2.512(1)	2.600(1)	1.955(2)	313.0	[101]
dmap–Al(Me_2)Sb($SiMe_3$)$_2$–$Ni(CO)_3$	2.680(2)	2.556(1)	1.965(4)	314.3	[102]
dmap–Ga(Me_2)As($SiMe_3$)$_2$–$Ni(CO)_3$	2.465(1)	2.419(1)	2.045(2)	316.3	[101]
dmap–Ga(Me_2)Sb($SiMe_3$)$_2$–$Ni(CO)_3$	2.647(1)	2.554(1)	2.046(2)	312.8	[101]

increase in the Ni–C bond order and a decrease in the C–O bond order in $Ni(CO)_3$-containing complexes vs. $Ni(CO)_4$. As reported for the simple Lewis acid–base adducts, the coordination to either a main group metal or a transition metal center typically increases the Si–E–Si and Al–E–Si bond angles, a result of the enhanced p-character of the *electron lone pair*. Analogous tendencies were observed with trialkylalanes and -gallanes analogues dmap–Al(R_2)E($SiMe_3$)$_2$–MR_3 (E = P, Sb; M = Al, Ga) (Fig. 16, Table 7) [84].

3.3 Organoaluminum Complexes with Other p-Block Metals (Sn, Pb, Te)

In sharp contrast to intermolecular complexes with direct Al/group 15 bonds, analogous molecular organoaluminum complexes with bonds to group 14 (Sn, Pb) and group 16 metals (Te) are rather rare. To date, compound [*t*-BuNSn]$_4$[$AlCl_3$]$_2$, prepared by reaction of [*t*-BuNSn]$_4$ with two equivalents of

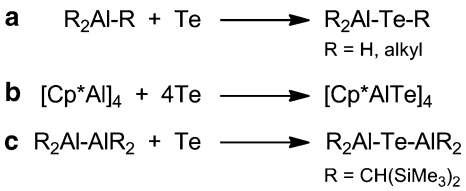

Fig. 17 General reaction pathways for the synthesis of organoaluminum telluride complexes

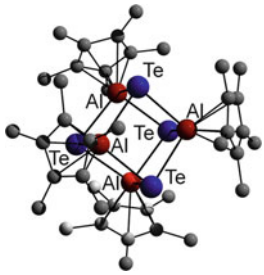

Fig. 18 Solid state structure of $[Cp^*AlTe]_4$

$[AlCl_3]$, constitutes the only structurally characterized complex containing a dative Sn–Al bond [105]. In addition, the synthesis of $Cp_2Sn–AlX_3$ (X = Cl, Br) was reported [106]. In these complexes, the Sn(II) atom coordinates through its electron lone pair to the Lewis acidic aluminum trihalides.

There are several examples of structurally characterized organoaluminum complexes containing at least one direct Al–Te bond. Such entities are typically prepared by an insertion reaction of elemental Te and an alane derivative containing either an Al–C [107, 108] or an Al–H bond [109–114] (Fig. 17a). Also, the reaction of the subvalent organoaluminum complex $[Cp^*Al]_4$ with elemental tellurium was found to proceed via the insertion of Te into the Al–Al bond and formation of the corresponding heterocubane $[Cp^*AlTe]_4$ [115] (Fig. 17b). In an analogous manner, the reaction of $[(Me_3Si)_2CH]_2Al–Al[CH(SiMe_3)_2]_2$ with elemental tellurium afforded monomeric $[(Me_3Si)_2CH]_2Al–Te–Al[CH(SiMe_3)_2]_2$ (Fig. 17c) [116].

The solid state molecular structures of these complexes essentially depend on the sterics of the organic groups (R). Typically, heterocubane-like structures $[RAlTe]_4$ (R = Cp* [115], Fig. 18, $Me_2(Et)C$ [108], *t*-Bu [107], and $C(SiMe_3)_3$ [111]) were observed. Geometries and thermodynamics of these group 13/16 heterocubanes $[RME]_4$ (M = Al, Ga, In; E = O, S, Se, Te) have also been estimated via DFT studies, suggesting their thermodynamic stability toward fragmentation reactions [117]. Interestingly, treatment of neat *t*-Bu_3Al with two equivalents of elemental tellurium yielded the dimeric complex [*t*-Bu_2AlTe(*t*-Bu)]$_2$, formally resulting from the insertion of Te into an Al–C bond. Prolonged heating of the latter (toluene, 100°C, 48 h) afforded the heterocubane $[t\text{-BuAlTe}]_4$. Alternatively, $[t\text{-BuAlTe}]_4$ may be formed via a controlled pyrolysis of [*t*-Bu_2AlTe(*t*-Bu)]$_2$ (300°C, 1 atm) [107].

Dimeric complexes of the type $[RAlTe]_2$ bearing either a sterically demanding substituent with a side-arm donor [110] or a chelating organic ligand [109, 113]

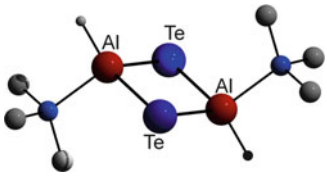

Fig. 19 Solid state structure of $[Me_3NAl(H)(\mu\text{-}Te)]_2$

Table 8 Selected bond lengths (Å) and angles (°) for organoaluminum tellurides

Complex	Al–Te	Te–Al–Te	Al–Te–Al	Reference
$[t\text{-}Bu_2AlTe(t\text{-}Bu)]_2$	2.732(3)	93.9(4)	86.1(4)	[107]
$[Cp^*AlTe]_4$	2.7500(9), 2.6883(9), 2.6917(9)	94.84(2), 96.29(2), 94.06(2)	84.86(2), 83.68(2), 85.51(2)	[115]
$[2\text{-}(NEt_2CH_2)\text{-}6\text{-}MeC_6H_3AlTe]_2$	2.581(8), 2.588(7)	103.70(3)	76.30(3)	[110]
$[N(SiMe_3)C(Ph)C(SiMe_3)_2AlTe]_2$	2.5619(12), 2.5765(14), 2.5768(14), 2.5753 (12)	103.12(4), 102.79(4)	76.88(4), 77.21(4)	[109]
$\{[HC\{C(Me)N(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_2]Al(\mu\text{-}E)\}_2$	2.575(3), 2.581(2)	97.9(1)	82.1(1)	[113]
$[Me_3N(PhTe)Al(\mu\text{-}Se)]_2$	2.610(2)	–	–	[118]
$[Me_3N(H)Al(\mu\text{-}Te)]_2$	2.586(4), 2.580(4)	103.6(1)	76.4(1)	[114]
$[(\eta^1\text{-}3,5\text{-}t\text{-}Bu_2pz(\mu\text{-}Al)H)_2Te]$	2.5621(12), 2.5763(11)	–	69.41(3)	[112]
$[(Me_3Si)_2CH]_2Al\text{–}Te\text{–}Al[CH(SiMe_3)_2]_2$	2.549(1)	–	110.4(1)	[116]
$Me_3N\text{–}Al(TePh)_3$	2.589(2), 2.585(2), 2.581(2)	11 1.21(7), 110.47(8), 110.1 1(7)	–	[119]

have been prepared. Moreover, the mixed chalcogenide complex *trans*-$[\{Me_3N(PhTe)Al(\mu\text{-}Se)\}_2]$, featuring a terminal Al–Te single bond, was synthesized by reaction of *trans*-$[\{Me_3N(H)Al(\mu\text{-}Se)\}_2]$ with diphenylditelluride Ph_2Te_2 [118]. The reaction of $Me_3N\text{–}AlH_3$ with Ph_2Te_2 occurred with Te–Te bond cleavage and hydrogen elimination and subsequent formation of $Me_3N\text{–}Al(TePh)_3$ [119] (Fig. 19).

Unlike their heavier group 13 counterparts (Ga and In), which have been prepared and structurally characterized (see the following and references cited therein: [120]), examples of monomeric organoaluminum tellurides RAlTe containing an Al=Te double bond have yet to be reported (Table 8).

Apart from being structural curiosities, such Al/Te intermetallic compounds may reveal of interest as single source precursors for the deposition of Al_2Te_3 thin films (via MOCVD), as demonstrated for the Ga and In analogues [121, 122].

4 Organoaluminum Complexes with d-Block Metals

Intermetallic complexes of group 13 metals and transition metals were first investigated by Ziegler and Natta as potentially active complexes in olefin polymerization. The first report on the structural characterization of "$[Cp_2TiAlEt_2]_2$," a model compound in the Ziegler–Natta catalytic system, claimed that such a complex contains direct Ti–Al bonds [123]. The latter complex along with others, including $[\{Co_3(CO)_9\}(\mu^3\text{-Al})]$ [124] and $[Cp(CO)_3M–AlMe_2]$ (M = Mo, W) [125, 126], was later unambiguously identified to be an hydride-bridged compound $[(C_5H_5)(C_5H_4)Ti(\mu\text{-H})AlEt_2]_2$ [127] and isocarbonyl-bridged M–CO–Al species, respectively [128–130]. Nevertheless, the interest in this type of intermetallic complexes has remained high since then. Additional impulses came with the development of monovalent group 13 diyles of the type RAl(I), susceptible to act as coordinating Lewis bases toward transition metal complexes. In this area, the report by Robinson et al. on a "ferrogallyne" 2,6-Mes^*_2–C_6H_3Ga–$Fe(CO)_4$ (Mes^* = 2,4,6-*i*-Pr_3-C_6H_2) containing a very short Fe–Ga bond (2.2248 Å) [131] thought to be a Fe≡Ga triple bond, promoted a very intense debate, yet sometimes regrettably personal, on the nature of bonding in the latter Fe–Ga complex [132, 133]. These discussions certainly stimulated the general interest in this class of complexes and several group 13-transition metal complexes were synthesized, structurally characterized in the following years and their bonding properties studied by computational calculations.

The unusual coordination properties of the ligands ECp* (E = Al, Ga, In) go beyond their isolobal CO or phosphine analogues. Species of the type ECp* not only stabilize unprecedented cluster structures, but may significantly influence the chemical reactivity of the resulting cluster complexes. By generating very electron rich and thus unusually reactive transition metal centers, unexpected C–H, Si–H, and even C–C bond activation reactions were observed with, for instance, $[Ni(AlCp^*)_4]$ [134], $[Fe(AlCp^*)_5]$, $[Ru(AlCp^*)_5]$ [135], and $[RhCp^*(CH_3)_2(GaCp^*)]$ [136].

Besides their fascinating bonding properties and unusual reactivity, these intermetallic complexes are of potential interest as single source precursors for the thin film deposition (MOCVD process) of alloys such as β-CoGa [137], $CuAl_2$ and α/β-CuAl [138], θ-CuE_2 (E = Al, Ga) and $Cu_{1-x}Al_x$ phases [139]. Also, such molecular entities may be useful molecular precursors for nanoparticles synthesis in solution, as reported for α-/β-NiAl nanoparticles [140].

The following section summarizes the synthesis, structures, and bonding properties of complexes containing at least one direct transition metal–aluminum bond. The metal derivatives incorporating M–X–M bridging organic groups (X = alkyl, hydride, alkoxides, amides, etc.) are excluded.

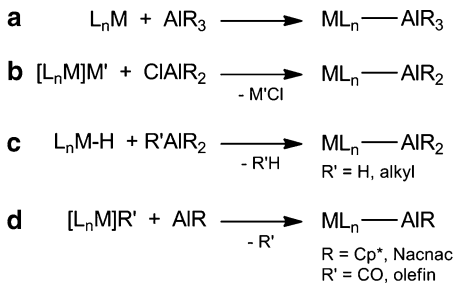

Fig. 20 Synthesis of aluminum-transition metal complexes

4.1 Synthesis

Numbers of group 13 diyl-transition metal complexes, mostly with gallanediyls (GaR) derivatives, have been prepared and structurally characterized in the last decade, as reviewed by Fischer and others [141–145]. Several general reaction protocols have been established over the past years for the synthesis of such species. In this domain, early studies mainly dealt with reactions of electron-rich, often anionic, transition metal complexes with triorganylalanes AlR_3, yielding the corresponding adducts of the type $L_nM–AlR_3$, in which the Lewis basic transition metal complex L_nM coordinates to the Lewis-acidic alane AlR_3 [146–149] (Fig. 20a). In addition, salt metathesis reactions between carbonyl metallates and $RAlX_2$ (X = Cl, I) [150–153] (Fig. 20b), as well as alkane elimination reactions between transition metal hydrides (containing an acidic M–H function) and alanes [147, 154] (Fig. 20c), have been thoroughly studied.

As initially reported by Schnöckel, substitution reactions between monovalent alanediyl RAl species and transition metal carbonyl olefin complexes certainly constitute the most attractive synthetic approach to access M–Al intermetallic complexes [135, 155–162] (Fig. 20d) [26]. Since then, variously substituted RE species (E = Al, Ga, In) have been studied, going from sterically bulky alkyl and aryl groups such as terphenyl ligands (2,4,6-$R_3C_6H_2$; 2,4-$R_2C_6H_3$) or $Ci(SiMe_3)_3$, which are anionic 2-electron substituents, to chelating 4-electron donors such as guanidinato and β-diketiminato-based ligands. The extent of σ-donating and π-accepting properties of these group 13 diyls depends on the nature of the metal center (Al, Ga, In) and the supporting ligand. As a consequence, the structures and chemical properties of the resulting aluminum-transition metal complexes may greatly differ.

In addition to the aforementioned general reaction pathways, complexes containing transition metal–Al bonds have been prepared by rather unusual reactions such as that between $[Cp^*Co(C_2H_4)_2]$ and $[Et_2AlH]$, resulting in the formation of the bimetallic complex $[\{Cp^*(\eta^2\text{-}C_2H_4)–Co–Al(C_2H_5)\}_2]$ [163].

Very recently, a Cr(I) aminopyridinate species containing a Cr–Cr quintuple bond was reported to react with $AlMe_3$ via insertion of the Cr–Cr quintuple bond into the Al–Me bond (carbalumination) to form the trimetallic compound LCr(μ-CH_3)(μ-$AlMe_2$)]CrL (L = (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-

pyridin-2-yl]-amine)[164]. This novel type of complex incorporates a formal Cr–Cr quadruple bond along with formally anionic Me and $AlMe_2$ groups and features elongated Cr–Al bonds (2.8945(14), 2.9076(14) Å).

4.2 Structure and Bonding

A large variety of intermetallic complexes containing terminal alanes AlR_3, terminal and bridging alanyls AlR_2 as well as terminal and bridging alanediyls AlR have been structurally characterized (see Table 9).

As stated above, alane complexes of the type $L_nM–AlR_3$ have typically been prepared via reaction between Lewis basic transition metal carbonyl complexes and AlR_3. The formation of a direct M–Al bond or an isocyanate-bridge M–CO–Al strongly depends on the Lewis basicity of the transition metal complex [146]. Comparisons of structural parameters for complexes containing the same metal centers may not be that meaningful given the limited number of structurally characterized complexes. However, the M–Al bond lengths of *alane complexes* $L_nM–AlR_3$ such as anionic $[Cp(CO)_2Fe–AlPh_3]^-$ (2.510(2) Å) were observed to be slightly longer than those of *alanyle complexes* $L_nM–AlR_2$ containing terminally bonded alanyl moieties (e.g., $[Cp(CO)_2Fe–Al(tmp)_2]$ 2.450(1) Å, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe–Al(CH_2)_3NMe_2)i\text{-}Bu]$ 2.456(1) Å) and in *alylene complexes* with bridging alanediyl groups $[L_nM]_2$ μ^2–AlR (e.g., $[CpFe(CO)_2]_2Al(2\text{-}Me_2NCH_2C_6H_4)]$ 2.468 (1), 2.496(1) Å). Homoleptic $M(AlR)_x$ and heteroleptic *alylene complexes* $L_nM–AlR$ with terminal alanediyl groups such as $[Fe(AlCp^*)_5]$ and $[(CO)_4Fe(AlCp^*)]$ typically show significantly shorter intermetallic bonds. The only exception was observed for the alane complex $(Cy_3P)_2Pt–AlCl_3$ (2.3857(7) Å) (Fig. 21), whose Pt–Al bond length is comparable to those observed in the alylene complexes with terminal alanediyl moiety $[(dcpe)Pt(AlCp^*)_2]$ (dcpe = 1,2-bis(dicyclohexylphosphanyl)ethane), 2.327(2), 2.335(2) Å).

The bonding situation in $L_nM–AlR_3$ is best described as that of a simple adduct between the Lewis-basic transition metal complex coordinated to the Lewis-acidic alane, as shown by computational calculations [169]. For instance, the geometry of compound $Cp^*(PMe_3)Ir(H)_2AlPh_3$ indicates that the Ir center in $Cp^*(PMe_3)Ir$ is Lewis basic, forming a dative two-electron bond to the aluminum center. This finding strongly contrasts with the bonding situation observed in alylene complexes such as $[(CO)_4Fe(AlCp^*)]$, where the electron transfer goes from the Lewis basic, two-electron donor alanediyl Cp*Al to the electron deficient $Fe(CO)_4$ fragment [147].

Terminally bound alanyle complexes of the type $L_nM–AlR_2$ contain an electron-deficient Al center that, in principle, may act as a Lewis acid moiety. Such complexes therefore tend to form intra- or intermolecularly coordinated structures as observed in base-stabilized complexes such as $[(\eta^5\text{-}C_5H_5)(CO)_2Fe–Al(CH_2)_3NMe_2)i\text{-}Bu]$ and in dimeric complexes such as $[(C_5H_4Me)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_3Me)Mo(\mu\text{-}Al(H)i\text{-}Bu)]$. Compound $[Cp(CO)_2Fe–Al(tmp)_2]$ is the only

Table 9 M–Al bond lengths (Å) in organoaluminum complexes with d-block metals

Complex	Al–M (Å)	Reference
Alane (AlR_3) complexes		
$[Cp^*(PMe_3)(H_2)Ir–AlPh_3]$	2.684(2)	[147]
$[Cp(CO)_2Fe–AlPh_3][NEt_4]$	2.510(2)	[146]
$[(Cy_3P)_2Pt\text{-}AlCl_3]$	2.3857(7)	[148]
Alanyle complexes with terminal AlR_2 groups		
$[Cp(CO)_2Fe–Al(tmp)_2]$	2.450(1)	[153]
$[(\eta^5\text{-}C_5H_5)(CO)_2Fe–Al(CH_2)_3NMe_2)$ *i*-Bu]	2.456(1)	[165]
Alanyle complexes with bridging AlR_2 groups		
$[\{(C_5H_4)_2MoAl_2Me_3]_2\}]$	2.685(3), 2.656(3)	[166]
$[(C_5H_5)(C_5H_4)]_2(H)MoAl_3Me_5]$	2.650(5), 2.657(4), 2.951(4), 2.996(5)	[166]
$[(C_5H_5)(C_5H_4)]_2(H)MoAl_3Me_5]$	2.662(6), 2.655(5), 2.944(6), 3.003(6)	[167]
$[\{(C_5H_4Me)(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_3Me)Mo(\mu\text{-}$ Al(H)*i*-Bu)	2.636(2), 2.944(2)	[154]
$[L_2Cr_2(\mu\text{-}CH_3)(\mu\text{-}AlMe_2)]$	2.8945(14), 2.9076(14)	[164]
Homoleptic alylene complexes with terminal alanediyls (AlR)		
$[Pd(AlCp^*)_4]$	2.2950(9)	[160]
$[Ni(AlCp^*)_4]$	2.1727(8)	[160]
$[Fe(AlCp^*)_5]$[a]	2.2124(15), 2.2419(15), 2.2404(15), 2.3686 (15), 2.3272(14)	[135]
$[Fe(AlCp^*)_5]$[a]	2.223, 2.378, 2.405, Fe1-Al4 2.444, 2.263	[135]
$[Ru(AlCp^*)_5]$[b]	2.294(2), 2.331(2), 2.337(2), 2.49(3), 2.434(2)	[135]
Heteroleptic alylene complexes with terminal alanediyls (AlR)		
$[(CO)_4Fe(AlCp^*)]$	2.231(3)	[151]
$[(CO)_5Cr(AlCp^*)]$	2.3761(6)	[157]
$[(dcpe)Pt(AlCp^*)_2]$	2.327(2), 2.335(2)	[158]
[(dvds)Pd{Al(ddp)}]	2.3702(10)	[162]
$[(Cp^*Al)_3Ni(\mu^2\text{-}H)Al(Ph)Cp^*]$	2.2105(11), 2.2062(10), 2.1688(11), 2.2912 (11)	[134]
$[(Cp^*Al)_3Ni(H)SiEt_3]$	2.203(8), 2.208(10), 2.180(7)	[134]
$[(DippNanacAl)Pd_2(\mu^2\text{-}$ $GaCp^*)_2(GaCp^*)_2]$	2.456(3), 2.559(3)	[161]
Base-stabilized heteroleptic alylene complexes with terminal alanediyls (AlR)		
$[(CO)_5W–Al(t\text{-}Bu)(tmpda)]$	2.741(4)	[152]
$[(CO)_5Cr–Al(Cl)(tmpda)]$	2.482(1)	[152]
$[(CO)_5W–Al(Et)(tmeda)]$	2.670(1)	[168]
$[(CO)_5W–Al[(Cl)(tmpda)]$	2.645(2)	[168]
Alylene complexes with bridging alanediyls (AlR)		
$[(CpNi)_2(\mu^2\text{-}AlCp^*)_2]$	2.274(2), 2.283(2)	[155]
$[(CO)_6Co_2(\mu^2\text{-}AlCp^*)_2]$	2.384(3), 2.369(3)/2.377	[156]
$[Pt_2(GaCp^*)_2(\mu^2\text{-}AlCp^*)_3]$	2.3310(7), 2.4259(16), 2.4237(17)	[159]
$[\{Pd(dvds)\}_2\{\mu^2\text{-}AlDippNacnac\}]$	2.4234(18), 2.4419(18)	[161]
$[\{Cp^*Ir(PMe_3)(\mu^2\text{-}AlEt)\}_2]$	2.456(1), 2.459(1)	[147]
$[\{Cp^*(\eta^2\text{-}C_2H_4)Co(\mu\text{-}AlEt)\}_2]$	2.336(2), 2.333(1)	[163]
$[CpFe(CO)_2]_2Al(2\text{-}Me_2NCH_2C_6H_4)]$	2.468(1), 2.496(1)	[150]

(continued)

Table 9 (continued)

Complex	Al–M (Å)	Reference
Alylene complexes with terminal and bridging alanediyls (AlR)		
$[Pd_3(AlCp^*)_2(\mu^2\text{-}AlCp^*)_2(\mu^3\text{-}AlCp^*)_2]$	2.592(5), 2.498(5), 2.563(5), 2.488(5), 2.401 (5), 2.369(5)	[159]
$[Pd_2(AlCp^*)_2(\mu^2\text{-}AlCp^*)_3]$	2.3230(18), 2.4559(18), 2.4559(18)	[159]

[a]Two C–H activated isomers containing a μ^2-bridging Fe–H–Al unit
[b]C–H activated isomer containing a μ^2-bridging Ru–H–Al unit

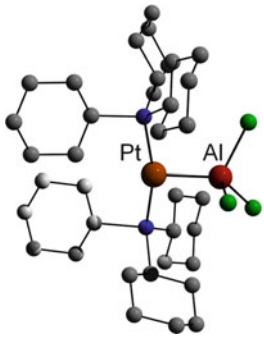

Fig. 21 Solid state structure of $(Cy_3P)_2Pt–AlCl_3$

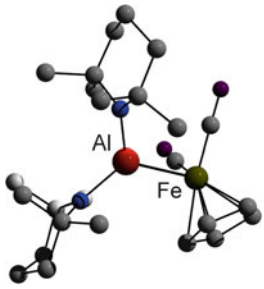

Fig. 22 Solid state structure of $[Cp(CO)_2Fe–Al(tmp)_2]$

structurally characterized alanyle complex containing a planar and three-coordinate Al center (Fig. 22).

Thus far reported homoleptic transition metal alylene complexes of the type $[M(AlCp^*)_x]$, which contain terminal alanediyls Cp*Al, incorporate up to four Cp*Al moieties acting as ligands toward transition metal centers. This has been observed with d^{10} metal complexes through the synthesis of $[Ni(AlCp^*)_4]$ and $[Pd(AlCp^*)_4]$ (Fig. 23). For the d^8 metal complexes, attempted preparations of the $[Fe(AlCp^*)_5]$ and $[Ru(AlCp^*)_5]$ derivatives, for which a trigonal bipyramidal structure was predicted [13], only yielded undesired C–H activation products. The hypothetic structure $[Fe(AlCp^*)_5]$ containing five Fe–Al bonds and bearing unactivated and terminal Cp* ligands appears unrealistic [135].

In contrast, compound $[(Ph_3P)_4RuCl_2]$ reacts with six equivalents GaCp* to afford $[Ru(GaCp^*)_6Cl_2]$, in which the Ru(II) center is surrounded by six GaCp*

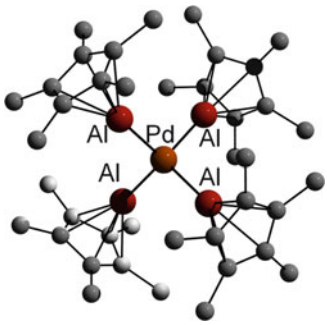

Fig. 23 Solid state structure of $[Pd(AlCp^*)_4]$

moieties and two bridging chloride ligands connect the two Ga centers to one another, hence blocking any C–H activation reactions [170]. The formation of $[Ru(GaCp^*)_6Cl_2]$ from $[(Ph_3P)_4RuCl_2]$ results from the substitution of four phosphine ligands by four Cp*Ga ligands, while two Cp*Ga groups insert into the Ru–Cl bonds.

In addition to homoleptic complexes, a large number of heteroleptic alylene complexes of the type $L_nM(AlR)_x$ have been structurally characterized, with the aluminum center bearing a Cp*, a β-diketiminate, or an alkyl ligand. Lewis-base stabilized heteroleptic complexes of the type L_nM–ECl(base) have also been reported. Unlike Cp*Al complexes, where the M–Al–Cp* moiety is almost linear, the M–Al–X angle significantly deviates from linearity in base-stabilized complexes such as $[(CO)_5$ W–Al(Et)(tmeda)] (121.4(2)°) and $[CO)_5$ W–Al[(Cl)(tmpda)] (124.2(1)°). According to theoretical calculations, the dissociation energies (D_e) of the W–Al bond in species of the type $[(OC)_5W–AlX(NH_3)_2]$ (X = H 100.9 kcal/mol, Cl 93.1 kcal/mol) essentially depend on the nature of the Al–X substituent. Replacement of an hydride by a chloride increases the s-character of the Al-based electron lone pair, which decreases donor–acceptor interactions. This goes along with a weakening of the Al–W bond strength because the Al–based donor orbital is more compact. Yet, the W–Al bond in $[(OC)_5$ W–AlCl$(NH_3)_2]$ is shorter than that in $[(OC)_5W–AlH(NH_3)_2]$. Comparable trends were experimentally observed for $[CO)_5W–Al[(Cl)(tmpda)]$ (2.645(2) Å) and $[(CO)_5W–Al(Et)(tmeda)]$ (2.670(1) Å) [168].

The bonding properties of the presently discussed alylene complexes have been exhaustively studied via quantum chemical calculations. Monovalent group 13 diyls RE are formally isolobal with carbon monoxide CO, phosphanes PR_3 and singlet carbenes CR_2. Since the HOMO of Cp*E predominantly consists of a large lobe on E pointing away from the Cp* ligand, Cp*E-type species exhibit σ-donor properties as already mentioned. Moreover, the presence of two orthogonal and degenerate LUMOs, which are π-antibonding with respect to the Cp*–E bond, should in principle allow for π-acceptor properties. However, numerous theoretical calculations both on neutral and cationic transition metal complexes of group 13 diyls ER (E = B–Tl; R = H, alkyl, aryl, Cp, silyl, amide, halide) clearly demonstrated that the diyls ER are strong σ-donating Lewis bases with rather

Fig. 24 Synthesis of complexes containing group 13/4f metal bonds

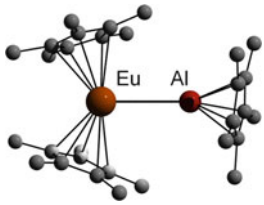

Fig. 25 Solid state structure of [Cp*$_2$Eu(AlCp*)]

weak π-accepting properties. As expected, the nature of the supporting ligand directly influences the donating/accepting abilities of the metal center. For instance, β-diketiminato-substituted diyls were found to be more Lewis basic than Cp*-substituted diyls, which is most likely due to the increased negative charge at the gallium atom on the latter [9, 12, 13, 158, 168, 171–175]. An in-depth analysis of the bonding situation in these complexes revealed that ionic contributions may also play an important role in the stability of these bimetallic entities. For instance, while the Al–Fe bond in [(CO)$_4$Fe(AlCp*)] [151] was initially described as a simple donor–acceptor single bond between the Al(I) center and the Fe(0) atom, subsequent DFT calculations were consistent with a more polar Fe–Al bond ($RAl^{2+}Fe(CO)_4^{2-}$) arising from a significant electron transfer from the Al atom to the transition metal center [156].

5 Organoaluminum Complexes with f-Block Metals

Unlike their well-established p- and d-block analogues, f-block metal complexes with direct f-element-Al metal bonds remain extremely rare. However, interest in such derivatives has grown in recent years and initial results on that matter were recently reviewed [176, 177].

The first complexes containing group 13 metal-f-element bonds were reported in 2006 [178]. Lewis acid–base adducts of the type [Cp*$_2$Ln(AlCp*)] (Ln = Eu or Yb) (Fig. 25) with direct aluminum(I)–lanthanide(II) bonds were prepared via a solvent-free route involving the reaction of [Cp*Al]$_4$ with a divalent lanthanocene Cp*$_2$Ln (Ln = Eu, Yb) in an evacuated glass ampule at 120°C (Fig. 24). Both lanthanide products dissociate in solution, indicating rather weak donor–acceptor interactions. The oxidation states of the metal centers are consistent with those of the starting complexes. DFT studies showed that the aluminum-4f-element bond in these adducts (about 30 kJ/mol) is essentially electrostatic with little charge transfer and covalent contributions.

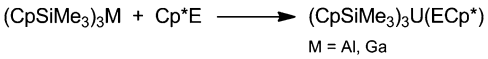

Fig. 26 Synthesis of group 13 diyl-uranium complexes

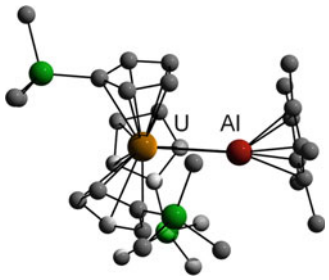

Fig. 27 Solid state structure of $[(CpSiMe_3)_3U(AlCp^*)]$

In addition, the formation of adduct complexes upon reaction of trivalent lanthanides with Cp*E (E = Al, Ga) was proven experimentally. $(CpSiMe_3)_3Ce–ECp^*$ complexes were observed in solution by variable-temperature paramagnetic NMR spectroscopy. Computational calculations using the model complexes $Cp_3Ln–ECp$ (Ln = La–Lu; E = Al, Ga) agree with shorter Ln–E bond distances across the Ln series. These theoretical studies also suggest the Ln–E bond to be stronger for Al vs. Ga adduct, unlike earlier reports on divalent lanthanide analogous complexes. Also, the Nd–Al bond dissociation energy (BDE) was found to be lower than the energy required (per Al) to disrupt the competitively formed $(Cp^*Al)_4$ tetramer. Therefore $(CpSiMe_3)_3Nd–AlCp^*$ was predicted not to be isolable. The highest BDE was calculated for the CpE–Gd donor–acceptor interaction. According to these calculations, the Ln–E bonding interactions are predominantly covalent with a nonpolar donor–acceptor character; the formation of a strong covalent bond is not observed because of resistance to reduction of an effectively divalent Ln center [179].

Group 13-actinide complexes have been even less studied thus far than lanthanide complexes. The U–Al compound $[(CpSiMe_3)_3U(AlCp^*)]$, arising from the reaction of Cp*Al with $(CpSiMe_3)_3U$, constitutes the first structurally characterized U–Al complex [180] (Fig. 26).

In compound $[(CpSiMe_3)_3U(AlCp^*)]$ (Fig. 27), the U–Al bond lengths of two crystallographically inequivalent molecules (3.117(3), 3.124(4) Å) are very close to the sum of the covalent radii. A calculated natural charge of 0.540 (0.560) for the AlCp fragment hints toward a small Al–U net charge transfer of 0.091. The Wiberg bond index between U and Al indicates a covalent bond order of ca. 0.5.

Arnold et al. also performed theoretical calculations to compare intermetallic group 13 metal complexes of 4f and 5f metals, these being synthesized by reaction of $(CpSiMe_3)_3Nd$ and $(CpSiMe_3)_3U$ with Cp*E (E = Al, Ga) [181]. While the uranium complexes were isolated on gram scales and characterized by single crystal X-ray diffraction, the Nd analogues were only observed spectroscopically.

DFT calculations revealed that Cp*Al is a slightly better donor than Cp*Ga, while U is a better acceptor than Nd for soft σ-donating ligands (by an order of magnitude) according to quantitative ^{1}H NMR studies. As a consequence, some gallanediyl complexes of 4f and 5f elements have been synthesized in the past [182–185]. Moreover, Cp*Al and Cp*Ga are both capable of binding 5f over 4f elements with an excellent selectivity, which, according to DFT calculations, primarily results from a strong σ-interaction. These calculations also excluded a stabilization of the 5f electrons (of the U metal center) through π-backbonding.

6 Conclusions and Outlook

The synthesis of monovalent alanediyls of the type AlR, behaving as excellent σ-donor properties, has opened the way to the synthesis of a large variety of intermetallic complexes including p-block, d-block and, to a lesser extent thus far, f-block metals. The derived organometallic complexes display a fascinating structural diversity and, in some instances, exhibit unprecedented chemical reactivity due to their interesting bonding properties. In such species, fine tuning of the group 13 metal-bound ligands allow further adjustments of the σ-donor/π-acceptor properties, hence enabling the synthesis of novel intermetallic complexes in the near future. In this regard, structurally characterized intermetallic organocompounds incorporating a direct Al–s-block–metal bond, unknown to date, would be of particular interest.

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Low Valent Organoaluminum (+I, +II) Species

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Abstract Since the isolation of the first stable molecular aluminum(II) compound $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$, the field of low oxidation state aluminum species has burgeoned tremendously. Organoaluminum(I) species $(RAl)_n$ stabilized with bulky substituents have been isolated and used as reducing agents, precursors to aluminum(III) compounds, ligands toward transition group metal complexes, and main group Lewis acids. Mixed valent aluminum compounds and numerous clusters such as the large aluminum anion $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ have provided insight into the stepwise formation of metallic aluminum from molecular precursors. It now appears likely that low oxidation state organoaluminum compounds will find their way into the organic and organometallic synthetic toolbox.

Keywords Aluminum · Aluminum clusters · Low valent organoaluminum · Mixed valent species

Contents

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Abbreviations

2e–2c	Two electrons–two centers
Ar′	2,6-$Mes_2C_6H_3$
Bbp	2,6-$\{(Me_3Si)_2CH\}_2C_6H_3$
Cp	Cyclopentadienide
Cp*	Pentamethylcyclopentadienide
Cp′	Tetramethylcyclopentadienide
Dipp	2,6-(*i*-Pr)$_2C_6H_3$
Dipp*	2,6-(2,6-(*i*-Pr)$_2C_6H_3)_2C_6H_3$
Do	Donor
EPR	Electron paramagnetic resonance
HOMO	Highest occupied molecular orbital
IDipp	1,3-Di-(2,6-(*i*-Pr)$_2C_6H_2$)imidazolin-2-ylidene
LUMO	Lowest occupied molecular orbital
Mes	Mesityl (=2,4,6-$Me_3C_6H_2$)
Mes*	2,4,6-(*t*-Bu)$_3C_6H_2$
NHC	N-heterocyclic carbene
NMR	Nuclear magnetic resonance
THP	Tetrahydropyran
TMEDA	Tetramethylethylenediamine
Trip	2,4,6-(*i*-Pr)$_3C_6H_2$
UV/Vis	Ultraviolet/visible
VT	Variable temperature

1 Introduction

The development of aluminum low oxidation state chemistry began with the isolation and structural characterization of the first stable dialane compound $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$, by Uhl and coworkers in 1988 [1]. Previously, aluminum(I) and aluminum(II) compounds could only be generated as high temperature gas-phase species (such as AlCl [4]), or as part of extended solid state structures, such as Al_7Te_{10} featuring staggered $Te_3Al–AlTe_3$ moieties [3]. In 1991 the Schnöckel group was able to prepare the first room temperature stable aluminum(I) compound, $(Cp^*Al)_4$, from a toluene/ether solution of metastable AlCl [2].

After these milestones numerous new compounds and synthetic routes were reported, contributing to a better understanding of low oxidation states of main group compounds, multiple bonding involving heavier main group compounds and cluster chemistry of main group metals. Several reviews and book chapters have summarized the progress in the low oxidation state chemistry of aluminum or, more generally, of group 13 compounds [5–11]. The present contribution reviews the chemistry of condensed phase molecular aluminum(I), aluminum(II), and mixed valence aluminum compounds including the literature until the winter of 2012. A brief summary of the major developments in aluminum cluster chemistry will also be presented. Compounds featuring bonds of aluminum to transition metals, lanthanide and actinides and selected main group elements are included in Chapter 2, "Organoaluminum complexes with bonds to s-block, p-block, d-block, and f-block metal centers".

While low oxidation state aluminum compounds may now be readily prepared in a typical organometallic laboratory, it should be pointed out that only the +3 oxidation state is thermodynamically stable at room temperature. For example, the disproportionation of gaseous aluminum(I) chloride to aluminum metal and aluminum(III) chloride is strongly exothermic (420 kJ/mol) [Eq. (1)] [12]. Similarly, based on the standard reduction potentials in an acidic environment the disproportionation of $Al^{+}(aq)$ is spontaneous ($\Delta E = 1.4$ V) [Eq. (2)] [12]:

$$3\ \mathrm{AlCl(g)} \longrightarrow 2\ \mathrm{Al(s)} + \mathrm{AlCl_3(s)} \quad \Delta H_R = 420\ \mathrm{kJ/mol} \tag{1}$$

$$\begin{aligned} &\mathrm{Al^{3+}(aq) + 3e^- \longrightarrow Al(s)}, && E^\circ = -1.662\ \mathrm{V} \\ &\mathrm{Al^{+}(aq) + e^- \longrightarrow Al(s)}, && E^\circ = +0.3\ \mathrm{V} \\ &\mathrm{Al^{3+}(aq) + 2e^- \longrightarrow Al^{+}(aq)}, && E^\circ = -2.7\ \mathrm{V} \end{aligned}$$

$$3\ \mathrm{Al^{+}(aq)} \longrightarrow 2\ \mathrm{Al(s)} + \mathrm{Al^{3+}(aq)} \quad \Delta E = 1.4\ \mathrm{V} \tag{2}$$

Hence, the synthesis and isolation of room temperature stable low oxidation state species require strategies preventing electron transfer processes leading to disproportionation reactions. The most common strategy involves a kinetic stabilization through the use of Al-bound ligands bearing large and bulky substituents including alkyl and aryl groups such as $(Me_3Si)_2CH$-, 2,4,6-$(t\text{-}Bu)_3C_6H_2$- (Mes*), or 2,6-$(2,6\text{-}i\text{-}Pr_2C_6H_3)_2C_6H_3$- (Dipp*) and bidentate anionic ligands such as $[ArNCMeCHCMeNAr]^-$ or $[ArNCH{=}CHNAr]^{2-}$ (Ar = Dipp = 2,6-i-$Pr_2C_6H_3$). These large substituents severely crowd up the redox active centers and inhibit facile electron transfers or other decomposition pathways. A combination of steric and electronic stabilization is probably at work in most other stable Al(I) derivatives bearing less sterically demanding ligands, such as $(Cp^*Al)_4$ (Cp^* = pentamethylcyclopentadienide) [2] or $Al_4(Br_4)(NEt_3)_4$ [13].

2 Aluminum(I) Compounds

2.1 Synthesis

Until 1989 aluminum(I) compounds were only known as high temperature species such as the binary species AlX (X = halide) [14] and AlH [15]. Aluminum(I) halide species have been generated by passing gaseous halogens or HX over liquid aluminum at high temperatures (1,200 K) and could be trapped in frozen nitrogen or noble gas matrices. IR, Raman, microwave, and EPR spectroscopic investigations of the gas-phase and matrix-trapped species provided structural and reactivity data. For example, AlCl exists as a monomer [d(Al–Cl) = 2.130 (1) Å] in the gas phase [16], whereas the argon matrix-trapped species is predominantly the halide-bridged dimer Al(μ-Cl)$_2$Al, whose experimental IR and Raman spectra agreed well with those predicted by quantum chemical calculations [17]. A metastable dark red solution of AlCl was finally obtained, when gaseous AlCl was co-condensed with toluene and ether at 77 K and allowed to warm to 160 K [4]. At room temperature, disproportionation into aluminum metal and $AlCl_3$ takes place within a few hours but this reaction is significantly slower at low temperatures: AlCl solutions can be stored at −50°C for weeks [5]. Although no crystalline aluminum(I) chloride species has been obtained to date, a few related aluminum(I) halides have been structurally characterized, namely $Al_4X_4(NEt_3)_4$ (X = Br [13]; X = I [18]) and $Al_4I_4(PEt_3)_4$ [19]. The compounds $Al_4X_4(NEt_3)_4$ were crystallized from AlX solutions in the presence of Et_3N, whereas $Al_4I_4(PEt_3)_4$ was prepared by a ligand exchange reaction involving $Al_4I_4(NEt_3)_4$ and Et_3P. The facile displacement of a hard ligand by a soft one agrees with the expected decrease in hardness in aluminum(I) compounds with respect to aluminum(III) analogues. In the solid state, these Al(I) species feature planar Al_4 rings, in which each aluminum center is further connected to one halide and one donor molecule.

The accessibility of metastable aluminum(I) halide solutions on a preparative scale quickly led to the isolation of the first room temperature stable aluminum(I) species, $(Cp^*Al)_4$ [2], isolated as an air and moisture sensitive yellow crystalline solid [Eq. (3)]:

$$2\ Cp^*_2Mg + 4\,AlCl \cdot x OEt_2 \xrightarrow[-78^\circ C]{\text{toluene/Et}_2O} (Cp^*Al)_4 + 2\,MgCl_2 \cdot 2OEt_2 + (4x-4)\ Et_2O \quad (3)$$

The molecular structure of $(Cp^*Al)_4$ consists of an Al_4 tetrahedron with each aluminum center coordinating to one Cp* ring in an η^5-fashion. Variable temperature ^{27}Al NMR spectroscopic investigations suggested that the tetrameric structure remains intact in solution at room temperature, but dissociation into Cp*Al monomers was observed at elevated temperatures [Eq. (4)]:

$$(Cp^*Al)_4 \rightleftharpoons 4\,Cp^*Al \quad (4)$$

This was further corroborated by the determination of the gas-phase structure of monomeric Cp*Al by electron diffraction [20]. In contrast, the parent compound $(AlCp)_n$, synthesized in an analogous manner to that developed for $(Cp^*Al)_4$, decomposed at −60°C [21], while compound $(AlCp')_4$ ($Cp' = C_5Me_4H$) was found to be stable at room temperature [22]. In a similar manner, the tetrameric species $(AlSi\textit{t}\text{-}Bu_3)_4$ has been prepared using $NaSi\textit{t}\text{-}Bu_3$ as a reactant and was isolated in a crystalline form when crystalline $(AlI{\cdot}NEt_3)_4$ was employed as the aluminum(I) source [23]. Likewise, the synthesis of the related $\{AlSi(SiMe_3)_3\}_4$ species required the use of $(AlBr{\cdot}NEt_3)_4$ [36]. A series of cyclopentadienide aluminum(I) compounds was obtained from $(Cp^*Al)_4$ [Eqs. (5) and (6)] [24]:

$$(Cp^*Al)_4 + 4/n\ Cp'_nM \longrightarrow (Cp'Al)_4 + 4/n\ Cp^*_nM \downarrow$$
$$Cp' = \text{substituted cyclopentadienide}$$
$$n = 1;\ M = Li, Na, K$$
$$n = 2;\ M = Mg \qquad (5)$$

$$(Cp^*Al)_4 + 1/2\ MgR_2 \longrightarrow (Cp^*Al)_3AlR + 1/2\ Cp^*_2Mg \downarrow$$
$$R = Cp,\ N(SiMe_3)_2 \qquad (6)$$

While aluminum(I) halide precursors benefit from their reactivity at low temperatures, hence allowing the preparation of thermolabile compounds such as $(AlCp)_n$, such a synthetic approach requires specialized equipments and well-trained personnel. To promote wider use and applications of Al(I) reagents, less demanding synthetic routes were clearly desirable. On that matter, the synthesis of $(Cp^*Al)_4$ by reduction of the readily available precursor $(Cp^*AlCl_2)_2$ with potassium in refluxing toluene (using standard Schlenk techniques) undoubtedly constituted a synthetic improvement to access well-defined Al(I) species [25]. Since then, the majority of Al(I) compounds has been synthesized by reduction of appropriate Al(III) precursors [Eq. (7)]. For these reductions, $RAlI_2$-type reactants hold a special place as they typically afford the desired reduced products in higher yields, which is probably related to the low Al–I bond energy (172 kJ/mol) [26].

$$RAlX_2 \xrightarrow[-KX]{K \text{ or } NaK_2} 1/n\ (RAl)_n \qquad (7)$$
$$R = Cp^*,\ Si(SiMe_3)_3,\ C(SiMe_3)_3;\ n = 4$$
$$R = 2,6\text{-}Dipp_2C_6H_3;\ n = 2$$
$$R = HC\{C(Me)NDipp\};\ n = 1$$

The formation of a transient dimer $(Dipp^*Al)_2$ ($Dipp^* = 2,6\text{-}Dipp_2C_6H_3$, $Dipp = 2,6\text{-}i\text{Pr}_2C_6H_3$) was suggested in the reduction of the bulky terphenyl substituted $Dipp^*AlI_2$ with KC_8 at room temperature [27]. The isolation of the first monomeric aluminum(I) compound was possible through the employment

of the monoanionic bulky bidentate substituent HC{C(Me)NDipp}$_2$ (nacnac) [28]. Attempts to prepare the anionic species [(DippNCH = CHNDipp)Al]$^-$ led to decomposition and deposition of aluminum metal [29]. Excess of reducing agent resulted in the isolation of the Na_2Al_2 cluster [Dipp*Al]$_2Na_2$ and the Na_2Al_3 cluster [Ar′Al]$_3Na_2$ (Ar′ = 2,6-$Mes_2C_6H_3$) [30]. Finally, the compounds (t-$BuCH_2Al)_4$ [31] and (t-$Bu_3SiAl)_4$ [32] were prepared via disproportionation and radical decomposition reactions.

2.2 Structures

Crystal structure analyses of fourteen aluminum(I) compounds have uncovered three structural motifs: (1) four-membered Al_4 rings for solvated aluminum(I) halides $(AlX{\cdot}Do)_4$, (2) Al_4 tetrahedra for aluminum(I) compounds with organic substituents $(RAl)_4$, and (3) a monomer for the nacnac derivative. In addition, a tetramer–monomer equilibrium for $(Cp^*Al)_4$ was established through VT NMR studies, and the gas-phase structure of Cp*Al was determined by electron diffraction [20]. A dimeric structure similar to that of (Dipp*Ga)$_2$ [33, 34] was suggested for the transient Dipp*Al species, a proposal based on the structure of the isolated cycloaddition product [27].

2.2.1 Aluminum(I) Halides

Stable crystalline aluminum(I) halides are accessible by treatment of metastable AlBr and AlI solutions with triethylamine. The triethylphosphine adduct $(IAlPEt_3)_4$ may subsequently be formed through ligand exchange. All these compounds feature a planar Al_4 ring, in which each aluminum is coordinated with one halide and one amine/phosphine ligand (Fig. 1). The average Al–Al distances (2.63 Å, Table 1), the Al–X, and Al–L distances are slightly longer than those observed for aluminum (III) compounds, in line with the larger covalent radius of Al(I). Unlike those in tetrahedral organoaluminum(I) compounds, the Al–Al bonds in these species can be described as two-electron two-center bonds.

2.2.2 Organoaluminum(I) Compounds

The majority of organoaluminum(I) compounds RAl form tetramers consisting of roughly symmetrical Al_4 tetrahedral cores (Fig. 2). Rather long Al–Al distances with values around 2.76 Å have been reported for π-bonded cyclopentadienide substituted species, whereas aluminum(I) compounds with σ-bonded substituents feature Al–Al bond lengths around 2.60 Å. This is particularly striking in $Cp^*_3(Me_3Si)_2NAl_4$, the only crystallographically characterized Al(I) compound bearing different substituents. The three Al–Al contacts involving aluminum

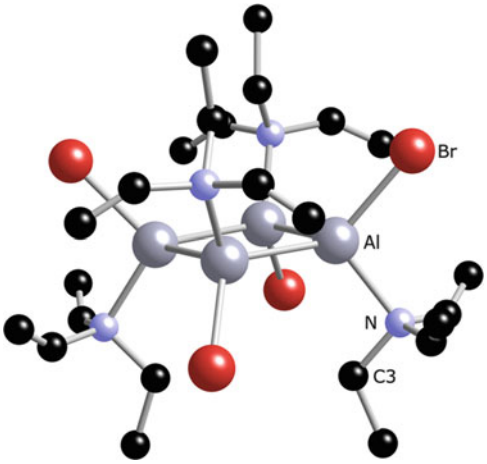


Fig. 1 Crystal structure of $(BrAlNEt_3)_4$ [13]

Table 1 Selected bond distances for isolated aluminum(I) halides (distances in Å)

Compound	d(Al–Al)	d(Al–X)	d(Al–L)	Reference
$(BrAlNEt_3)_4$	2.643 (3)	2.417 (2)	2.095 (6)	[13]
$(IAlNEt_3)_4$	2.653 (5)	2.641 (3)	2.060 (11)	[18]
$(IAlPEt_3)_4$	2.597 (3)	2.630 (2)	2.403 (2)	[19]

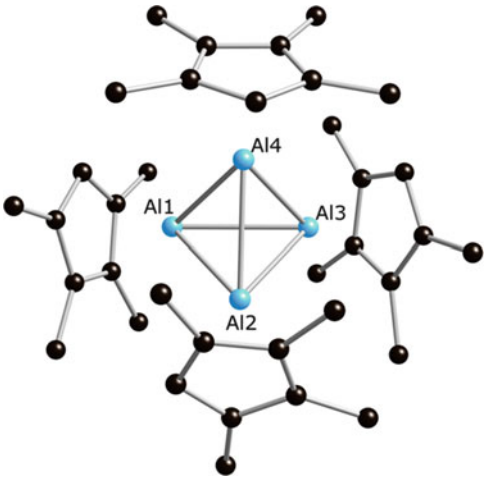


Fig. 2 Crystal structure of $(Cp'Al)_4$ [22]

centers substituted by Cp* average 2.758 Å, whereas those involving the amide substituted aluminum center average 2.664 Å. This value is longer than those found for the homoleptic compounds because two different aluminum centers are

Table 2 Isolated organoaluminum(I) compounds (distances in Å)

Compound	d(Al–Al)	d(Al–X)	Synthetic procedure	Color	Reference
$(Cp^*Al)_4$	2.769 (avg.)	2.334 (avg.)	A, B	Yellow	[2, 25, 26]
Cp^*Al[a]		2.388 (7)			[20]
$(Cp'Al)_4$[b]	2.709 (avg.)	2.32 (avg.)	A	Pale yellow	[22]
$\{(Me_3Si)_3CAl\}_4$	2.739 (avg.)	2.028 (avg.)	B	Orange	[35]
$\{(Me_3Si)_3SiAl\}_4$	2.602 (avg.)	2.445 (avg.)	A	Blue–violet	[36]
$(t\text{-}Bu_3SiAl)_4$	2.604 (avg.)	2.499 (avg.)	A, C	Violet	[23, 32]
$\{DippN(SiMe_3)Al\}_4$	2.619 (avg.)	1.815 (avg.)	B	Yellow	[37]
$Cp^*_3(Me_3Si)_2NAl_4$	2.758 (avg.)[c] 2.664 (avg.)[d]	2.316 (avg.)[e] 1.847 (2)	D	Yellow	[24]
$[\{(Me_3Si)_3SiAl\}_3AlSi(SiMe_3)_2]^-[Li(THF)_4]^+$	2.594 (avg.)	2.455 (avg.)	A	Dark red	[38]
$HC\{C(Me)NDipp\}_2Al$		1.957 (avg.)	B	Light yellow	[28]
$HC\{C(t\text{-}Bu)NDipp\}_2Al$		1.964 (2)	B	Red	[39]

[a]Monomeric gas-phase structure
[b]$Cp' = C_5Me_4H$
[c]For Al_{Cp}–Al_{Cp}
[d]For Al_{Cp}–Al_N
[e]For Al_{Cp}–C
Synthetic procedures: Method A: AlX + RM, Method B: reduction of $RAlX_2$, Method C: decomposition of R_2AlAlR_2, Method D: $(Cp^*Al)_4 + LiN(SiMe_3)_2$

connected with each other. Exceptions involve $(Cp'Al)_4$ (Cp' = tetramethylcyclopentadienide) and $\{(Me_3Si)_3CAl\}_4$. The former features shorter Al–Al bonds due to the smaller size of the Cp' substituent (Fig. 2) [22], while the Al–Al bonds in the latter compound are significantly elongated due to the very bulky $(Me_3Si)_3C$ substituents [35] (Table 2).

For $(RAl)_4$ tetramers, there are six Al–Al contacts per tetrahedron and only eight valence electrons (two from each aluminum). The bonding in such tetrahedral unit is best described in terms of molecular orbitals in analogy with well-established boron clusters such as $(t\text{-}BuB)_4$. The linear combination of four sets of frontier orbitals for each monomeric fragment (one filled HOMO and two empty degenerate LUMOs) results in the formation of one filled bonding orbital, three degenerate essentially non-bonding or weakly bonding orbitals and eight antibonding orbitals with π-symmetry (Fig. 3). The interaction of the ligand π-orbitals with these antibonding orbitals leads to the observed weakening and elongation of the Al–Al bonds in the corresponding cyclopentadienide compounds.

The Al(I) compounds with short Al–Al distances are deeply colored reflecting a small HOMO–LUMO gap. This gap is widened through the interaction of substituent orbitals of π-symmetry, primarily cyclopentadienide-type ligands, with the π-orbitals of the Al_4 clusters; hence the observed yellow colors. The pale yellow color of the amido derivative $\{(SiMe_3)(Dipp)NAl\}_4$ can be rationalized by a larger HOMO–LUMO gap caused by a lower energy HOMO in aluminum(I) compounds with electronegative substituents [21].

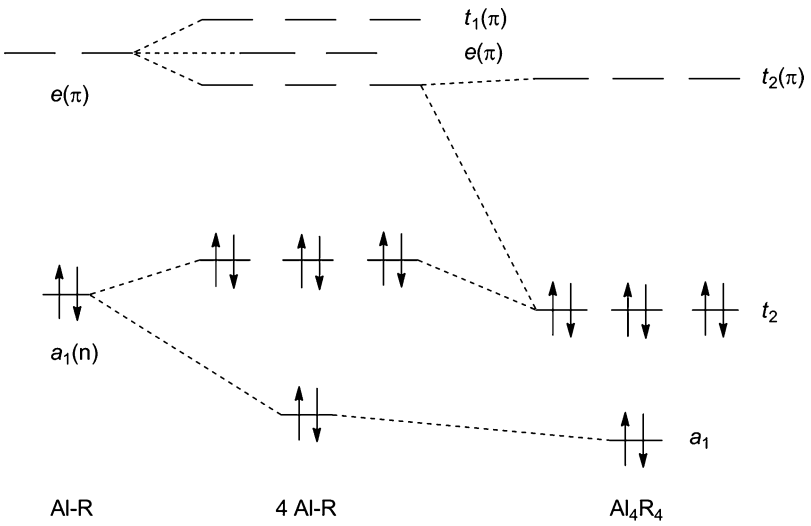


Fig. 3 Qualitative MO scheme for $(RAl)_4$ tetramers. Adapted from [9, 40]

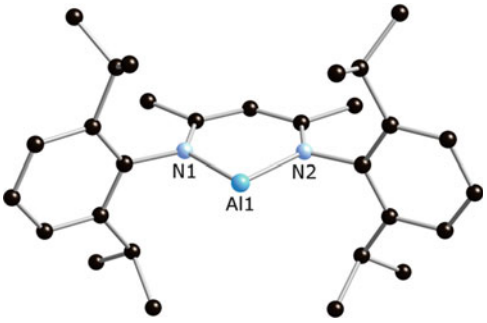


Fig. 4 Crystal structure of HC{C(Me)NDipp}$_2$Al [28]

The first aluminum(I) compound to be monomeric in the solid state, HC{C(Me)NDipp}$_2$Al, was reported in 2000 and its molecular structure is shown in Fig. 4 [28]. This species may be viewed as an aluminum analogue of an N-heterocyclic carbene (NHC) and has since been joined by a *t*-butyl substituted relative, HC{C(*t*-Bu)NDipp}$_2$Al [39]. Both compounds feature an essentially planar six-membered AlN_2C_3 core with the aluminum center being framed and protected by bulky aryl substituents. X-ray data and theoretical calculations are in agreement with the presence of a lone pair at aluminum in an sp-type orbital in the plane of the ring [28, 41]. The Al–N distances in both compounds are slightly longer (1.96 Å) than those for comparable Al(III) nacnac compounds (1.90–1.94 Å) [28, 39], most likely a result of less polar Al–N bonds in Al(I) compounds.

2.3 Reactivity

There are five distinct types of reactions that aluminum(I) compounds can undergo: (1) substitutions, (2) disproportionations, (3) redox reactions (4), carbene-like reactions, and (5) Lewis acid base reactions. The latter will only be briefly mentioned as it is dealt with in detail in Chap. 2.

2.3.1 Substitution Reactions

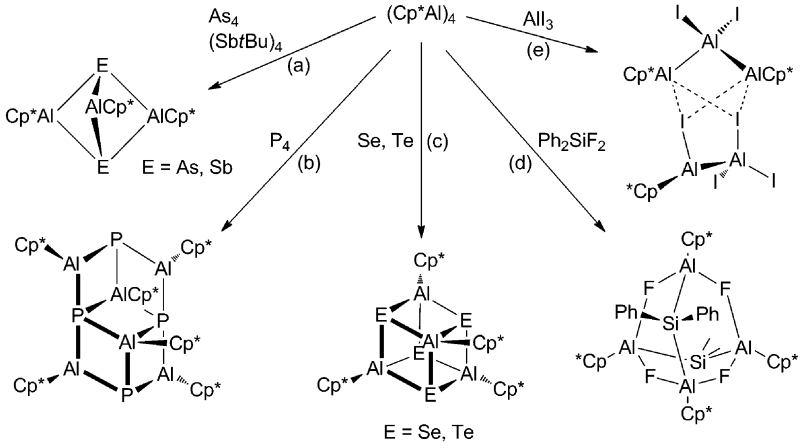
Aluminum(I) halides are excellent precursors to access various organoaluminum(I) species through the reaction with organolithium, organosodium, Grignard, or diorganomagnesium reagents [Eq. (3)]. The aluminum(I) halides are usually generated in situ; yet, in some cases, a crystalline precursor may be required for the isolation of the desired product. For example, albeit initially synthesized in 1991 [42], compound $(t\text{-Bu}_3\text{SiAl})_4$ was only isolated as a pure crystalline product in 1999 upon use of isolated $(\text{IAlNEt}_3)_4$ as reactant [23]. As discussed earlier [Eqs. (5) and (6)], one or all Cp* substituents in $(\text{Cp*Al})_4$ can also be displaced by other cyclopentadienide-type ligands and the bulky amido moiety $\text{N(SiMe}_3)_2$.

2.3.2 Disproportionation Reactions

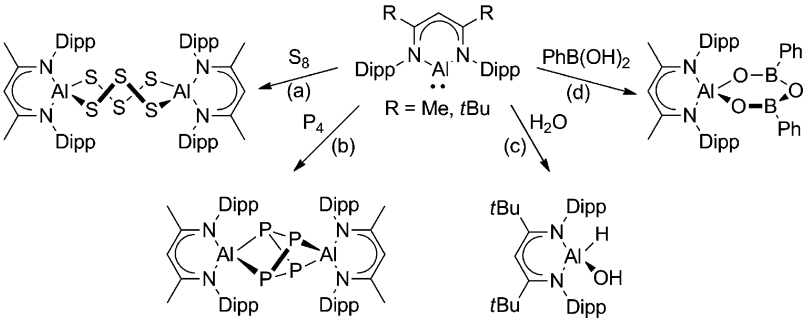
Unless protected by bulky substituents aluminum(I) compounds are subject to facile disproportionation into aluminum(III) species and aluminum metal, even at low temperatures. Under certain conditions large metal-rich (metalloid) clusters such as $[\text{Al}_{77}\{\text{N(SiMe}_3)_2\}_{20}]^-$ [43] and $\text{Al}_{50}\text{Cp*}_{12}$ [44] can be isolated. Theoretical calculations have found that the latter compound is stable toward disproportionation for steric reasons [45]. On the other hand, less sterically demanding cyclopentadienide ligands such as Cp or Cp′ do not form stable $\text{Al}_{50}\text{Cp}_{12}$ or $\text{Al}_{50}\text{Cp'}_{12}$ species, which is indicative of a ready decomposition of the parent aluminum(I) precursor. The subject has been extensively reviewed and the readers may refer to this in-depth analysis for further information [11, 46–51].

2.3.3 Redox Reactions

Aluminum(I) compounds are strong reducing agents $[E^\circ(\text{Al}^{3+}/\text{Al}^+) = -2.7\ \text{V}]$ [12], and the majority of their reactions involve redox chemistry. In some cases, aluminum(I) compounds have been employed as reducing agents. For instance, the attempted generation of $(\text{Cp*Mg})_2$ through the reaction of $(\text{IAlNEt}_3)_4$ with Cp*MgCl has been carried out [52]. As $(\text{Cp*Al})_4$ and $\text{HC}\{\text{C(Me)NDipp}\}_2\text{Al}$ can readily be prepared in most organometallic laboratories, the chemistry of



Scheme 1 Reactivity of $(Cp^*Al)_4$ with various inorganic and organometallic substrates



Scheme 2 Reactivity of $HC\{C(R)NDipp\}_2Al$ with various inorganic substrates

these two compounds has been investigated in much detail [5, 53, 54] and will be the focus of the following discussion (Schemes 1 and 2).

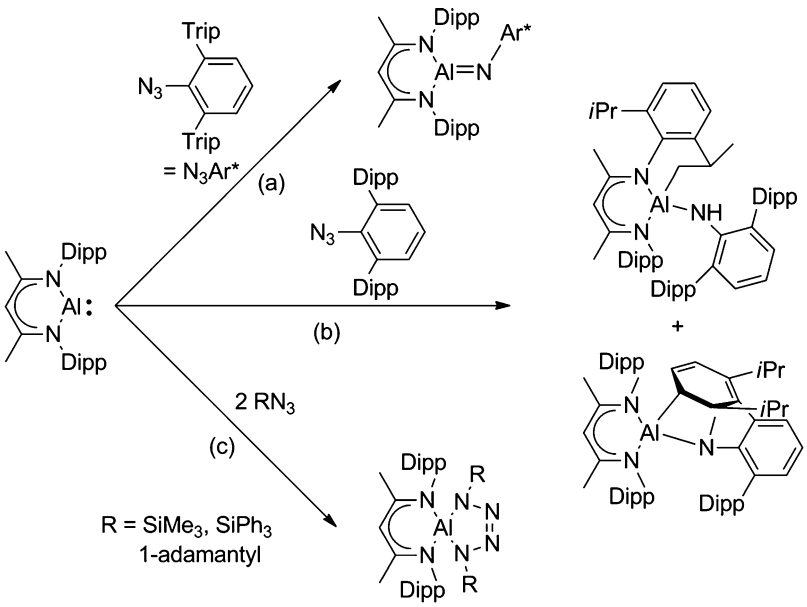
Most aluminum(I) compounds cleanly react with elements of groups 15 and 16. For example, the reactions of $(Cp^*Al)_4$ with white phosphorus and arsenic afforded the interesting cage compounds $(Cp^*Al)_6P_4$ [55] and $(Cp^*Al)_3As_2$ (Scheme 1a, b) [56]. The analogous antimony compound $(Cp^*Al)_3Sb_2$ is also accessible via reaction of $(Cp^*Al)_4$ with $(t\text{-BuSb})_4$ and proceeds with loss of the *t*-butyl groups (Scheme 1a) [57]. In contrast, the monomeric compound $HC\{C(Me)NDipp\}_2Al$ reacts with P_4 to yield a species resulting from the breakage of only two P–P bonds, which is most likely due to the larger size of the β-diketiminate substituents (Scheme 2b) [58]. Heterocubanes of the type $(Cp^*AlE)_4$ (E = Se, Te) may readily be prepared upon treatment of $(Cp^*Al)_4$ with Se and Te (Scheme 1c) [25], whereas the reaction of $HC\{C(Me)NDipp\}_2Al$ with O_2 and S_8 resulted in the respective formation of a rare dimeric aluminoxane $(HC\{C(Me)NDipp\}_2Al\mu\text{-}O)_2$, [59], and a peculiar species featuring a puckered Al_2S_6 core $(HC\{C(Me)NDipp\}_2Al\mu\text{-}S_3)_2$

(Scheme 2a) [60]. The reaction of $(t\text{-Bu}_3\text{SiAl})_4$ with oxygen was reported to afford the heterocubane $(t\text{-Bu}_3\text{SiAlO})_4$ [61], adopting an unprecedented aluminoxane structure. Surprisingly, very few efforts have been devoted to the oxidation of aluminum(I) compounds with halogens. One example includes the reaction of $(\text{Cp*Al})_4$ with four equivalents of I_2 to afford Cp*AlI_2 [62]. The use of 2 eq. of I_2 did not result in the formation of an aluminum(II) compound as could be expected, but in a mixture of Cp*AlI_2 and unreacted $(\text{Cp*Al})_4$. The addition of water to $(\text{HC}\{\text{C}(t\text{-Bu})\text{NDipp}\}_2\text{Al})$ afforded the mixed hydride hydroxide species $(\text{HC}\{\text{C}(t\text{-Bu})\text{NDipp}\}_2\text{Al(H)OH})$ with an excellent yield (Scheme 2c) [39]. Similarly, the addition of 2 eq. of phenylboronic acid to $(\text{HC}\{\text{C(Me)NDipp}\}_2\text{Al})$ produced a mixed aluminoxane boroxine compound with a cyclic AlB_2O_3 core (Scheme 2d) [63].

Reactions of aluminum(I) species with H_2 have been limited to gas-phase and matrix reactions. For instance, gaseous monomeric Cp*Al was co-condensed with H_2 in an argon matrix at 12 K and photolyzed to afford Cp*AlH_2 [64]. Compound $(\text{Cp*Al})_4$ was found to react with the Lewis acids Ph_2SiF_2 and AlI_3 by insertion into Si–F and Al–I bonds, respectively, to eventually afford the cage compounds $\{(\text{Cp*AlF})_2\text{SiPh}_2\}_2$ [57] and $\text{Cp*}_3\text{Al}_5\text{I}_6$ (Scheme 1d, e) [65]. The formation of these compounds most likely proceeds through initial adducts, such as $\text{Cp*Al} \rightarrow \text{SiPh}_2\text{F}_2$ or $\text{Cp*Al} \rightarrow \text{AlI}_3$, that subsequently rearrange into the observed products. In contrast, a ligand exchange reaction takes place upon reaction between $AlCl_3$ and $(\text{Cp*Al})_4$ to form the ionic species $[\text{Cp*}_2\text{Al}]^+[\eta^1\text{-Cp*AlCl}_3]^-$, which contains an aluminocenium cation [66]. Likewise, the reaction of $(\text{Cp*Al})_4$ with BiI_3 forms $[\text{Cp*}_2\text{Al}][\text{Cp*Bi}(\mu\text{-AlI}_4)](\text{AlI}_4)_2$ [67]. An insertion reactivity was observed when $(\text{Cp*Al})_4$ was reacted with $(\text{P}t\text{-Bu})_3$, with the formation of species $\text{Cp*Al}(\text{P}t\text{-Bu})_3$ [68].

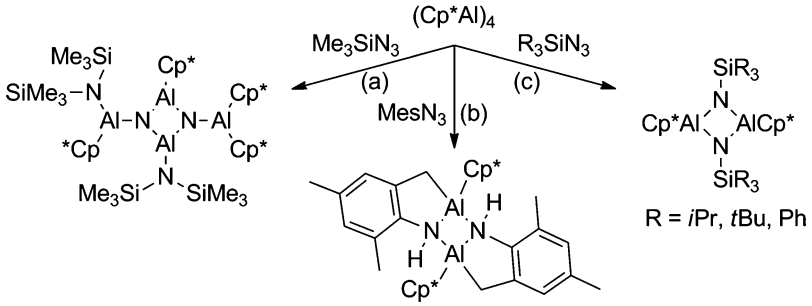
2.3.4 Carbene-Like Reactions

The frontier orbitals of monomeric aluminum(I) compounds are analogous to those of NHCs, and this similarity is reflected in their chemical properties [53, 54, 69]. The formation of complexes with Lewis acids and transition metals will be discussed later. For instance, just as singlet carbenes readily add to alkynes to afford cyclopropenes, the Al(I) compound $\text{HC}\{\text{C(Me)NDipp}\}_2\text{Al}$ is converted to aluminum cyclopropenes $\text{HC}\{\text{C(Me)NDipp}\}_2\text{Al}(\eta^2\text{-C}_2\text{R}_2)$ upon reaction with various alkynes, although no reaction was observed with $\text{Me}_3\text{SiC}{\equiv}\text{CSiMe}_3$ [70–72]. Alternatively, such metallacycles have been accessible by reduction of $\text{HC}\{\text{C(Me)NDipp}\}_2\text{AlI}_2$ with potassium in the presence of an alkyne source. The latter reaction most likely proceeds via a mechanism that does not involve an aluminum(I) species [70]. In contrast, solutions of metastable AlCl have been reported to react with 1 eq. of 3-hexyne or 2-butyne to form 1,4-dialumina-2,5-hexadiene and 1,4,7,10-tetralumina-2,5,8,11-cyclododecatetraene. These compounds may be viewed as ring-opened oligomers of an aluminumcyclopropene and constitute the first examples of aluminum(III) compounds featuring Al···olefin π-interactions in the solid state [73, 138]. $\text{HC}\{\text{C(Me)NDipp}\}_2\text{Al}$ also adds readily to azobenzene PhN═NPh to

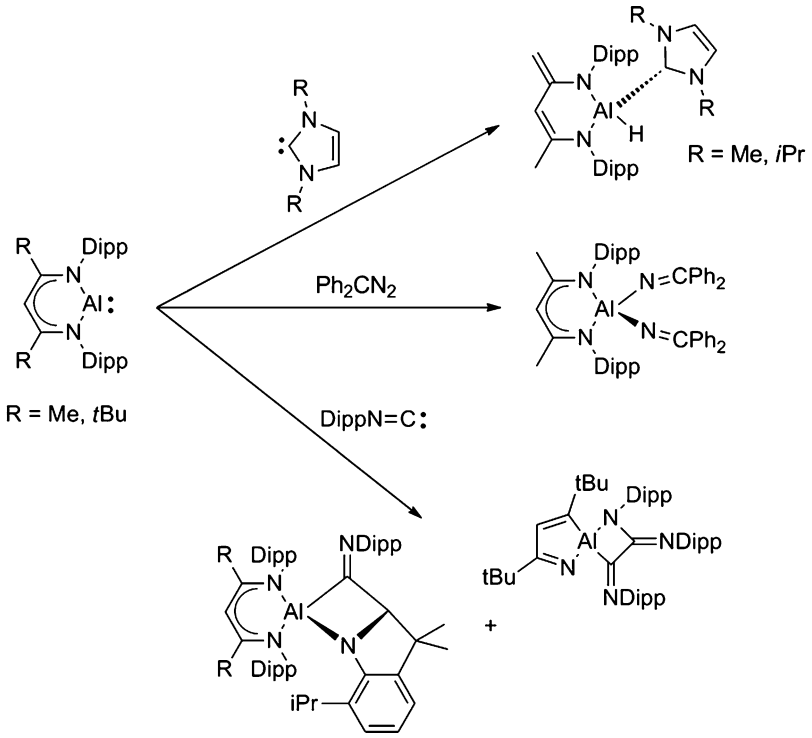


Scheme 3 Reactions of the aluminum(I) HC{C(Me)NDipp}$_2$Al species with organic azides

afford the corresponding [1+2] cycloaddition product, which then rearranges via C–H activation and N–N bond breakage to an *o*-phenylene diamide featuring a five-membered AlN_2C_2 core [74]. The reaction with organic azides is strongly dependent on the type of substrates. In all cases, a Staudinger-type reaction, leading to an aluminum imide with a formal Al–N double bond, can be assumed to be the first step. As aluminum derivatives containing Al=X multiple bonds may only be stabilized by steric protection, most of the imides undergo consecutive reactions. A stable monomeric aluminum imido derivative was nevertheless isolated and characterized through the combination of HC{C(Me)NDipp}$_2$Al with the very bulky azide $Trip_2C_6H_3N_3$ (Scheme 3a) [75]. The slightly less bulky azide $Dipp_2C_6H_3N_3$ resulted in the formation of two products, arising from either a C–H activation reaction or a formal [2+2] cycloaddition of the Al imido intermediate and one of the flanking arene rings (Scheme 3b) [76]. Medium-sized azides afforded aluminum tetrazole derivatives, thought to form through a cycloaddition reaction involving an intermediate aluminum imide species and excess azide (Scheme 3c) [77, 78]. The reaction of silylazides with $(Cp^*Al)_4$ yields the dimeric aluminum imides $\{Cp^*Al(\mu\text{-}NSiR_3)\}_2$ (R = *i*Pr, Ph, *t*-Bu) containing a central Al_2N_2 core (Scheme 4c) [79, 80]. A more complicated product, $(Me_3Si)_2NAlCp^*(\mu^3\text{-}N)_2(\mu^2\text{-}AlCp^*)\{\mu^2\text{-}AlN(SiMe_3)_2\}AlCp^*$, was isolated upon reacting $(Cp^*Al)_4$ with Me_3SiN_3 (Scheme 4a) [81]. Mesitylazide afforded a dimeric Al amido complex, presumably through C–H activation of one *o*-methyl group in the putative imides $(Cp^*AlNMes)_n$ ($n = 1$, 2) (Scheme 4b) [81]. As a comparison, N-heterocylic carbenes react with organic azides to give triazenides. N_2 extrusion



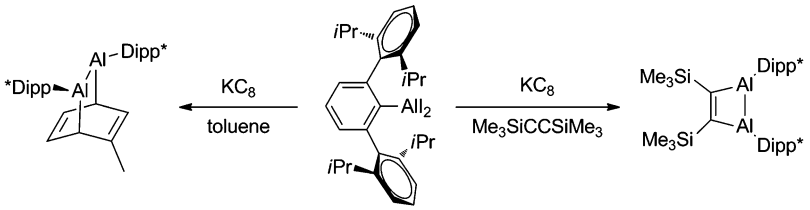
Scheme 4 Reactions of the aluminum(I) $(Cp^*Al)_4$ species with organic azides



Scheme 5 Reactions of $HC\{C(R)NDipp\}_2Al$ species with selected organic Lewis bases

and formation of Staudinger-type products, 2-iminoimidazolines, require heating above 100°C [82].

Lewis adducts of the type RAl···NHC (with the formation of an Al–C bond with a double bond character) do not readily form upon reaction of AlR and NHCs derivatives, which further supports that both classes of compounds exhibit related properties. However, prolonged heating of $HC\{C(Me)NDipp\}_2Al$ with imidazol-2-ylidenes produced a carbene adduct of a rearranged aluminum(III) hydride



Scheme 6 Reduction of Dipp*AlI_2 in the presence of $Me_3SiCCSiMe_3$ or toluene

(Scheme 5) [83]. The reaction of Ph_2CN_2, a triplet carbene precursor, with HC{C(Me)NDipp}$_2$Al did not result in a carbene adduct, but rather in the formation of a diiminyl complex. Such a reaction may proceed via an Al(I)-catalyzed decomposition of Ph_2CN_2 to $Ph_2C{=}N{-}N{=}CPh_2$ and its subsequent oxidative addition to the Al(I) center (Scheme 5) [83]. Similarly, the bulky isonitrile DippN=C species allowed access to two unexpected products, both resulting from coupling of the isonitrile carbon centers followed by C–H activation or insertion reactions (Scheme 5) [39].

Reduction of the bulky terphenyl substituted aluminum iodide Dipp*AlI_2 with KC_8 in the presence of toluene [27] or $Me_3SiCCSiMe_3$ [84] afforded novel Al–Al metallacycle species, possibly formed through [2 + 4] or [2 + 2] cycloaddition reactions between the dialuminene intermediate Dipp*Al=AlDipp* and an arene or alkyne source (Scheme 6). However, the exact mechanism remains to be studied and may well involve stepwise ionic or radical processes. For that matter, theoretical calculations suggested the existence of a partial diradical character in dialuminene species [85].

2.3.5 Adducts with Lewis Acids

Due to their intrinsic electronic properties, aluminum(I) compounds are Lewis bases, and their adducts with numerous Lewis acids including transition metal complexes have been isolated. The first stable and structurally characterized Al(I) Lewis adduct was generated via reaction of $(Cp^*Al)_4$ with the strong Lewis acid $B(C_6F_5)_3$ and isolated in moderate yields as a colorless solid (Fig. 5) [86]. The synthesis of the aluminum analogue $Cp^*Al \rightarrow Al(C_6F_5)_3$, which may also be viewed as a valence isomer of an aluminum(II) compound $R_2Al{-}AlR_2$, followed shortly thereafter [87]. Interaction with the monomeric species *t*-Bu_3Al afforded the adduct $Cp^*Al \rightarrow M$*t*-Bu_3, logically exhibiting a significantly longer Al–Al distance than that in the $Al(C_6F_5)_3$ analogue [2.689 (2) Å vs 2.591 (2) Å] [88]. In contrast, the reaction of $(Cp^*Al)_4$ with $In(C_6F_5)_3$ resulted in the formation of $Cp^*Al(C_6F_5)_2$ through a C_6F_5 ligand migration and a redox reaction [86]. The authors suggested that the higher stability of indium(I) drove the latter reaction. A series of Lewis adducts of the type Cp*Al/substituted 9-borafluorenes displayed slightly shorter Al–B distances than $Cp^*Al \rightarrow B(C_6F_5)_3$ [2.133 (avg.) Å vs 2.169 (3) Å], presumably due to the smaller size of the 9-borafluorene moiety [89]. When reacted with

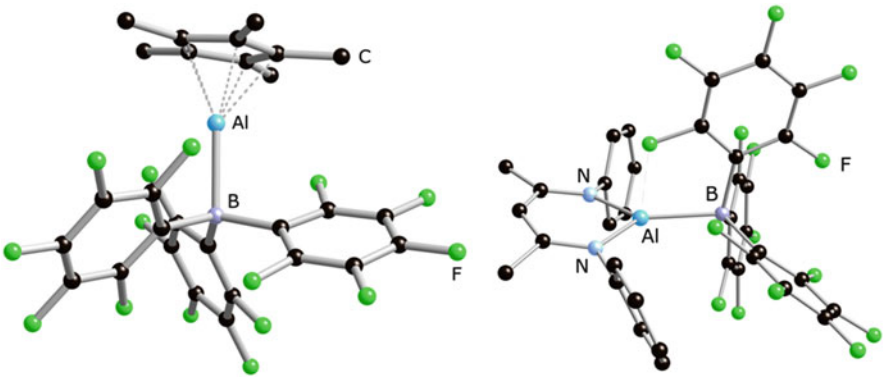
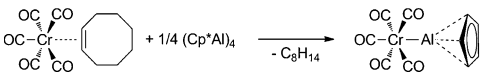


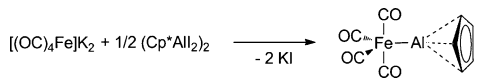
Fig. 5 Crystal structures of Cp*Al → $B(C_6F_5)_3$ [86] and $HC\{C(Me)NDipp\}_2Al$ → $B(C_6F_5)_3$ [90] (*i*-Pr groups have been omitted for clarity)

$B(C_6F_5)_3$, the monomeric compound $HC\{C(Me)NDipp\}_2Al$ formed a Lewis adduct that features a short Al···F interaction with one of the *o*-fluorines of the $B(C_6F_5)_3$ group (Fig. 5) [90]. The fluorine atom essentially donates electron density to the formally empty *p*-orbital located on the aluminum center, as supported by theoretical calculations [90, 91]. This is the first example of an aluminum compound containing an Al center behaving as a Lewis amphoter.

The analogy between organoaluminum(I) and NHCs derivatives also extends to their coordination behavior toward transition metal complexes. Beginning with compound $(CpNi)_2(\mu\text{-}AlCp^*)_2$ [92], closely related to $(CpNi)_2(\mu\text{-}CO)_2$, the coordination chemistry of $(Cp^*Al)_4$ toward transition metal species has been relatively well investigated, unlike that of $HC\{C(R)NDipp\}_2Al$ (R = Me, *t*-Bu) that remains in its infancy. Overall, the donor ability of organoaluminum(I) species compares well with those of phosphines, NHCs and even CO. This area has been very recently reviewed [93] (see also Chap. 2). Typically, these complexes are available either through the reaction of RAl with a transition metal complex containing labile ligands or that of anionic transition metalate complexes with $RAlX_2$ reagents, as exemplified by the reactions in Eqs. (8) and (9) [94, 95].



(8)



(9)

3 Aluminum(II) Compounds

As mentioned previously, the first stable molecular aluminum(II) compound $\{(Me_3Si)_2CH\}_2Al\text{–}Al\{CH(SiMe_3)_2\}_2$ was reported by Uhl and coworkers in 1988 [1, 8]. Earlier claims involving the synthesis of $R_2Al\text{–}AlR_2$ (R = *i*-Bu, Me_3CH_2)

could not be independently substantiated [31, 96]. However, a careful reinvestigation of the reduction of *i*-Bu_2AlCl with potassium led to the isolation of the cluster anion $[Al_{12}i\text{-}Bu_{12}]^{2-}$, the first heavy analogue of the borate cluster $[B_{12}H_{12}]^{2-}$ [97]. Subsequent results showed that bulky substituents such as $(Me_3Si)_2CH$ [1], Trip [98], or $(t\text{-}Bu)_3Si$ [32] are required to prevent disproportionation reactions such as that shown below [Eq. (10)] [99].

$$i\text{-}Bu_2AlCl \xrightarrow[-KCl]{K} {}''i\text{-}Bu_2Al\text{-}Ali\text{-}Bu_2{}'' \longrightarrow 2i\text{-}Bu_3Al + Al \xrightarrow{KCl} K[i\text{-}Bu_3AlCl] \tag{10}$$

In some instances, aluminum(II) halides may be trapped as donor-stabilized species of the type $LX_2Al–AlX_2L$ during the slow decomposition process of metastable aluminum(I) halides [100].

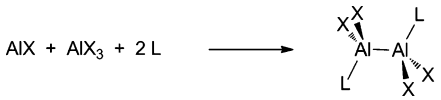
3.1 Synthesis

Aluminum(II) compounds are typically prepared using two synthetic approaches: (1) the reduction of an aluminum(III) halide precursor [Eq. (11)] and (2) the oxidation/disproportionation of aluminum(I) compounds. The first stable molecular aluminum(II) compound to be reported, $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$, was synthesized by potassium reduction of the aluminum halide precursor $\{(Me_3Si)_2CH\}_2AlCl$ in hexane [1]. The $Trip_2Al–AlTrip_2$ and $(t\text{-}Bu_3Si)_2Al–Al(Sit\text{-}Bu_3)_2$ analogues were subsequently isolated using similar approaches [98], although the reduction of $(t\text{-}Bu_3Si)_2AlCl$ was carried out using $NaSi(t\text{-}Bu)_3$ instead of potassium [32].

$$\begin{aligned} &2R_2AlX \xrightarrow{\text{red.}} R_2Al\text{-}AlR_2 \\ &R = (Me_3Si)_2CH;\ X = Cl;\ \text{red.} = K \\ &R = Trip;\ X = Br;\ \text{red.} = K \\ &R = t\text{-}Bu_3Si;\ X = Cl;\ \text{red.} = NaSit\text{-}Bu_3 \end{aligned} \tag{11}$$

As deduced from various studies, the key feature to access stable Al(II) compounds of the type $R_2Al–AlR_2$ lies in the use of sterically demanding Al–R substituents protecting the aluminum center and preventing facile decomposition. However, the very large size of the $t\text{-}Bu_3Si$ substituent ("supersilyl") weakens the Al–Al bond; thus, compound $(t\text{-}Bu_3Si)_2Al–Al(Sit\text{-}Bu_3)_2$ may be subject to radical decomposition (vide infra). Cp*- and *m*-terphenyl-substituted aluminum(II) species bearing one iodide and one organic substituent, namely Cp*(I)Al–Al(I)Cp* [62] and Dipp*(I)Al–Al(I)Dipp* [27], have been synthesized. The bromo-substituted complex Bbp(Br)Al–Al(Br)Bbp (Bbp = 2,6-$\{(Me_3Si)_2CH\}_2C_6H_3$) was also prepared via reduction of the Al(III)-Et_2O adduct $Al(Et_2O)(Br_2)Bbp$ with KC_8

[109]. These compounds may be viewed as intermediates in the reduction of organoaluminum(III) dihalides to organoaluminum(I) compounds. The first aluminum(II) hydride IDipp(H_2)Al–Al(H_2)(IDipp) (IDipp = 1,3-di-(2,6-(*i*-Pr)$_2$C$_6$H$_2$) imidazolin-2-ylidene) could be generated by reduction of the corresponding NHC adduct (IDipp)·AlH_3 with the magnesium(I) compound (nacnac)Mg–Mg(nacnac) [101]. Several amidinate and guanidinate substituted aluminum(II) hydrides were synthesized following the same reduction route. The compound IDipp(H_2)Al–Al(H_2)IDipp is related to the donor-stabilized aluminum(II) dihalides $LX_2Al–AlX_2L$, which, prior to this, could only be accessed from metastable aluminum(I) halides in the presence of an appropriate donor ligand [100, 102, 103]. For that matter, it is possible that the formation of aluminum(II) compounds resulted from a comproportionation reaction of metastable aluminum(I) halides with aluminum(III) halides [Eq. (12)], with the latter Al(III) compounds arising from the disproportionation of some aluminum(I) halides in solution [see Eq. (1)]. Alternatively, the aluminum(II) halides may result from disproportionation of aluminum(I) halides [Eq. (13)] [52].



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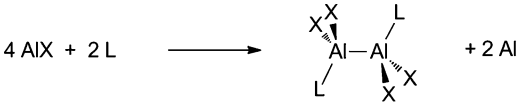


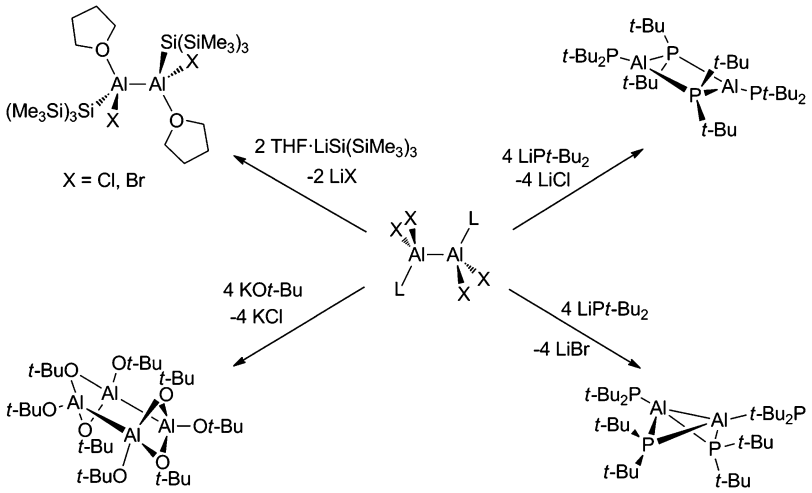
(13)

X = Cl, Br, I
L = THF, OEt_2, MeOPh, NEt_3, Me_3SiNMe_2,

Employment of an aza-allyl ligand allowed the synthesis of the mixed halide species L(I)Al–Al(Cl)L (L = $[(Me_3Si)_2CC(Ph)NSiMe_3]^-$) through potassium reduction of the corresponding precursor LAlClI [104]. Also, compound (Et_3P)I_2Al–AlI_2(PEt_3) was prepared through a ligand exchange reaction between solid (PhOEt)I_2Al–AlI_2(PhOEt) and an excess of PEt_3 [100].

In a few instances, the Schnöckel group reported on the synthesis of aluminum (II) compounds via a salt metathesis route involving preformed aluminum(II) halides and organolithium reagents (Scheme 7) [105–107]. For example, the THF adducts $(Me_3Si)_3Si(X)(THF)Al–Al(THF)(X)Si(SiMe_3)_3$ (X = Cl, Br) were prepared by reaction of crude $(Me_3Si)Me_2N(X_2)Al–Al(X_2)NMe_2(SiMe_3)$ with THF_3·$LiSi(SiMe_3)_3$. In contrast, starting from an AlBr solution only yielded the aluminum(III) species $(Me_3Si)_3SiAlBr_2$ [105].

Cycloaddition reactions of the putative dialuminene species Dipp*Al = AlDipp* with toluene or $Me_3SiC{\equiv}CSiMe_3$ were found to afford novel organoaluminum(II) compounds (Scheme 6) [27, 84]. The radical anion $[(t\text{-}Bu_2MeSi)_3Al]^{\bullet-}$, formally an aluminum(II) anion, was generated by potassium reduction of the neutral precursor (t-Bu_2MeSi)$_3$Al [108]. There again, the use of the bulky substituents, such as the t-Bu_2MeSi group, appears to be crucial for the stability of the produced Al(II) anionic species.



Scheme 7 Salt metathesis reactions using well-defined Al(II) precursors

3.2 Structures

For the most part, thus far isolated aluminum(II) compounds contain an Al–Al single bond. The X-ray characterized radicaloid $\{t\text{-Bu}_2\text{PAl}(\mu\text{-P}t\text{-Bu}_2)_2\}_2$ (Scheme 7) constitutes a noteworthy exception [107]. Also, spectroscopic and chemical evidence suggests that the very bulky dialane $(t\text{-Bu}_3\text{Si})_2\text{Al–Al}(\text{Si}t\text{-Bu}_3)_2$ partially dissociates in solution to afford the radical species $(t\text{-Bu}_3\text{Si})_2\text{Al}^{\bullet}$ [32].

In (R)(R′)Al–Al(R)(R′) species (R, R′ = organic group), two three-coordinate aluminum centers are connected by an Al–Al single bond. Depending on the R and R′ substituents, the Al–Al bond was reported to range from 2.495 to 2.751 Å while the twist angle between the two R–Al–R′ planes varies from 4° to 90°. For instance, in $(\text{Dipp*Al})_2(\mu\text{-Me}_3\text{SiC}{=}\text{CSiMe}_3)$, the short Al–Al distance (2.495 Å) most likely results from the strained dialuminumcyclobutene ring [84]. In $(t\text{-Bu}_3\text{Si})_2\text{Al–Al}(\text{Si}t\text{-Bu}_3)_2$, the rather long Al–Al distance (2.751 Å) and the large torsion angle (90°) are due to the very large $t\text{-Bu}_3\text{Si}$ substituents [32]. The core of the nearly coplanar dialane $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Al–Al}\{\text{CH}(\text{SiMe}_3)_2\}_2$ is shown in Fig. 6 [1].

The Al–Al distances in diorganodihaloalanes (R)(X)Al–Al(X)(R) (R = organic group, X = halide) are generally a bit shorter (ranging from 2.532 to 2.609 Å) than those in the more sterically bulky (R)(R′)Al–Al(R)(R′) species (Table 3).

The Al–Al distances in most organoaluminum compounds of the type (L)(R)(X)Al–Al(X)(R)(L) are close to 2.60 Å (Table 4). Thus, despite the higher coordination of the Al centers, the latter Al–Al distances are comparable to those in (R)(X)Al–Al(X)(R).

The Al–Al distances in $(\text{L})(\text{X})_2\text{Al–Al}(\text{X})_2(\text{L})$ average 2.55 Å with the aluminum (II)–NHC hydride species $\text{IDipp}(\text{H}_2)\text{Al–Al}(\text{H}_2)\text{IDipp}$ being the lone exception with

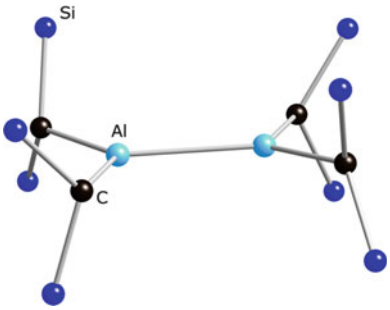


Fig. 6 Core of the structure of $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ [1]

Table 3 Selected structural parameters for organoaluminum(II) compounds (distances in Å, angles in degree)

Compound	d(Al–Al)	d(Al–X)	Twist angle	Color	Reference
$\{[(Me_3Si)_2CH]_2Al\}_2$	2.660 (1)	1.984 (avg.)	4.3	Colorless	[1]
$(Trip_2Al)_2$	2.647 (3)	1.996(3)	44.8	Yellow–green	[98]
$\{(t\text{-}Bu_3Si)_2Al\}_2$	2.751 (2)	2.717 (1)	90	Ruby	[32]
(Dipp*Al)$_2$(μ-2,5-C_6H_5Me)	2.5828 (7)	1.997 (avg., Dipp*) 2.002 (avg.)	30.3	Red	[27]
(Dipp*Al)$_2$(μ-$Me_3SiC = CSiMe_3$)	2.4946 (9)	1.978 (avg., Dipp*) 2.006(avg.)	–[a]	Orange-red	[84]
(Dipp*AlI)$_2$	2.609 (2)	1.964 (4) 2.502 (1)	0	Yellow	[27]
(BbpAlBr)$_2$	2.592 (3)	1.952 (5) 2.302 (2)	0	Colorless	[109]
(Cp*AlI)$_2$	2.5321 (10)	1.891 (avg., centroid) 2.639 (avg.)	89	Yellow	[62]

[a]The coordination at the Al centers is slightly pyramidal with ∑(angles) = 352 and 353°

a rather long Al–Al bond [2.637 (1) Å]. In such species, the donor molecules are usually oriented *anti* with respect to each other, although the Al-amino adducts $Et_3N(X)Al–Al(X)NEt_3$ (X = Br, I) were found to crystallize as two different rotamers [100, 110]. The bond shortening in compounds $(L)(X)_2Al–Al(X)_2(L)$ vs (R)(X)Al–Al(X)(R) may be rationalized by less electrostatic repulsion between the positively charged aluminum centers in the former compounds (Table 5) [102].

Table 4 Selected structural parameters for organoaluminum compounds of the type (L)(R)(X)Al–Al(X)(R)(L) (distances in Å)

Compound	d(Al–Al)	d(Al–X)	d(Al–L)	Color	Reference
$\{t\text{-Bu}_2\text{PAl}(\mu\text{-P}t\text{-Bu}_2)\}_2$	2.587	2.370 (avg., terminal) 2.394 (avg.)		Y	[107]
$\{(t\text{-BuO})_4\text{Al}_2\}_2$	2.6168 (7)	1.706 (avg., terminal) 1.874		PY	[107]
$\{\text{MeC(DippN)}_2\text{AlH}\}_2$	2.5756 (11)	1.947 (avg.) 1.52 (3)		C	[101]
$\{(p\text{-tolyl})\text{C(DippN)}_2\text{AlH}\}_2$	2.630 (3)	1.953 (avg.) 1.53 (5)		C	[101]
$\{t\text{-BuC(DippN)}_2\text{AlH}\}_2$	2.6144 (9)	1.945 (avg.) 1.54 (3)		C	[101]
$\{i\text{-Pr}_2\text{NC(DippN)}_2\text{AlH}\}_2$	2.6751 (13)	1.944 (avg.) 1.53 (2)		C	[101]
$\{i\text{-Pr}_2\text{NC(DippN)}_2\text{AlI}\}_2$	2.6083 (19)	1.919 (avg.) 2.5797 (12)		C	[101]
L(Cl)Al–Al(I)L[a]	2.593 (2)	2.100 (avg., Al–C) 1.964 (avg., Al–N) 2.316 (avg., Al–Cl) 2.550 (avg., Al–I)		Y–O	[104]
$\{(\text{Me}_3\text{Si})_3\text{Si(Cl)(THF)Al}\}_2$	2.588 (2)	2.1947 (9) (Al–Cl) 2.4892 (9) (Al–Si)	1.931 (2)	C	[105]
$\{(\text{Me}_3\text{Si})_3\text{Si(Br)(THF)Al}\}_2$	2.628(2)	2.3666 (9) (Al–Br) 2.4926 (11) (Al–Si)	1.929(2)	C	[105]

Color code: *C* colorless, *Y* yellow, *PY* pale yellow, *Y–O* yellow–orange
[a]L = $(\text{Me}_3\text{Si})_2\text{CC(Ph)NSiMe}_3$

Table 5 Selected structural parameters for organoaluminum compounds of the type (L)$(X)_2$Al–Al$(X)_2$(L) (distances in Å)

Compound	d(Al–Al)	d(Al–X)	d(Al–L)	Color	Reference
$\{(\text{Me}_3\text{Si})\text{Me}_2\text{NAlCl}_2\}_2$	2.573 (5)	2.168 (avg.)	2.001 (3)	Colorless	[100]
$\{(\text{PhOMe})\text{AlBr}_2\}_2$	2.527 (6)	2.306 (avg.)	1.930 (8)	Yellow	[102]
$\{(\text{Me}_3\text{Si})\text{Me}_2\text{NAlBr}_2\}_2$	2.564 (4)	2.332 (avg.)	1.999 (4)	Colorless	[100]
$(\text{Et}_3\text{NAlBr}_2)_2$	2.585 (2)	2.346 (avg.)	2.034	Yellow	[110]
$(\text{Et}_3\text{NAlBr}_2)_2$	2.571 (2)	2.342 (avg.)	2.035	Yellow	[110]
$(\text{Et}_2\text{OAlI}_2)_2$	2.52 (2)	2.542 (avg.)	1.86 (2)	Colorless	[100]
$(\text{Et}_2\text{OAlI}_2)_2$	2.531 (13)	2.550 (avg.)	1.86 (avg.)	Colorless	[100]
$(\text{Et}_3\text{PAlI}_2)_2$	2.546 (3)	2.562 (avg.)	2.440 (2)	Colorless	[100]
$(\text{THFAlI}_2)_2$	2.521 (3)	2.550 (avg.)	1.855 (avg.)	Colorless	[103]
$(\text{IDippAlH}_2)_2$	2.6375 (8)	1.54 (avg.)	2.086 (1)	Yellow	[101]

3.3 Reactivity

Depending on their substitution pattern, aluminum(II) compounds have been shown to undergo various types of reactions including: (1) substitution, (2) reduction, (3) oxidation, and (4) Lewis acid base chemistry.

3.3.1 Substitution Reactions

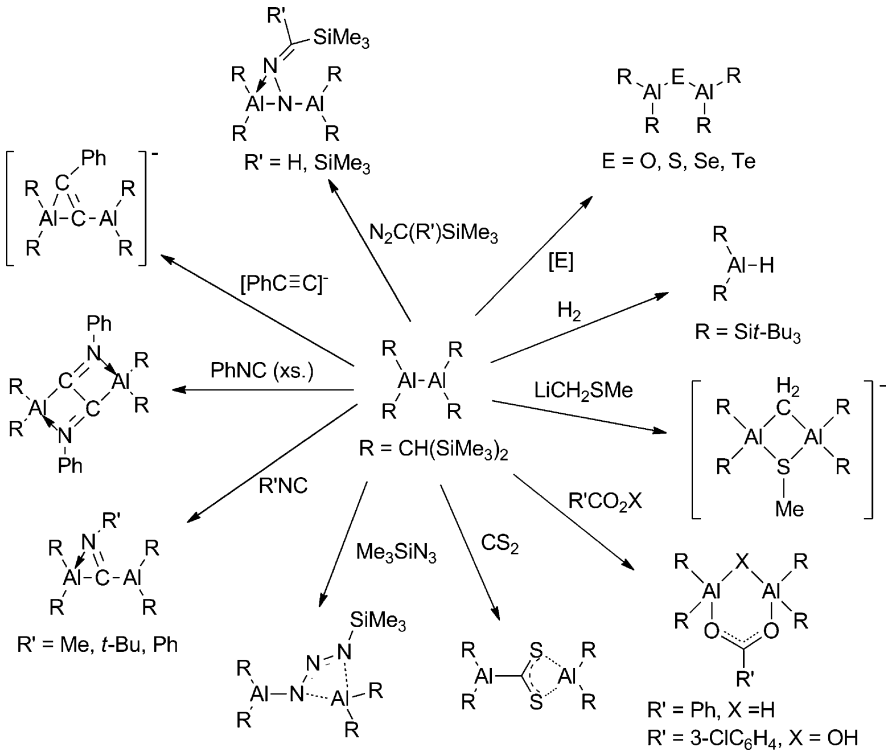
The donor-stabilized aluminum(II) compounds $(L)(X)_2Al–Al(X)_2(L)$ may readily undergo L-ligand exchange reactions, as observed in the synthesis of $(Et_3P)I_2Al–AlI_2(PEt_3)$ from solid $(PhOEt)I_2Al–AlI_2(PhOEt)$ and excess PEt_3 [100]. Also, halide substitution reactions of such Al(II) species with various organolithium and -potassium compounds are summarized in Scheme 7 (vide supra). Although such metathesis reactions may be seen as attractive routes to access aluminum(II) compounds, they remain of limited use because aluminum(II) halide precursors are not readily available [105–107].

3.3.2 Reductions

Species Cp*(I)Al–Al(I)Cp* along with the tetraorganodialane compounds $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ and $Trip_2Al–AlTrip_2$ have been reduced with sodium metal to, respectively, afford the Al(I) species $(Cp^*Al)_4$ [62] and the corresponding radical anions $[R_2Al–AlR_2]^{\bullet-}$ [98, 111, 112]. Structural data for the $[R_2Al–AlR_2]^{\bullet-}$ anions, such as the shortening of the Al–Al bonds (by 5% and 6% vs the neutral analogues), the coplanarity of the aluminum coordination planes and EPR data, agree with the additional electron being located in a π-orbital formed by overlap of the two empty p-orbitals on the aluminum centers. The one electron π-bond leads to an Al–Al bond order of 1.5. As mentioned earlier, the very crowded dialane $(t\text{-}Bu_3Si)_2Al–Al(Sit\text{-}Bu_3)_2$ partially dissociates in solution into the radical $(t\text{-}Bu_3Si)_2Al^{\bullet}$. It may also lose a $t\text{-}Bu_3Si^{\bullet}$ radical upon photolysis to afford the room temperature stable black-green radical species $[(t\text{-}Bu_3Si)_2Al–AlSit\text{-}Bu_3]^{\bullet}$ [32]. The EPR spectra of a solution of $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ after irradiation with UV light show signals that are compatible with those expected for the radicals $\{(Me_3Si)_2CH\}_2Al^{\bullet}$ and $[\{(Me_3Si)_2CH\}_2Al–AlCH(SiMe_3)_2]^{\bullet}$ [99].

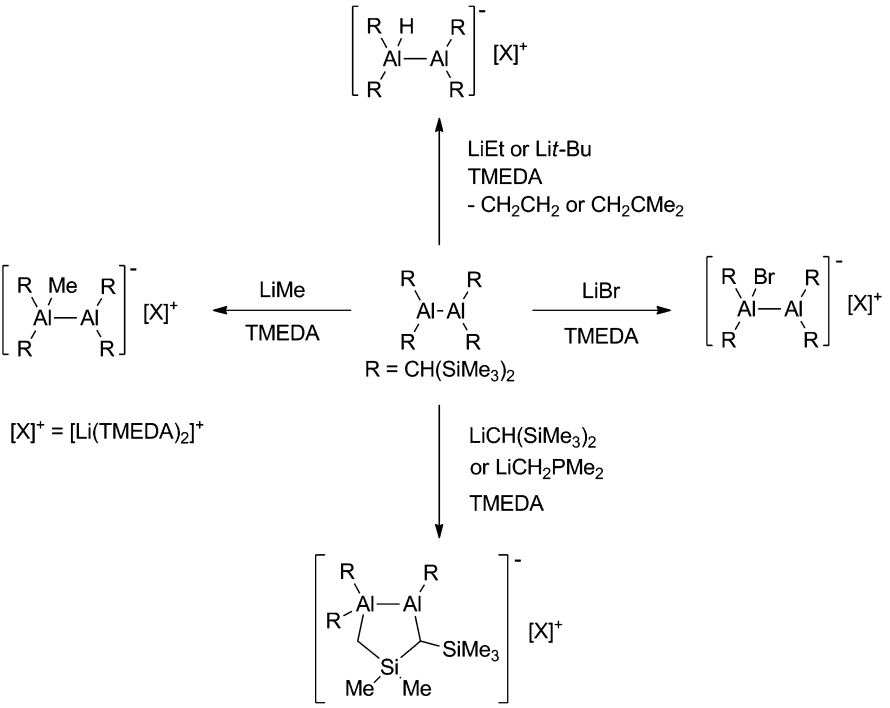
3.3.3 Oxidations

Reactivity studies of aluminum(II) species towards organic substrates and chalcogen atom donors have primarily been investigated with the dialane precursor $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ by Uhl and coworkers (Scheme 8) [7]. In all cases, the Al–Al bond was cleaved, and the aluminum centers were oxidized. Interestingly, the reaction of the very crowded dialane $(t\text{-}Bu_3Si)_2Al–Al(Sit\text{-}Bu_3)_2$ with H_2 cleanly afforded the hydride species $(t\text{-}Bu_3Si)_2AlH$ [32], this constituting the only instance where H_2 was reacted with an aluminum(II) species. Chalcogen atom donors such as CS_2 [113], RNCS (R = *t*-Bu, Ph) [114], Et_3PSe [115], and Et_3PTe [116] were reported to react with $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ through a formal insertion of the chalcogen atom into the Al–Al bond to produce the bent compounds $\{(Me_3Si)_2CH\}_2Al–E–Al\{CH(SiMe_3)_2\}_2$ (E = S, Se, Te).



Scheme 8 Reactivity of $R_2Al–AlR_2$ species with various small molecules

Upon reaction with DMSO, the linear Al–O–Al species $\{(Me_3Si)_2CH\}_2Al–O–Al\{CH(SiMe_3)_2\}_2$ along with small amounts of the trimeric hydroxide $[\{(Me_3Si)_2CH\}_2Al(\mu\text{-}OH)]_3$ were isolated [117, 118]. The linearity of the Al–O–Al bond results both from the significant steric crowding around the metal centers and from the highly ionic character of the Al–O bond. Furthermore, CS_2 also inserts into the Al–Al bond to form dinuclear aluminum complexes of the type η^2-*S,S*-$\{R_2AlCS_2\}AlR_2$, in which a dithiocarboxylato moiety effectively η^2-chelates an Al center [113]. The reaction of $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ with isothiocyanates affords compound $\{(Me_3Si)_2CH\}_2Al–S–Al\{CH(SiMe_3)_2\}_2$, arising from a desulfurization along with isonitrile side products. The latter species readily insert into the dialane Al–Al bond to form aluminaazacyclopropenes. Higher yields were achieved with isonitrile substrates, and a dialuminadiazabicyclohexadiene was isolated upon reaction with an excess of PhNC [114, 119]. Also, an excess of *t*-BuNC eventually led to the formation of the trimeric aluminum cyanide species $[\{(Me_3Si)_2CH\}_2Al(\mu\text{-}CN)]_3$ featuring a nine-membered $Al_3C_3N_3$ ring [120]. Additional compounds incorporating AlC_2 or AlN_2 three-membered rings were obtained with the acetylenide moiety $PhC{\equiv}C^-$ [121] and with diazomethane derivatives [122]. An interesting AlN_3 four-membered ring



Scheme 9 Reactivity of $R_2Al–AlR_2$ species with various Lewis bases

(formed upon reaction with trimethylsilyl azide, Scheme 8) was observed to further react with additional Me_3SiN_3 under photolysis conditions to afford the trimeric aluminum azide $[\{(Me_3Si)_2CH\}_2Al(\mu\text{-}N_3)]_3$ [123]. Notably, the carbenoid $LiCH_2SMe$ formally undergoes a CH_2 insertion reaction into the Al–Al bond along with the formation of an Al-μ-S(Me)-Al bridging thiolate [124]. Finally, the reactions of benzoic acid and 3-chloroperbenzoic acid afforded the corresponding carboxylate bridged hydride and hydroxide species [125, 139].

3.3.4 Lewis Acid Base Chemistry

The three-coordinate and thus electron deficient aluminum centers in $R_2Al–AlR_2$ compounds may, under certain conditions, react with Lewis bases without breakage of the Al–Al bond. Again, most of studies in the area have thus far been performed with compound $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ [7]. When activated by a chelating ligand such as TMEDA, unhindered Lewis bases such as LiBr and LiMe add to one of the aluminum centers to yield anionic dialuminum species (Scheme 9) [126, 128]. In contrast, the organolithium reagents EtLi and *t*-BuLi serve as hydride transfer reagents through β-hydrogen elimination to produce anionic Al (II) hydride species [126, 127]. Bulky bases such as $LiCH(SiMe_3)_2$ or $LiCH_2PMe_2$ do not undergo β-hydrogen elimination; rather, they deprotonate one of the Si-Me

Table 6 Selected structural parameters for organoaluminum compounds of the type $[R_2Al(X)\text{-}AlR_2]^-$ (distances in Å)

Compound	d(Al–Al)	d(Al–X)	Reference
$[\{(Me_3Si)_2CH\}_2Al(Me)\text{-}Al\{CH(SiMe_3)_2\}_2]^-$	2.752 (3)		[126]
$[\{(Me_3Si)_2CH\}_2Al(H)\text{-}Al\{CH(SiMe_3)_2\}_2]^-$	2.667 (3)		[126]
$[\{(Me_3Si)_2CH\}_2Al(Br)\text{-}Al\{CH(SiMe_3)_2\}_2]^-$	2.643	2.476	[128]
$[\{(Me_3Si)_2CH\}_2Al\{\mu\text{-}CH_2SiMe_2(CHSiMe_3)\}\text{-}AlCH(SiMe_3)_2]^-$	2.665 (3)		[127]

groups leading to the formation of a siladialuminacyclopentane that features a central C_2Al_2Si core [127]. Access to the THF adducts Bbp(THF)BrAl–Al(Br)Bbp and Bbp(THF)BrAl–AlBr(THF)Bbp was established by UV–vis and NMR spectroscopy [109]. For the most part, these bimetallic Al–Al compounds contain a four-coordinate and a three-coordinate aluminum center. While the Al–Al bond distances in the bromide and hydride adducts are comparable to those of the Al(II) precursors, that of the methyl adduct is significantly lengthened (2.752 vs 2.660 Å) [126] (Table 6).

4 Mixed Valence Compounds and Clusters

The dianionic icosahedral aluminum anion $[i\text{-}Bu_{12}Al_{12}]^{2-}$, serendipitously prepared in low yield upon an attempted synthesis of $i\text{-}Bu_2Al\text{–}Ali\text{-}Bu_2$ through reduction of $i\text{-}Bu_2AlCl$ with potassium, constituted the first structurally characterized aluminum cluster to be reported (Fig. 8) [97]. Shortly after, the synthesis of mixed valent aluminum compounds such as the radical anions $[R_2Al\text{–}AlR_2]^{\bullet-}$ (R = $CH(SiMe_3)_2$ [111, 112], Trip [98]), featuring aluminum centers in a 1.5 formal oxidation state, was achieved. General synthetic procedures to prepare mixed valent compounds and clusters involve reduction reactions of aluminum(II) or (III) precursors or controlled decomposition of aluminum(I) species. In some cases, homolytic bond cleavage in aluminum(II) compounds also afforded mixed valent compounds. This area has been thoroughly reviewed [10, 11, 40, 47], and aluminum cluster compounds will only be briefly mentioned.

4.1 Synthesis

4.1.1 Reductions of Aluminum(II) and (III) Precursors

The outcome of the reduction reactions involving organoaluminum halides $RAlX_2$ and R_2AlX strongly depends on the size and electronic properties of the R substituents. Similarly, the choice of the halide substituent may also be critical. In general and as previously mentioned, the reduction of aluminum iodides allows for better yields and more tractable reaction mixtures. In most instances, the reduction of Al(III) halide species $RAlX_2$, with R being a bulky ligand such as Cp*,

$(Me_3Si)_3C$, DippN($SiMe_3$) or HC{C(Me)NDipp}$_2$, affords the corresponding Al(I) species, as discussed above [see Eq. (7) and Table 2]. Yet it was found that the reduction of Ar*AlI_2 (Ar* = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$) with sodium metal yielded the dianionic cluster $[(Ar^*Al)_3]^{2-}$, whose trigonal Al_3 core contains two π-electrons resulting in a formal Al–Al bond order of 1.33 [30]. Reduction of the dialanes $\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2$ [111, 112] and $Trip_2Al–AlTrip_2$ [98] with lithium or potassium led to the formation of the aforementioned radical anions $[R_2Al–AlR_2]^{\bullet-}$. Compound $K_2[Al_{12}i\text{-}Bu_{12}]$, which incorporates an icosahedral dianionic $[i\text{-}Bu_{12}Al_{12}]^{2-}$ moiety, was isolated from the reduction of $i\text{-}Bu_2AlCl$ with excess potassium metal [97].

4.1.2 Controlled Decomposition of Aluminum(I) Precursors

Controlled decomposition of metastable solution of aluminum(I) halides (see Sect. 2.1) may be achieved upon fine-tuning experimental parameters such as temperature, solvent, co-ligands, and reactants. This has led to the isolation of several mixed valent molecular compounds and various clusters. Thus, depending on the reaction condition, products range from aluminum(I) compounds such as $(Cp^*Al)_4$ [2] or $Al_4Br_4(NEt_3)_4$ [13] to electron precise mixed valent species ($[Al_5Br_6\cdot 6THF]^+[Al_5Br_8\cdot 4THF]^-$, [103]) and metalloid clusters $Al_{22}Br_{20}\cdot 12THF$ [129], $[Al_{77}\{N(SiMe_3)_2\}_{20}]^-$ [43], $Al_{50}Cp^*_{12}$ [44]. The disproportionation of aluminum(I) compounds to aluminum metal and aluminum(III) compounds is a complicated reaction involving multiple steps and intermediates. The latter mixed valent species and clusters can be viewed as likely intermediates along this path. Nevertheless, despite numerous studies on the formation of such mixed valent systems over the past 20 years, there remains much to be understood. Some trends have, however, become apparent [11]:

- Strong Lewis base donors such as NEt_3 favor the formation of smaller units such as $Al_4Br_4(NEt_3)_4$ [13] and $Al_4I_4(NEt_3)_4$,[18] whereas weaker donors such as THF or THP may allow the isolation of larger clusters such as $Al_{22}X_{20}\cdot 12L$ (X = Cl, Br; L = THF, THP) [129, 130].
- The use of sterically demanding ligands including Cp*, $N(SiMe_3)_2$, $C(SiMe_3)_3$ or P*t*-Bu_2 appears crucial to stabilize and cap a given cluster. For example, cluster compounds such as $Al_4(Pt\text{-}Bu_2)_6$ and $Al_4X(Pt\text{-}Bu_2)_5$ (X = Cl, Br) were prepared by reaction of AlX solutions with Li*t*-Bu_2 [131].
- The size of the Al cluster may be controlled via the choice of an appropriate aluminum(I) halide precursor and various temperature conditions. For instance, the product of the reaction between AlCl and $LiN(SiMe_3)_2$ greatly depends on the reaction temperature, with the formation of $[Al_7R_6]^-$ at −7°C [132], $[Al_{12}R_8]^-$ at room temperature [133], and $[Al_{69}R_{18}]^{3-}$ at 60°C [R = N($SiMe_3$)$_2$] [134]. Also, when reacted with $LiN(SiMe_3)_2$, a solution of AlI was reported to afford the anionic cluster $[Al_{14}R_6I_6]^-$ at room temperature [135], while its counterpart $[Al_{77}R_{20}]^-$ was isolated when the reaction was carried out at 60°C [43].

4.1.3 Radical Processes and Adduct Formations

Due to the large size of the silyl substituents the dialane $(t\text{-Bu}_3\text{Si})_2\text{Al–Al}(\text{Si}t\text{-Bu}_3)_2$ readily undergoes Al–Al and Al–Si bond homolysis. Thus, its thermolysis at 80°C affords the radical species $[(t\text{-Bu}_3\text{Si})_2\text{Al–Al}(\text{Si}t\text{-Bu}_3)]^{\bullet}$ and $[(t\text{-Bu}_3\text{Si})_4\text{Al}_3]^{\bullet}$ [136]. While the former species formally contains an Al(II) and an Al(I) center, the latter compound features an aluminum(II) and two aluminum(I) centers. The related species $[\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Al–AlCH}(\text{SiMe}_3)_2]^{\bullet}$ could be generated via photolysis and was characterized by EPR spectroscopy [99].

The carbenoid Cp*Al forms 1:1 adducts with the Lewis acids $\text{Al}(\text{C}_6\text{F}_5)_3$ and $\text{Al}t\text{-Bu}_3$ [87, 88]. These Lewis pairs contain an aluminum(I) and an aluminum(III) center and may be considered as valence isomers of tetraorganodialanes species of the type $\text{R}_2\text{Al–AlR}_2$. It is also noteworthy that the reaction of Cp*Al with AlI_3 afforded the mixed valence species $\text{Cp}^*_3\text{Al}_5\text{I}_6$, best described as a $[(\text{Cp}^*\text{Al})_2\text{AlI}_2]^+[\text{Cp}^*(\text{I})\text{Al-AlI}_3]^-$ contact ion pair [65].

4.2 Structures

The structural data for mixed valence compounds containing Al–Al bonds either essentially localized 2e–2c (σ bond) or with an additional π bonding character are summarized in Table 7. For instance, the radical anions $[\text{R}_2\text{Al–AlR}_2]^{\bullet -}$ feature nearly planar Al_2C_4 cores with short Al–Al distances (2.53 and 2.470 Å) due to the partial π bond between the aluminum centers [98, 111, 112]. Based on the structural and EPR spectroscopical data, the extra electron resides in a π orbital arising from the interaction of two empty p orbitals (one on each trigonal planar aluminum center), thus resulting in a formal Al–Al bond order of 1.5. Likewise, the unpaired electron in the radical $[(t\text{-Bu}_3\text{Si})_2\text{Al–Al}(\text{Si}t\text{-Bu}_3)]^{\bullet}$ also occupies a π orbital [136]. In the dianionic Al cluster $[(\text{Ar}'\text{Al})_3]^{2-}$ ($\text{Ar}' = 2,6\text{-Mes}_2\text{C}_6\text{H}_3^-$), the two extra electrons are delocalized over the trigonal Al_3 core in a Hückel-type aromatic orbital ($4n + 2$, $n = 0$), although quantum chemical calculations indicate that the sodium ions bear some electron density. Hence the structure may be better described as an Al_3Na_2 cluster (Fig. 7) [30].

Unlike mixed valent Al compounds just discussed, the cluster radical $[(t\text{-Bu}_3\text{Si})_4\text{Al}_3]^{\bullet}$ consists of a trigonal Al_3 core containing Al atoms that are held together by five electrons in σ orbitals, i.e. one electron less than required for three standard 2e–2c bonds [136]. Alternatively, despite rather comparable Al–Al bond distances, species $[(t\text{-Bu}_3\text{Si})_4\text{Al}_3]^{\bullet}$ may be viewed as an adduct of the $(t\text{-Bu}_3\text{Si})_2\text{Al}^{\bullet}$ radical to the dialuminene $(t\text{-Bu}_3\text{Si})\text{Al}{=}\text{Al}(\text{Si}t\text{-Bu}_3)$ (Scheme 10).

As for the salt compound $[\text{Al}_5\text{Br}_6{\cdot}6\text{THF}]^+[\text{Al}_5\text{Br}_8{\cdot}4\text{THF}]^-$ [103] (Scheme 11a) and the contact ion pair $[(\text{Cp}^*\text{Al})_2\text{AlI}_2]^+[\text{Cp}^*(\text{I})\text{Al-AlI}_3]^-$ [65] (Scheme 11b), they both feature mixed valent Al centers connected to one another by 2e–2c σ-bonds.

Table 7 Selected structural data for mixed valent Al species (distances in Å)

Compound	d(Al–Al)	d(Al–X)	Color	Reference
$[\{(Me_3Si)_2CH\}_2Al–Al\{CH(SiMe_3)_2\}_2]^{\bullet-}$	2.53 (1)	2.04 (avg.)	Black violet	[112]
$[Trip_2Al–AlTrip_2]^{\bullet-}$	2.470 (avg.)	2.021 (avg.)	Dark green	[98]
$[(t\text{-}Bu_3Si)_2Al–Al(Sit\text{-}Bu_3)]^{\bullet}$	2.537[a]	2.572 (avg.)[a]	Black green	[136]
$[(t\text{-}Bu_3Si)_4Al_3]^{\bullet}$	2.703 (3) 2.737 (2) Al–$AlSi_2$ 2.776 (2) Al–$AlSi_2$	2.554 (avg.)	Black green	[136]
$[(Ar'Al)_3]^{2-b}$	2.520 (2)	2.021 (3)	Red	[30]
$[Al_5Br_6\cdot 6THF]^{+}$	2.532 (avg.)	2.346 (avg.) 2.380 (avg.) 1.884 (avg.)	Colorless	[103]
$[Al_5Br_8\cdot 4THF]^{-}$	2.543 (avg.)	2.368 (avg.) 1.905 (avg.)	Colorless	[103]
$[(Cp^*Al)_2AlI_2]^{+}$	2.526 (avg.)	2.554 (avg.)	Colorless	[65]
$[Cp^*(I)Al\text{-}AlI_3]^{-}$	2.53*(7)	2.569 (avg.) 2.811 (7)	Colorless	[65]
$Cp^*Al\rightarrow Al(C_6F_5)_3$	2.591 (2)	1.810 Al–Cp^*_{centr} 1.993 (avg.)	Yellow	[87]
$Cp^*Al\rightarrow Alt\text{-}Bu_3$	2.689 (2)	1.858 Al–Cp^*_{centr} 2.032 (avg.)	Colorless	[88]

[a]From DFT calculations
[b]$Ar' = 2,6\text{-}Mes_2C_6H_3$

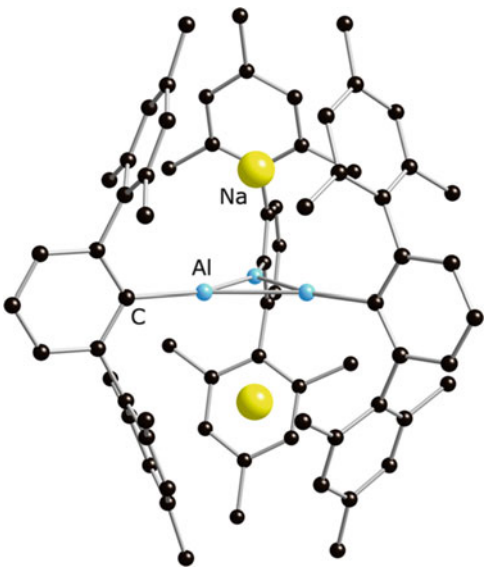
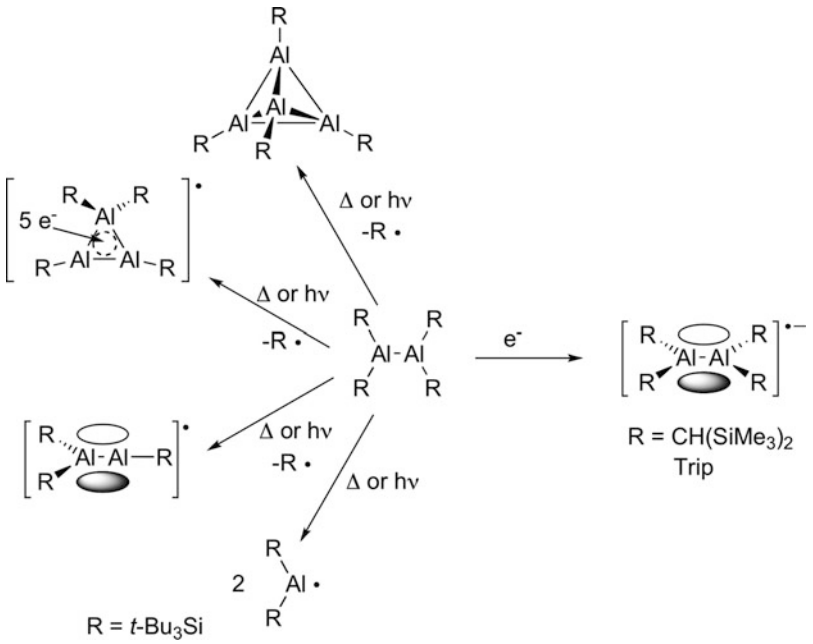
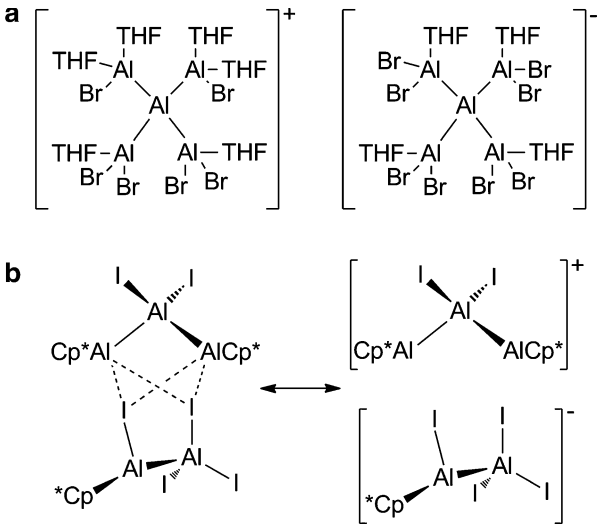


Fig. 7 Structure of $[(Ar'Al)_3]Na_2$ [30]



Scheme 10 Various reaction pathways to access mixed valent Al species from $R_2Al–AlR_2$



Scheme 11 Salt-like compounds $[Al_5Br_6{\cdot}6THF]^+[Al_5Br_8{\cdot}4THF]^-$ and $[(Cp^*Al)_2AlI_2]^+[Cp^*(I)Al\text{-}AlI_3]^-$ $[(Cp^*Al)_2AlI_2]^+[Cp^*(I)Al\text{-}AlI_3]^-$

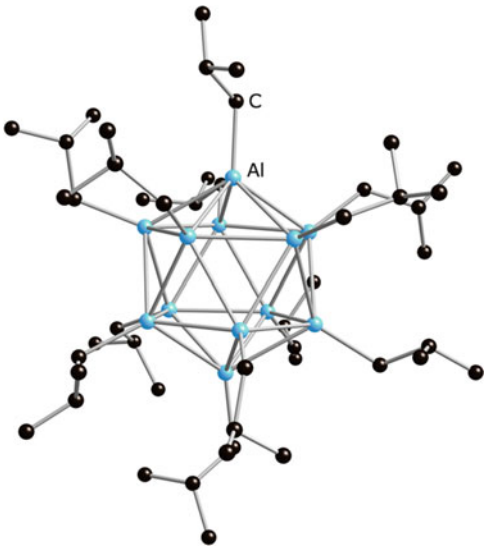


Fig. 8 Structure of the dianion $[i\text{-}Bu_{12}Al_{12}]^{2-}$ [97]

The bond distances in the Lewis adducts Cp*Al → $Al(C_6F_5)_3$ and Cp*Al → Al*t*-Bu_3 [2.591 (2) and 2.689 (2) Å, respectively] reflect a more Lewis acidic Al(III) center in $Al(C_6F_5)_3$ vs Al(*t*-Bu)$_3$ [87, 88].

Aluminum clusters can be divided into metalloid and non-metalloid clusters Al_nR_m, with $m < n$ for metalloid clusters and $m \geq n$ for non-metalloid clusters [11, 47]. In other words, metalloid clusters may be viewed as fragments of the parent metal structure, including possible modifications yet to be observed. Non-metalloid clusters have been described in previous sections, with a compound such as $(Cp^*Al)_4$ being a prototype for many organoaluminum(I) compounds. The molecular structure of the large non-metalloid cluster $[i\text{-}Bu_{12}Al_{12}]^{2-}$ consists of isolated Al_{12} isohedra obeying the Wade rules (Fig. 8) [97].

The field of metalloid aluminum clusters was established with the isolation of the large Al_{77} cluster $[Al_{77}\{N(SiMe_3)_2\}_{20}]^-$ in 1997 [43]. The anion $[Al_7\{N(SiMe_3)_2\}_6]^-$, the smallest metalloid cluster to date [132], features an aluminum center sandwiched between two planar $\{AlN(SiMe_3)_2\}_3$ rings. The Al_7 moiety corresponds to a somewhat distorted section of the aluminum metal structure. The polyhedral subhalides $Al_{22}X_{20}\cdot 12L$ (X = Cl, Br; L = THF, THP) all contain an Al_{12} icosahedral core with ten aluminum centers each connected to an $AlX_2\cdot L$ unit and two metal centers to the donor ligand L. Therefore, such polyhedral structures are best formulated as $Al_{12}(AlX_2\cdot L)_{10}\cdot 2L$ [129, 130]. Such a structural motif bears some resemblance to that of β-rhombohedral boron [129] or even α-boron as they both possess B_{12} icosahedral units [137]. It might therefore be possible to crystallize a new β-aluminum phase via a controlled disproportionation of aluminum(I) precursors. The largest aluminum cluster made of aluminum,

carbon and hydrogen atoms, $Al_{50}Cp^*_{12}$, contains an Al_{38} core capped by 12 AlCp* units that provide an effective hydrocarbon shell, hence contributing to its stability. For additional information on the booming field of large metalloid clusters the reader may refer to more comprehensive accounts in the area [11, 40, 47].

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Organoaluminum Species in Homogeneous Polymerization Catalysis

Samuel Dagorne and Christophe Fliedel

Abstract This chapter highlights the most recent and representative results on the use of organoaluminum compounds in polymerization catalysis with a special emphasis on discrete Al-incorporating catalysts. The first part of this contribution summarizes recent and noteworthy developments on well-defined Al-based initiators for the controlled (and stereocontrolled) polymerization of various monomers including isobutene, styrene, epoxides, methyl methacrylate, cyclic esters, and cyclic carbonates. The second part discusses the latest significant advances on the synthesis and structural characterization of polynuclear organoaluminum/transition (and f-block) metal complexes relevant to Ziegler–Natta-type catalysis.

Keywords Aluminum · Cyclic esters · Epoxides · Lewis acids · Olefins · Polymerization · Ziegler–Natta catalysts

Contents

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Abbreviations

Acac	Acetyl acetonate
BHT	2,6-Di-*tert*-butyl-4-methyl-phenolate
BU	1,3-Butadiene
CBR	Commercial butyl rubber
CHO	Cyclohexene oxide
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cp′	Tetramethylcyclopentadienyl
DAMEB	1,4-Bis(1-azido-1-methylethyl)benzene
DEAC	Diethylaluminum chloride
DMAP	4-Dimethylaminopyridine
DTBMA	Bis(2,6-di-*tert*-butyl-4-methyl-phenolate)methylaluminum
DTBP	2,6-Di-*tert*-butyl-pyridine
EADC	Ethylaluminum dichloride
EO	Ethylene oxide
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
IB	Isobutene
IBEA	(Isobutoxy)ethyl acetate
IP	Isoprene
LA	Lactide
MAO	Methylaluminoxane
Mes-NHC	1,3-Di-mesityl-butylimidazolin-2-ylidene
MMA	Methyl methacrylate
PDI	Polydispersity
PDLA	Poly[(D)-lactic acid]
PE	Polyethylene
PIB	Poly(isobutene)
PIP	Poly(isoprene)
PLA	Poly(lactic acid)
PLLA	Poly[(L)-lactic acid]
PMMA	Poly(methyl methacrylate)
PO	Propylene oxide
Porph	Porphyrin

PPNCl	Bis(triphenylphosphine)iminium chloride
PPO	Poly(propene oxide)
PS	Poly(styrene)
PTMC	Poly(trimethylene carbonate)
ROP	Ring-opening polymerization
Salen	*N*,*N*′-Bis(salicylidene)-1,2-ethylenediamine
SEC	Size exclusion chromatography
TBP	Tributylphosphate
t-Bu-NHC	1,3-Di-*tert*-butylimidazolin-2-ylidene
TEA	Triethylaluminum
TFPP	5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin
TMA	Trimethylaluminum
TMC	Trimethylene carbonate
TPP	5,10,15,20-Tetraphenylporphyrin
UHMWPE	Ultra-high molecular weight polyethylene
XRD	X-ray diffraction
ε-CL	ε-Caprolactone

1 Introduction

The use of organoaluminum species in polymerization catalysis was first studied and developed by Ziegler and Natta, who were awarded the Nobel prize in 1963 for the discovery of low pressure olefin polymerization with organoaluminum/transition metal catalysts. Their seminal work opened up novel opportunities for aluminum-based compounds whether in polymerization catalysis or in organometallic chemistry. As of today, simple reagents such as AlX_xR_{3-x} (X = halide and R = alkyl), produced on industrial scale, remain primarily used as cocatalysts in Ziegler–Natta-type polymerization. The ready availability of AlX_xR_{3-x} Lewis acids also promoted their successful use as initiators in various Lewis acid-mediated polymerization processes, thereby allowing the cationic-like polymerization of various monomers (such as styrene, isobutene, diene substrates, epoxides) in a straightforward manner. On that matter, it is noteworthy that the prominent industrial process for the production of commercial butyl rubber (CBR), an isobutene–isoprene copolymer, uses an $AlCl_3/H_2O$ initiating system. More recently, the use of ligand-supported and discrete aluminum complexes for their subsequent use as *single site* polymerization catalysts (for polar monomer polymerization) has undoubtedly attracted both industry and academia so that to improve polymerization control and stereocontrol and thus the properties of the resulting materials.

This chapter highlights the most recent and representative results on the use of organoaluminum compounds in polymerization catalysis with a special emphasis on discrete Al catalysts. The first part of this contribution deals with the latest trends and developments on the use of well-defined Al-based polymerization catalysts

while the second summarizes the key results on polynuclear organoaluminum/transition (and f-block) metal complexes relevant to Ziegler–Natta-type catalysis. Also, closely related, yet formally inorganic, aluminum compounds such as $AlCl_3$ and various ligand-supported Al–X derivatives (X = halide, alkoxide, amido) are also discussed.

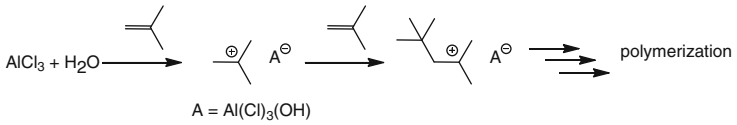
2 Lewis Acid-Promoted Olefin Polymerization by Organoaluminum Species

2.1 Polymerization of Isobutene, Isoprene, and Styrene by Organoaluminum Lewis Acids

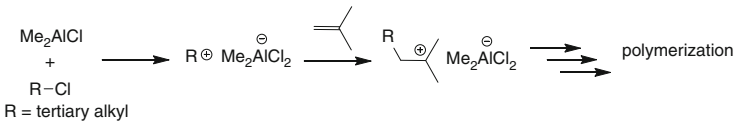
2.1.1 Isobutene and Isoprene

Due to the industrial importance of the resulting polymers, the use of simple organoaluminum species as Lewis acids for the initiation/co-initiation of the carbocationic polymerization of isobutene (IB) remains an active and prolific field of research so that to outperform the catalytic performance of the thus far well-established initiators [1–3]. The most important material derived from isobutene–isoprene is undoubtedly CBR, a isobutene–isoprene copolymer (<2.5 mol.% in isoprene) [4]. It is a sought-after material for its excellent gas barrier properties and its outstanding dampening characteristics [5, 6]. As such, this copolymer is widely used as inner tubes of car tires as well as for electrical insulation. The prominent industrial process for the production of CBR uses an initiating system based on $AlCl_3$ in CH_3Cl in the presence of water. In such a process, low temperature (ca. −95°C for the industrial process) is required so that to minimize chain transfer reactions and access high molecular weight CBR. This proton-initiated polymerization proceeds by a cationic mechanism with H_2O acting as proton source for the generation of a carbocation, acting as the propagating species (Scheme 1) [5, 6].

The main drawbacks of the latter process include [2]: (1) high energy consumption, (2) production of aluminum- and chlorine-containing waste, (3) the use of toxic MeCl as a solvent, and (4) limitation of the isoprene content in commercial polymers. To overcome these limitations, recent studies have focused on the use of novel initiating systems for the controlled and living polymerization of isobutene at somewhat higher temperatures: on that matter, mixtures of alkyl aluminum halides and tertiary halides have been successfully used for the direct generation of carbocationic entities that will subsequently chain grow after reaction with the C═C bond of the monomer. Alternatively, well-defined and ligand-supported cationic aluminum complexes have also been studied for the direct Lewis acid-assisted cationic polymerization of isobutene. Both of these approaches have recently been reviewed [1, 2, 7]. In addition, an up-to-date comprehensive account



Scheme 1 Proton-initiated isobutene polymerization initiated by $AlCl_3$ and H_2O



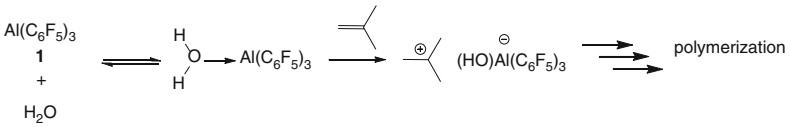
Scheme 2 Me_2AlCl/RCl-mediated isobutene polymerization

covering all aspects of living cationic polymerization is also available [8]. Thus, this section just highlights the key results in the area.

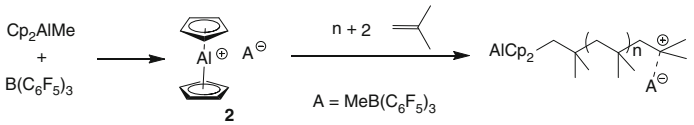
A living and well-controlled cationic polymerization of isobutene co-initiated by an organoaluminum species was reported by Cheradame and coworkers in 1996 using the binary initiating system $AlEt_2Cl$/DAMEB [$-50°C$, CH_2Cl_2, DAMEB = 1,4-bis(1-azido-1-methylethyl)benzene] to afford relatively narrow-disperse poly (isobutene) (PIB) ($1.2 < PDI < 1.4$), yet with a moderate M_n (<50 kDa) [9]. As expected, all PIB samples were isolated as azido end-group-functionalized polymers, indicating that the azido group (from DAMEB) is essentially responsible for chain termination. It is worth highlighting that PIBs bearing a reactive chain end are rather scarce, despite their potential interest for subsequent functionalization. In related studies, a Me_2AlCl/tertiary alkyl chloride combination was found to rapidly polymerize isobutene in a controlled and living manner to yield high molecular weight PIB ($PDI \approx 1.3$, $M_n > 100$ kDa) within 15 min at $-80°C$ (Scheme 2) [10]. Kinetic studies on the latter system agree with an apparent first-order dependence in monomer, as commonly observed for this type of polymerization, and with a second-order with respect to Me_2AlCl, this being consistent with its dimeric nature under the studied conditions. It may be noted that high molecular weight PIB of the type produced here is of particular interest for use as a midsegment for PS–PIB–PS triblock copolymers with optimal thermoplastic elastomer properties.

The nature of the aluminum alkyl group in AlR_xCl_{3-x} appears to be crucial in these Lewis acid-assisted polymerizations. Thus, changing the Al co-initiator from Me_2AlCl to Et_2AlCl (under otherwise identical conditions) resulted in a poorly controlled polymerization process, indicating the presence of terminated chains incapable of reinitiation as the polymerization proceeds. In this regard, it should be noted that alkylation and β-hydride transfer have long been identified as termination pathways in Et_2AlCl-mediated polymerizations of related monomers such as 3-methyl-1-butene and 4-methyl-1-butene [11].

Despite tedious drying procedures, polymerization of isobutene is very frequently observed in the sole presence of strong Lewis acids such as $R_{3-x}AlCl_x$, which may reasonably be ascribed to the presence of trace amount of water in the reaction



Scheme 3 Proton-initiated isobutene polymerization initiated by $Al(C_6F_5)_3$ in an aqueous medium



Scheme 4 Direct isobutene polymerization initiated by the aluminocenium cation **2**

medium [2]. This may be problematic as water/Lewis acid-initiated carbocationic polymerization may compete with that initiated by other systems such as R_2AlCl/tertiary alkyl halide systems, this being detrimental to polymerization control and to the properties of the resulting material. Such a drawback may be limited, at least to some extent, via the use of a proton trap such as 2,6-di-*tert*-butyl-pyridine (DTBP), a sterically demanding pyridine derivative, precluding proton-initiated polymerization. In a remarkable example, Faust and coworkers reported on the use of the ternary initiating system (1/1 $Me_2AlCl/MeAlCl_2$)/tertiary alkyl halide/DTBP for the controlled and living polymerization of isobutene (consumption of 600 equiv. of isobutene within 2 min, −80°C, 40/60 hexane/MeCl) to afford chain-length controlled and narrow disperse PIB (PDI $\leq$ 1.1) [12]. As a comparison, the (1/1 $Me_2AlCl/MeAlCl_2$)/H_2O system was found to yield PIB and isobutene–isopropene copolymers with broad polydispersities (2 < PDI < 3). Thorough kinetic studies on isobutene polymerization by R_xAlCl_{3-x}/tertiary alkyl halide/DTBP (R = Me, $x = 2$; R = Et, $x = 1$) concluded on chain propagation rate constants being independent of temperature and the nature of the Lewis acid [13]. The overall polymerization rates are however significantly affected by the solvent polarity and the nature of the Lewis acid, which can be attributed to different concentrations in active centers upon variation of the latter parameters. As may be anticipated, the reaction is slower with decreasing solvent polarity and Lewis acid strength and faster as the temperature is raised. Apart from alkyl aluminum halides, one should note that more robust organoaluminum Lewis acidic species such as $Al(C_6F_5)_3$ (compound **1**, Scheme 3) have very recently been shown to mediate the cationic polymerization of isobutene in an aqueous medium with a moderate level of control (1.2 < PDI < 1.6): this organic-solvent-free polymerization certainly constitutes an attractive approach from an environmental point of view [14].

Well-defined and discrete cationic organoaluminum species, which are of interest due to an enhanced Lewis acidity vs. that of their neutral analogues, may readily initiate the direct carbocationic polymerization of isobutene and/or isoprene in the absence of any co-initiator [2, 15]. In a seminal example, Bochmann and coworkers reported the aluminocenium cation Cp_2Al^+ [as a $MeB(C_6F_5)_3^-$ salt] (**2**, Scheme 4)

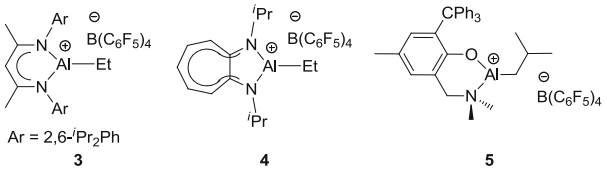


Fig. 1 Representative discrete Al organocations for isobutene and/or isoprene polymerization

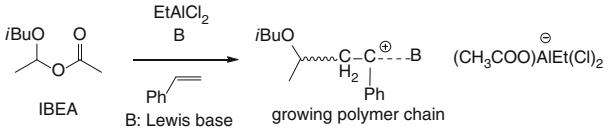
to be an effective initiator of the cationic polymerization of isobutene at low temperature [16]. Cation **2** also copolymerizes isobutene and isoprene (2–5 vol.% of isoprene) to yield a polymer containing about 2.7% isoprene with a 1,4-*trans* structure. As depicted in Scheme 4, it is likely that weak interactions with the counterion stabilize the propagating cationic species.

Subsequent polymerization studies on related aluminocenium systems, such as the $Cp^*_2Al^+$ and Cp'_2Al^+ cations, showed that both the sterics of the Cp-type ligand and the nature of the counterion may greatly affect the polymerization activity [17, 18]. For instance, it was recently reported that Cp_2Al^+ is more active in isobutylene polymerization when associated with the $Al(OR^F)_4^-$ vs. $MeB(C_6F_5)_3^-$ anion, which was attributed to weaker $Cp_2Al^+/Al(OR^F)_4^-$ interactions [$R^F = C(CF_3)_3$] [18]. Other representative discrete aluminum cations (compounds **3**–**5**, Fig. 1) found to readily undergo the direct cationic polymerization of isobutene or/and isoprene are depicted above [15, 19].

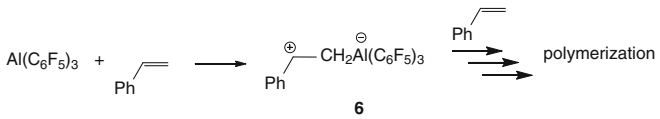
2.1.2 Styrene and Related Monomers

The controlled cationic polymerization of styrene is generally more difficult than that of IB, due to the fact that the growing species (as the polymerization proceeds) is more prompt to undergo chain transfer via various pathways. Also, styrene is a less reactive monomer than IB. While less studied than their B(III), Sn(IV), and Ti(IV) Lewis acidic counterparts, simple organoaluminum species have proven their suitability as Lewis acid components for styrene (and related monomers) polymerization. In this area and for instance, simple organoaluminum species such as $EtAlCl_2$, combined with an appropriate cationogen such as 1-(isobutoxy)ethyl acetate (IBEA) or 1-phenylethyl trifluoroacetate, effectively polymerize styrene in a controlled and living-like fashion at low temperature ($M_n \approx 15$ kDa, $1 < PDI < 1.5$, 0°C) in the presence of $CHCl_2CO_2Me$ (an added Lewis base) in C_6H_5Cl (Scheme 5) [20]. There again, for these initiating systems, the solvent polarity appears to be crucial for the stability of the propagating polymer chain and therefore for a well-behaved polymerization reaction. Thus, carrying out styrene polymerization in toluene (under otherwise identical conditions) only afforded ill-defined oligomers.

The key role of polar solvents and/or external Lewis bases for the stabilization of the propagating carbocationic chain, so that to prevent undesirable chain-transfer and termination reactions, is well-documented [8]. Using related $EtAlCl_2$-incorporating initiators but in the presence of $SnCl_4$, allowed for the highly



Scheme 5 Controlled cationic styrene polymerization involving $EtAlCl_2$ as the Lewis acid component



Scheme 6 Direct cationic polymerization of styrene initiated by $Al(C_6F_5)_3$

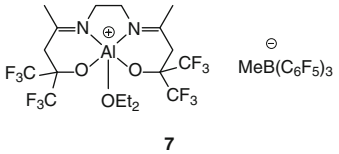


Fig. 2 A penta-coordinate Al cation for the direct polymerization of α-methylstyrene

effective and controlled polymerization of *p*-methoxystyrene and α-methylstyrene [21]. Likewise, the cationic polymerization of related monomers such as vinylethers (for instance, isobutyl vinyl ether) may be readily achieved by three-component catalysts of the type $EtAlCl_2$/IBEA/Lewis base for the production of well-defined linear or star-shaped poly(vinylethers) [22].

Albeit little studied, a couple of well-defined organoaluminum species have been used as Lewis acids for the direct polymerization of styrene derivatives, yet with a poor polymerization control so far. Chen and coworkers reported that $Al(C_6F_5)_3$ directly initiates a very rapid styrene polymerization at −78°C to quantitatively convert 1,000 equiv. of styrene to poorly defined PS (PDI = 3.9) within 5 min (TON = 22,800 h^{-1}), via a process likely to involve the zwitterionic styrene–alane adduct **6** (Scheme 6) [23]. In an analogous manner, the N_2O_2-supported penta-coordinate Al cation **7** (Fig. 2) was found to readily mediate α-methylstyrene polymerization, yet to produce a broadly disperse material [24]. Overall, the direct polymerization of styrene-type monomers by discrete aluminum cationic initiators is beneficial to catalytic activity; however, the poor control of such polymerization reactions certainly hampers their potential usefulness at this stage.

2.2 *Polymerization of Other Olefins by Organoaluminum Compounds*

Organoaluminum species have been known and used for over 50 years as cocatalysts in Ziegler–Natta-type olefin polymerization catalysis (vide infra). There are also a few instances in which transition-metal-free Al derivatives such as low-coordinate organoaluminum derivatives were found to polymerize ethylene and propene. In the late 1990s, Jordan and coworkers reported on several families of *N*,*N*-supported three-coordinate Al alkyl cations able to catalyze ethylene polymerization with moderate activity [25, 26]. Related subsequent studies in other three- and four-coordinate Al cations further substantiated these initial findings and this work has been reviewed [15]. Various combined experimental and theoretical studies of these systems clearly indicated that mononuclear Al alkyl cations do not polymerize olefins via a classical coordination/insertion mechanism (as that observed in olefin polymerization mediated by early-transition-metal alkyl cations), as initially thought. In particular, theoretical calculations concluded that the energy barrier for chain transfer is energetically favored over propagation [27]. In fact, the propagation/chain transfer balance for the modeled three-coordinate Al alkyl cations appears to be worse (higher preference for chain transfer) than that for Me_2AlEt, an ethylene oligomerization catalyst (Aufbau reaction). These studies suggest that a coordination/insertion polymerization mechanism would be more likely for multinuclear Al alkyl species. Alternatively, a Lewis acid-assisted cationic polymerization of ethylene, in which Al alkyl cations would act as strong Lewis acids, may not be excluded.

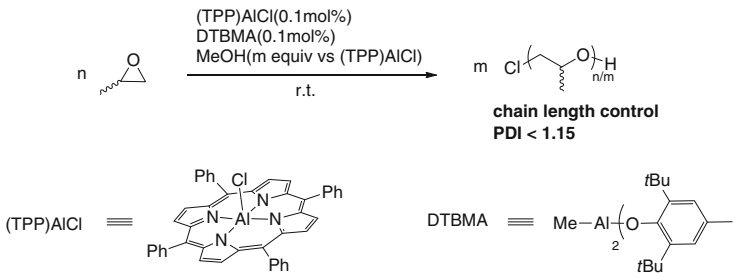
A couple of reports have also shown that organoaluminum species may well polymerize α-olefins such as propene, albeit with low activity. For instance, Al-incorporating catalytic systems such as $AlEt_3/B(C_6F_5)_3$ and $MAO/B(C_6F_5)_3$ are apparently capable of homo- and copolymerizing of ethylene and propene [28]. A cationic Al species that would readily form upon ionization of $AlEt_3$ or MAO by $B(C_6F_5)_3$ may be responsible for the observed polymerization activity.

3 Organoaluminum Species for the Polymerization of Polar Monomers

3.1 *Polymerization of Epoxides and Methyl Methacrylate by Organoaluminum Species*

3.1.1 Epoxides Homopolymerization

The ring-opening polymerization (ROP) of epoxides such as ethylene oxide (EO) and propylene oxide (PO) that initiated various organoaluminum species have been



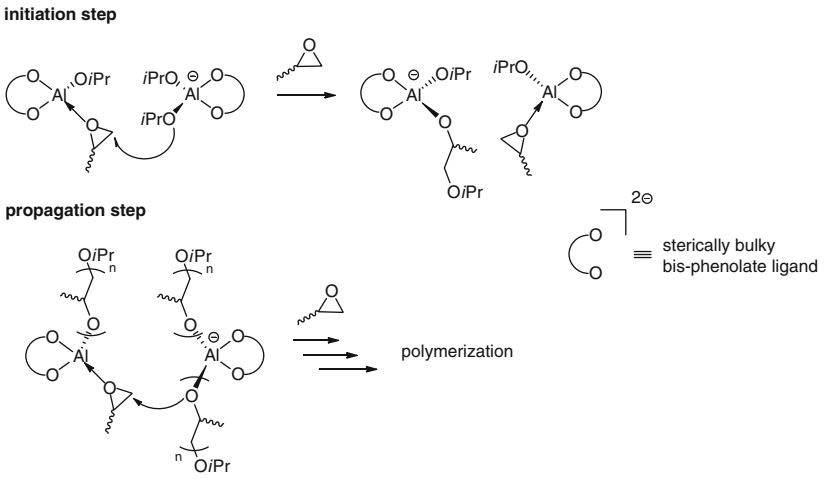
Scheme 7 Living and immortal propylene oxide polymerization by a two-component Al-based initiator

known since the 1960s with the seminal work of Vanderberg and coworkers, who first demonstrated that a combination of trialkylaluminum reagents with water, diethylether, or 2,4-pentanedione may promote the ROP of EO and substituted epoxides [29, 30]. More recently, various discrete and ligand-supported Al initiators, such as neutral (L′)Al(X) and (L′ = X_2^{2-}, LX_2^{2-} or $L_2X_2^{2-}$ dianionic chelating ligand; X = halide, alkyl , alkoxide), have been successfully developed for the ROP of epoxides (primarily propylene oxide and cyclohexene oxide). Depending on the initiating system, Al-mediated epoxide polymerizations may proceed either via an anionic, coordination/insertion or a cationic mechanism [31]. Thus far, coordination/insertion and anionic polymerization of epoxides mediated by Al-based species has led much better results than the (Lewis acid-assisted) cationic polymerization as the former frequently involve living and well-controlled processes, allowing the production of well-defined and valuable materials. For the most part, recent progresses in Al-initiated ROP of epoxides are included in several reviews [32–34]. We thus here highlight key representative results in the area along with the most relevant latest results.

Major breakthroughs in Al-mediated epoxide ROPs were reported in the 1980s and 1990s by the group of Inoue. For instance, well-defined porphyrinato-Al complexes of the type (Porph)AlX (X = halide, alkyl, alkoxide; Porph = porphyrin), when associated with a sterically bulky aluminum Lewis acid such as, for instance, bis(2,6-di-*tert*-butyl-4-methyl-phenolate) methyl aluminum (DTBMA), were reported to be excellent initiators for the living ROP of a wide array of epoxides affording the corresponding regioregular polymers with controlled molecular weights and narrow PDIs [34, 35]. In addition, such polymerizations may be carried out in an "immortal" manner (as coined by the authors) in the presence of an alcohol source (Scheme 7) [35].

Since then, in Al-mediated epoxide polymerization, no significant improvements have been reported whether regarding catalytic performance and the well-defined nature of the resulting PPO. Rather, recent studies in the area have provided insight as to the possible mechanisms in these polymerization reactions.

While the polymerization of PO by (TPP)AlCl (TPP = 5,10,15,20-tetraphenyl-porphyrin) was unequivocally showed to proceed via a coordination–insertion



Scheme 8 Bimetallic anionic polymerization of PO initiated by Al alkoxide derivatives

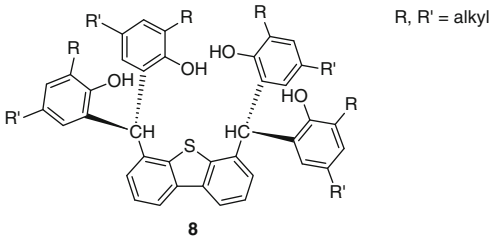
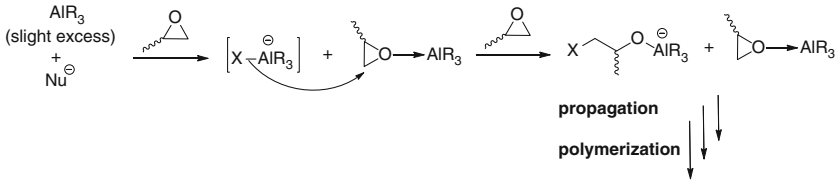


Fig. 3 Sulfur-bridged tetraphenol pro-ligands used for the synthesis of discrete dinuclear Al initiators effective in EO polymerization

mononuclear mechanism in the absence of an external Lewis acid source [36, 37], that in the presence of bulky Lewis acids such as DTBMA remains to be addressed. Recent studies using (L′)Al(X) initiators (L′ = X_2^{2-}, LX_2^{2-}, or $L_2X_2^{2-}$ dianionic chelating ligand; X = halide, alkyl, alkoxide) suggested that a bimetallic polymerization pathway might well take place in some instances. Evidences for such a mechanism have been provided by Okuda et al. through studies of a series of mono- and bi-component Al alkoxide complexes supported by bis-phenolate ligands [38]. It was then concluded that the ROP of PO cannot occur at mono-site Lewis acidic centers, but that the presence of an external nucleophilic Al ate species is required for the initiation and propagation steps (Scheme 8). The present process is thus best described as a coordination anionic polymerization with chain transfer.

Parallel studies by Chisholm and coworkers on PO polymerization by bis-phenolate Al species also convincingly ruled out a coordination–insertion mechanism occurring at a single metal center [39]. Of relevance to the subject, Wasserman and coworkers designed and synthesized a family of dinuclear Al complexes supported by sulfur-bridged-tetraphenolate-supported mononuclear of



Scheme 9 AlR_3-mediated PO polymerization via nucleophilic attack/monomer activation sequence

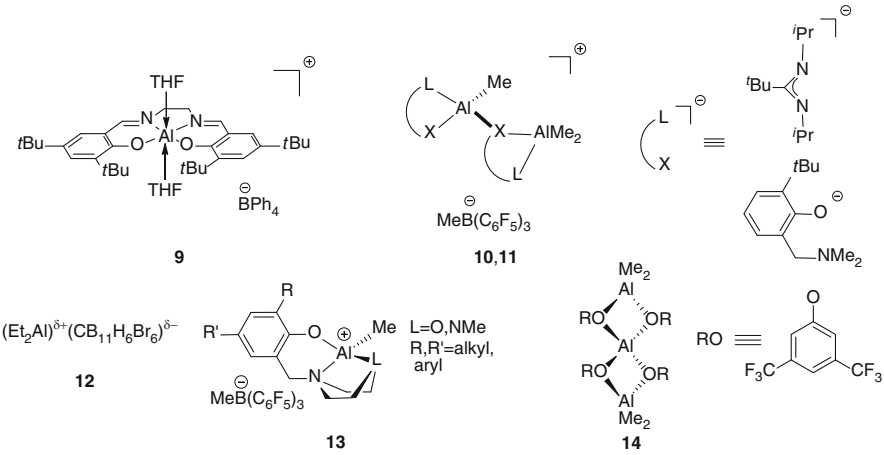


Fig. 4 Representative Al species initiating epoxide polymerization via a cationic-like mechanism

type **8** (Fig. 3) and found the dinuclear Al derivatives to be up to ten times more active than their mononuclear counterparts in the ROP of EO, which is consistent with a ROP process being favored as two metal centers are in close vicinity [40].

The bimetallic nature of Al-mediated anionic polymerization was recently further exploited by Deffieux and coworkers using simple AlR_3/nucleophile two-component catalysts for the high-speed, living and controlled polymerization of PO and epichlorohydrin to afford the corresponding well-defined regioregular polyethers. In these systems, the crucial point lies on the use of a slight excess of AlR_3 with respect to the nucleophilic source (typically a tetraalkylammonium halide salt) so that to allow coordination, and thus activation, of the monomer to AlR_3 (Scheme 9) [41, 42]. Such an approach has also been applied for the regioselective ROP of perfluoroalkyl-substituted epoxides using $Al(iBu)_3$/Nu (Nu = $[MePPh_3][Br]$, NaO*i*Pr) as a two-component initiator [43].

Various well-defined aluminum compounds, essentially cationic derivatives, have also been recently and successfully used as discrete Lewis acids for the direct cationic ROP of PO and CHO [44–49] and representative examples of such compounds are depicted above (compounds **9–14**, Fig. 4). For the most part, these electrophilic species are extremely efficient initiators for the direct ROP of epoxides such as PO and CHO, with polymerization reactions presumably

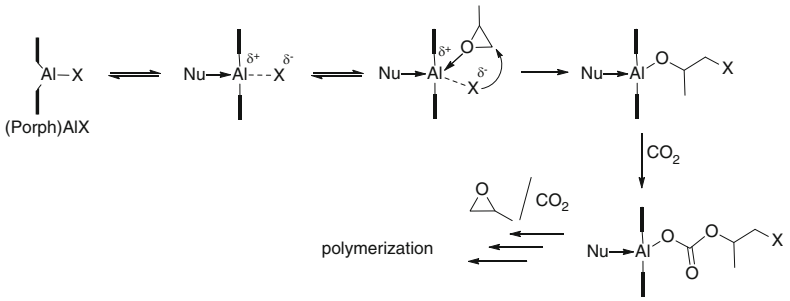
proceeding via a cationic mechanism. Nevertheless, these cationic polymerizations are poorly controlled, thus limiting the utility of such catalysts.

Overall, in the area of Al-mediated homopolymerization of epoxides, it should be noted that the design and synthesis of effective Al catalysts for the stereoselective and living ROP of substituted epoxides is essentially unexplored and thus remains an ongoing challenge as the derived materials may feature improved thermal and mechanical properties vs. their atactic analogues [50].

3.1.2 Epoxide/CO_2 Copolymerization

Although known since the late 1960s, the alternating CO_2/epoxide copolymerization has witnessed a growing attention over the past few years as a promising route to activate and use CO_2, a renewable, abundant, and inexpensive C1 source [51, 52]. Such a transformation may be carried out through the use of various ligand-supported metal catalysts [metal = Zn(II), Cr(III), Co(III), Al(III)] to access valuable aliphatic polycarbonate copolymers, of interest for their thermal and mechanical properties (high glass transition temperature and tensile strength). (Porph)AlX complexes, when combined with a nucleophilic cocatalyst (typically an ammonium/phosphine-iminium halide salt or a neutral nucleophile such as DMAP), have long been known to polymerize the controlled copolymerization of CO_2 and epoxides (primarily cyclohexene oxide or propylene oxide) with a moderate catalytic activity [53–55]. Recent improvements in the area include the following: (1) the use of (salen)AlX/nucleophile catalytic systems for the CO_2/epoxide copolymerization found to exhibit comparable catalytic features to those of (Porph)AlX [53–55] and (2) mechanistic insights into the (Porph)AlX-mediated CO_2/epoxide copolymerization [37]. In general, the thus far reported Al compounds are rather poor catalysts when compared to their Co(III) and Cr(III) analogues [51, 52]. Compound (TFPP)AlCl (in the presence of PPNCl), in which the Al center is supported by an electron-withdrawing porphino chelating ligand, lies among the most effective Al-based initiators for the CO_2/epoxide copolymerization [54, 55]. It quantitatively copolymerizes at room temperature 150 equiv. of PO and CO_2 (50 bar) to afford the corresponding polycarbonates within 24 h. As a comparison, the (TFPP)AlCl system is twice more active than the (TPP)AlCl initiator originally developed by Inoue and coworkers, thus indicating that an enhanced Lewis acidity of the Al center appears to be beneficial to catalytic activity. It should be noted that, in the absence of a nucleophilic cocatalyst, both the (salen)AlX and (Porph)AlX compounds only homopolymerize PO or CHO in the presence of CO_2, highlighting the key role of the nucleophile for CO_2 incorporation.

Detailed mechanistic studies on CO_2/epoxide promoted by various Al porphyrin initiators in the presence of a nucleophile concluded on a mono-metallic pathway with the polycarbonate chain growing on one side of the (Porph)Al backbone and with the opposite side being occupied by the Al-coordinated Lewis base cocatalyst (Scheme 10) [37]. In particular, investigations on a (TPP)AlX/DMAP catalytic systems for CO_2/PO copolymerization showed that coordination of the nucleophile/



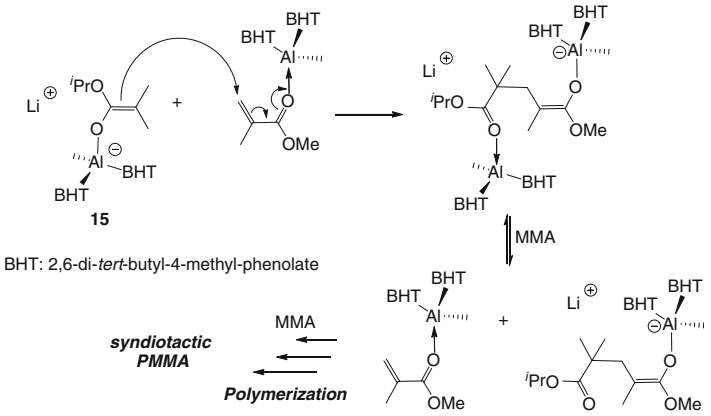
Scheme 10 Mechanism of the PO/CO_2 copolymerization mediated by (Porph)AlX species

cocatalyst (DMAP) to the Al metal center appears crucial as it promotes the insertion of CO_2 into the Al-alkoxide of the growing chain and labilizes the carboxylate ligand toward subsequent ROP of PO.

Yet, in related studies, mechanistic studies and theoretical calculations on (salen)AlX/nucleophile-mediated formation of cyclic carbonates from CO_2 and PO, the authors proposed a bi-metallic mechanism, involving a nucleophilic attack at an Al-coordinated epoxide species by an Al-bound nucleophile adduct [56]. Subsequent CO_2 insertion into the newly formed Al-alkoxide bond, likely to be the rate-determining step of the all process, would then afford the corresponding Al-carboxylate derivative. Overall, further studies are certainly required for a complete understanding of the factors controlling and affecting Al-mediated CO_2/epoxide copolymerization reactions so that to allow the development of more active Al catalytic systems.

3.1.3 Methyl Methacrylate Polymerization

Anionic organometallic initiators are routinely used to polymerize polar vinyl monomers such as methacrylates to technologically important functionalized vinyl polymers [57]. In particular, the use of alkyllithium polymerization initiators in combination with common organoaluminum compounds, the latter being often added in excess, is a well-established strategy for the production of stereoregular poly(methyl methacrylate) (PMMA) materials [58–63]. Yet, the frequent poor chain length control of the resulting material, which can be ascribed to the multisite nature of these nondiscrete initiators, results in polymers with ill-defined chain structures [64], thus prompting the development of *single site* initiators. Initial work by Inoue on the use of single-site catalysts for the controlled polymerization of methyl methacrylate (MMA) included the use of the aluminum porphyrin complex (TPP)AlMe for the living and immortal polymerization of MMA [65]. The rate of MMA polymerization by (TPP)AlMe can be substantially accelerated (by a factor of 10^4) via the addition of a sterically crowded organoaluminum Lewis acid such as DTBMA with no detrimental effects on polymer yield and chain length control

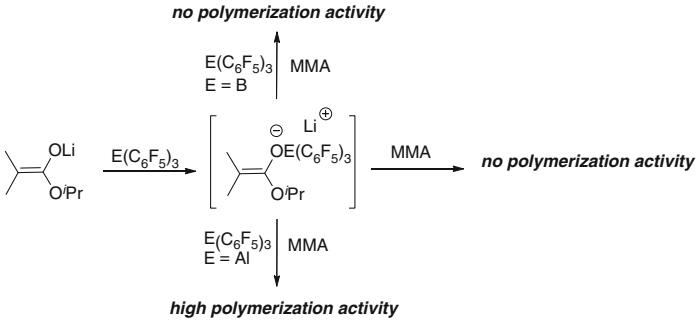


Scheme 11 Bimetallic pathway for MMA polymerization by the $MeAl(BHT)_2$/**15** two-component system

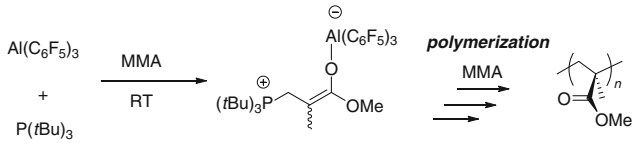
[66]. Recent reviews on the coordination polymerization of polar vinyl monomers constitute excellent and comprehensive accounts regarding the latest developments in Al-mediated alkyl methacrylate polymerization [67–69]. Noteworthy results in this area are highlighted in this section.

Intending to develop single-site anionic polymerization of MMA using discrete aluminate species, Chen and coworkers recently isolated and characterized various well-defined lithium enolaluminate complexes such as $Li^+[Me_2C = C(O^iPr)OAlMe(BHT)_2]^-$ (**15**, Scheme 11), readily generated by reaction of α-lithioisobutyrate $Li^+[Me_2C = C(O^iPr)O]^-$ with DTBMA, for subsequent use as discrete catalysts for alkyl methacrylates polymerization [70]. The well-controlled and highly active polymerization of MMA for the production of syndiotactic PMMA can be achieved using the DTBMA/**15** two-component system (1/1 ratio) and proceeds via a bimetallic chain propagation pathway, as illustrated in Scheme 11. The proposed mechanism involves an initial Michael addition of the enolaluminate propagator to the Al-activated monomer. Subsequent displacement by MMA of the ester-end-coordinated DTBMA complex regenerates the aluminate propagating species along with the MMA–DTBMA adduct. Repeated Michael additions of the propagating chain to the Al-coordinated MMA adduct produce PMMA in a controlled fashion.

Thorough kinetic studies unambiguously established these polymerizations to be first-order with respect to monomer and catalyst concentrations, which is thus consistent with a bimolecular, activated-monomer anionic polymerization mechanism via single-site ester enolaluminate propagating centers. Notably, a critical point in these initiating systems, which are typically generated upon addition of 2 equiv. of Al Lewis acids to 1 equiv. of a lithium enolester derivative, lies on the ability of the Al Lewis acids to generate both the discrete enolaluminates and the activated-monomer complexes. On that matter, among the various organoaluminum compounds tested so far, the alane $Al(C_6F_5)_3$ was found to afford the



Scheme 12 Influence of the Lewis acidic component [$B(C_6F_5)_3$ vs. $Al(C_6F_5)_3$] on the MMA polymerization initiated by lithium ester enolates



Scheme 13 Polymerization of methyl methacrylate initiated by $P(t\text{-Bu})_3/Al(C_6F_5)_3$

most active and controlled MMA polymerization system when combined with $Li^+[Me_2C = C(O^iPr)O]^-$ [70, 71]. As a comparison, under identical conditions, its boron analogue $B(C_6F_5)_3$ is inactive in MMA polymerization [72], further highlighting the suitability of Al Lewis acids for the present process (Scheme 12).

The strong Lewis acidity and steric hindrance of $Al(C_6F_5)_3$ was further exploited for MMA polymerization via the use of frustrated Lewis pairs of the type Lewis base/$Al(C_6F_5)_3$ (Lewis base = $P(t\text{-Bu})_3$, *t*-Bu-NHC, *Mes*-NHC) [73]. These pairs rapidly polymerize MMA in a somewhat controlled manner. For instance, at best, the 1/2 Lewis base/Al $P(t\text{-Bu})_3/Al(C_6F_5)_3$ yields the quantitative conversion of 800 equiv. of MMA (room temperature, <4 min) to syndiotactic-enriched high molecular weight PMMA (73.5% rr, PDI = 1.52). The polymerization is thought to proceed via the formation of zwitterionic phosphonium or imidazolium enolaluminate species that would subsequently chain grow in an analogous manner to that observed for related enolaluminate species/Al Lewis acid systems described above [67–69] (Scheme 13).

With regard to $Al(C_6F_5)_3$-mediated MMA polymerizations, one may add that: (1) zirconocenium methyl cations associated with the methyl aluminate anion $MeAl(C_6F_5)_3^-$ have also been reported to polymerize MMA for the production of syndiotactic PMMA via a process involving the formation of the enolaluminate moiety $[Me(Et)C{=}C(O^iPr)OAl(C_6F_5)_3]^-$ acting as the propagator [74, 75] and (2) a $KH/Al(C_6F_5)_3$ mixture (in 1/2 ratio) was very recently reported to effectively polymerize MMA to produce syndiotactic PMMA with a narrow molecular weight distribution (PDI = 1.04) [76]. In the latter, the implication of the aluminate salt $K^+[HAl(C_6F_5)_3]^-$ in the polymerization process has been proposed.

Unrelatedly, on a couple of occasions, the addition of $Ni(acac)_2$ to catalytically inactive $L_2AlR/AlMe(BHT)_2$ systems has been demonstrated to promote the polymerization of MMA to afford syndiotactic PMMA [77, 78].

Overall, the anionic polymerization of MMA by single-site Al-based anionic catalysts associated with an appropriate Al Lewis acid clearly witnessed significant progress over the past few years whether regarding catalytic performance or mechanistic understanding. The design and synthesis of Al-based "anionic bimetallic" initiating systems for the highly effective and controlled MMA (and related vinyl monomers) appear much more promising than the use of cationic Al species for the Lewis acid-mediated cationic polymerization MMA, which typically exhibit a low catalytic activity and afford ill-defined PMMA materials [79, 80].

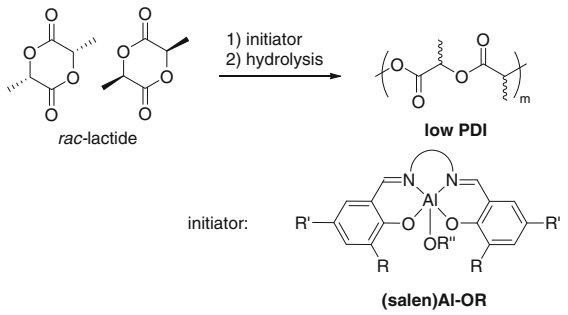
3.2 Polymerization of Cyclic Esters and Cyclic Carbonates

3.2.1 Polymerization of Cyclic Esters

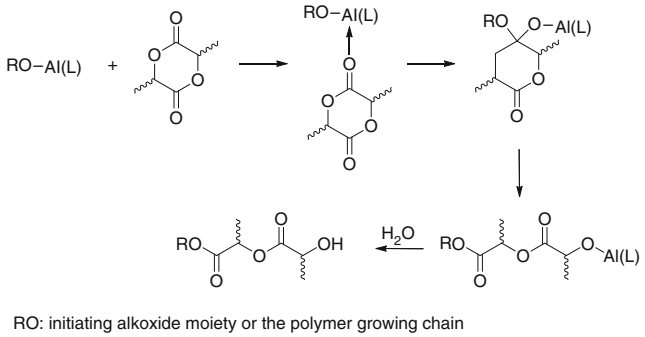
Biodegradable polyesters, such as polylactide (PLA) and poly(ε-caprolactone) (ε-PCL), have received considerable interest in recent years due to their important biomedical and pharmaceutical applications and as a viable alternative to petrochemical-based plastics [81–84]. The ROP of cyclic esters [lactide (LA), ε-caprolactone (ε-CL), for instance] by discrete metal-based alkoxide initiators [metal = Al(III), Zn(II), Sn(II), Mg(II), Ca(II), group 4 transition metals and rare earths (III)] has undoubtedly established itself as a method of choice to access well-defined, narrowly disperse and, possibly, stereoregular polyesters [85–92]. In this area, pioneering studies by Spassky and coworkers in the late 1990s on ligand-supported aluminum alkoxide species, such as (salen)AlOR derivatives (Scheme 14), historically hold a special place as some of these Al-based complexes constitute the first ROP initiators shown to stereoselectively polymerize *rac*-lactide for the production of stereoregular PLA [93, 94]. These investigations, along with those of Inoue on the living and immortal ROP of LA and ε-CL by (Porph)AlX-type complexes, paved the way to further studies in this domain [34].

As a result, the synthesis of Al alkoxides supported by various chelating ligands for their subsequent use in the ROP of cyclic esters, primarily LA, ε-CL and β-lactones, has received great attention over the past 10 years for the efficient and controlled production of well-defined and/or stereoregular polyesters. For the most part, the ROP of cyclic esters mediated by Al alkoxide species typically occurs through a well-established coordination/insertion mechanism, as depicted below (Scheme 15) [31].

Several comprehensive reviews thoroughly covering the area have recently been published in the literature [85–92]. With the exception of the most interesting and representative developments, readers can refer to reviews for exhaustive and in-depth information on the subject. In general, when compared to other alkoxide complexes of oxophilic metals initiating the ROP of cyclic esters, aluminum



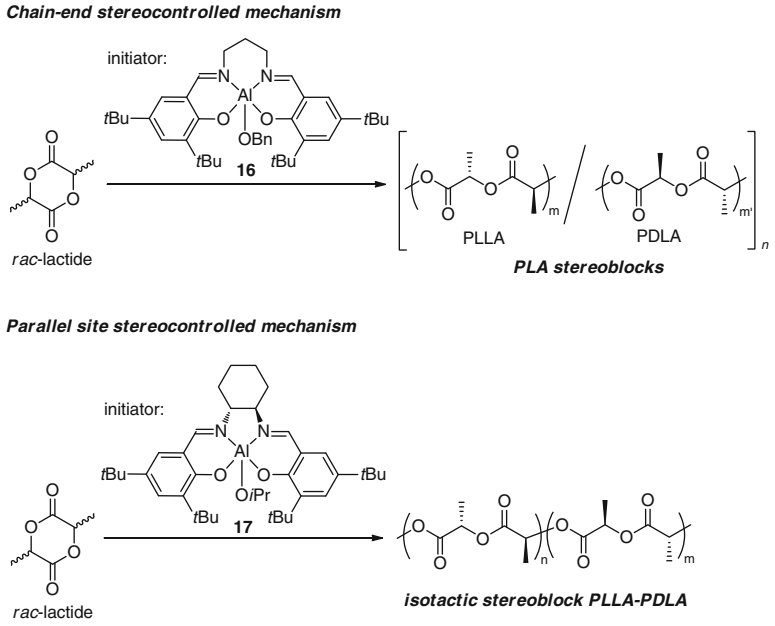
Scheme 14 Ring-opening polymerization of *rac*-lactide by (salen)Al–OR complexes



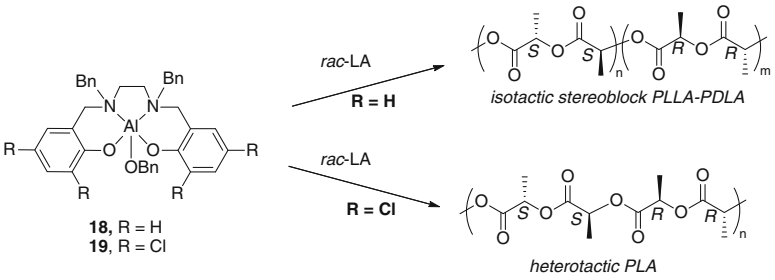
Scheme 15 General coordination/insertion mechanism for the ROP of cyclic esters initiated (taking the example of lactide) by aluminum alkoxide complexes

analogues are typically less reactive and exhibit lower catalytic activities. Rather, as shown by recent developments in the area, the attractive features of Al derivatives lie on the controlled and, most importantly, the stereocontrolled character they may promote upon initiating the ROP of racemic cyclic esters such as *rac*-lactide.

In principle, *rac*-lactide, a racemic mixture of D- and L-lactide, may be polymerized in a stereoselective fashion. Depending on the stereoselection as the ROP proceeds, the resulting polymer may thus exhibit different stereoregularities; these directly influence the thermal and mechanical properties of the produced PLAs. In this regard, isotactic PLA stereoblocks and PLA stereocomplexes, which are of interest for their thermal and mechanical properties, may be produced via the ROP of *rac*-lactide initiated by an achiral derivative, provided the polymerization proceeds via a chain-end stereocontrolled mechanism; i.e., the last inserted lactide unit stereo-controls the insertion of the incoming monomer. This strategy has been first validated using salen-based aluminum complexes such as **16** (Scheme 16, top) to produce PLLA–PDLA isotactic stereoblocks [95, 96]. Alternatively, the chiral racemic salen aluminum complex **17** was found to be suitable for the parallel stereoselective synthesis of isotactic poly(D-lactide) and poly(L-lactide) from *rac*-



Scheme 16 Aluminum-based initiators for the stereoselective ROP of *rac*-lactide



Scheme 17 Tacticity switch in the ROP of *rac*-lactide initiated by (salen)Al–OR complexes

lactide (Scheme 16, bottom) to eventually yield PLLA–PDLA isotactic stereoblocks [97–101]. In this case, each enantiomer of the aluminum catalyst preferentially polymerizes one lactide enantiomer via a metal-site (or enantiomorphic) stereocontrolled mechanism.

A remarkable and unprecedented stereocontrol switch has also been achieved in the ROP of *rac*-lactide initiated by aluminum complexes supported by tetradentate aminophenoxide salan-type ligands (Scheme 17). Thus, apart from the well-controlled and living character of these ROP reactions, it was found that the

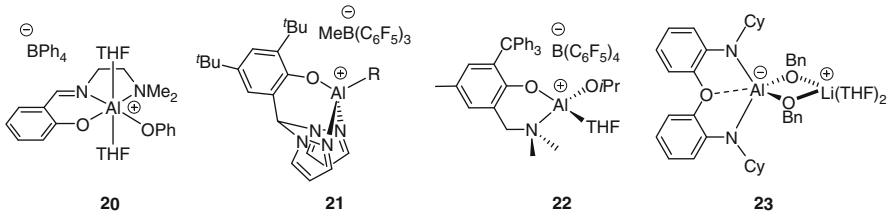


Fig. 5 Representative cationic and anionic Al complexes initiating the ROP of cyclic esters

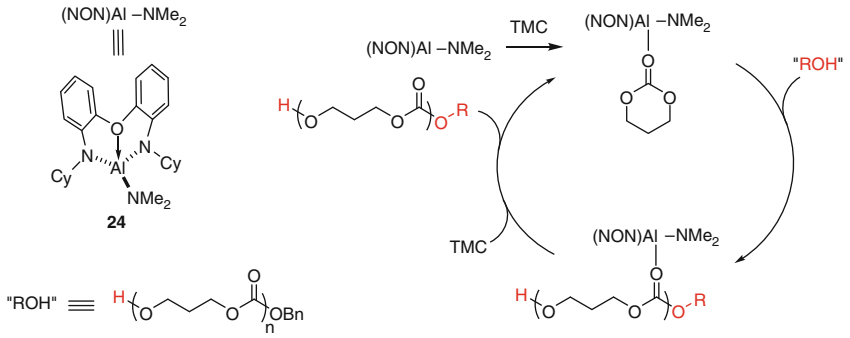
Al initiator **18** affords highly isotactic PLA while its analogue **19** yields highly heterotactic PLA [102]. This dramatic switch in PLA tacticity first clearly illustrated that the chelating ligand substitution pattern, including that of remote substituents, may be crucial both to the nature and the level of stereocontrol in these ROP reactions.

While the vast majority of Al-based ROP initiators of cyclic esters are neutral derivatives, several reports have recently highlighted that ligand-supported cationic or anionic Al complexes may mediate the polymerization of cyclic esters such as LA and ε-CL. For instance, the Al cations **20**–**22** (Fig. 5), thought to be of interest for their enhanced Lewis acidity, indeed exhibit an excellent activity in the ROP of ε-CL, but are all inactive in the ROP of *rac*-lactide [19, 103, 104]. In contrast, the Al alkoxide anion **23** (Fig. 5), which incorporates two nucleophilic alkoxide moieties, was found to polymerize lactide in a controlled manner and under milder conditions (room temperature) than those typically required for neutral Al alkoxide analogues [105].

3.2.2 Polymerization of Cyclic Carbonates

Aliphatic polycarbonates are currently receiving attention due to their biomedical and pharmaceutical applications arising from their biocompatibility and biodegradability. Of special interest, poly(trimethylene carbonate) (PMTC), produced by the ROP of trimethylene carbonate (TMC), is being investigated as drug-delivery vehicles and flexible suture materials [84].

The ROP of TMC mediated by discrete Al compounds has recently been the subject of a few studies so that to access well-defined and narrowly disperse PTMC through precise chain length control. In this area, it was shown that (salen)Al–OR compounds may readily polymerize TMC, presumably via a coordination/insertion mechanism similar to that taking place in Al-mediated ROP of cyclic esters (vide supra), to afford ill-defined PTMC materials (PDI $>$ 1.5), likely reflecting a poorly controlled ROP process [106, 107]. In contrast, the use of Al Lewis acid/ROH two-component initiators for the ROP of TMC, such as $Al(OTf)_3$/ROH and **24**/ROH (Scheme 18), was very recently demonstrated to be a superior approach for the production of chain-length controlled and tailor-made PTMC material [108, 109].

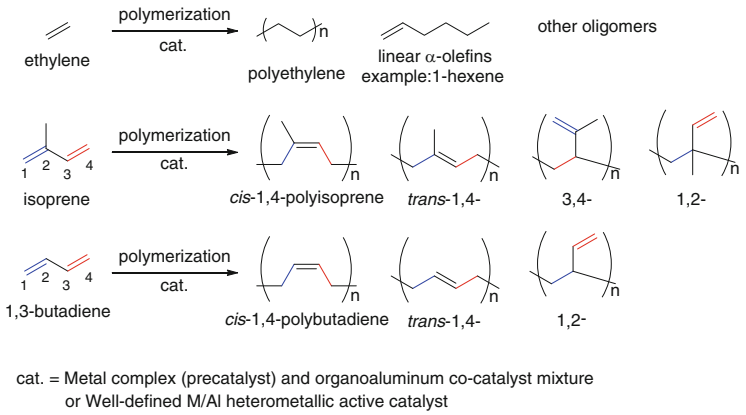


Scheme 18 Controlled and immortal ROP of TMC by **24**/BnOH via an activated-monomer mechanism

For instance, the **24**/BnOH initiating system polymerizes TMC in a highly controlled, immortal manner and under mild conditions (room temperature). Unlike that mediated by (salen)Al–OR, the ROP of TMC performed by **24**/BnOH is thought to proceed via an activated-monomer mechanism, as illustrated in Scheme 18.

4 Recent Developments on Organoaluminum Species as Cocatalysts in Olefin Polymerization

Ziegler–Natta-type ethylene polymerization catalysts were initially based on a $TiCl_4/AlEt_2Cl$ system. Since their discovery, most of catalytic systems reported for olefin polymerization combine a transition metal salt or complex and an aluminum cocatalyst. In this area, catalyst activity and selectivity are strongly dependent upon the structure and the stoichiometry of the aluminum activator. Numerous investigations have been thus carried out to gain insight into the role of the organoaluminum compounds in the formation of the catalytically active species. For the most part, it is now well established that the Al cocatalyst may act as a Lewis acid, alkylating, and/or reducing agent. This part aims at highlighting representative results and recent achievements on the use of well-defined and characterized M/Al polynuclear species in olefin polymerization catalysis (Scheme 19).



Scheme 19 Olefin polymerization reactions discussed in this section

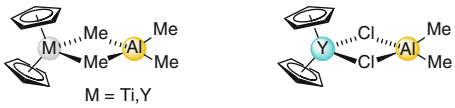


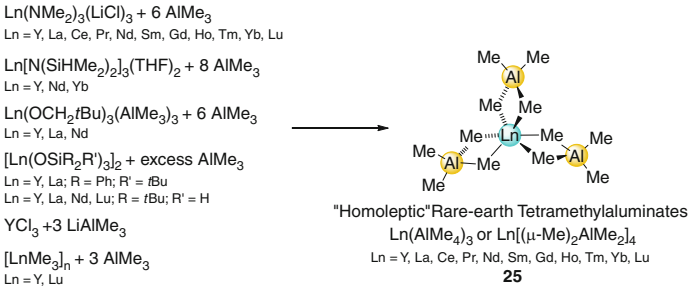
Fig. 6 First structurally characterized alkyl- or chloride-bridged M/Al complexes

4.1 Group 3 and Lanthanide/Organoaluminum Species

Following initial studies on the $(C_5H_5)_2TiCl_2/Et_2AlCl$ system for ethylene polymerization, the alkylation of Ti(III) and Ln(III) species by organoaluminum reagents was thoroughly studied by Pearce and Lappert in the late 1970s (Fig. 6) [110, 111]. These initial structural studies constituted the basis for the *Lanthanide Ziegler–Natta Model* and encouraged subsequent work on the structural elucidation of products arising from the reaction of rare-earth metal complexes and organoaluminum derivatives. Fischbach and Anwander comprehensively reviewed the subject in 2006 and an additional contribution by Zimmerman and Anwander on rare-earth complexes containing organolanthanides fragments was provided in 2010 [112, 113]. We here focus on recent, representative and significant examples of structurally characterized rare-earth metal/organoaluminum complexes of interest as (pre)catalysts in olefin polymerization.

4.1.1 Homoleptic Rare-Earth Tetramethylaluminate Precursors

Rare-earth tetramethylaluminate complexes have been identified as key intermediates in Ziegler–Natta-type olefin polymerization and may be readily prepared by reaction of rare-earth precursors with organoaluminum reagents [112]. The first homoleptic $Ln(AlR_4)_3$ species (Ln = Y, Nd; R = Me) were reported by Evans et al. in 1995 [114]. The synthesis of these heterobimetallic



Scheme 20 Different synthetic methods for the preparation of "homoleptic" rare-earth tetramethylaluminate complexes

Table 1 Polymerization of isoprene with $Ln(AlMe_4)_3$ precatalysts of type **25**

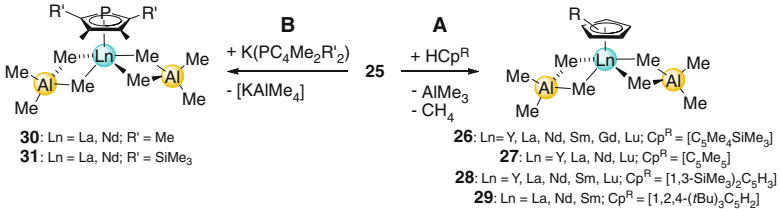
Ln[a]	Et_2AlCl[b] (equiv.)	Yield[c] (%)	*Cis*-1,4[d] (%)	M_n[e] ($\times 10^{-3}$)	PDI[e]	Ln[a]	Et_2AlCl[b] (equiv.)	Yield[c] (%)	*Cis*-1,4[d] (%)	M_n[e] ($\times 10^{-3}$)	PDI[e]
Y	2	97	75.9	101	3.95	Pr	1	>99	>99	386	1.90
La	1	92	>99	128	4.25	Pr	2	>99	>99	320	2.30
La	2	99	>99	184	3.26	Nd	1	>99	>99	228	3.45
Ce	1	>99	>99	160	2.41	Nd	2	>99	>99	117	2.78
Ce	2	>99	>99	152	3.08	Gd	2	>99	>99	146	2.58

[a]General conditions: 8 mL hexane, 0.02 mmol precatalyst, 0.02–0.04 mmol Et_2AlCl, 20 mmol isoprene, 24 h, $T = 40°C$
[b]Catalyst preformation 30 min at room temperature
[c]Gravimetrically determined
[d]Determined by ^{13}C NMR
[e]Determined by gel permeation chromatography (GPC) with polystyrene standards

complexes is now described for a large variety of rare-earth(III) centers, starting from various precursors (Scheme 20) [112, 113, 114–116]. Since the synthesis of such complexes is now well established and involves good yield procedures, they have been used as starting reagents to (1) develop novel olefin polymerization catalysts and (2) gain a better understanding of the role of organoaluminum cocatalyst in polymerization catalysis (see sections below).

When treated with Et_2AlCl as a cocatalyst, $Ln(AlMe_4)_3$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd) afforded highly active and selective catalysts for isoprene (IP) polymerization affording poly(isoprene) (PIP) with a 1,4-*cis* structure (Table 1) [116, 117]. The best results were generally observed with the use of 2 equiv. of cocatalyst.

NMR investigations on the Ln/Et_2AlCl catalyst mixture evidenced the presence of various alkylated products (in accordance with a chloride transfer from the Al center to the alkylated rare-earth metal center). Compounds of type $[Me_2LnCl]_n$/$[MeLnCl_2]_n$ have been suggested as possible active catalysts in the industrial diene



Scheme 21 Synthesis of half-sandwich rare-earth bis(tetramethylaluminate) complexes from homoleptic tris(tetramethylaluminate) rare-earth precursors

Table 2 Isoprene polymerization by half-sandwich bis(tetramethylaluminate) precatalysts **26**–**31**

					Selectivity (%)[c]				
Precatalyst[a]	Cocatalyst[b]	Time (h)	Temperature (°C)	Yield (%)	*Trans*-1,4	*Cis*-1,4	3,4-	M_n[d] ($\times 10^5$)	PDI[d]
26: La	A	24	40	>99	95.6	2.2	2.2	2.0	1.26
27: Y	A	24	40	>99	93.6	1.9	4.5	0.9	1.78
27: La	A	24	40	>99	99.5	–	0.5	2.4	1.18
27: Nd	A	24	40	>99	92.4	3.8	3.8	1.3	1.35
28: La	A	24	40	>99	89.3	–	10.7	3.3	1.52
29: La	A	24	40	>99	90.0	6.0	4.0	1.1	1.41
30: La[e]	B	2	30	90	87	8	5	0.5	2.33
31: Nd[e]	B	2	30	>99	50	18	32	0.4	1.68

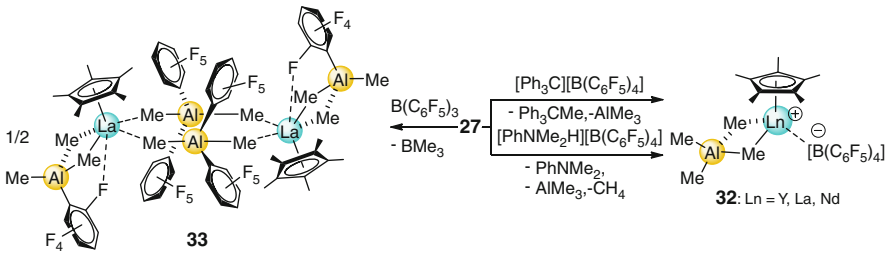
[a]General conditions: 8 mL toluene, 0.02 mmol precatalyst, 1 equiv. cocatalyst, 20 mmol isoprene
[b]Cocatalyst: A = $B(C_6F_5)_3$, B = $[PhNMe_2H][B(C_6F_5)_4]$; catalyst preformation 20 min at 40°C
[c]Determined by ^1H and ^{13}C NMR in $CDCl_3$
[d]Determined by GPC with polystyrene standards
[e]Catalyst preformation: 15 min at 30°C

polymerization process using $Nd(AlMe_4)_3/Et_2AlCl$ mixtures [118], yet with no clear-cut structural characterization supporting the proposed formulation.

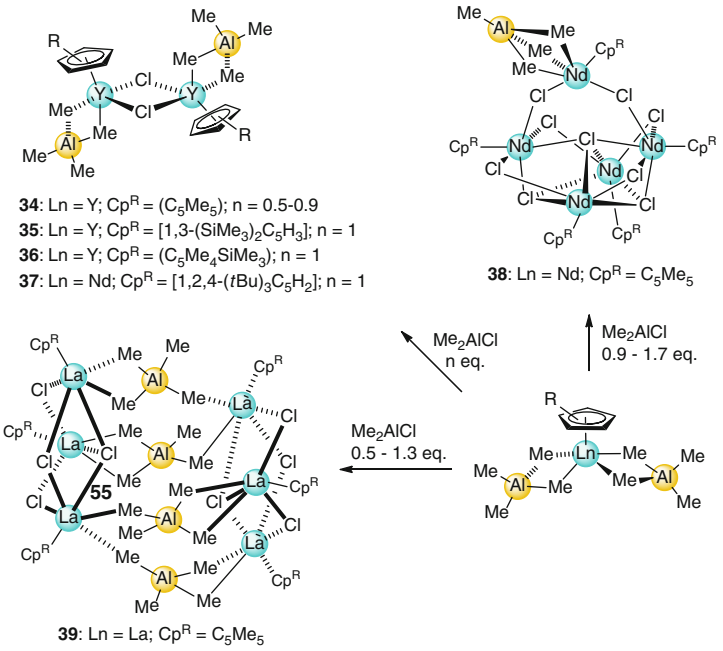
4.1.2 Half-Sandwich Rare-Earth Tetramethylaluminate Precursors

Various half-sandwich rare-earth bis(tetramethylaluminate) complexes have been readily synthesized by methane elimination reactions between $Ln(AlMe_4)_3$ derivatives and appropriate HCp^R ligands (Scheme 21, **A**) [119–121]. Reaction of homoleptic tetramethylaluminate derivatives with phospholide salts also allowed access to the corresponding half-sandwich bis(tetramethylaluminate) complexes through a salt-metathesis route (Scheme 21, **B**) [122].

Upon activation with boron cocatalysts, these half-sandwich heterobimetallic complexes were found to be efficient catalysts for IP polymerization, with a selectivity strongly dependent on the size of the metal center, the Cp substituents, and the nature of the cocatalyst (Table 2) [119, 122].

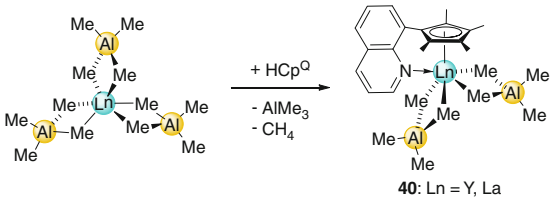


Scheme 22 Reactivity of half-sandwich tetramethylaluminates toward various cationizing reagents



Scheme 23 Reactivity of half-sandwich tetramethylaluminates toward Me_2AlCl

Anwander et al. worked on the identification of the active species formed upon treatment of the $Ln(Cp^R)(AlMe_4)_2$ with boron activators [123]. Cationization with activators such as $[Ph_3C][B(C_6F_5)_4]$ and $[PhNMe_2H][B(C_6F_5)_4]$ quantitatively produced the corresponding $[Ln(Cp^R)(AlMe_4)][B(C_6F_5)_4]$ complexes (**32**, Scheme 22). NMR investigations on the latter showed the presence of highly electron-deficient rare-earth metal centers and suggested the existence cation/anion interactions. In contrast, when the mono(Cp^R) bis(tetraaluminate) lanthanum complex was treated with $B(C_6F_5)_3$, the dimeric ion pair $[\{[(C_5Me_5)La\{(\mu\text{-}Me)_2AlMe(C_6F_5)\}][Me_2Al(C_6F_5)_2]\}_2]$ (**33**, Scheme 22) instantly and quantitatively formed, as unambiguously established by XRD studies. The salt species **33** behaves as a single component IP



Scheme 24 Synthesis of $[(Cp^Q)Ln(AlMe_4)_2]$ from homoleptic tetramethylaluminate precursors

Table 3 Isoprene polymerization with $[(Cp^Q)Ln(AlMe_4)_2]$ precursors

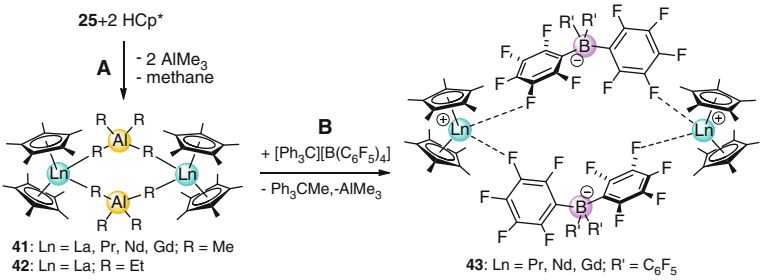
					Selectivity (%)[c]				
Precatalyst[a]	Cocatalyst[b]	Solvent	Time (h)	Yield (%)	*Trans*-1,4	*Cis*-1,4	3,4-	M_n[d] ($\times 10^5$)	PDI[d]
40: Y	A	Tol.	2	>99	85.9	1.3	12.8	7.4	1.14
40: Y	B	Hex.	2	>99	88.4	0.6	11.0	9.2	1.07
40: La	B	Hex.	24	>99	93.1	2.1	4.9	15.9	1.28

[a]General conditions: 8 mL (toluene or hexane), 0.02 mmol precatalyst, 1 equiv. cocatalyst, 20 mmol isoprene, $T = 40°C$
[b]Cocatalyst: A = $[Ph_3C][B(C_6F_5)_4]$, B = $[PhNMe_2H][B(C_6F_5)_4]$; catalyst preformation 30 min at 40°C
[c]Determined by ^1H and ^{13}C NMR in $CDCl_3$
[d]Determined by GPC with polystyrene standards

polymerization catalyst and selectively produces (99%) *trans*-1,4-polyIP in high yield (>99%) with narrow polydispersity (PDI = 1.19) [123].

Further investigations on $Ln(Cp^R)(AlMe_4)_2$ derivatives allowed the isolation of unusual and structurally interesting compounds. Thus, treatment of the half-sandwich tetramethylaluminates with Me_2AlCl afforded mixed tetramethylaluminate/chloride compounds (Scheme 23) [116, 124]. For the less crowded Cp^R ligand ($Cp^R = C_5Me_5$), the nature of the final product was found to be influenced by the size of the rare-earth metal center. While the small Y center afforded a chloro-bridged dimer $[Y_2Al_2]$ (**34**), larger centers, such as La and Nd, yielded higher nuclearity assemblies, $[La_6Al_4]$ (**39**) and $[Nd_5Al]$ (**38**), respectively [124]. In the case of more sterically hindered Cp^R rings ($Cp^R = [1,3\text{-}(SiMe_3)_2C_5H_3]$, $(C_5Me_4SiMe_3)$, or $[1,2,4\text{-}(t\text{-}Bu)_3C_5H_2]$), the formation of dimeric structures (**35**–**37**) is favored [116].

To conclude this section, one should highlight recent studies on N-functionalized cyclopentadienyl ligands. The $[(Cp^Q)Ln(AlMe_4)_2]$ precatalysts (**40**), generated via a protonolysis reaction of $Ln(AlMe_4)_3$ with HCp^Q (Scheme 24), were reported to be active in IP polymerization under various conditions (cocatalyst, solvent, temperature, time) and the best results are summarized in Table 3 [125]. Allyl-lanthanides complexes of an N-functionalized Cp* (N = amino) were also reported by Cui et al. to be efficient catalysts for the living and block copolymerization of IP in the presence of organoaluminum (5–70 equiv.) and boron cocatalysts [126].



Scheme 25 Synthesis of rare-earth metallocene via a protonolysis pathway (**A**) and subsequent formation of cationic lanthanidocenes as borate salts (**B**)

4.1.3 Rare-Earth Metallocene Tetraalkylaluminate Precursors

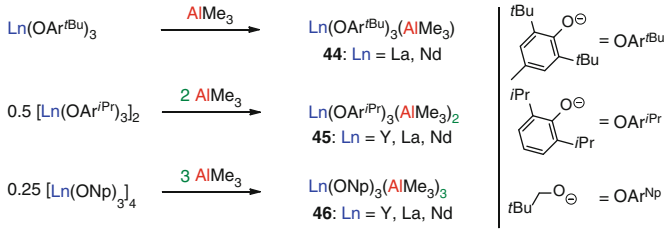
The synthesis of rare-earth metallocene tetraalkylaluminates was first reported in the late 1980s [112, 127]. Yet, the protonolysis reaction of $La(AlMe_4)_3$ or $La(AlEt_4)_3$ with HCp* was only recently applied to the formation of bismetallocene tetraalkylaluminates $[(Cp^*)_2La(AlR_4)]$ (Scheme 25, **A**) [128, 129]. This is an interesting finding since complexes $[(Cp^*)_2Ln(AlMe_4)]_2$, dimeric in the solid state, can be ionized to afford efficient catalysts for the selective polymerization of butadiene (BU) (Scheme 25, **B**) [130–132]. For instance, when activated with 5 equiv. iBu$_3$Al as cocatalyst, the Gd derivative of type **43** polymerizes 500 equiv. BU within 3 min at 50°C to afford a PBU material with a 97.5% *cis*-1,4-selectivity, along with a narrow polydispersity (PDI = 1.73) [129].

4.1.4 Rare-Earth Aryl-, Alk-, or Siloxide Alkylaluminate Precursors

The formation and characterization of rare-earth Ln–OR (R = aryl-, alkyl-, or silyl-) alkyl aluminate complexes have been reviewed [112, 113]. These complexes are essentially accessible via two routes: (1) alkylaluminum adduct formation starting from a homoleptic rare-earth aryl(alk)oxide precursor and (2) protonolysis of the corresponding phenol/alcohol/silanol source by alkane elimination. The outcome of the reaction between homoleptic aryl(alk)oxides with $AlMe_3$ is determined by the bulkiness of the aryl(alk)oxide ligand (Scheme 26) [133]. In the resulting dinuclear complexes, the TMA units are linked through (μ-OR) and (μ-Me) bridges.

The protonolysis reaction of $Sm(AlMe_4)_3$ (generated in situ) with a sterically hindered bis-phenol was reported to yield the dimeric bis(aryloxide) samarium(III) tetramethylaluminate **47** (Fig. 7), found to behave as a single-component ethylene polymerization catalyst for the production of UHMWPE (600 psi ethylene, 70°C) [134].

The aryl(alk)oxide heterometallic complexes of types **44**–**46** and the siloxide derivative **48** were tested in IP polymerization [116, 133]. While the mono-TMA



Scheme 26 Synthesis of TMA adducts of rare-earth aryl(alk)oxide species

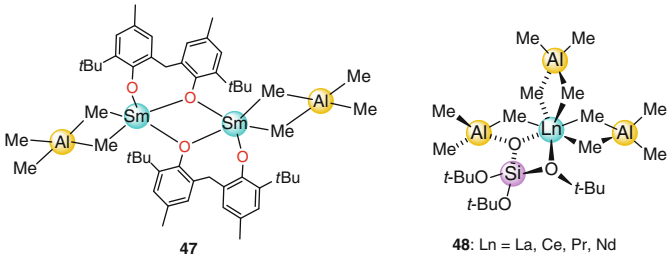


Fig. 7 Dimeric Sm(III) bis(aryloxide) (**47**) and heteroleptic rare-earth siloxide alkylaluminate complexes (**48**)

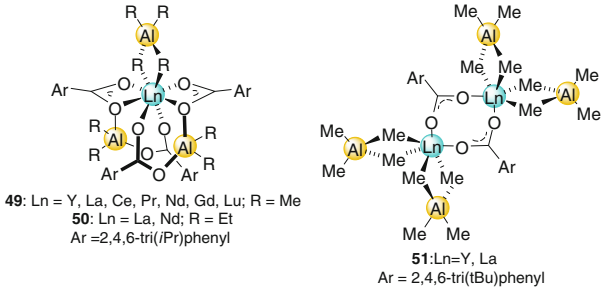


Fig. 8 Mixed carboxylate-alkylaluminate catalyst precursors active in olefin polymerization

adducts **44** are inactive, the Nd derivatives of both the bis- and tris-TMA adducts (**45** and **46**, respectively) as well as some derivatives of type **48** (Fig. 7) feature an excellent polymerization activity upon activation with 1–2 equiv. of Et_2AlCl (1,000 equiv. IP, 24 h, 40°C, quantitative conversion, >98% selective in *cis*-1,4-enchainments).

4.1.5 Rare-Earth Carboxylate Alkylaluminate Precursors

The excellent polymerization activity of Ln–OR derivatives prompted further studies in the area. In particular, the synthesis of mixed [OCO^-]-carboxylate/

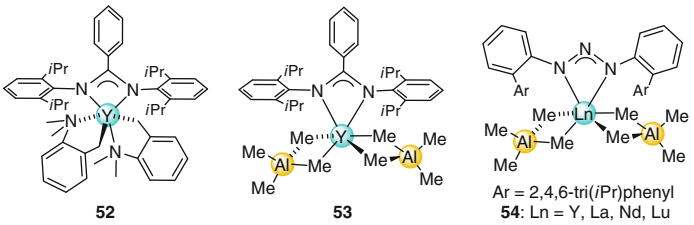
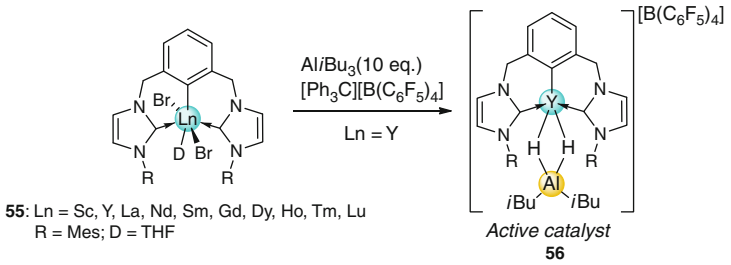


Fig. 9 Rare-earth monoanionic [NN] precursors showing activity in olefin polymerization



Scheme 27 Well-defined [CCC]-pincer bis-NHC lanthanide complexes active in isoprene polymerization

alkylaluminates heterobimetallic precursors has been investigated [116, 135]. Those exhibiting the highest activities in Ziegler–Natta-type olefin polymerization are depicted in Fig. 8 [112, 113, 116, 135]. As may be anticipated, the nuclearity and connectivity of the formed heterobimetallic complexes are directly influenced by the bulkiness of the carboxylate ligand. IP polymerization catalyzed by species **49**–**51** in the presence of various amounts of DEAC (2–3 equiv.) proceeded with good activity (1,000 equiv. IP within 24 h at 40°C) and a high selectivity for a *cis*-1,4-structured PIP (>95.6%).

4.1.6 Other Rare-Earth Precursors Containing Mono- or Dianionic Ligands

Over the past few years, rare-earth metal/aluminum precursors bearing mono- or dianionic, chelating or pincer ligands have received an increasing attention; yet, to date, most of them have not been evaluated in olefin polymerization [112, 113]. Representative examples of mono-anionic–[NN] complexes of rare-earth metals tested in Ziegler–Natta-type polymerization are included in Fig. 9 [136, 137]. For catalyst **52**, the selective formation of a 3,4-structure PIP (>96%) was observed using either $AlEt_3$ or $AliBu_3$ as a cocatalyst. In contrast, when TMA was used as a cocatalyst, the selective formation of *cis*-1,4-structured PIP proceeded in high yield (>91%). Complex **53** preferentially produced *cis*-1,4-PIP in the absence of an Al cocatalyst or using TMA as a cocatalyst [137]. Precatalysts of the type **54** exhibit a

good activity in IP polymerization after activation with a boron-based cocatalyst, but with a moderate selectivity (<92% *trans*-1,4) [136].

We conclude this section by the recent investigations of Lv and Cui. These authors reported on the synthesis and highly selective *cis*-1,4 polymerization of IP promoted by [CCC^{-}]-pincer bis-NHC rare-earth complexes (Scheme 27) [138]. The presumed active species, containing two Al-(μ-H)-Y bridging hydrides, was characterized upon mixing the yttrium precatalyst of type **55** with Al(*i*Bu)$_3$ (10 equiv.) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (Scheme 27, **56**). The binary systems consisting of complexes **55** (Y, Nd, Gd or Dy)/TEA were found to be best suited for IP polymerization (500 equiv. IP, 15–30 min, room temperature, quantitative conversion, 96.3–98.6% *cis*-1,4-selectivity, 1.73 < PDI < 2.27). It is noteworthy that the isolated "active catalyst" **56** polymerizes IP with comparable activity and selectivity but with an improved polymerization control vs. the in situ formed catalyst (PDI = 2.83 vs. 3.81).

4.2 Group 4/Organoaluminum Species

4.2.1 Group 4 Metallocenes, Half-Metallocenes and Associated Derivatives

In 2001, Chen and coworkers reported unprecedented "double activation" reactions between group 4 dialkyl complexes and the strong Lewis acid Al(C$_6$F$_5$)$_3$ [139]. Thus, the reaction of CGC-TiMe$_2$ [CGC = Me$_2$Si(η^5-Me$_4$C$_5$)(*t*-BuN)] and SBI-ZrMe$_2$ [SBI = *rac*-Me$_2$Si(η^5-Ind)$_2$] with 1 equiv. of Al(C$_6$F$_5$)$_3$ afforded the corresponding stable and isolable cationic complexes CGC-TiMe(μ-Me)Al(C$_6$F$_5$)$_3$ and SBI-ZrMe(μ-Me)Al(C$_6$F$_5$)$_3$, respectively (**57**, Fig. 10). Interestingly and unlike its boron analogue B(C$_6$F$_5$)$_3$, a second equiv. of Al(C$_6$F$_5$)$_3$ was found to further ionize species **57** to form the dicationic bis-aluminate complexes CGC-Ti[(μ-Me)Al(C$_6$F$_5$)$_3$]$_2$ and SBI-Zr[(μ-Me)Al(C$_6$F$_5$)$_3$]$_2$ (**58**, Fig. 10). The structures of complexes **57** and **58** were confirmed by XRD. The influence of such a double activation on catalytic activity was evaluated in ethylene/1-octene copolymerization at 140°C by in situ activation of the dialkyl precatalysts using various amounts of Al(C$_6$F$_5$)$_3$. Higher Al/Ti ratios increased both the initial polymerization exothermicity (from 0.3°C to 30.6°C) and efficiency (from 0.32 to 2.40 g polymer/μg Ti). A similar behavior was observed with the Zr precatalyst, which produced a high-density copolymer (d = 0.926). More recently, the zirconocene species **59**, prepared via reaction of Cp*$_2$ZrMe$_2$ with B(C$_6$F$_5$)$_3$ and AlMe$_3$, was also characterized [140]. Solid state and NMR data as well as DFT calculations support the formation of Cp*$_2$ZrMe^{+}/Me Al(C$_6$F$_5$)$_3^{-}$ ion pairs for compound **59**.

Roesky and coworkers studied the reactivity of commonly used olefin polymerization group 4 precatalysts, such as Cp$_2$MMe$_2$ and Cp*MMe$_3$, toward well-defined organoaluminum hydroxide reagents to access the corresponding Al/group 4 metal complexes bearing methylaluminoxane-type cores [141–145]. Complex **60** reacted with Cp$_2$MMe$_2$ and Cp*MMe$_3$ via a methane elimination pathway to afford the

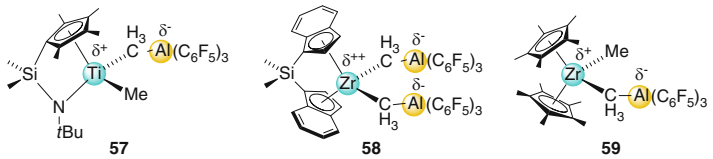
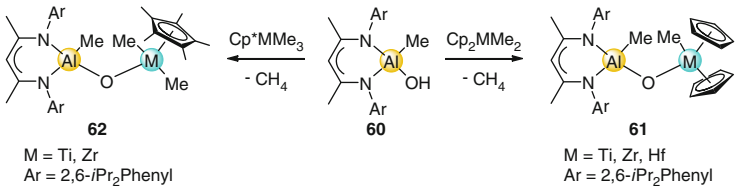
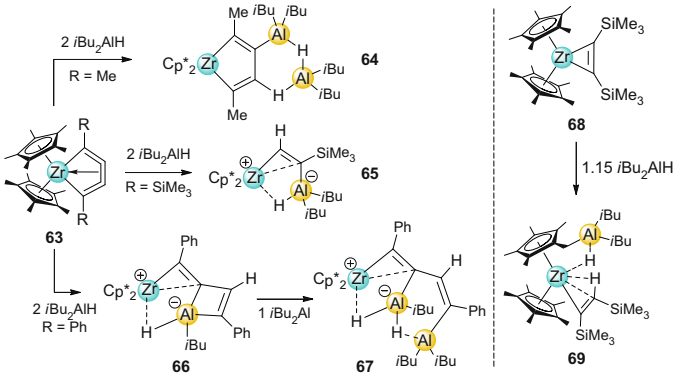


Fig. 10 Examples of ion pairs resulting from simple and double activation of group 4 metallocene complexes with $Al(C_6F_5)_3$



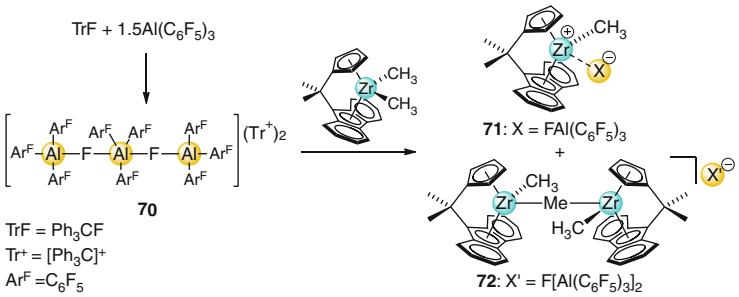
Scheme 28 Synthesis of Al–O–M Al/group 4 metallocenes heterobimetallic complexes for use in ethylene polymerization



Scheme 29 Reactivity of organozirconocene complexes towards $i\text{Bu}_2\text{AlH}$ reagent

oxo-bridged bimetallic complexes of type **61** and **62** (Scheme 28). These complexes were tested in ethylene polymerization with additional use of MAO and found to be more active than standard metallocene catalysts. In particular, the Zr derivative of **61** was reported to be significantly more efficient (by an order of magnitude of 2) than Cp_2ZrMe_2 [141]. The introduction of a chemically grafted (Me)Al–O moiety thus clearly appears to be beneficial to catalytic activity.

Rosenthal, Baumann, and coworkers investigated the reactivity of organozirconocene complexes (**63** and **68**) toward di-*iso*butylaluminum hydride and evaluated the resulting mixture in ethylene polymerization [146, 147]. The structure of heterometallic complexes **65–67** and **69** could be unambiguously



Scheme 30 Synthesis and reactivity of a polynuclear perfluoroarylaluminum cocatalyst

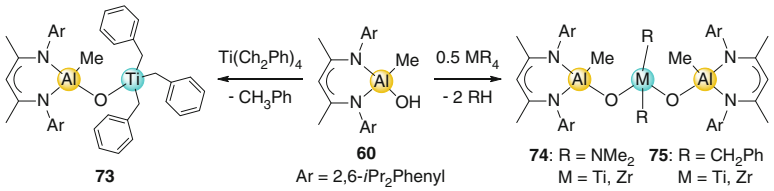
determined by XRD, while that of **64** was deduced from NMR data and chemical derivatization with CO_2 (Scheme 29). The interesting feature of complexes **64**, **65**, **67**, and **69** lies on their ability to polymerize ethylene in the absence of any additional cocatalyst, with the production of up to 220 kg of PE/(mol h). Yet, for complexes **64** and **65**, a thermal activation (90°C, 2 h) is required for the polymerization to proceed [146, 147].

In 2004, Marks and coworkers reported the synthesis of a novel polynuclear perfluoroarylaluminum cocatalyst **70**, which was subsequently reacted with an *ansa*-zirconocene precursor [148]. NMR data of the resulting mixture are consistent with the formation of two products: i.e., monomeric complex **71** and the μ-Me Zr dimer **72** (Scheme 30), indicating that the Al species **70** acts as an alkyl abstracting agent. The in situ generated **71/72** mixture efficiently and stereoselectively polymerizes propene for the production of highly syndiospecific polypropylene [activity: 7.9×10^6 g polymer/((mol of catalyst) atm. h) in 3 min at 25°C, 89.3% rrrr] [148].

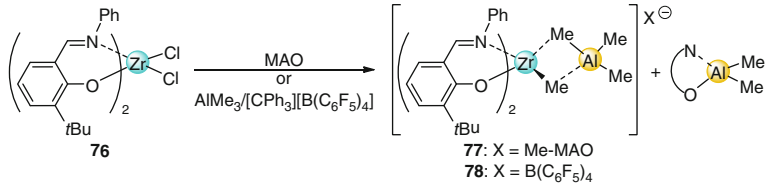
4.2.2 Group 4 Non-metallocenes

Recent work on the reactivity of non-metallocene group 4 precursors toward the organoaluminum hydroxide derivative **60** should also be briefly highlighted. By analogy with the metallocene derivatives (see Sect. 4.2.1) [141, 149, 150], the objective was to generate heterometallic complexes containing a methylaluminoxane core (Me)Al–O–M, taking advantage of the acidic character of the Al–OH moiety. This concept was successfully applied to the formation of bimetallic Al–O–M species **73** and trimetallic Al–O–M–O–Al complexes **74** and **75** (Scheme 31). These complexes only exhibited a low (for catalysts **73** and **75**) to moderate (catalyst **74**) activity in ethylene polymerization [149, 150].

The reaction of bis(phenoxyimino)zirconium dichloride precursors with MAO or mixture of $AlMe_3$/$[CPh_3][B(C_6F_5)_4]$ was also thoroughly NMR investigated by Talsi and coworkers [151]. Activation of the *t*-Bu precursor **76** with MAO resulted in a mixture of the heterobimetallic ion pair **77** and the ligand transfer product [$(NO^{tBu})AlMe_2$] (Scheme 32). Complex **77** was found to be unstable at room temperature as it



Scheme 31 Synthesis of Al–O–M group 4/Al heterobi- and heterotrimetallic non-metallocene complexes for use in ethylene polymerization

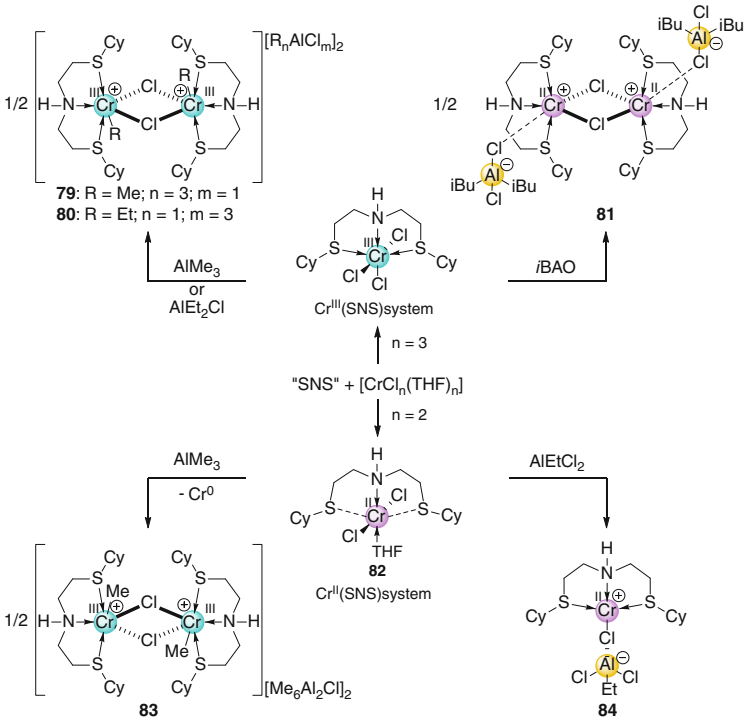


Scheme 32 Activation of $(NO^{tBu})ZrCl_2$ with MAO or $AlMe_3/[CPh_3][B(C_6F_5)_4]$

rapidly decomposes to $[(NO^{tBu})AlMe_2]$ and other side products. The identity of species **77** was further confirmed via reaction of precursor **76** with a 10/1 $AlMe_3/[CPh_3][B(C_6F_5)_4]$ mixture that led to the quantitative formation of the ion pair species **78** (Scheme 32). Both **76**/MAO and **76**/$AlMe_3/[CPh_3][B(C_6F_5)_4]$ exhibited high ethylene polymerization activities (1,820 and 450 kg of PE/mol of Zr, respectively) outperforming the Cp_2ZrCl_2-based catalysts [151]. While the catalyst system **76**/MAO produced low molecular weight and narrow disperse PE ($M_w = 9.4 \times 10^3$, $M_w/M_n = 2.2$), the **76**/$AlMe_3/[CPh_3][B(C_6F_5)_4]$ mixture afforded a slightly higher molecular weight PE ($M_w = 14 \times 10^3$, $M_w/M_n = 2.6$) [151].

4.3 Chromium-Based Catalysts

Chromium-based catalysts, typically associating a Cr precursor and an organoaluminum cocatalyst, lie undoubtedly among the most active and selective systems for olefin oligomerization. Accordingly, the selective trimerization of ethylene catalyzed by Cr/Al systems have been the subjects of numerous patents and publications over the last two decades. This research area has been well reviewed by Morgan et al. in 2004 [152] and, more recently, by McGuinness in 2011 [153]. Besides the development of novel systems along with improvements of those currently used, numerous studies have been conducted to elucidate the mechanism of the Cr-based selective oligomerization [154, 155]. Various mechanisms have been proposed and appear to depend upon the oxidation state of the active chromium center (after activation of the Cr precursor by the aluminum cocatalyst). To gain insight and substantiate mechanistic proposals, many investigations have dealt



Scheme 33 Coordination of the "SNS" ligand with Cr(III) and Cr(II) precursors and reactivity toward various organoaluminum reagents

with the isolation and characterization of catalytically active Cr/Al species resulting from the reaction of the chromium precatalyst and the aluminum activator. The most recent and representative advances in this field are detailed in the following parts.

4.3.1 "SNS" Pincer Ligands-Based Chromium Catalysts: *New Insight into the "Sasol Catalyst"*

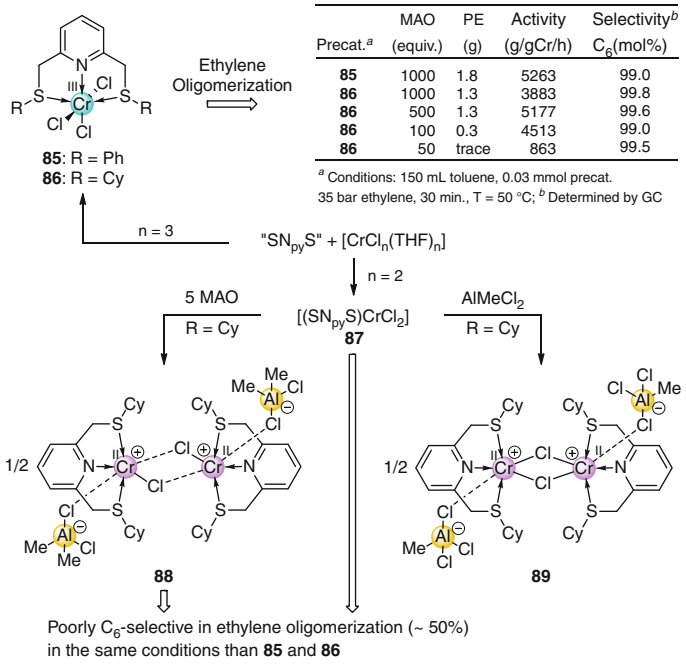
Historically, McGuinness and Wasserscheid first reported on the preparation of bis (phosphino)amine chromium(III) chloride complexes, which, upon activation with MAO, act as highly selective catalysts for the production of 1-hexene from ethylene [156]. Bis(sulfanyl)amine-type ligands were subsequently found to be less expensive and easier to prepare [157]. These systems were then optimized by researchers at Sasol Technology and patented as selective catalysts for the formation of 1-hexene (>97%) using a low amount of MAO (30–100 equiv.) [158].

Recent investigations on related systems allowed the characterization of potentially catalytic active species upon treatment of Cr precursors with an aluminum cocatalyst [159–162]. In 2006, Gambarotta and Duchateau investigated the role of the

Table 4 Comparative oligomerization activities and selectivities of Cr(III) and Cr(II) "SNS" systems

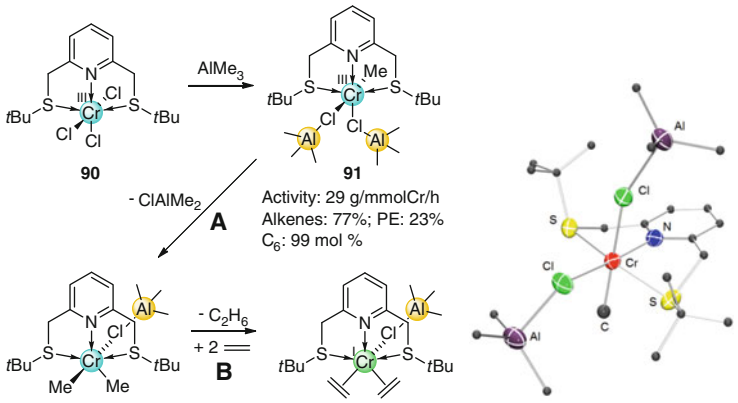
Precatalyst[a]		MAO (equiv.)	PE (g)	Activity (g/g Cr/h)	Selectivity[b] (mol.%)		
					C_6	C_8	C_{10}
Cr^{III}	**79**	1,000	0.80	1,510	>98	Traces	Traces
	80	1,000	0.80	9,383	>98	Traces	Traces
	83	1,000	0.80	6,903	>98	Traces	Traces
Cr^{II}	**81**	1,000	0.86	2,588	70.8	9.2	8.6
	81	300	0.70	4,530	>98	0.36	0.4
	82	1,000	2.6	2,912	>98	Traces	Traces
	84	1,000	0.64	2,265	>98	1.5	0.6

[a]General conditions: 150 mL of toluene, 0.03 mmol precatalyst, 35 bar ethylene, 1 h, $T = 50°C$
[b]Determined by GC



Scheme 34 Cr(III) and Cr(II) precursors supported by the "$SN_{py}S$" ligand, their reactivity toward organoaluminum reagents and use in catalytic ethylene oligomerization

Cr oxidation state on the selectivity of these systems, by identifying the products of the reaction of Cr(II) and Cr(III) complexes supported by SNS-type ligands with various organoaluminum reagents (Scheme 33). The resulting complexes were tested in ethylene oligomerization in the presence of MAO (Table 4). To determine the influence of the metal oxidation state on the oligomerization process, the performances of complexes **79** and **81** in ethylene polymerization were compared [160]. The observed similar selectivity allowed the authors to suggest that "the

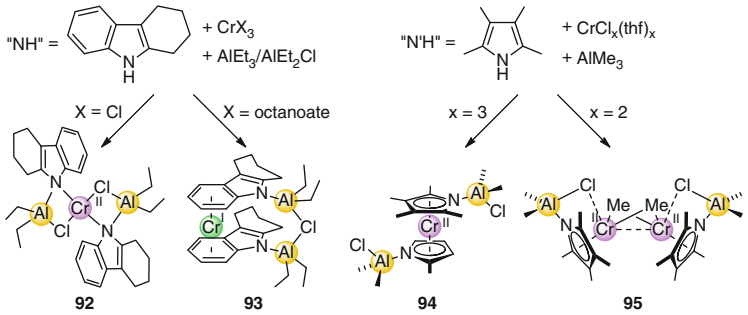


Scheme 35 Synthesis and solid-state molecular structure of complex **91** and its proposed self-activation pathway (**A**, **B**) for ethylene trimerization

trivalent oxidation state is a precursor to a Cr(II) species which, in turn, is a precursor to the catalytically active species" and that the Al-based Lewis acidic cocatalyst acts as a cationizing agent. Yet, treatment of the Cr(II)(SNS) complex with $AlMe_3$ afforded a Cr(III) dimer exhibiting a oligomerization selectivity similar to that observed for the Cr(III) species **79** and **80** and Cr(II) species **81** (300 equiv. MAO) (Scheme 33, Table 4) [159]. Interestingly, precatalyst **84**, resulting from the activation of compound **82** with $AlEtCl_2$, shows no structural similarity with the previously described complexes but was found to exhibit comparable catalytic performances to those observed for the dimeric Cr derivatives (**79**–**81** and **83**), thus indicating that the observed oligomerization selectivity may not solely depend on Cr oxidation state. Since then, various mechanistic studies (structural characterization, theoretical studies, and isotope labeling experiments) provided additional data, consistent with a mechanism involving metallacyclic intermediates and the selective production of 1-hexene or 1-octene via 3,7-H (hexene), 3,9-H (octene) shift, or a β-H elimination reaction followed by a reductive elimination. These sequential reactions would proceed through mixed-valent Cr(n)/Cr(n + 2) (n = 1 or 2) species [154, 155].

The proposal that catalyst activation is likely to go through a Cr(III) to Cr(II) reduction was also ruled out by studies on pyridine-centered "$SN_{py}S$" Cr systems (Scheme 34) [163]. For these systems, a loss of selectivity (in ethylene trimerization) was observed when going from Cr(III) to Cr(II) analogues (Scheme 34, insert). Complex **88**, resulting from the activation of the Cr species **87** by MAO, was structurally characterized, confirming the presence of a cationic Cr(II) center.

Very recent studies in the area allowed the isolation of a single Cr/Al-based catalyst for ethylene oligomerization (**91**, Scheme 35) [161]. The molecular structure of compound **91** clearly evidences the double role of the organoaluminum cocatalyst acting both as an alkylating agent and a Lewis acid (i.e. a cationazing agent). The self-activation of species **91** (for ethylene polymerization catalysis) may occur through dissociation of a neutral Me_2AlCl moiety with concomitant



Scheme 36 Synthesis of self-activating ethylene oligomerization catalysts as analogues to the Phillips trimerization catalyst

Table 5 Ethylene oligo- and polymerization activities for catalysts depicted in Scheme 36

Catalyst[a]	Activity (g/mmol Cr/h)	PE (g)	Oligo (mL)	1-Hexene[b] (%)
92	320	3.2	None	–
93	220	Traces	2.2	93
94[c]	800	8.0	None	–
95[d]	670	Traces	20.2	95

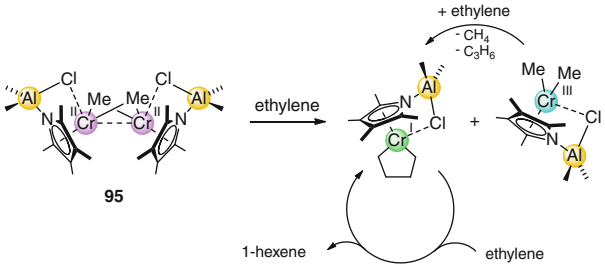
[a]Conditions: methylcyclohexane, 0.02 mmol catalyst, V_{total} 100 mL, 600 psi ethylene, 30 min, 115°C
[b]Determined by GC
[c]Toluene, 0.01 mmol catalyst, 110°C, 1 h
[d]0.03 mmol catalyst, $T = 105$°C, 36 bar ethylene, 1 h

alkyl transfer (Scheme 35, **A**), and a subsequent reductive elimination affording a catalytically active monovalent Cr species (Scheme 35, **B**).

4.3.2 Pyrrolyl-Based Chromium/Organoaluminum Catalysts: *New Insight into the "Phillips Ethylene Trimerization Catalyst"*

The Phillips catalyst, based on a Cr/2,5-dimethylpyrrole precursor and TEA as a cocatalyst, is the only commercial catalytic system for ethylene trimerization [164] and has thus been extensively studied [139, 140]. Based on DFT calculations, a redox mechanism involving a Cr(II)/Cr(IV) couple has been proposed [154, 165]. Also, the pyrrole derivative ligand, able to interact with one or two metal centers through the nitrogen lone pair and/or the aromatic π-system, may play a key role for the stabilization of heterodinuclear Cr/Al species formed after activation.

Recently, the research groups of Gambarotta and Duchateau reported the isolation and characterization of Cr/Al polynuclear adducts resulting from the reaction of a Cr precursor, a pyrrolide ligand and an organoaluminum activator [166, 167]. Depending on the chromium source, the resulting Cr/Al complexes were found to exhibit different structures and/or oxidation state (for the Cr center), thus resulting in different ethylene polymerization reactivity (Scheme 36, Table 5). While complexes **93** and **95** are single-component catalysts for the selective trimerization



Scheme 37 Disproportionation of the dinuclear Cr(II) complex **95** upon exposure to ethylene

of ethylene, complexes **92** and **94** react with ethylene to yield polyethylene. The formation of Cr/Al adducts could be unambiguously established by XRD analysis. Although dissociation of these adducts may well occur as the polymerization proceeds, the nature of the resulting polymers indicates that the initial structural differences do matter and influence the polymerization outcome [166]. Complex **92** acts as a self-activating ethylene polymerization catalyst, with an active species possibly resulting from the dissociation of a neutral ["N"AlEtCl] moiety and an alkyl transfer. In contrast, complex **93** was described as an unprecedented single component trimerization catalyst producing essentially 1-hexene with only traces of PE, through a redox pathway [Cr(I)/Cr(III)] after initial dissociation of a ["N"$AlEt_2$] residue [166]. Catalytic activities differ when going from the "chromocene" complex **94**, a self-activating and single-site catalyst for the production of UHMWPE, to the dimeric mono-pyrrolyl complex **95** working as a self-activating trimerization catalyst. These differences are explained by the fact that complex **94** retains a divalent Cr center during the catalytic process while complex **95** disproportionates into a monovalent Cr active species and a latent Cr(III) complex when exposed to ethylene (Scheme 37) [167].

4.3.3 Other Bi- and Tridentate Ligands-Based Chromium Catalysts

The first example of *diphosphinoamine [PN(R)PR] ligands*-based Cr systems for the selective ethylene trimerization was reported in 2002 by researchers at BP. Such catalysts combine ligands of type **96**, a Cr source and MAO as a cocatalyst (Fig. 11) [168]. These systems were found to be highly active (TOF $> 1.8 \times 10^6$ h^{-1}, 20 bar) and selective toward 1-hexene formation (80–90%). Activities and selectivities of the [PN(R)P] Cr systems along with mechanistic studies have been comprehensively reviewed [152, 153, 169].

Theoretical studies on the role of MAO in Cr-catalyzed ethylene tri- and tetramerization were performed using [PN(R)P] Cr systems and suggest the formation of a chromacycloheptane interacting with "a MAO anion" (**97**, Fig. 11) [170]. A Cr(II) cationic complex $\{[(PNP)_2Cr(\mu\text{-}Cl)AlMe_3][Me_3AlCl]_{0.34}[Me_4Al]_{0.66}\}$ (**98**) could also be isolated and structurally characterized after treatment of a dimeric Cr(III) precursor $[(PNP)CrCl_3]_2$ with TMA (Fig. 11) [171]. Compound **98** requires the addition of MAO for ethylene oligomerization activity.

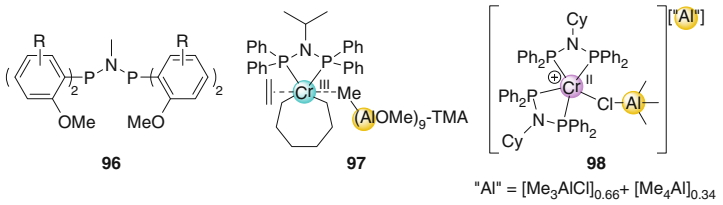
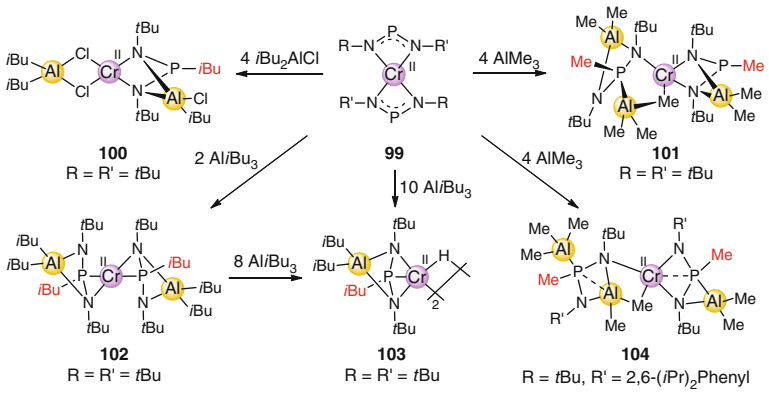


Fig. 11 Examples of [PN(R)P] ligands and related Cr/Al complexes



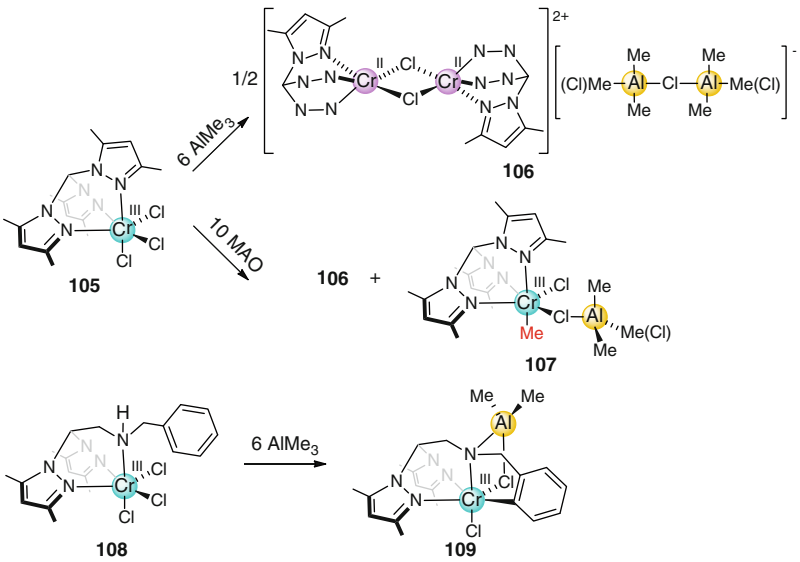
Scheme 38 Synthesis of single-component (NPN) type-Cr/Al complexes for ethylene oligo- or polymerization

Table 6 Self-activating (NPN)Cr/Al catalysts for ethylene oligo- or polymerization

Catalyst[a]	Activity (g/mmol Cr/h)	PE (g)	M_n ($\times 10^3$)[b] (g/mol)	PDI	Oligo (g)	1-Hexene[b] (%)
100	2,240	11.2	38	3.2	0	–
101	3,300	16.5	27	2.8	0	–
102[c]	820	8.2	1,300	3.2	–	–
103[c]	1,450	14.5	1,400	3.0	–	–
104[d]	600	–	–	–	3	99.9
104[e]	100	–	–	–	0.5	99.9

[a]Conditions: 100 mL toluene, 35 bar ethylene, 30 min., 50°C, 0.01 mmol catalyst
[b]Determined by GC
[c]0.02 mmol catalyst
[d]0.01 mmol catalyst
[e]0.01 mmol catalyst, 25°C

Since 2008, the reactivity of *bidentate [NPN] ligands based*-Cr complexes toward organoaluminum reagents has been thoroughly investigated, allowing the synthesis and characterization of single-component ethylene oligo- or polymerization catalysts [172–174]. As summarized in Scheme 38, compound **99**, consisting of a Cr(II) metal center surrounded by two mono-anionic chelating NPN ligands, was reacted with various Al activators to afford diverse Cr/Al heterometallic complexes. In all these reactions, alkylation of the NPN ligands phosphorus



Scheme 39 Reactivity of pyrazolyl-based [NNN] chromium complexes toward organoaluminum reagents

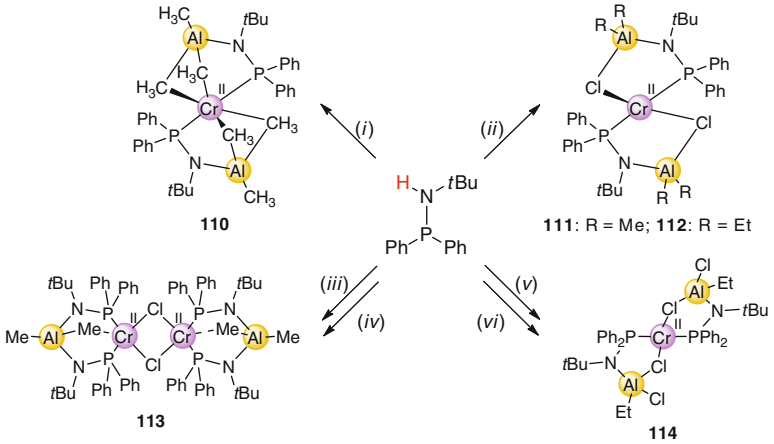
Table 7 Ethylene oligomerization catalyzed by pyrazolyl-based chromium precatalysts

			Selectivity (mol%)				
Catalyst[a]	Amt of Cr (μmol)	PE (%)	C_6	C_8	C_{10}	1-C_6	Activity (g/g Cr/h)
105	8.7	<0.1	97.6	1.3	1.0	98.4	32,400
106	8.0	<0.1	92.1	3.5	3.9	98.7	10,500
107	5.5	<0.1	98.7	1.2	0	99.1	36,300
107[b]	6.1	<0.1	97.8	2.1	0	99.1	630
108	5.3	<0.1	97.8	1.1	1.0	99.3	37,400
109	8.9	<0.1	93.0	3.7	3.2	98.3	13,300

[a]General conditions: 60 mL of toluene, 200 equiv. MAO, 30 bar ethylene, 80°C, 30 min
[b]50 equiv. TMA

atoms by the Al reagent is observed and the resulting products all incorporate organoaluminum residues coordinating through various μ-N and μ-P bridging modes. All heterometallic complexes were found to be active either in ethylene oligo- or polymerization as shown in Table 6. The catalytic performances of these complexes can be modulated through the use of excess cocatalysts [172–174]. Catalysts **100–103** produce polyethylene with a good polydispersity ($2.8 < PDI < 3.2$) while complex **104** selectively yields 1-hexene.

Chromium complexes supported by *tridentate [NNN] ligand* have also been widely studied as ethylene oligomerization catalysts since the early 2000s. A combination of Cr-based, MAO or trialkylaluminum reagents and *scorpionate pyrazolyl-based [NNN] ligands* were reported to be efficient catalysts for the



Scheme 40 Synthesis of (PN)Cr(II) complexes and their reactivity toward organoaluminum reagents

Table 8 Ethylene oligomerization performed with complexes **110–114**

Catalyst[a] (μmol)	MAO (equiv.)	Activity (g/mmol Cr/h)	PE (g)	M_w (g/mol)	PDI	Oligo (mL)	Selectivity (mol%)		
							C_6	C_8	C_{10}
110 (50)	0	236	1.2	–	–	4.7	25.0	10.0	–
110 (25)	1,000	4,616	2.7	72,150	2.5	55.0	14.1	26.4	23.4
111 (10)	1,000	7,200	8.0	–	–	28.0	18.9	24.9	20.2
111 (25)	1,000	6,200	9.5	969,950	17.6	68.0	20.0	27.2	16.7
112 (50)	0	0	0	–	–	–	–	–	–
112 (25)	1,000	6,280	8.5	561,380	8.6	70.0	35.6	22.2	16.7
113 (50)	0	20	0.5	–	–	–	–	–	–
113 (10)	1,000	10,400	0.2	2,500	2.5	51.0	15.0	21.5	18.5
114 (10)	1,000	–	1.0	–	–	68.0	22.2	23.9	19.2

[a]General conditions: V(tot) = 100 mL in toluene, 40 bar ethylene, 50°C, 30 min

selective ethylene trimerization at the Tosoh Corporation [175]. More recently, Hor and coworkers studied related Cr/Al systems [176–178], allowing the unambiguous characterization of novel Cr/Al heterometallic complexes upon activation of the [(NNN)$CrCl_3$] with TMA or MAO (Scheme 39) [178]. The preparation of such heterometallic derivatives further highlights the role of the Al activator acting as an alkylating and/or a cationizing agent. In the presence of MAO, these complexes are highly active and selective catalysts for ethylene oligomerization, producing essentially 1-hexene (Table 7).

A brief overview on the very recent use of Cr complexes bearing *[PN] bidentate ligands* as ethylene oligomerization precatalysts should also be mentioned. As summarized in Scheme 40, Cr(II) amidophosphine complexes **110–114** were

Table 9 Ethylene oligomerization performed with complexes **110–114** in methylcyclohexane

Catalyst[a] (μmol)	MAO (equiv.)	Activity (g/mmol Cr/h)	PE (g)	M_w (g/mol)	PDI	Oligo (mL)	Selectivity 1-C_6 (%)
110 (25)	150	1,760	16.0	90,040	2.9	6.0	>99.9
111 (10)	1,000	2,660	8.0	–	–	5.3	>99.9
111 (25)	150	1,880	19.0	241,880	8.5	4.5	>99.9
112 (25)	150	2,160	18.0	1,645,820	3.9	9.0	>99.9
112 (10)	1,000	2,560	5.4	–	–	7.4	>99.9
113 (11)	150	5,700	27.0	237,280	32	1.5	>99.9
114 (10)	150	2,120	20.0	551,790	10.1	5.5	>99.9

[a]General conditions: V(tot) = 100 mL in methylcyclohexane, 40 bar ethylene, 60°C, 30 min

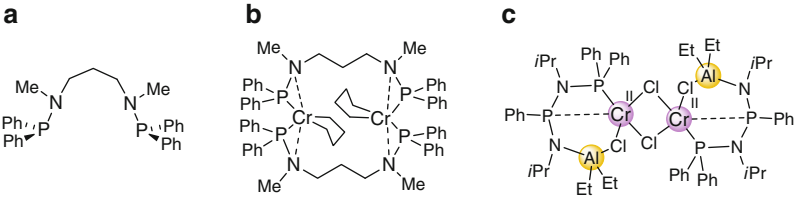


Fig. 12 (**a**) Bis-[PN] ligand, (**b**) possible intermediate in selective ethylene tetramerization, (**c**) [NPNP]Cr/Al precursor for selective trimerization of ethylene

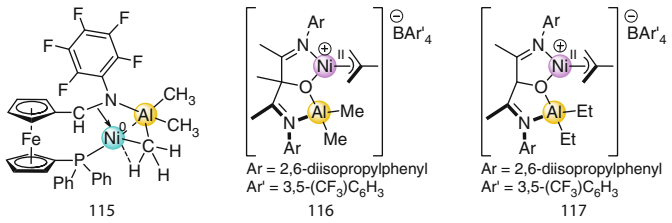


Fig. 13 Ni/Al polynuclear complexes acting as single component ethylene oligo/polymerization catalysts

observed to readily react with AlR_3 reagents to form various heterometallic complexes, whose ethylene oligomerization activity is summarized in Tables 8 and 9 [179]. In toluene, only complex **110** behaves as a single component catalyst, forming either PE or oligomers, while the other complexes (except **114**) are nonselective ethylene oligomerization catalysts, yielding a Schulz–Flory distribution of oligomers (Table 8). Interestingly, when using methylcyclohexane instead of toluene as a solvent, the highly selective formation of 1-hexene was observed in all cases, along with that of PE as a side-product (Table 9).

The architecture and coordination properties of the ligand(s) chelating the Cr metal center may greatly influence the catalytic performance of the resulting catalyst. For instance, the use of a novel ligand consisting of two [PN] moieties

linked through a flexible alkyl linker for coordination to Cr(II) allowed access to a highly selective ethylene tetramerization catalyst (Fig. 12a, b) [180]. The authors suggested that the observed selectivity is likely be related to the preferable formation of a dimeric species bearing two bridging ligands (Fig. 12b).

Recently, Rosenthal, Müller, and coworkers investigated the reactivity of a novel [PNPN]-Cr system toward AlR_3 reagents and were able to isolate a dimeric Cr/Al heterometallic complex that, in the presence of TEA, mediates the selective trimerization of ethylene (Fig. 12c) [181].

4.4 Nickel-Based Catalysts

Although numbers of Ni-based catalysts for olefin polymerization have been reported over the past 50 years, examples of structurally characterized Ni/Al heterometallic complexes resulting from the reaction of a Ni-based precatalyst and an organoaluminum cocatalyst were only recently reported [182, 183] (Fig. 13). Complex **115** oligomerizes ethylene with a moderate activity in the absence of any cocatalyst to selectively form 1-butene, while species **116** and **117** polymerizes ethylene in a controlled manner.

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Preparation of Organoalanes for Organic Synthesis

Paul Knochel, Tobias Blümke, Klaus Groll, and Yi-Hung Chen

Abstract Organoaluminums have become more and more important in organic synthesis due to their excellent reactivity and chemoselectivity. Several methods are available for the preparation of various organoaluminums: transmetalation of organomagnesium or lithium reagents, direct insertion of aluminum powder, deprotonation reactions using aluminate bases (metalation), hydro- and carboalumination of unsaturated compounds, and cycloaddition reactions. These methods provide access to aryl, alkynyl, alkenyl, alkyl, allylic, benzylic, and propargylic organoaluminums which all have interesting properties, and can be readily used in organic synthesis.

Keywords Aluminum · Carboalumination · Hydroalumination · Organoalane · Organoaluminum

Contents

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Abbreviations

acac	Acetyl acetonate
Bn	Benzyl
Bu	Butyl
c-Hex	Cyclohexyl
CuTC	Copper thiophenecarboxylate
dba	Dibenzylideneacetone
DIBAL-H	Diisobutylaluminiumhydride
dppe	1,2-Bis(diphenylphosphino)ethane
dr	Diastereomeric ratio
ee	Enantiomeric excess
Hex	Hexyl
*i*Bu	*iso*-Butyl
*i*Pr	*iso*-Propyl
M	Molar
NMI	Neomenthylindenyl
NMP	*N*-Methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance
OAc	Acetate
PEPPSI	[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl) palladium(II) dichloride
PMDTA	*N*,*N*,*N*′,*N*′,*N*″-Pentamethyldiethylenetriamine
TMP	2,2,6,6-Tetramethylpiperidyl
ttmpp	Tris(2,4,6-trimethoxyphenyl)phosphine
ZACA	Zirconium-catalyzed asymmetric carboalumination

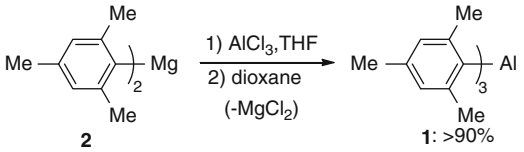
1 Introduction

Organoaluminums have received considerable attention in recent years [1] due to their unexpectedly high chemoselective reactivity, but also because of the attractive price of aluminum (<1$/kg) and moderate toxicity. Their preparation has therefore been reexamined and several mild methods have been devised recently. This chapter summarizes the available preparation methods and shortly describes the reactivity pattern of these useful organometallic intermediates. Aryl, alkynyl, allylic, and propargylic aluminum derivatives by far have found the most applications.

2 Preparation of Aluminum Organometallics

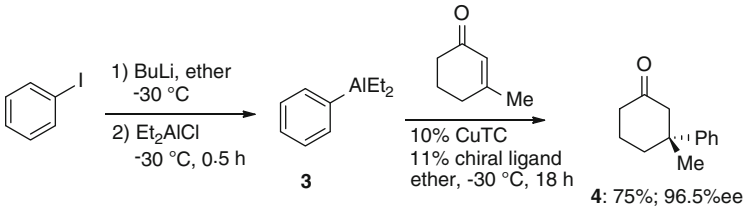
2.1 By Transmetalation

The preparation of arylaluminums has been realized by transmetalation starting from aryllithium or arylmagnesium reagents. Thus, for example the sterically hindered trimesitylaluminum (**1**) is obtained in high yield from dimesitylmagnesium (**2**) [2]. The magnesium salts formed in the course of the reaction are precipitated by the addition of dioxane [Eq. (1)]. Various triarylaluminums prepared in this way undergo highly enantioselective additions to aldehydes in the presence of $Ti(OiPr)_4$ and catalytic amounts of a chiral 1,2-aminoalcohol [3].



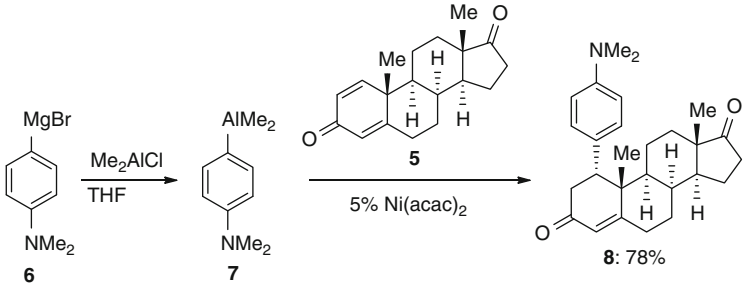
(1)

Starting from phenyllithium the preparation of diethylphenylaluminum (**3**) is readily performed. This aluminum reagent undergoes an efficient asymmetric addition to 3-methyl-1-cyclohexanone in the presence of copper salts and a chiral ligand, leading to the ketone **4** with 96.5% ee [Eq. (2)] [4].



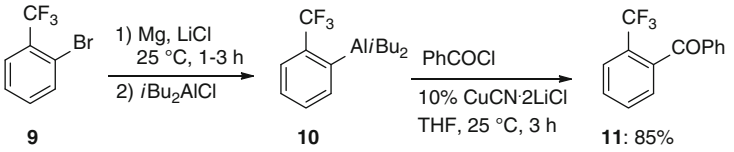
(2)

A related Ni-catalyzed Michael addition allows the functionalization of steroids, such as **5**. The transmetalation of 4-dimethylaminophenylmagnesium bromide (**6**) with Me_2AlCl provides the aluminum reagent **7** which smoothly undergoes a 1,4-addition to **5** at 0°C in the presence of 5% $Ni(acac)_2$ leading to the diketone **8** in 78% yield [Eq. (3)] [5].



(3)

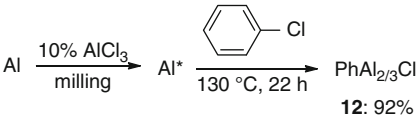
An in situ preparation of arylmagnesium reagents using magnesium turnings in the presence of LiCl [6] also allows an expeditive preparation of arylaluminum species. Thus, the reaction of 1-bromo-2-trifluoromethylbenzene (**9**) with Mg turnings and LiCl at 25°C is complete within 1–3 h providing the aluminum reagent **10** after the addition of iBu$_2$AlCl [7]. The organometallic reagent is readily benzoylated by PhCOCl in the presence of CuCN·2LiCl [8] affording the aromatic ketone **11** in 85% yield. No competitive transfer of the *iso*-butyl group is observed under these reaction conditions [Eq. (4)] [7].



9 **10** **11**: 85% (4)

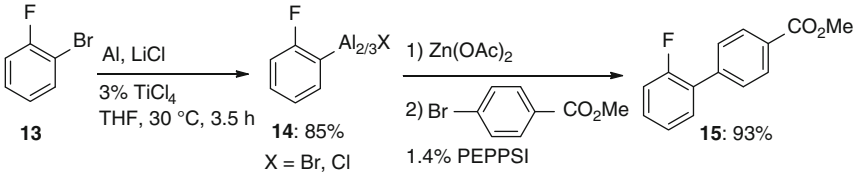
2.2 By the Direct Insertion of Aluminum

Aluminum powder is covered by an oxide layer making it kinetically unreactive towards a direct insertion to organic halides (passivation). Surface activation of aluminum or a catalysis by metallic salts is required to achieve an insertion to aryl halides. Thus, it has been shown that the grounding of aluminum powder with small amounts of aluminum chloride allows the insertion of aluminum powder to aryl iodides, bromides, and chlorides [Eq. (5)] [9].



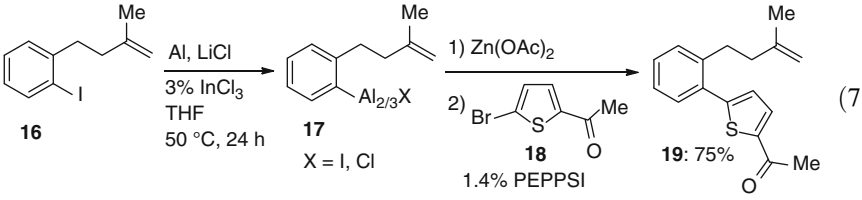
12: 92% (5)

In the case of chlorobenzene, a temperature of 130°C is required for the formation of the aluminum reagent **12** in 92% yield. By adding dry lithium chloride and small amounts of a metallic salt additive, such as $TiCl_4$, $BiCl_3$, $InCl_3$, or $PbCl_2$ to Al powder a smooth insertion to various aryl iodides and bromides can be performed between 25°C and 50°C in THF [10]. Thus, the treatment of 1-bromo-2-fluorobenzene (**13**) with aluminum powder (3 equiv.), LiCl (1.5 equiv.), and 3 mol% $TiCl_4$ in THF for 3.5 h at 30°C provides the arylaluminum **14** in ca. 85% yield without significant aryne formation [Eq. (6)]. This organometallic undergoes a Pd-catalyzed cross-coupling reaction in the presence of 1.4 mol% of PEPPSI [11] after transmetalation with $Zn(OAc)_2$.



(6)

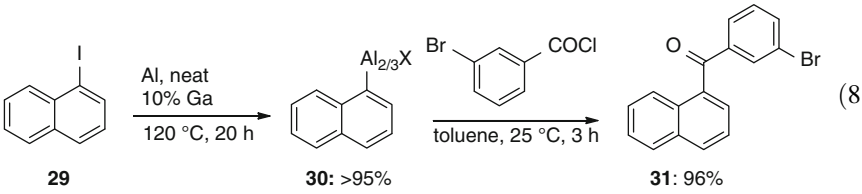
Thus, by cross-coupling with methyl 4-bromobenzoate the biphenyl **15** is obtained in 93% isolated yield. The use of $InCl_3$ [12] proves to be advantageous and of general utility. No long living free radical species seems to be generated in the insertion step since the aryl iodide **16** bearing a remote double bond undergoes the expected Al-insertion (50°C, 24 h) without any radical ring closure leading to the aluminum reagent **17** [Eq. (7)].



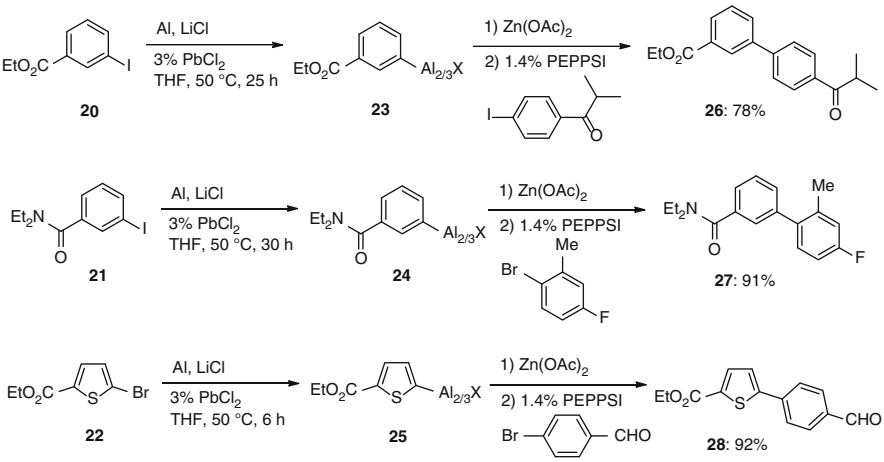
(7)

After $Zn(OAc)_2$ transmetalation Pd-catalyzed cross-coupling with the bromothiophene **18** provides the substituted thiophene **19** in 75% yield. The presence of carbonyl groups (ester or amide) precludes the use of $TiCl_4$, $BiCl_3$, or $InCl_3$ as additives. However, by employing 3% $PbCl_2$ a smooth insertion reaction with several functionalized iodides, such as **20** and **21**, or with the bromide **22** (Scheme 1) [10] occurs, providing the derived functionalized aluminum reagents **23**–**25** in good yields.

After a transmetalation with $Zn(OAc)_2$, Pd-catalyzed cross-coupling reactions with various aryl iodides or bromides furnish the polyfunctional biaryls **26**–**28** in 78–92% yield (Scheme 1). Interestingly, 10 mol% of Ga also catalyzes the aluminum insertion and 1-naphthyl iodide (**29**) reacts neat at 120°C with Al powder furnishing the 1-naphthylaluminium derivative **30** in >95% yield. Its reaction in toluene with an acid chloride leads to the desired ketone **31** in 96% yield [Eq.(8)] [13].

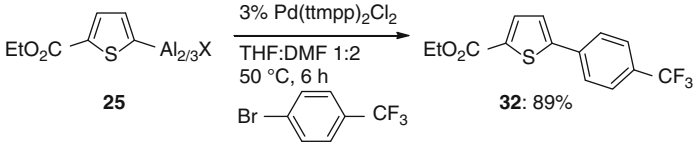


(8)



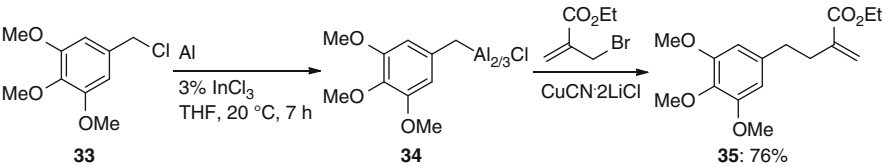
Scheme 1 $PbCl_2$-catalyzed Al insertion to aryl halides bearing carbonyl groups

Most cross-coupling reactions involving arylaluminum reagents required a preceding transmetalation with Zn salts in order to perform efficiently. However, by screening various ligands, it was possible to find an optimum ligand for performing a direct cross-coupling of the aluminum reagent. Thus, the reaction of the aluminum reagent **25** with 1-bromo-4-trifluoromethylbenzene in 1:2 THF:DMF and 3% of $Pd(ttmpp)_2Cl_2$ (ttmpp: tris(2,4,6-trimethoxyphenylphosphine) is complete at 50°C within 6 h providing the cross-coupling product **32** in 89% yield [Eq. (9)] [Groll K, Blümke TD, Knochel P (2011) unpublished work].



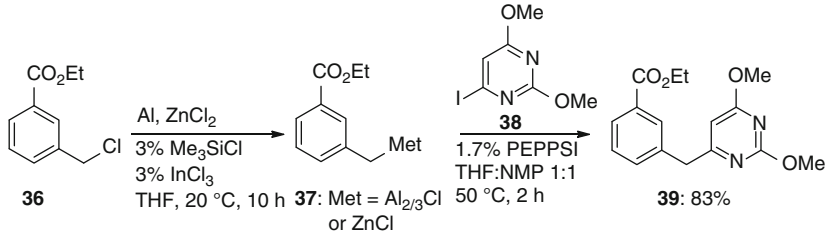
(9)

The insertion reaction can also be extended to benzylic chlorides. Thus, the reaction of the benzylic chloride **33** with Al dust in the presence of 3% $InCl_3$ in THF at 20°C for 7 h furnishes the corresponding aluminum reagent **34**. Transmetalation with $Zn(OAc)_2$ followed by a copper(I)-catalyzed allylation with ethyl (2-bromomethyl)acrylate leads to the substituted acrylate **35** in 76% yield [Eq. (10)] [14].



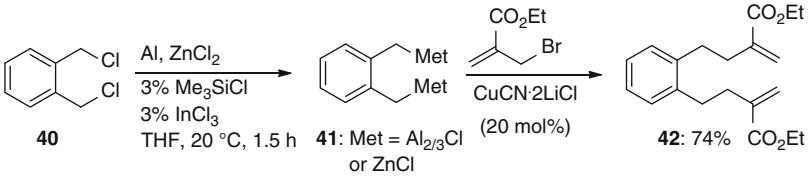
(10)

By performing the insertion in the additional presence of $ZnCl_2$ (1 equiv.), the insertion is also compatible with polar functional groups. This additional presence of $ZnCl_2$ in fact leads to a mixture of aluminum and zinc organometallics according to ^{1}H-, ^{13}C-, and ^{27}Al-NMR spectroscopy studies. Thus, the treatment of ethyl 3-chloromethylbenzoate (**36**) with the metallic cocktail of aluminum powder, $ZnCl_2$, 3% Me_3SiCl, and 3% $InCl_3$ in THF at 20°C provides after 10 h reaction time the desired organometallic reagent (**37**). Its Pd-catalyzed cross-coupling with an iodouracil derivative (**38**) provides the heterocycle **39** in 83% yield [Eq. (11)] [14].



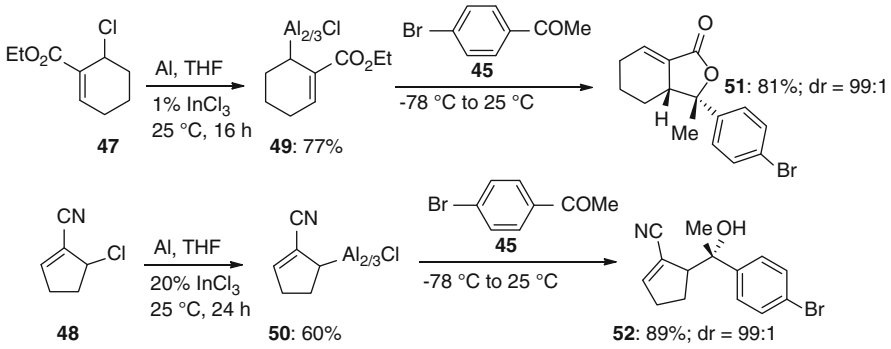
(11)

Interestingly, bis-metallic reagents were also prepared by this mixed metal approach. Thus, the reaction of 1,2-bis(chloromethyl)benzene (**40**) with Al dust in the presence of 3% Me_3SiCl and 3% $InCl_3$ furnishes the bis-metallic species **41** at 20°C within 1.5 h. Its allylation with ethyl (2-bromomethyl)acrylate in the presence of 20% CuCN·2LiCl furnishes the expected bis-allylated product **42** in 74% yield [Eq. (12)] [14].



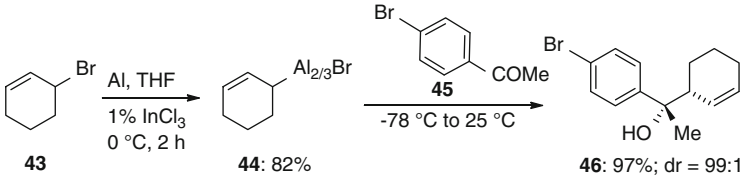
(12)

Allylic halides insert aluminum powder much more readily and do not require extensive metal activation. Especially attractive is the allylation of imines with in situ generated allylic lead reagents using Al as reducing reagent [15, 16]. Well-defined allylic aluminum reagents can, however, be generated by treating various allylic bromides with aluminum powder activated by 1 mol% $InCl_3$ [17]. Thus, the reaction of 3-bromocyclohexene (**43**) with Al powder in the presence of 1% $InCl_3$ in THF (0°C, 2 h) gives the corresponding aluminum reagent **44** in 82% yield (according to iodometric titration). Remarkably, these allylic aluminum reagents add smoothly to aldehydes and ketones with high diastereoselectivity. Thus, the



Scheme 2 Addition of functionalized allylic organoaluminums to carbonyl groups

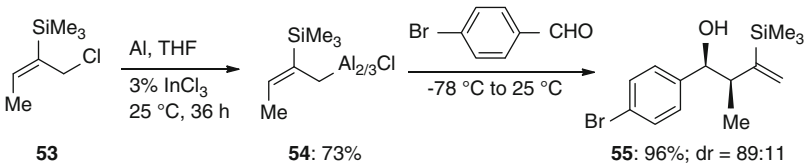
reaction of the aluminum reagent **44** with 4-bromophenylmethylketone (**45**) furnishes the homoallylic alcohol **46** in 97% yield and a diastereoselectivity of 99:1 [Eq. (13)].



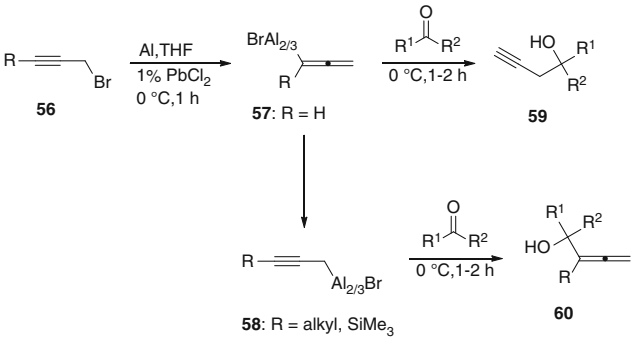
(13)

Due to the excellent functional group tolerance of the organoaluminum reagent the preparation of functionalized allylic aluminum reagents is possible. Thus, the ester-substituted allylic chloride (**47**) and the nitrile-substituted allylic chloride (**48**) were converted in 60–77% yield to the corresponding aluminum reagents **49** and **50**. Their reaction with 4-bromophenylmethylketone (**45**) provides the lactone **51** and the hydroxynitrile **52** with very high diastereoselectivity (Scheme 2).

Although the diastereoselectivity of the addition of crotylaluminum halides to aromatic aldehydes is moderate, by introducing a trimethylsilyl group in position 2, an excellent *syn*-diastereoselectivity is obtained. Thus, the reaction of the allylic chloride **53** with Al powder and 3% $InCl_3$ in THF at 25°C (36 h) gives the desired aluminum reagent **54** in 73% yield. Its reaction with 4-bromobenzaldehyde provides the desired homoallylic alcohol **55** in 96% yield and a diastereoselectivity of 89:11 [Eq. (14)] [17].



(14)

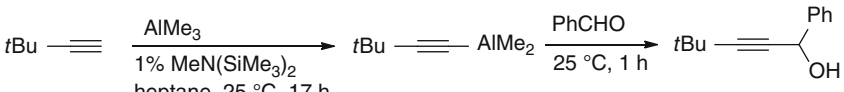


Scheme 3 Propargylic organoaluminums show a different constitution depending on the substituents

Propargylic bromides display a similar reactivity as allylic bromides and various propargylic bromides of type **56** react well with aluminum powder in the presence of 1% $PbCl_2$ in THF (0°C, 1 h). Depending on the nature of the substituent R, different aluminum organometallic species are produced. If R = H, the allenylaluminum reagent **57** is obtained. On the other hand, if R ≠ H (for example R = Hex, TMS, $Cl(CH_2)_3$, *c*-Hex) then propargylic aluminum compounds of type **58** are rather formed. After reaction with carbonyl derivatives, either homopropargylic alcohols of type **59** or homoallenic alcohols of type **60** are obtained (Scheme 3) [18].

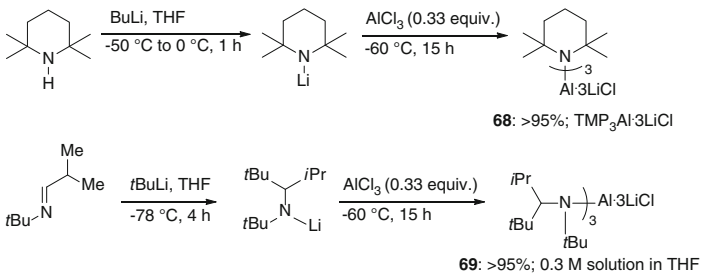
2.3 By Directed Alumination

The directed alumination of aromatics, heteroaromatics, and alkynes is an efficient method for preparing organoaluminum derivatives. The alumination of alkynes such as **61** proceeds smoothly in the presence of catalytic amounts of MeN $(SiMe_3)_2$ in heptane affording alkynylaluminums such as **62** which after addition to benzaldehyde leads to propargylic alcohols like **63** [Eq. (15)] [19, 20].



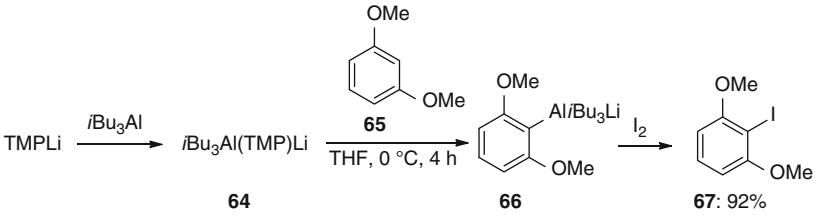
(15)

Similar aluminations on aromatic systems require much stronger bases. Thus, aluminum ate bases such as $iBu_3Al(TMP)Li$ (**64**), which is readily prepared by mixing iBu_3Al with TMPLi (TMP = 2,2,6,6-tetramethylpiperidyl), aluminate readily



Scheme 4 Preparation of LiCl-monomerized aluminum amide bases

various aromatic and heterocyclic rings. Thus, the reaction of 1,3-dimethoxybenzene (**65**) with *i*Bu$_3$Al(TMP)Li (**64**) in THF at 0°C for 4 h affords an aluminum reagent **66** which after iodolysis furnishes the aryl iodide **66** in 92% yield [Eq. (16)] [21].



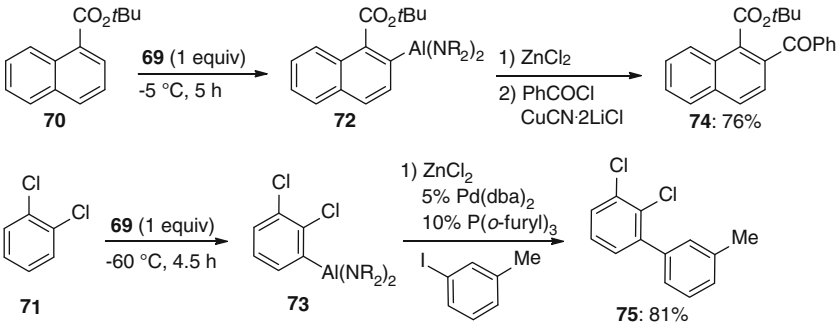
(16)

The regioselectivity, reactivity, and structure of the aluminum adducts of type **65** and of the aluminum ate base **64** have been carefully studied [22, 23]. Alternatively, LiCl-monomerized TMP bases such as **68** and **69** allow the smooth deprotonation of various aromatic and heterocyclic compounds. These bases are soluble in THF (ca. 0.3 M) and decompose in THF at 25°C within 12 h. They are prepared in almost quantitative yield from corresponding lithium amides (Scheme 4) [24].

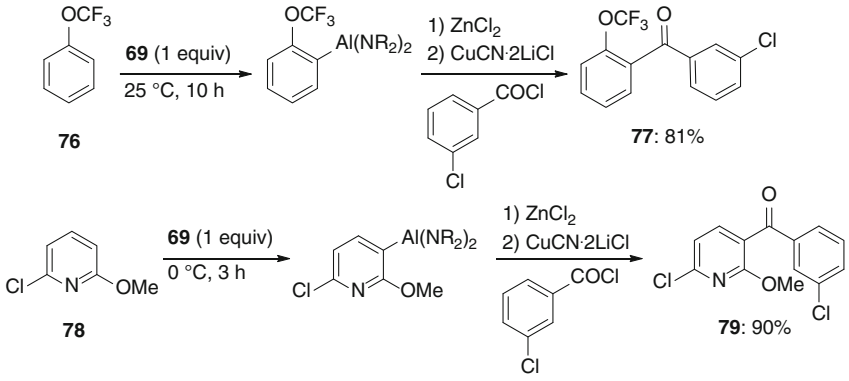
These bases readily deprotonate various functionalized aromatics like the *t*-butylester **70** and 1,2-dichlorobenzene (**71**) respectively at −5°C (3 h) and −60°C (4.5 h) leading to the expected arylaluminum reagents **72** and **73**. Benzoylation or Pd-catalyzed cross-coupling furnishes the expected products **74** and **75** in 76% and 81% yield, respectively (Scheme 5) [24].

Interestingly, aromatics and heterocycles bearing donor substituents are readily aluminated at 0–25°C. Thus, the aryl ether **76** is metalated with the amide **69** (1 equiv.) at 25°C in 10 h. After acylation the ketone **77** is obtained in 81% yield [24]. Similarly, the 2-methoxypyridine **78** is metalated in position 3. Acylation furnishes the pyridyl ketone **79** in 90% yield (Scheme 6) [24].

In the case of mixed *S*,*O*- and *N*,*S*-heterocycles the metalation occurs in proximity of the best donor heteroatom. This heteroatom more readily forms a complex with the aluminum base and therefore directs the alumination (Scheme 7) [24, 25].



Scheme 5 Directed alumination of aromatics using the sterically hindered Al-base **69**

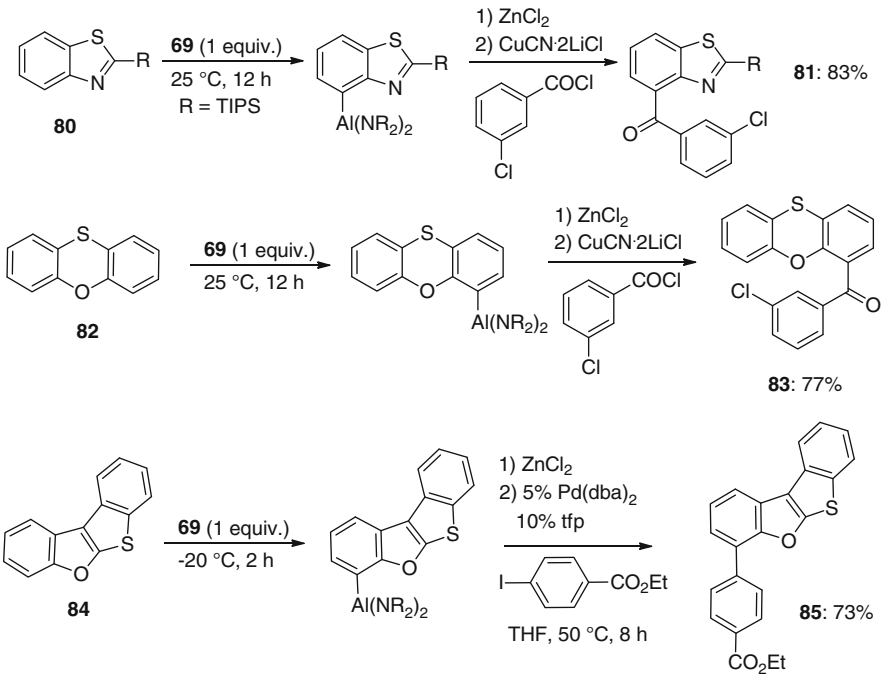


Scheme 6 Directed alumination of alkoxy-substituted aromatics and heteroaromatics

Thus, benzothiazole (**80**) is aluminated at the α-position to nitrogen providing the ketone **81** in 83% yield after acylation. Similarly, the heterocycles **82** and **84** are selectively deprotonated at the α-position to oxygen furnishing the ketone **83** or the ester-derivative **85** in 77% and 73% yield after a copper(I)-mediated acylation or a Pd-catalyzed cross-coupling reaction (Scheme 7) [24, 25].

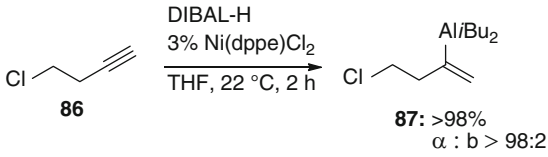
2.4 By Carbo- or Hydroalumination Reactions

The hydroalumination of alkynes using DIBAL-H (diisobutylaluminumhydride) is a general method for preparing various alkenylaluminum reagents [26]. Recently, it has been shown that this hydroalumination can be catalyzed with 3% $Ni(dppe)Cl_2$ in THF at 22°C within 2 h. This hydroalumination tolerates some functional groups. Thus, the



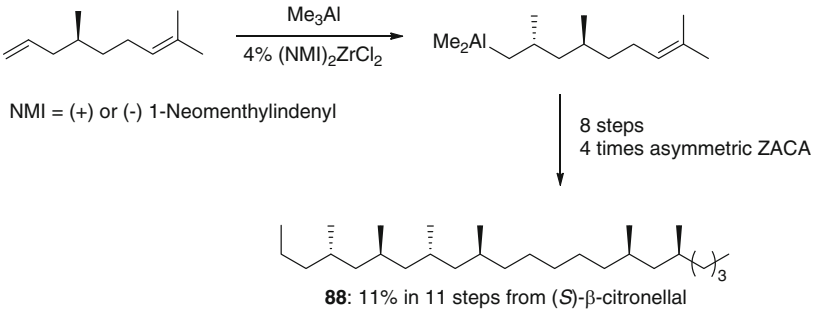
Scheme 7 Regioselective alumination with the aluminum base **69**

chloroalkyne **86** is converted in this way to the aluminum reagent **87** showing an opposite regioselectivity for the hydroalumination performed in the absence of a Ni-catalyst [Eq. (17)] [27].



(17)

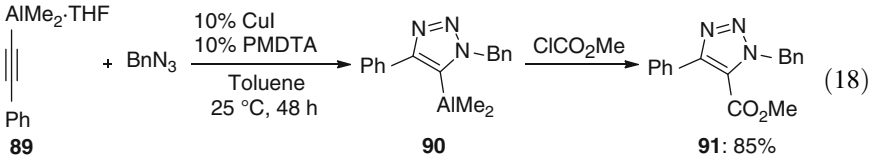
The carbometalation reaction has been reviewed recently [28–30]. Negishi has demonstrated that zirconium(IV) complexes catalyze the carboalumination of Me_3Al to various alkynes and enynes [31]. Also the Zr-catalyzed asymmetric carboalumination of alkenes (ZACA reaction) [32–34] has found important applications in the synthesis of natural products [35–37]. Especially efficient was the asymmetric synthesis of insect pheromones such as (*S*,*R*,*R*,*S*,*R*,*S*)-4,6,8,10,16,18-hexamethyldocosane (**88**) (Scheme 8) [38].



Scheme 8 Zirconium-catalyzed asymmetric carboalumination (ZACA)

2.5 *By Cycloaddition Reactions*

Recently, it could be shown that cycloaddition reactions can be used to generate unsaturated organoaluminums [39]. Thus, the aluminum acetylide **89** is reacting with benzylazide in the presence of 10% of CuI and a ligand, forming the aluminum reagent **90**, which after quenching with different electrophiles leads to 1,4-disubstituted triazoles such as **91** [Eq. (18)]. Noteworthy is the exclusive formation of only one regioisomer as shown by deuterolysis.



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Reactions Triggered by Lewis Acidic Organoaluminum Species

Yuki Naganawa and Keiji Maruoka

Abstract The use of organoaluminum-based Lewis acids (AlR_nX_{3-n}; R = alkyl, alkynyl, X = halide or pseudohalide) in the period 2000 to mid-2011 is overviewed with a focus on: (1) stoichiometric reactions in which one of the organoaluminum substituents is transferred to the substrate (e.g., the opening of epoxides, 1,2-additions to carbonyl compounds, coupling with C–X, and Reissert chemistry) and (2) asymmetric, often catalytic, reactions promoted by Lewis acid catalysts derived from organoaluminum species (e.g., use of auxiliaries with alanes, Diels–Alder, and related cycloaddition reactions, additions to aldehydes and ketones, and skeletal rearrangement reactions).

Keywords Cycloaddition reaction · Lewis acid · Nucleophilic addition · Rearrangement reaction · Substitution reaction

Contents

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1 Introduction

One of the most significant features of organoaluminum reagents, bearing sp^2 aluminum centers, is definitely its strong Lewis acidity arising from the presence of one vacant p-orbital. Such organoaluminums favorably make a coordination bond with Lewis basic heteroatoms in order to complete electron octets, and thus a variety of electrophiles (i.e. carbonyls, imines, ethers, amines, haloalkanes) can be activated for reaction with nucleophilic species under the influence of properly selected organoaluminum reagents (Fig. 1).

In some cases, organoaluminums behave not only as Lewis acid catalysts but also as nucleophilic reagents. Namely, aliphatic or aromatic substituents on the aluminum center migrate to be incorporated into the corresponding products. For example, reaction of cyclohexanone and Me_3Al giving 1-methylcyclohexanol is composed of (1) the activation of carbonyl group by Me_3Al and (2) the following intramolecular migration of methyl group on aluminum to afford the methylation product (Scheme 1) [1].

This chapter presents the concentrated overview concerning the recent advances of such organic reactions induced by Lewis acidic organoaluminum reagents.

The first part of this chapter focuses on the recent examples of C–C bond forming reactions using Lewis acidic organoaluminum species. In order to remain focused and concise, this overview covers the reactions whereby one, or more, of the R–Al substituents of simple organoaluminum species (i.e., Me_3Al) is introduced into the products. The second part of this chapter describes the notable progress in the field of the development of chiral aluminum Lewis acids for asymmetric reactions, showing high selectivity or unique reactivity. For the more comprehensive information about Lewis acidic aluminum including both organo- and non-organoaluminum reagents (i.e., $AlCl_3$, $Al(O\mathit{i}Pr)_3$, etc.) ("organoaluminum" defined herein should be as aluminum(III) species bearing more than one aliphatic or aromatic substituent on the metal center, and hence catalysis by non-organometallic reagents was excluded from this review), several recent and referable books are available [2–7].

2 Alkylaluminums and Their Related Compounds

Alkylaluminums (R_nAlX_{3-n}; $n = 1$–3, R = alkyl, X = halide or pseudohalide) are the main subclass of typical Lewis acidic organoaluminum reagents used both in laboratory and in industry. These reagents have been applied to a wide variety of reactions for highly selective and effective conversion of organic molecules. This subchapter organizes the recent progress of the reactions promoted by Lewis acidic alkylaluminum reagents. In addition, reactions using the related organoaluminums (alkenylaluminums, alkynylaluminums, and arylaluminums) are also dealt with herein due to their similar reactivities.

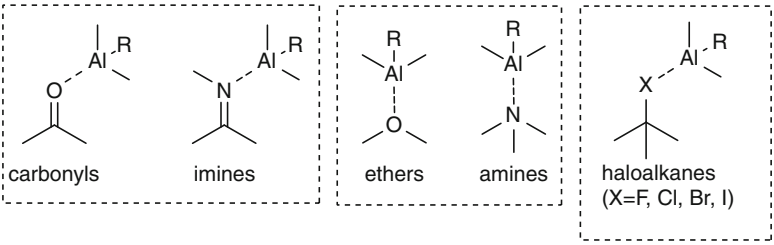
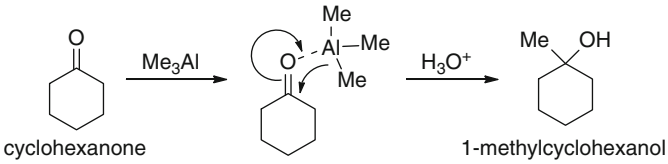
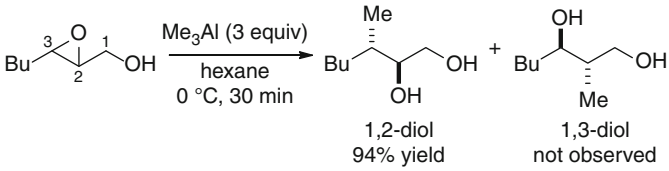


Fig. 1 Activation modes for organoaluminum



Scheme 1 Example of combined Lewis acid/nucleophilic trap chemistry

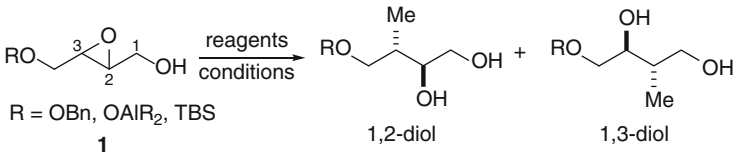


Scheme 2 Stereoselective opening of epoxides by $AlMe_3$

2.1 Reactions Involving Al–O Coordination

In general, Lewis acidic aluminums have high oxophilicity (cf. the bond energy of Al–O = 580 kJ mol^{-1}) [3] and oxygen-containing substrates should be good reaction partners in aluminum Lewis acid catalysis in non-coordinating solvents. Among them, epoxides have been employed as highly reactive and useful functionalities to furnish the building blocks with oxygen function. Since the first primitive report in 1970 [8], trialkylaluminums have been studied broadly as reagents for opening and alkylation of epoxides. The most considerable issue in these reactions is the regio- and stereoselectivity of the corresponding products realized by either the control of the stability of reaction intermediates, or of the coordination between substrate and metal. One early example is the reaction of 2,3-epoxy-1-alkanol reported by Oshima et al. (Scheme 2) [9, 10]. This reaction proceeds with high regioselectivity to furnish the corresponding 1,2-diol. This opening of epoxy alcohols using trialkylaluminums renders a reliable procedure to prepare stereodefined 1,2-diols of practical use, unless $AlEt_3$ is used [10]. For example, the protocols have been applied to recent total syntheses of natural compounds [11–13].

Table 1 Regiochemical control in epoxide opening via organoalane choice



Reagents	Conditions	1,2-Diol/1,3-diol	Yield (%)
Me_3Al (3 equiv.)	CH_2Cl_2, 0°C, 30 min	92/8	87
n-BuLi (1.1 equiv.) then Me_3Al (3 equiv.)	CH_2Cl_2, −30°C to 0°C, 120 min	8/92	93

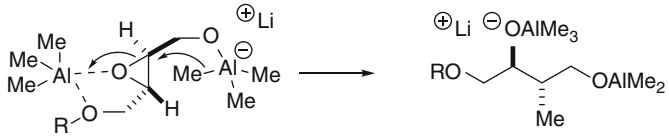
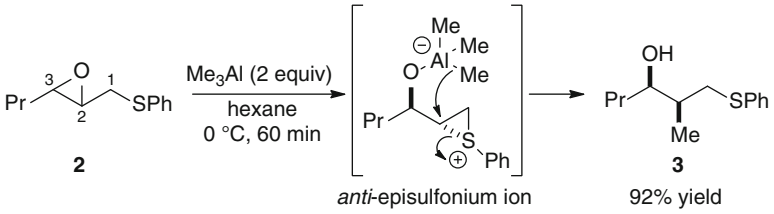


Fig. 2 Proposed origin of reversed regiochemistry

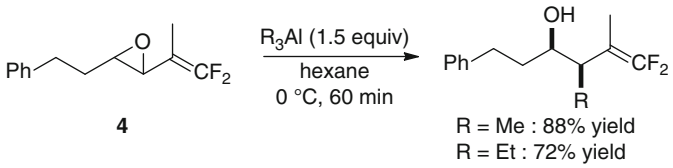


Scheme 3 Opening of *trans*-epoxy sulfides **2** using $AlMe_3$

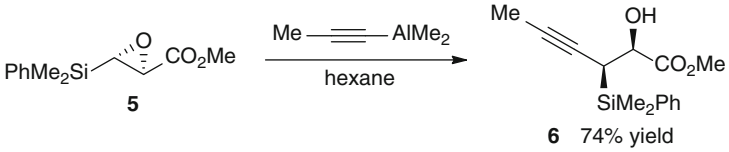
Later, Miyashita et al. reported the switching of this regioselectivity in the ring opening of *trans*-epoxy alcohol **1** using methylaluminum ate complexes prepared from *n*-BuLi and Me_3Al (Table 1) [14]. This reaction provides 1,3-diol with high regioselectivity through a plausible transition state wherein pentacoordinate aluminum Lewis acid plays an important role (Fig. 2).

Conversely, the opening of *trans*-epoxy sulfides **2** using Me_3Al results in the substitution occurring at the C2 position to provide the corresponding products **3** with retention of the configuration (Scheme 3) [15, 16]. The possible reaction intermediate is *anti*-episulfonium ion, and overall double inversion of the stereochemistry is observed. In a related report, it was revealed that a reaction of epoxy selenides proceeds with the similar stereochemical outcome via an episelenonium ion intermediate [17].

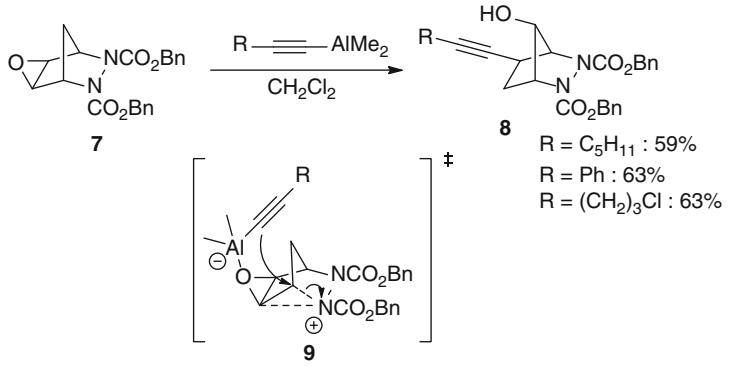
This unusual retention of the configuration is also observed in the Al-mediated ring opening reaction of *gem*-fluorinated vinyloxiranes **4**, which become precursors



Scheme 4 Ring opening reaction of *gem*-fluorinated vinyloxiranes **4**



Scheme 5 Fragment for bistramide A synthesis

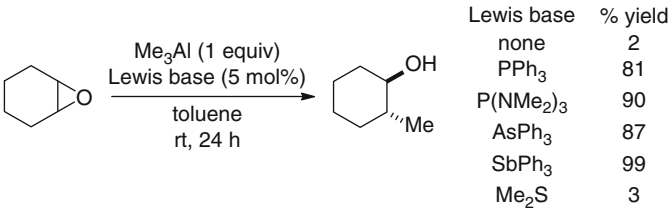


Scheme 6 Rearrangement of a bicyclic hydrazine-epoxide by an aziridinium cation intermediate

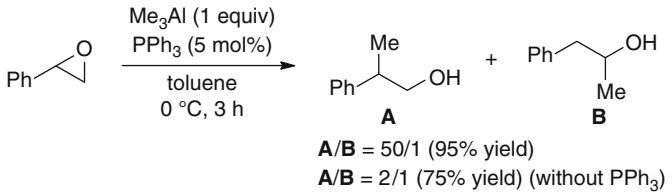
of various fluorine-functionalized organic molecules with unique biological, chemical, and physical properties (Scheme 4) [18]. (For the review on the unique selectivity in the ring opening of fluoro epoxides, see [6].)

The epoxy-opening using alkylalkynylaluminum reagent generally furnishes an alkynylated product in preference to an alkylated product [9, 10]. For a recent example, Panek et al. prepared chiral hydroxy ester **6** using reaction of epoxide **5** and diethylpropynylaluminum in their recent total synthesis of bistramide A (Scheme 5) [19].

Micouin et al. found that the nucleophilic substitution of bicyclic hydrazine-epoxide **7** using alkynylaluminum reagent led to the formation of hydroxy group-rearranged product **8** (Scheme 6) [20]. The plausible mechanism of this unique reaction involves (1) the initial formation of aziridinium cation intermediate catalyzed by aluminum Lewis acid and (2) the intramolecular nucleophilic migration of alkynyl group, as in transition state **9**.



Scheme 7 Chemoselectivity effects of Lewis base additives



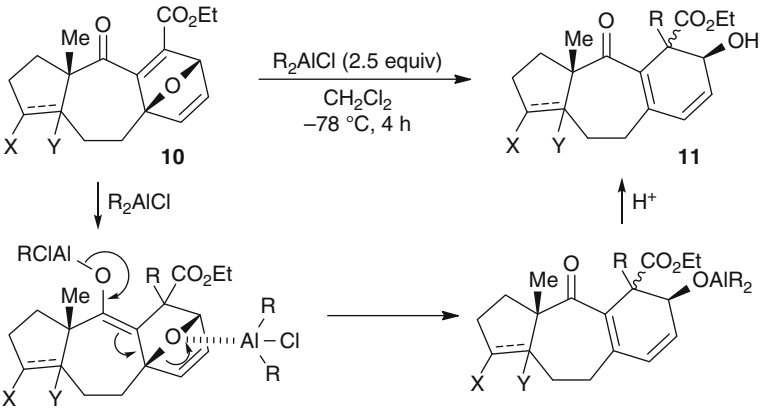
Scheme 8 Regioselectivity effects of Lewis base additives

Schneider et al. reported that the reactivity of trialkylaluminum to epoxides was dramatically enhanced under the influence of catalytic amount of Lewis base additives such as triphenylphosphine (Scheme 7) [21, 22]. The authors explain that the coordination between organoaluminum reagents and Lewis base is important for the breakage of trialkylaluminum dimer and the formation of a monomeric aluminum–phosphine adduct from which the alkyl substituent easily migrates. In addition, this procedure was found to improve not only chemical yields but also regioselectivity in the reactions of terminal epoxides (Scheme 8) [22].

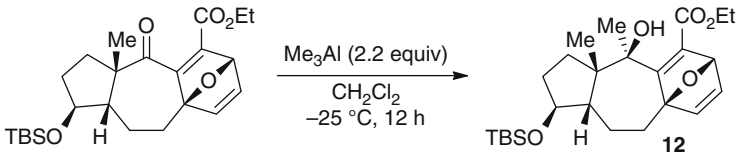
Not only structurally strained epoxides but also other sizes of heterocycles with oxygen function can be employed in the reaction promoted by organoaluminum reagents [3]. One of very recent examples is R_2AlCl-mediated ring-opening reaction of oxatricyclic compounds **10** for the construction of **11** with an all-carbon quaternary center reported by Quan and Yang et al. (Scheme 9) [23]. In the reaction using R_3Al instead of R_2AlCl, however, the alkylation of keto moiety selectively occurs to give **12** consisting of the different framework from **11** (Scheme 10).

As shown in the examples of Schemes 5–10, recent investigations have yielded the new insights about organoaluminum-mediated addition to carbonyl groups. Knochel et al. developed the novel protocols for preparation of allylic aluminum reagents from allyl halides and aluminum powder [24], and examined its application for diastereoselective addition to a series of carbonyl compounds [25]. For example, 3-bromocyclohexene **13** is converted to the corresponding allylic aluminum reagent and reacts with 4′-bromoacetophenone to give allylic alcohol in good yield and with excellent diastereoselectivity (Scheme 11).

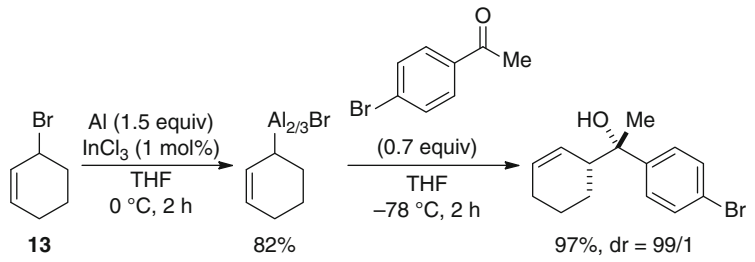
With this procedure, organoaluminum reagents bearing ester moiety **15** can be prepared from allylic chloride **14** without suffering from the intramolecular addition to ester functionality (Scheme 12). The reaction of **15** and 4′-bromoacetophenone provides bicyclic lactone as a single diastereomer.



Scheme 9 Construction of **11** reported by Quan and Yang et al.



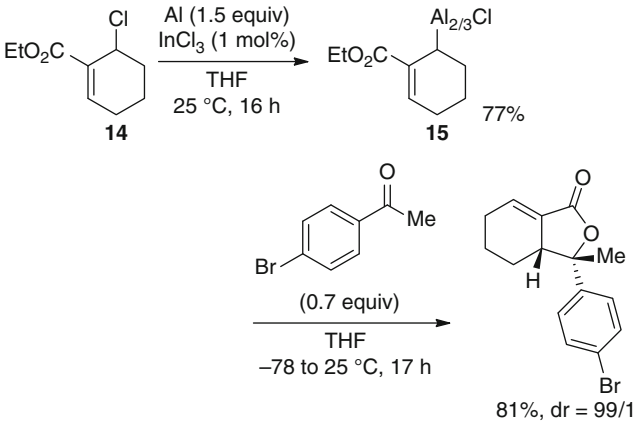
Scheme 10 Reagent effects in Quan's chemistry



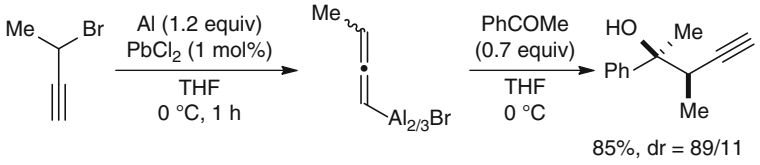
Scheme 11 Application of directly prepared allylaluminum species

A similar protocol enables the preparation of allenylaluminum reagents from propargylic bromides. The reaction of these aluminum reagents and aldehydes or ketones affords the corresponding homopropargylic alcohols in a diastereoselective manner (Scheme 13) [26].

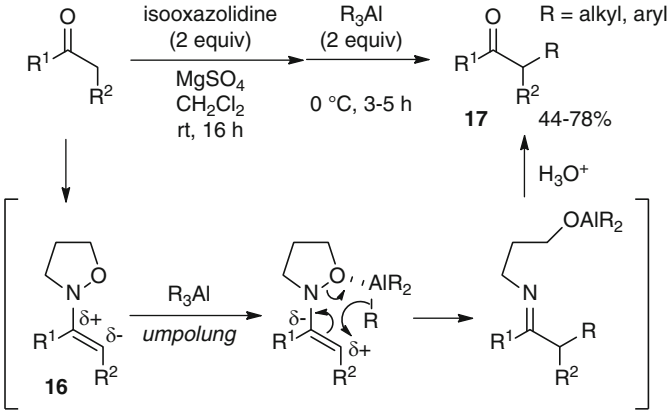
In a recent distinctive report, using carbonyl compounds and organoaluminum reagents, Miyata et al. developed a new umpolung reaction of *N*-alkoxyenamines **16** derived from ketones with trialkyl- or triarylaluminum reagents (Scheme 14) [27]. The final products are α-alkylated or arylated carbonyl compounds **17** through (1) the coordination between oxygen atom of isooxazolidine and organoaluminum



Scheme 12 Functional group tolerant organoalanes



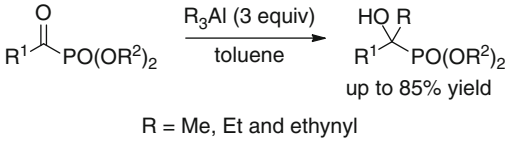
Scheme 13 Preparation of allenylaluminum reagents



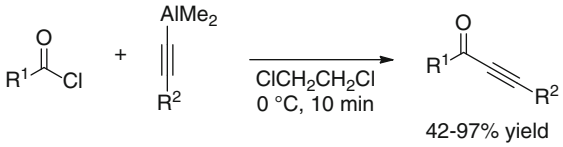
Scheme 14 Miyata's umpolung reaction of *N*-alkoxyenamines

reagents, (2) the N–O bond cleavage, and (3) the nucleophilic addition of alkyl or aryl group.

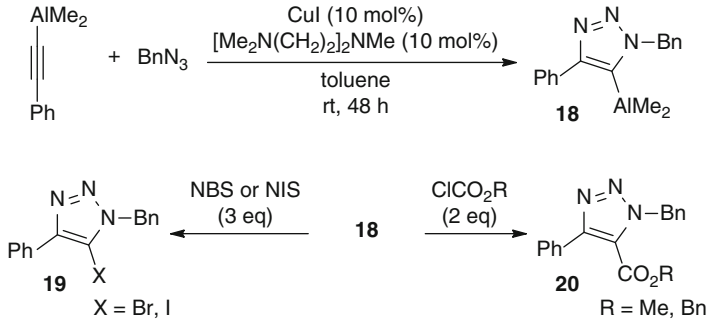
Other than listed above, new entries of oxygen-containing electrophiles were reported to react with Lewis acidic organoaluminum reagent in this decade. Demir



Scheme 15 Reaction of aryl phosphonates organoaluminum reagents



Scheme 16 Direct synthesis of ynones



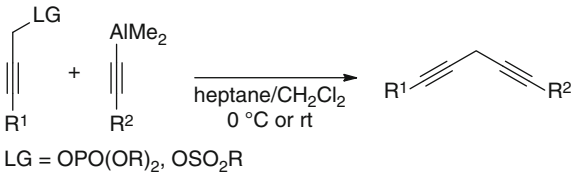
Scheme 17 Copper-catalyzed cycloaddition of organic azides and dimethylalkynylaluminums

et al. introduced the reaction of aryl phosphonates organoaluminum reagents (Scheme 15) [28]. This protocol provides a straightforward entry for the synthesis of secondary and tertiary α-hydroxy phosphonates, which are important building blocks of enzyme inhibitors.

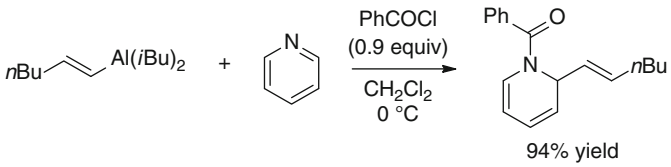
Micouin et al. reported the direct synthesis of ynones by the reaction of dimethylalkynylaluminum reagent and acid chlorides (Scheme 16) [29].

The same research group described the preparation method of organoaluminum reagents **18** via copper-catalyzed cycloaddition between organic azides and dimethylalkynylaluminums. Thus-generated organoaluninum reagents **18** can react with *N*-halo-succinimides or chloroformates to give the corresponding functionalized triazoles **19** or **20** (Scheme 17) [30].

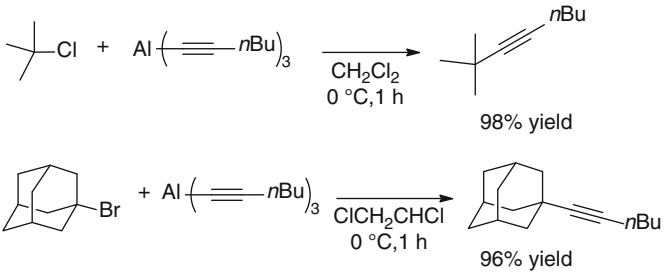
Wendeborn et al. developed the novel synthesis of skipped diynes by performing the reaction of propargylic electrophiles and dimethylalkynylaluminum reagents (Scheme 18) [31, 32].



Scheme 18 Reaction of propargylic electrophiles and dimethylalkynylaluminums



Scheme 19 Organoaluminum Reissert-type chemistry



Scheme 20 C–X couplings of trialkynylaluminum reagents

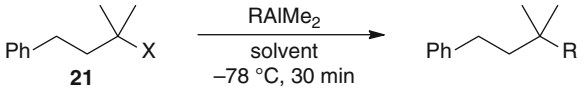
Menicagli et al. reported the one-pot Reissert-type reaction using acid chlorides, pyridine, quinoline or isoquinoline derivatives, and organoaluminum reagents (Scheme 19) [33].

2.2 *Reactions Involving Al–Halogen Coordination*

The synthetic strategy for C–C bond forming process utilizing the high affinity between halogen atom and aluminum atom has been paid much attention in modern organic chemistry [6]. For example, Megishi et al. elaborated the alkyl–alkynyl coupling between *tert*-alkyl chlorides or bromides and trialkynylaluminum reagents (Scheme 20) [34].

An emerging topic in this area is the activation of inert and stable C–F bond (ca. 460 kJ mol^{-1}, cf. the bond energy of Al–F = 663 kJ mol^{-1}) [35] using organoaluminum reagents [36]. Maruoka et al. utilized *tert*-alkyl fluorides

Table 2 C–F bond activation by organoaluminum reagents



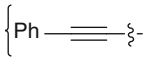
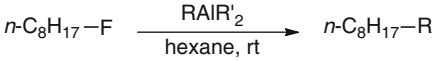
X	R	Solvent	Yield (%)
F	Me	CH_2Cl_2	70
F		Toluene	70
Cl		Toluene	No reaction

Table 3 Activation of primary alkyl fluorides



R	R′	Yield (%)
Et	Et	93
n-Hex	*i*-Bu	90 (*E*/*Z* = 90/10)
n-Hex	Et	94

(**21** X = F) as promising alkylation or alkynylation reagents for C–C bond forming reactions with organoaluminum reagents (Table 2) [37]. It should be noted that the reactions using **21** (X = Cl) didn't proceed at all. This result suggests that the strong interaction between fluorine and aluminum is necessary to convert the inert fluorine substituent to a good leaving group.

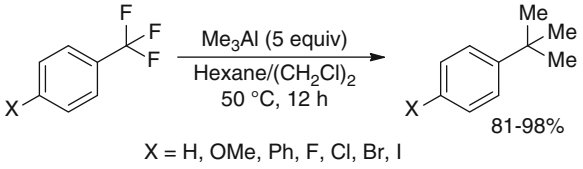
Later, Terao and Kambe et al. disclosed that primary alkyl fluorides were also employed in the alkylation reaction using organoaluminum reagents (Table 3) [38].

Very recently, the conversion of C–F bonds of a series of benzotrifluorides into C–C bonds was developed by using organoalunimun reagents (Scheme 21) [39, 40].

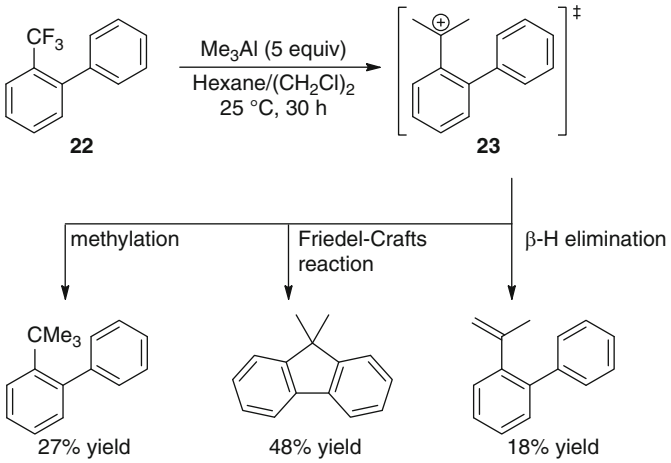
The treatment of *o*-phenyl-substituted benzotrifluoride **22** led to the formation of mixture of three products as shown in Scheme 22 [39]. This result can be explained as the common benzyl cation intermediate **23** underwent direct methylation, intramolecular Friedel–Crafts-type reaction, or β-H elimination to be converted into each product.

2.3 Asymmetric Addition to Chiral Substrates

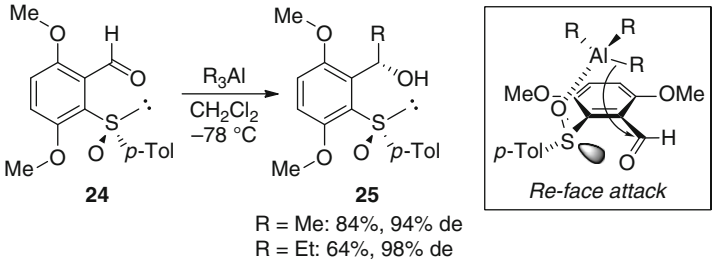
The asymmetric addition of organoaluminum to carbonyl compounds has been accomplished by using substrates involving chiral auxiliaries. In this section, recent examples published in this decade (to mid-2011) are overviewed.



Scheme 21 Exhaustive deflourination of CF_3 groups



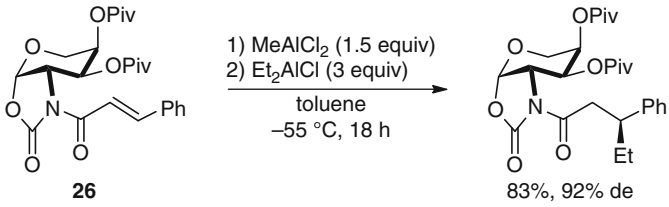
Scheme 22 Carbocation intermediates in deflourination



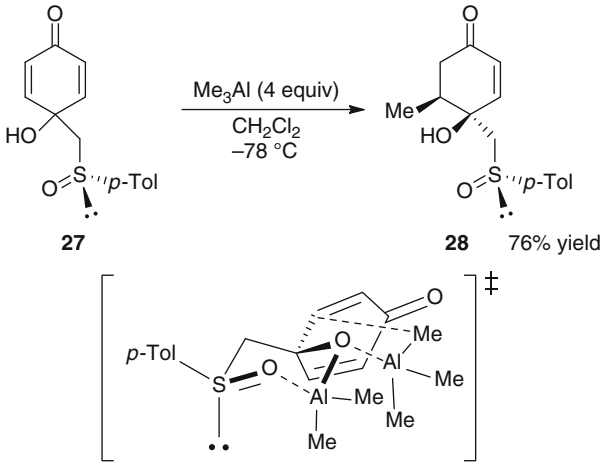
Scheme 23 Sulfinyl-directed additions to aldehydes

Carreño and Urbano et al. examined nucleophilic additions of alkylaluminum reagents to benzaldehyde **24** bearing a chiral sulfinyl group (Scheme 23) [41]. The effective association between aluminum atom and oxygen atom of sulfinyl moiety could be required to determine the stereochemical outcome of the alkylated products **25**.

Stereoselective conjugate addition of organoaluminum reagents has been performed by employing α,β-unsaturated carbonyl compounds having chiral auxiliary. Kunz et al. have demonstrated the asymmetric 1,4-addition of α,β-unsaturated



Scheme 24 Reaction of organoaluminum reagents with α,β-unsaturated *N*-acyloxazolidinones **26**

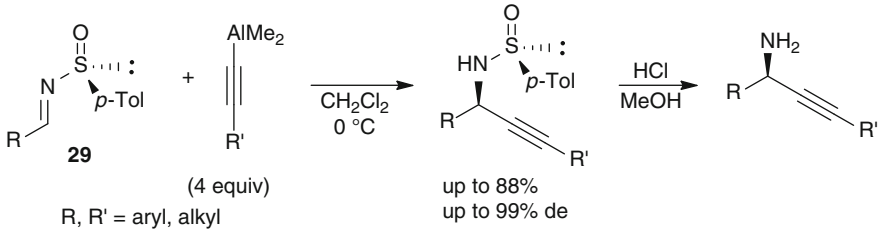


Scheme 25 Carreño's asymmetric synthesis of cyclohexenone **27**

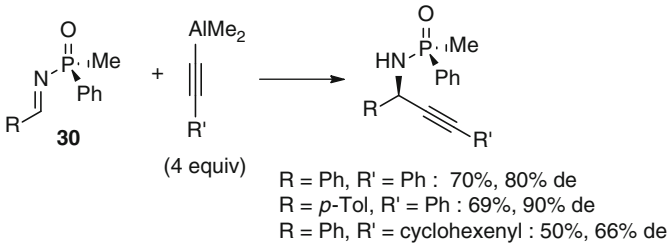
carbonyl compounds with a series of chiral oxazolidinones derived from various natural compounds [42]. The recent example is the reaction of organoaluminum reagents and α,β-unsaturated *N*-acyloxazolidinones **26** derived from carbohydrates (Scheme 24) [42]. Before the treatment of organoaluminum nucleophiles, an extra strong Lewis acid reagent ($MeAlCl_2$) must be added in order to achieve the satisfying results.

Carreño et al. realized the asymmetric synthesis of cyclohexanone **28** from [*p*-(tolylsulfinyl)methyl]-*p*-quinol **27** and trimethylaluminum (Scheme 25) [43, 44]. The possible transition state for the present reaction, explaining the observed stereochemistry is also shown in Scheme 25. The reaction of a stoichiometric amount of trimethylaluminum and **27** initially generates aluminum alkoxide which is associating with the sulfinylic oxygen to form pseudo-chair conformation. The second trimethylaluminum could coordinate with alkoxide oxygen and the nucleophilic attack of methyl group selectively undergoes from one of diastereotopic faces to furnish the corresponding product **28**.

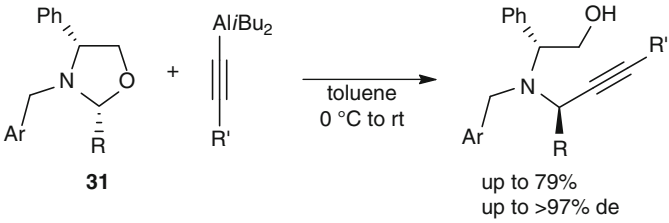
The addition of organometallic species to imines is one of general ways to produce substituted amines. Use of imines bearing chiral auxiliary on the nitrogen atom leads to the synthesis of optically active amine compounds. Among them, reactions using alkynylaluminum and chiral imine derivatives have been developed



Scheme 26 Diastereoselective alkynylation of *N*-tolylsulfiniylimines



Scheme 27 Additions to chiral phosphinoylimines

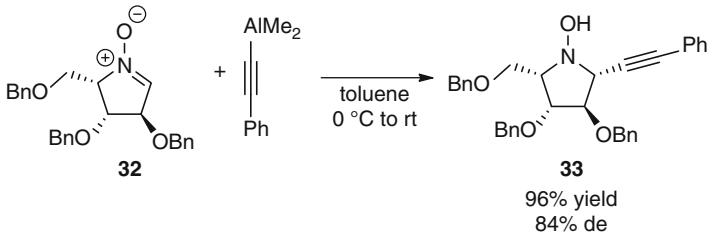


Scheme 28 Dialkylalkynylaluminum opening of chiral oxazolidinones

to furnish chiral propargylamines. Royer et al. investigated the diastereoselective alkynylation of *N*-tolylsulfiniylimines **29** (Davies imines) and dialkylalkynylaluminums (Scheme 26) [45]. The reaction proceeds cleanly to afford optically active propargyl amines in good yields and with high diastereoselectivities. Chiral auxiliary can be removed easily with the treatment of aqueous 3 M HCl solution in MeOH.

The same group tested the use of chiral phosphinoylimines **30** instead of **29** and the corresponding propargyl amines were obtained in up to 90% de (Scheme 27) [46].

Husson et al. performed the synthesis of enantiomerically pure propargylamines by the reaction of chiral oxazolidinones **31** and dialkylalkynylaluminum reagents (Scheme 28) [47, 48]. Lewis acid catalyzed hemiaminal cleavage at C–O bond occurs to generate reactive iminium intermediate. The following addition of alkynyl groups gives the final products in high diastereomeric excesses. Later the same group reported the modification and application of this protocol [49, 50].



Scheme 29 Addition of dialkylalkynylaluminums to nitrones

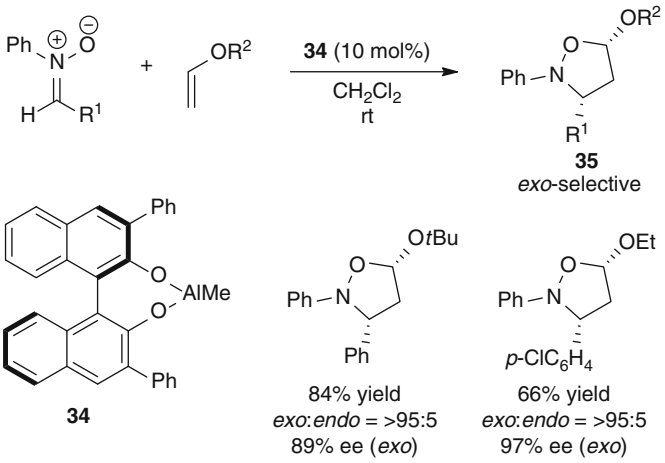
Nitrones also works as precursors of amines via nucleophilic addition of organoaluminum species. Desvergnes and Py et al. described the effective addition of dimethylalkynylaluminum reagents to carbohydrate-derived chiral nitrones **32** (Scheme 29) [51]. This strategy enables diastereoselective access to optically active *N*-hydroxy pyridine derivatives **33** having four stereogenic centers.

3 Chiral Organoaluminum for Asymmetric Reactions

The development of catalytic asymmetric reactions using chiral Lewis acid has become a major research field in modern synthetic organic chemistry. High efficiency and selectivity have been realized with the approach based on the sophisticated molecular design of chiral ligands. Among them, chiral organoaluminum complexes, which are usually generated in situ by mixing a chiral ligand and a typical achiral organoaluminum reagent such as Me_3Al, have attracted much attention as effective catalysts to promote asymmetric reactions with high enantioselectivity over decades. This section describes the current studies concerning chiral organoaluminum Lewis acid catalyzed asymmetric syntheses reported from 1999 through mid-2011. (For the review on chiral Al–Lewis acid catalyzed asymmetric reactions reported before 1998, see [7].)

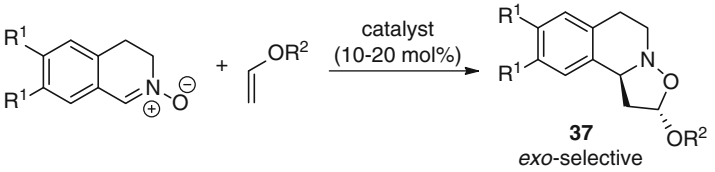
3.1 Cycloaddition Reactions

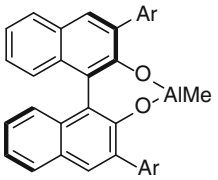
Cycloaddition reactions, as represented by 1,3-dipolar cycloaddition and Diels–Alder reaction, serve powerful ways for the construction of various carbocycles. Chiral organoaluminum reagents have been identified as promising catalysts to promote asymmetric cycloaddition reactions. In 1999, Jørgensen et al. developed the first catalytic inverse-electron demand 1,3-dipolar cycloaddition reaction of aromatic nitrones and vinyl ethers catalyzed chiral aluminum complex **34** (Scheme 30) [52]. The nitrones are activated by chiral Lewis acid **34**, and the cycloaddition reaction with vinyl ethers furnishes the corresponding *exo*-isomer of isooxazolidines **35** in good yields and with high up to >95% de and 97% ee.



Scheme 30 Jørgensen's inverse-electron demand 1,3-dipolar cycloaddition

Table 4 Catalytic cycloaddition routes to 1,2,3,4-tetrahydroisoquinolines **37**

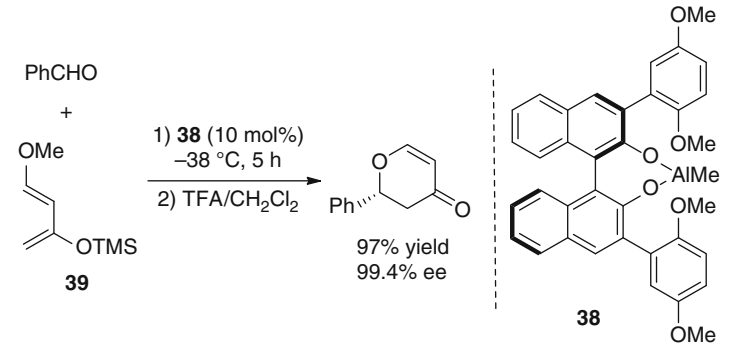


	R^1	R^2	Cat	Yield (%)	*Exolendo*	ee (*exo*) (%)
	H	Et	**36**	85	96/4	85
	OMe	Et	**34**	76	97/3	70
	H	*t*Bu	**34**	86	95/5	70
	OMe	*t*Bu	**34**	92	100/0	65
	H	Ph	**34**	24	>95/5	10

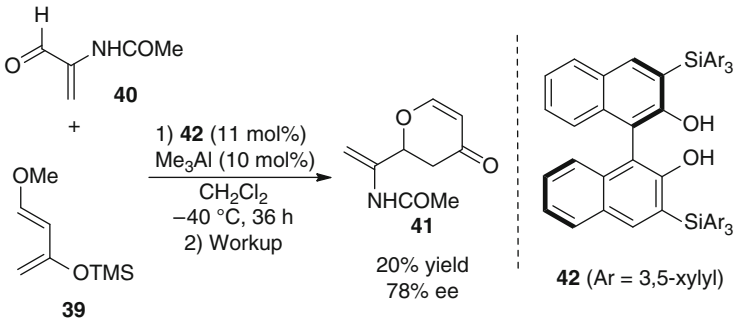
34 Ar = Ph
36 Ar = 2,5-$(OMe)_2C_6H_3$

The chiral Lewis acid **34** or **36** catalyzed-cycloaddition reaction of cyclic nitrones and vinyl ethers provided the 1-substituted 1,2,3,4-tetrahydroisoquinolines **37** in a highly *exo*-selective manner (Table 4) [53].

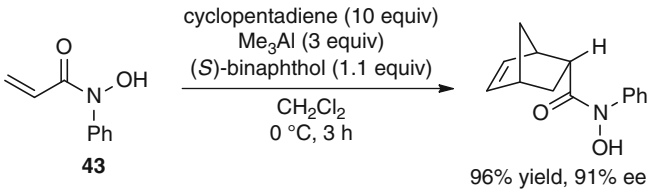
In 2000, the same group evaluated the catalytic activity of similar chiral aluminum complexes **38** in enantioselective hetero-Diels–Alder reaction of benzaldehyde and Danishefsky's diene **39** (Scheme 31) [54]. The mechanism for this hetero-Diels–Alder reaction has been investigated from a theoretical point of view using semiempirical and ab initio calculations [55].



Scheme 31 Enantioselective hetero-Diels–Alder reactions



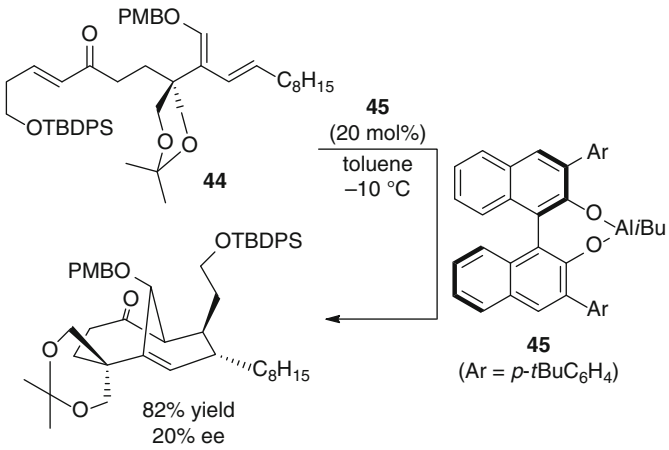
Scheme 32 Pu's asymmetric hetero-Diels–Alder reaction



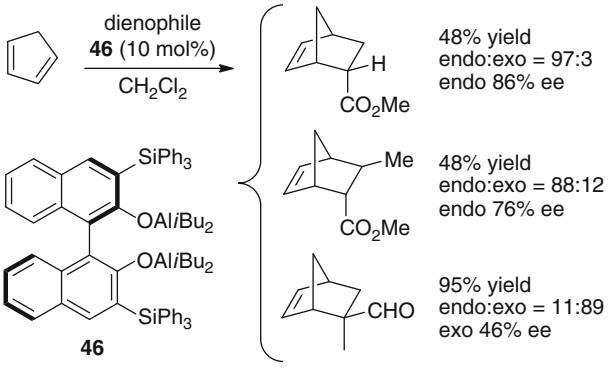
Scheme 33 Diels–Alder reactions of *N*-hydroxy-*N*-phenylacrylamide

In 2000, Pu et al. demonstrated asymmetric hetero-Diels–Alder reaction of enamide **40** and Danishefsky's diene **39** to give compound **41** as a precursor to natural compound fumonisins (Scheme 32) [56]. The most effective ligands for this reaction were 3,3′-disilyl substituted binaphthol ligand **42**, and enantioselectivity of **41** reached 78% ee.

In 2002, Renaud et al. reported enantioselective Diels–Alder reactions of *N*-hydroxy-*N*-phenylacrylamide **43** and cyclopentadiene catalyzed by chiral aluminum Lewis acid prepared by mixing (*S*)-binaphthol with 3 equiv. of Me_3Al (Scheme 33) [57].



Scheme 34 Intramolecular Diels–Alder reaction in CP-molecule synthesis

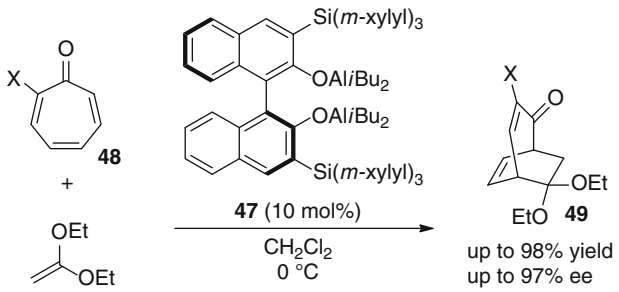


Scheme 35 Scope of bis-aluminum Lewis acid catalyst **46**

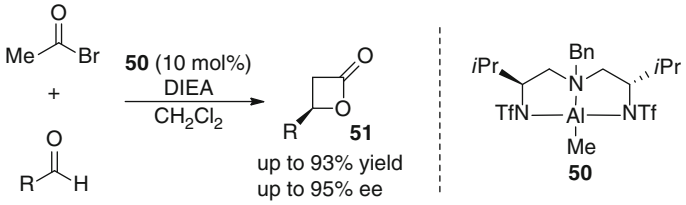
In the study of total synthesis of the CP-molecules by Nicolaou group, the asymmetric intramolecular Diels–Alder reaction of prochiral triene compound **44** was conducted under the influence of chiral aluminum Lewis acid catalyst **45**, albeit the low level of enantioselectivity (Scheme 34) [58, 59].

Significant effects of bis-aluminum Lewis acid catalyst for enantioselective Diels–Alder reactions have been discovered by Yamamoto et al. For example, the asymmetric Diels–Alder reaction of cyclopentadiene and α,β-unsaturated carbonyl compounds underwent with the aid of chiral bis-aluminum Lewis acid **46** (Scheme 35) [60].

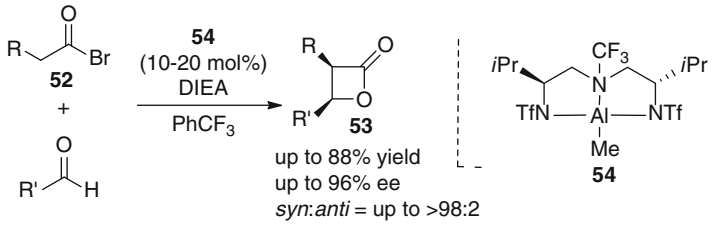
In 2009, Yamamoto et al. developed chiral bis-aluminum **47** catalyzed inverse electron demand Diels–Alder reaction of tropones **48** to give the functionalized bicyclo[3.2.2] ring structures **49** with high enantioselectivities (Scheme 36) [61].



Scheme 36 Diels–Alder reaction of tropones

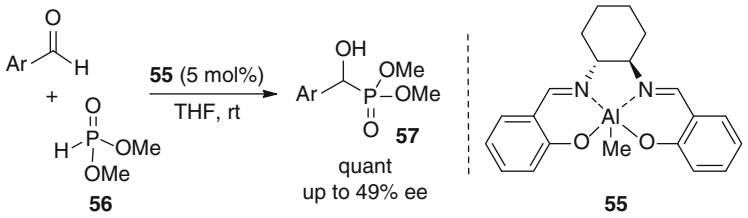


Scheme 37 Asymmetric [2+2] cycloaddition reactions of ketene and aldehydes

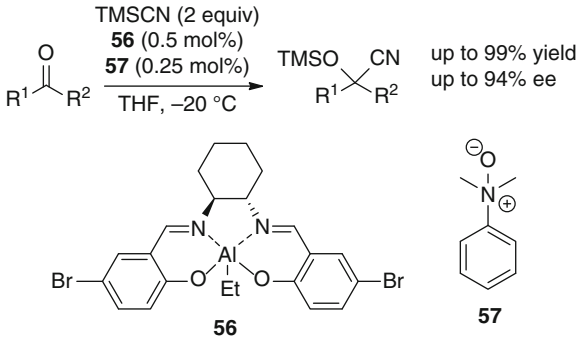


Scheme 38 Asymmetric [2+2] cycloaddition reactions of substituted ketene

In 1999, Nelson et al. developed chiral triamine-based organoaluminum complex **50** for asymmetric [2+2] cycloaddition reactions of ketene and aldehydes (Scheme 37) [62, 63]. Ketene generated in situ from acetyl bromide reacts with a series of aldehydes to furnish the optically active β-lactones **51**, which become key compounds in their study of natural compound synthesis in order to demonstrate the utilities of the present methodology [64–67]. The reaction of acid bromide **52** and aldehydes provided the corresponding *syn*-isomer of chiral β-lactones **53** having contiguous chiral centers with the aid of chiral organoaluminum species **54** (Scheme 38) [68, 69].



Scheme 39 Asymmetric catalytic Pudovik reaction



Scheme 40 Enantioselective cyanosilylation of ketones

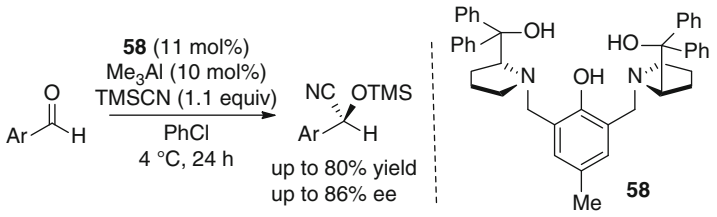
3.2 Addition to Carbonyl Compounds

Enantioselective addition of various nucleophiles to carbonyl compounds has received significant attention in modern asymmetric synthesis. This objective has been accomplished with the aid of chiral organoaluminum complexes. Kee et al. examined organoaluminum–chiral salen complex **55** catalyzed addition of dialkylphosphites **56** to aldehydes, known as Pudovik reaction, to give α-hydroxyphosphonates **57** (Scheme 39) [70, 71].

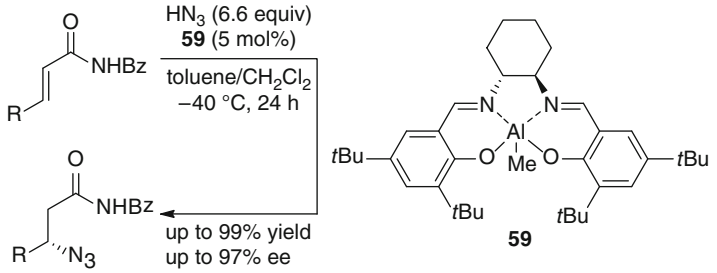
In 2004, Feng et al. reported enantioselective cyanosilylation of ketones catalyzed by chiral organoaluminum complex **56** (Scheme 40) [72, 73]. Their strategy involves the simultaneous activation of electrophiles by chiral Lewis acid **56** and of nucleophiles (TMSCN) by achiral Lewis base **57**.

In 2005, Trost et al. developed enantioselective addition of TMSCN to aldehydes using chiral aluminum Lewis acid catalyst based on their inventive chiral ligand **58** (Scheme 41) [74].

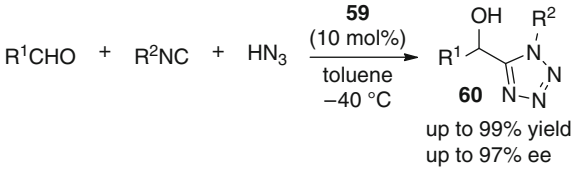
Other than listed above, the asymmetric conjugate addition to α,β-unsaturated carbonyl compounds has been also conducted by using organoaluminum species. In 1999, Jacobsen et al. described the highly enantioselective conjugate addition of hydrazoic acid (HN_3) to α,β-unsaturated imides catalyzed chiral salen–organoaluminum complex **59** (Scheme 42) [75].



Scheme 41 Enantioselective addition of TMSCN to aldehydes



Scheme 42 Asymmetric conjugate addition of azide

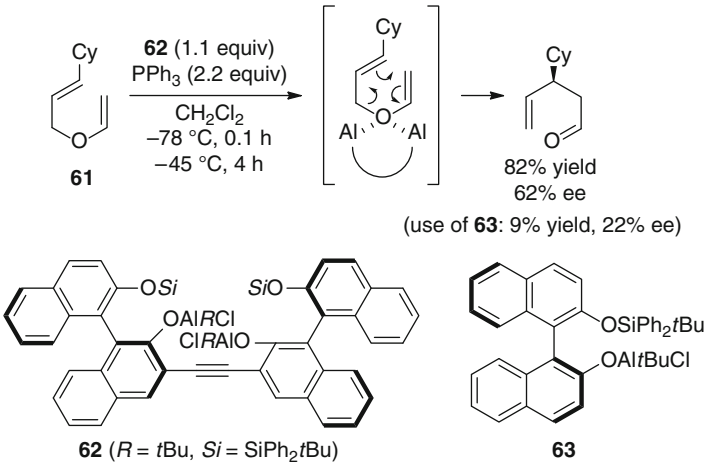


Scheme 43 Catalytic enantioselective Ugi reaction

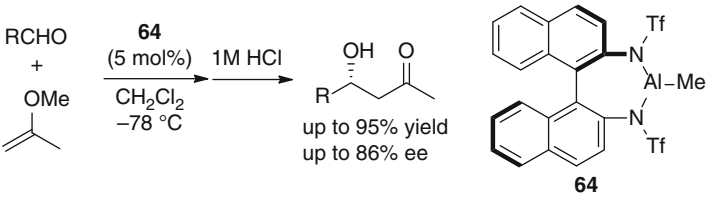
Furthermore, multicomponent reactions, as represented by Ugi reaction and Biginelli reaction, are attractive strategies for the selective construction of complex organic molecules from several simple starting materials in a single operation. Recently, Wang and Zhu et al. reported asymmetric synthesis of 5-(1-hydroxyalkyl)tetrazoles **60** from aldehydes, isocyanide, and hydrazoic acid via chiral salen–organoaluminum complex **59** catalyzed asymmetric Passerini-type reaction (Scheme 43) [76].

3.3 Rearrangement Reactions

Rearrangement reactions, as represented by Wagner–Meerwein rearrangement and Claisen rearrangement, often occupy a unique place in organic synthesis, due to the feasibility of giving organic molecules that are hard-to-access by other strategies.



Scheme 44 Claisen rearrangement induced by a chiral bis-organoaluminum



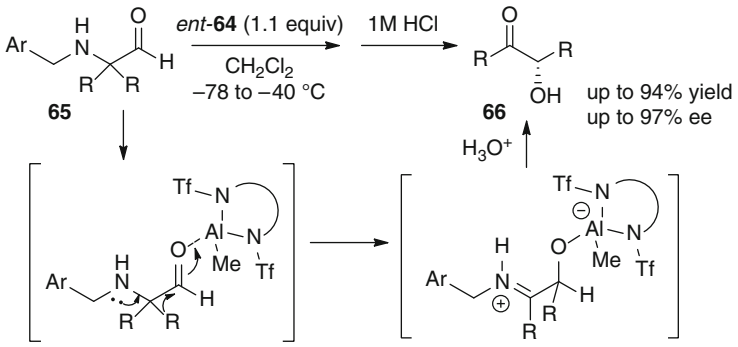
Scheme 45 Enantioselective hetero-carbonyl-ene reaction

It has been shown that chiral organoaluminum species could catalyze such asymmetric rearrangements of organic flameworks incorporating oxygen function with good enentioselectivity.

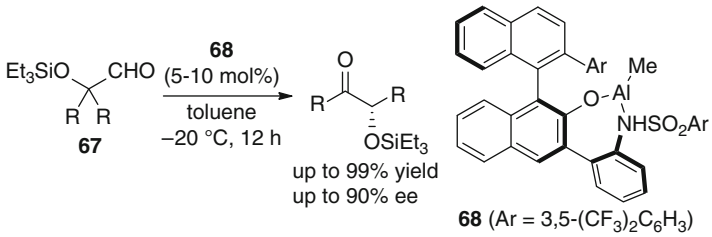
In 2002, Maruoka et al. reported the enantioselective Claisen rearrangement of allyl vinyl ethers **61** induced by chiral bis-organoaluminum complex **62** (Scheme 44) [77]. Reactions using mono-organoaluminum complex **63** resulted in the decrease of both chemical yields and enantiomeric excess, indicating the importance of the double coordination between carbonyl group and two aluminum centers of **62**.

As an example of asymmetric intermolecular sigmatropic rearrangement, chiral Lewis acid promoted carbonyl-ene reactions have been utilized as the powerful tool for stereocontrolled carbon–carbon bond formation processes. In 2004, Maruoka et al. demonstrated enantioselective hetero-carbonyl-ene reaction of aldehydes and 2-methoxypropene catalyzed by chiral organoaluminum complex **64**, giving enantiomerically enriched β-hydroxymethylketones (Scheme 45) [78].

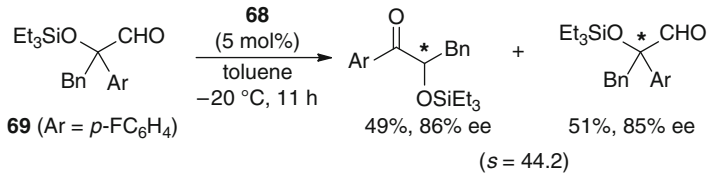
Maruoka et al. demonstrated a series of asymmetric skeletal rearrangements involving 1,2-carbon-to-carbon migration catalyzed by chiral organoaluminum complexes. In 2003, they described the enantioselective skeletal rearrangement of



Scheme 46 Enantioselective skeletal rearrangement



Scheme 47 Catalytic asymmetric 1,2-migration

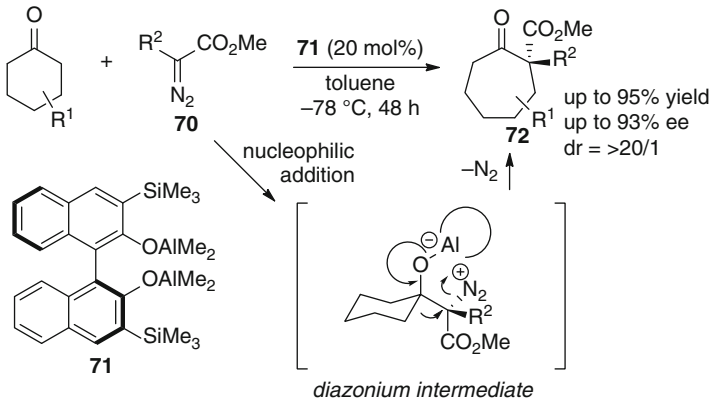


Scheme 48 Kinetic resolution of α,α-disubstituted α-siloxy aldehydes

symmetrically α,α-disubstituted α-amino aldehydes **65** using chiral organoaluminum complex *ent*-**64** to give optically active α-hydroxy ketones **66** (Scheme 46) [79].

They successively developed the first example of *catalytic* asymmetric 1,2-migration. They demonstrated the enantioselective 1,2-skeletal rearrangement of α,α-disubstituted α-siloxy aldehydes **67** using chiral organoaluminum Lewis acid **68** (Scheme 47) [80]. With this protocol, they also examined a kinetic resolution of racemic, differently α,α-disubstituted α-siloxy aldehydes **69** wherein the *s* values reached up to 44.2 (Scheme 48) [80]. Later, they investigated the related mechanistic study shedding light on the reason for the expression of this migration aptitude in the 1,2-migration by using achiral organoaluminum species [81, 82].

In 2011, Maruoka et al. reported desymmetrizing asymmetric ring expansion of substituted cyclohexanones with α-diazoacetates **70** catalyzed chiral bis-aluminum



Scheme 49 Desymmetrizing asymmetric ring expansion

Lewis acid **71**. This procedure gave the corresponding seven-membered products **72** with high enantio- and diastereoselectivity (Scheme 49) [83]. This reaction involves (1) the nucleophilic addition of **70** to acid activated cyclohexanones and (2) the subsequent 1,2-skeletal rearrangement of diazonium intermediate with the evolution of nitrogen. It should be noted that this protocol overcame the difficulty of stereocontrolled addition to *symmetric* ketones without a prochiral face.

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Hydro-, Carbo-, and Cycloalumination of Unsaturated Compounds

Usein M. Dzhemilev and Vladimir A. D'yakonov

Abstract This chapter gives a survey and a systematic account of modern achievements in the synthesis of acyclic and cyclic organoaluminum compounds using thermal and catalytic hydro- and carboalumination of unsaturated compounds. Here we consider a new, versatile catalytic cycloalumination reaction of olefins, acetylenes, and 1,2-dienes of various structures with alkyl and halogen alkyl Al catalyzed by Zr and Ti complexes to give previously unknown classes of OACs: aluminacyclopropanes, aluminacyclopropenes, aluminacyclopentanes, aluminacyclopentenes, aluminacyclopentadienes, and aluminamacrocarbocycles. Much attention is given to applications of hydro-, carbo-, and cycloalumination reactions for the synthesis of practically important natural carbo- and heterocyclic compounds.

Keywords Alkenes/alkynes · Aluminacyclopentane · Alumination · Dienes · Organoaluminum compounds

Contents

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Abbreviations

COD	1,5-Cyclooctadienyl
Cp	η^5-Cyclopentadienyl, C_5H_5
Cp*	η^5-Pentamethylcyclopentadienyl, C_5Me_5
Hex	*n*-C_6H_{13}
OAC	Organoaluminum compound
ZACA	Zr-catalyzed asymmetric carboalumination of alkenes

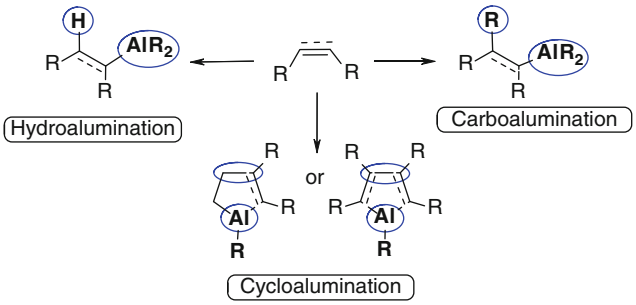
1 Introduction

A significant achievement of OAC chemistry in the second half of the twentieth century was K. Ziegler's discovery (in 1954) of an effective synthetic route to trialkylalanes based on the reaction of Al metal with an olefin and hydrogen [1]. The industrial implementation of this preparative method for trialkylalanes stimulated the broad development of organoaluminum synthesis and commercialization of highly important processes such as oligo- and polymerization of olefins and dienes, metathesis of olefins and acetylenes, alkylation of aromatic compounds, and the synthesis of higher alcohols. Modern chemical industry branches are difficult to imagine without organoaluminum compounds, which have now become ingrained in the practice of synthetic organic and organometallic chemistry as effective reducing agents for carbonyl compounds, esters and nitriles, as effective methylenation reagents of carbonyl compounds, as reagents for regio- and stereoselective reduction of alkenes and acetylenes, and as components of catalytic systems for fine and industrial organic synthesis.

In view of the limited size of the review presented to the reader, we will consider mainly the catalytic hydro-, carbo-, and cycloalumination of unsaturated compounds aimed at the development of effective synthetic methods for the construction of Al–C, C–C, and C–H bonds promising for the application both in the laboratory practice and in industry in the areas of Scheme 1.

Since the mid-twentieth century when the simplest OACs became widely known, a large number of publications have appeared dealing with the reaction of alkylaluminum hydrides and trialkylalanes with olefins and acetylenes to give hydro- and carboalumination products. In the vast majority of cases, these reactions occur under vigorous conditions (high temperature, pressure, long reaction time) and, therefore, these methods have not found wide use in the modern laboratory practice.

Upon the advent of metal complex catalysis techniques in organic and organometallic synthetic practice, the journey from thermal hydro- and carboalumination to high-tech and energy-saving catalytic versions of these reactions providing OACs of the desired structure under mild conditions with high regio- and stereoselectivity was attained over a short period of time. These studies were further developed in pioneering works dealing with the efficient catalytic replacement of the transition metal atoms in metallacarbocycles by main group [2]. In 1989, these investigations



Scheme 1 Hydro-, carbo-, and cycloalumination of unsaturated compounds

resulted in the discovery of the catalytic cycloalumination reaction of unsaturated compounds with simple trialkyl- and alkylhaloalanes catalyzed by Ti- and Zr-containing complexes to afford previously unknown classes of three- and five-membered and macrocyclic aluminacarbocycles. The above-mentioned achievements opened up new effective ways of the design, in one preparative step, of a broad range of practically valuable metallacarbocycles starting from olefins, dienes, acetylenes, allenes, and alkyl aluminum derivatives with participation of complex catalysts based on transition metals [3–6].

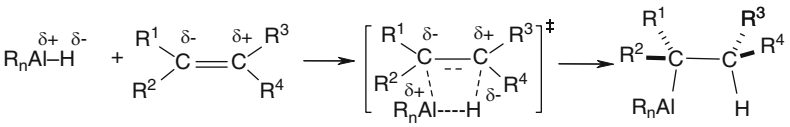
In view of the foregoing, in this review, the attention is focused on the catalytic hydro-, carbo-, and cycloalumination reactions and the application of these reactions in organic and organometallic syntheses. In some cases, the thermal versions of hydro- and carboalumination are considered to compare the efficiency and the selectivity of these methods.

2 Hydroalumination of Unsaturated Compounds

2.1 Hydroalumination of Alkenes

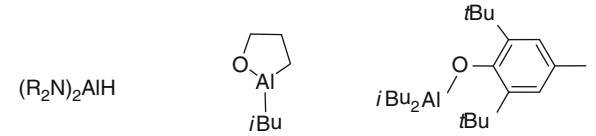
The thermal and catalytic hydroalumination of unsaturated compounds is covered rather comprehensively in a number of reviews [4, 7, 8] and monographs [9, 10] published in the last 10–15 years. Uncatalyzed hydroalumination of olefins with R_nAlH goes through a four-centre transition state in which the Al–H bond is cleaved and main group metal adds to the most electronegative carbon atom of the starting olefin (depending on the olefin nature and substituent structure) while the hydrogen atom, in turn, adds to the electropositive carbon atom [10] (Scheme 2).

Traditionally, alkenes are hydroaluminated using inorganic aluminum hydrides (AlH_3, $AlHCl_2$, $AlHBr_2$, $LiAlH_4$, $NaAlH_4$) or organoaluminum reagents represented most often by diisobutylaluminum hydride (iBu$_2$AlH), diethylaluminum hydride (Et$_2$AlH), triisobutylaluminum (Bu$_3$Al), and diisobutylaluminum chloride (iBu$_2$AlCl) [10]. The hydride alanes iBu$_2$AlH, iBu$_3$Al, and $LiAlH_4$ are most popular as



Scheme 2 Hydroalumination of unsaturated compounds

hydroaluminating reagents. The utilization of aluminum dialkylamides, cycloalumoxane, and diisobutylaluminum phenoxide as hydroaluminating reagents was reported [10].



aluminum dialkylamides

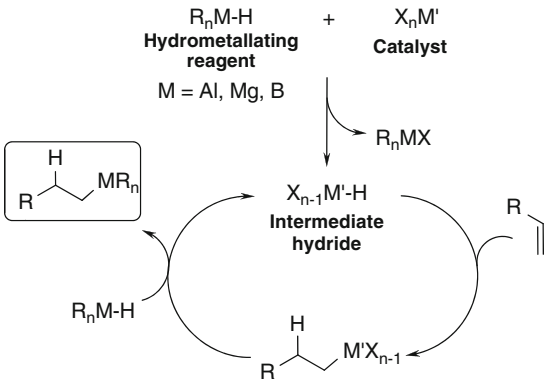
cycloalumoxane

diisobutylaluminum phenoxide

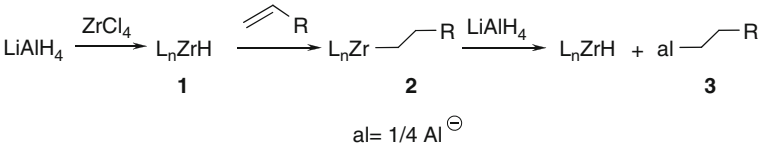
The thermal hydroalumination of olefins with alanes is known to suffer from a number of limitations and shortcomings. In particular, the reactions occur at elevated temperature (70–150°C) and are only applicable to a limited range of olefins, because the reaction is complicated by the presence of functional groups in the olefin. The use of catalysts for such reactions eliminates many of the limitations, allowing hydroalumination under milder conditions and with increased reaction rate. In some cases, hydroalumination occurs only in the presence of a catalyst. In addition, catalysts based on transition metals affect the regio- and stereochemistry of hydroalumination of unsaturated compounds. With the advent of metal complex catalysis techniques in organic and organometallic chemistry, it became possible to perform chemo-, regio-, and stereoselective, in particular, enantioselective, hydroalumination of unsaturated compounds under mild conditions in high yields [10].

The role of the catalyst in these reactions is reduced to the activation of the initial substrate through coordination to the catalyst central atom and to the formation of intermediate transition metal hydride complexes. These complexes, being more reactive as hydrometallating reagents, add to alkenes under mild conditions and then undergo transmetallation by an excess of the initial hydride reagent to give the target organometallic compounds according to Scheme 3.

An efficient hydroaluminating reagent for α-olefins is $LiAlH_4$; the reaction is carried out under mild conditions (0–20°C) in the presence of catalytic amounts of Ti and Zr complexes and gives lithium tetraalkylalanates in 60–100% yields [11]. During this reaction, intermediate zirconium hydride complexes **1** are generated; they hydrozirconate the initial olefins to give intermediate Zr alkyl complexes **2**. Transmetallation of complex **2** with the initial $LiAlH_4$ affords again hydride complexes **1** (Scheme 4) and the target higher trialkylalanes.



Scheme 3 Schematic mechanism of the catalytic hydrometallation of olefins

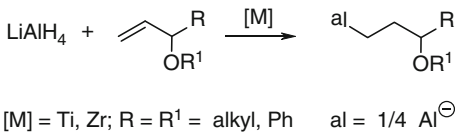


Scheme 4 Zr-Catalyzed hydroalumination of alkenes with $LiAlH_4$

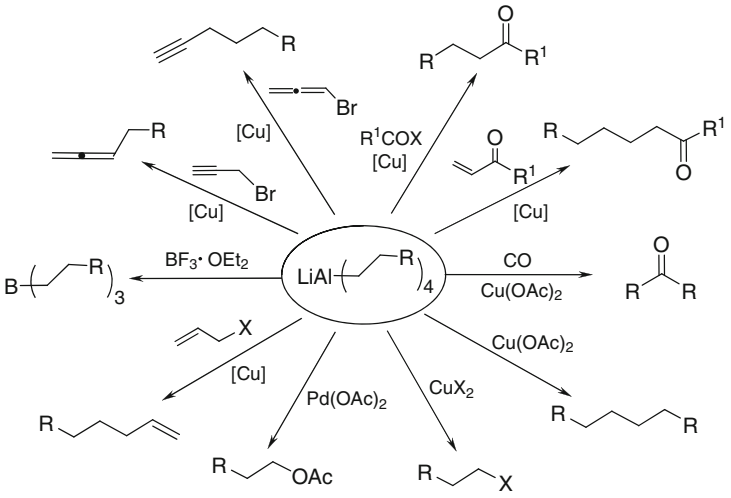
In hydroalumination of 1-hexene with $LiAlH_4$ it was found [12] that, apart from $ZrCl_4$, high catalytic activity in olefin hydroalumination is also attained with $TiCl_4$, VCl_4, Cp_2TiCl_2, and Cp_2ZrCl_2. Hydroalumination of terminal alkyl olefins with $LiAlH_4$ catalyzed by $Cp^*_2TiCl_2$ [13] or $Cp^*_2ZrCl_2$ [14] proceeds over 3–5 h at 0°C to give products in 93–99% yields. When Cp_2TiCl_2 is used, hexane is formed in appreciable amounts together with the hydroalumination products [15]. In terms of their reactivity toward hydroalumination, aluminum hydrides and initial olefins are arranged in the following series: $LiAlH_4 > AlH_3 > AlH_2Cl > AlHCl_2$; $RCH = CH_2 > R_2C = CH_2 > RCH = CHR$ [16]. Other metal complexes used as hydroalumination catalysts include: Co, Ni, Fe, Cr, U compounds [17–21] and transition metal complexes immobilized on inorganic or polymer supports [22].

In addition to the high regio- and stereospecificity, the catalytic hydroalumination has one more advantage over the thermal version of this reaction, namely, there appears the possibility to hydroaluminate at least some functionally substituted olefins, for example, allyl alcohols and ethers (Scheme 5).

The lithium tetraalkylalanates obtained in situ from these reactions are easily involved in the subsequent transformations. Cross-coupling of lithium tetraalkylalanates with allyl halides in the presence of copper compounds (CuBr, CuI, CuCN, CuCl, $Cu(OAc)_2$) furnishes olefins that differ from the initial ones by three carbon atoms [23], and CuCl-catalyzed reaction with propargyl bromide produces terminal allenes in high yields [24]. Such cross-couplings were also performed with allene bromide [25], carboxylic acid halides [26], acrolein [27], and methyl vinyl ketone



Scheme 5 Catalytic hydroalumination of allyl ethers by $LiAlH_4$



Scheme 6 Some transformations of $LiAlH_4$-derived alkyl alanes

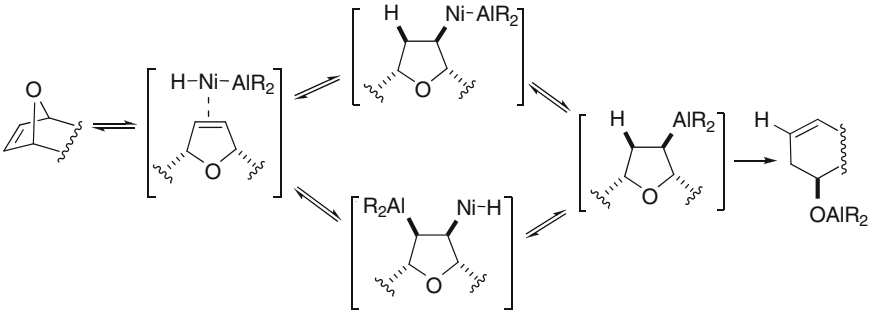
[27, 28]. The catalytic hydroalumination with $LiAlH_4$ and the subsequent functionalization of the alkylalanes thus allows a one-pot route for conversion of the initial olefins to organic halides [29], acetates [30], or organoboron compounds [31] (Scheme 6).

Oxabicyclic alkenes were hydroaluminated with iBu$_2$AlH using Ni(COD)$_2$ or its combination with phosphines as a catalyst. The regio- and enantioselectivity of the reactions depend on the ligand environment of the catalyst central atom, the catalyst concentration and component ratio, the nature of the solvent, and the rate of introduction of iBu$_2$AlH into the reaction mixture [32–35] (Scheme 7).

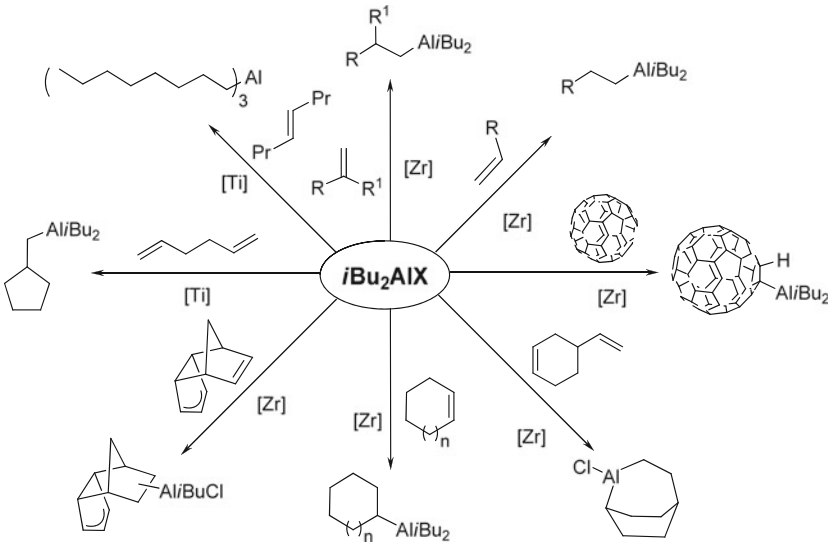
Catalytic hydroalumination has been widely used in relation to terminal, 1,2-disubstituted and cyclic alkenes and α,ω-dienes, norbornenes, and polyene systems, for example, C_{60} fullerene [36–48] (Scheme 8).

2.2 *Hydroalumination of Alkynes*

Hydroalumination of mono- and disubstituted acetylenes finds wide use in synthetic organic chemistry for the preparation of practically important trisubstituted



Scheme 7 Reaction of oxabicyclic alkenes with iBu$_2$AlH in the presence of Ni(COD)$_2$

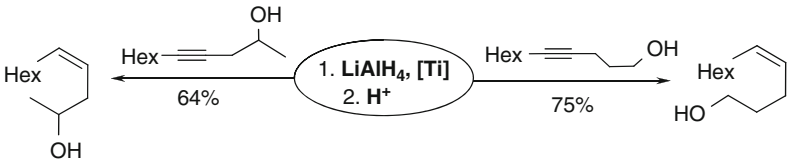


Scheme 8 Catalytic hydroalumination of unsaturated compounds (X = H, Cl)

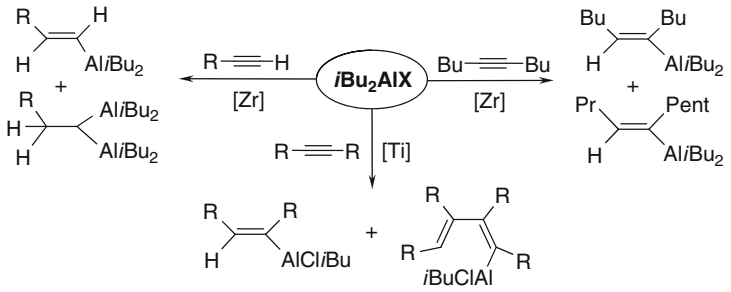
olefins [49], allyl alcohols [50], substituted 1,3-dienes [51], alkyl-1-en-3-ynes [52], alkenyl silanes and alkenyl sulfones [53, 54], (E)-vinylphosphonates [55], 1-halo-2-alkylcyclopropanes [56], unsaturated acids [57], etc.

Unlike alkenes, disubstituted acetylenes are hydroaluminated under mild conditions by means of iBu$_2$AlH and iBu$_3$Al without a catalyst. However, often it is impossible to avoid undesired side reactions and the subsequent transformations of vinyl alanes. Hydrolysis of the vinylalanes gives rise to 1,2-disubstituted olefins of *Z*- or *E*-configuration depending on the nature of the hydroaluminating reagent used [58], the structure of the initial acetylene [59], and the solvent [59].

In the presence of catalytic amounts of Cu, Fe, Ni, Ti, and Zr complexes or salts [13, 18, 60–64, 178], hydroalumination of acetylenes with iBu$_2$AlH, LiAlH$_4$,



Scheme 9 Ti-Catalyzed hydroalumination of alkynols



Scheme 10 Hydroalumination of alkynes with $i\text{Bu}_2\text{AlX}$ (X = *i*Bu, Cl)

$NaAlH_4$, $LiAlMe_3H$, $NaAlMe_3H$, $(i\text{Pr}_2\text{N})_2AlH$, $NaAl(OCH_2CH_2OCH_3)_2H_2$ can be performed with high selectivity to give up to 100% yields of target alkenyl alanes, especially from internal alkynes.

Thermal hydroalumination of alkynols using $LiAlH_4$ in diglyme at 150°C results in the formation of (E)-alkenols [65]. When this reaction is catalyzed by Cp_2TiCl_2 (10 mol%), (*Z*)-alkenols are formed as major products (*Z*/*E* ~ 10:1) [66] (Scheme 9). It was suggested [66] that under conditions of the above reaction, reactive complexes [Ti]-H are generated and hydrotitanate the triple bond. The subsequent transmetallation of the Ti alkenyl complexes results in (*syn*)-alkenyl alanes and regeneration of the hydride complexes [Ti]-H.

Worthy of note are the reagents $i\text{Bu}_2\text{AlCl}$–$[Cp_2TiCl_2]$ and Et_3Al–$[Cp_2TiCl_2]$ used for selective hydroalumination of disubstituted acetylenes to the corresponding unsaturated OACs [67, 68]. The OACs thus formed are hydrolyzed to afford *Z*-olefins. Depending on the structure of the initial acetylenes and reaction conditions, the reaction gives ~5–30% of alkadienyl alanes apart from alkenyl alanes. The structures of the unsaturated OACs were established by spectral methods [69–71] (Scheme 10). Unlike hydroalumination with the Et_3Al–Cp_2TiCl_2 system [68], the reaction of disubstituted acetylenes with $n\text{Pr}_3\text{Al}$ in the presence of Cp_2ZrCl_2 is less selective and gives a mixture of isomeric alkenyl alanes in ~60% overall yield [70].

The data presented in the literature indicate that in most cases, catalytic hydroalumination of acetylenes occurs under mild conditions to give alkenyl alanes, which are hydrolyzed to give *Z*-olefins in high yields.

Scheme 11 Ti-Catalyzed hydroalumination of norbornenes by Et_2AlCl

3 Carboalumination of Unsaturated Compounds

3.1 Carboalumination of Alkenes, Norbornenes, and Dienes

The stereo- and regioselective addition of OAC to olefins and acetylenes accompanied by Al−C bond cleavage is quite valuable from the synthetic viewpoint, because this affords simultaneously new metal–carbon and carbon–carbon bonds.

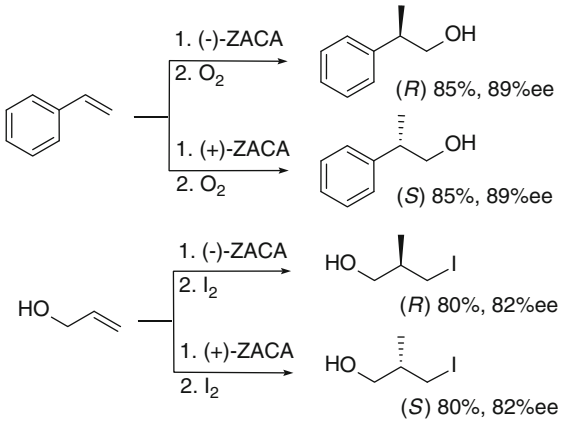
Thermal carboalumination of α-olefins occurs most often under vigorous conditions and is accompanied by hydro- and dehydroalumination side reactions [72]. In the presence of metal complex catalysts, carboalumination can be accomplished under milder conditions and with high selectivity. The catalytic carboalumination of olefins and acetylenes was surveyed in a number of publications [73–78].

Although quite a lot of metal complexes capable of catalyzing these reactions are known to date, carboalumination using Zr-compounds, yielding the target OACs with high regio- and stereoselectivity, has found the widest use in the synthetic practice. The first examples of catalytic carboalumination of olefins for the preparation of higher dialkylhaloalanes were reported in 1979 [79]. The method was based on the successive ethylene insertion into the Al–C bond induced by low-valence Ti complexes, resulting in higher dialkylaluminum chlorides containing from 4 to 30 carbon atoms. Dialkyl haloalanes such as Et_2AlCl, Me_2AlCl readily carboaluminate substituted norbornenes in the presence of catalytic amounts of Ti complexes (Cp_2TiCl_2, $Ti(acac)_2Cl_2$, $TiCl_4$), to give alkyl-substituted norbornanes with high stereoselectivity [80, 81] (Scheme 11).

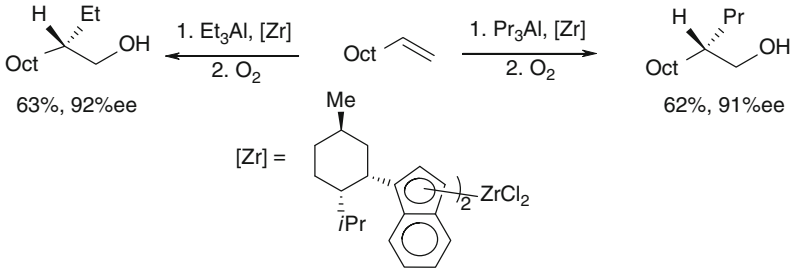
The carboalumination of terminal olefins with Me_3Al in the presence of chiral zirconium catalysts [bis(1-neomenthylindenyl)zirconium dichloride, bis (1-neo-*iso*-menthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride and so on], ZACA reaction, followed by oxidation of the chiral alanes is suitable for preparing optically active alcohols with high enantioselectivity [82] (Scheme 12).

These studies culminated in the development of a versatile method for the enantioselective carboalumination of terminal olefins with trialkylalanes in the presence of catalytic amounts of chiral zirconium catalysts [83] (Scheme 13).

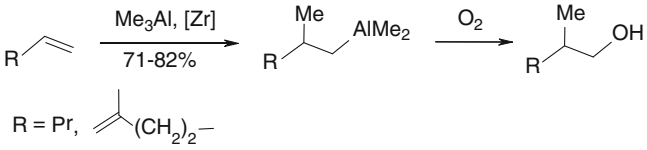
The highest selectivity of the α-olefin carboalumination with Me_3Al is achieved by using the two-component catalyst Cp_2*$ZrMe_2$–$B(C_6F_5)_3$ in toluene (0°C, ~3 h) [84] (Scheme 14).



Scheme 12 Zr-Catalyzed enantioselective methylalumination of olefins



Scheme 13 Zr-Catalyzed enantioselective carboalumination of olefins

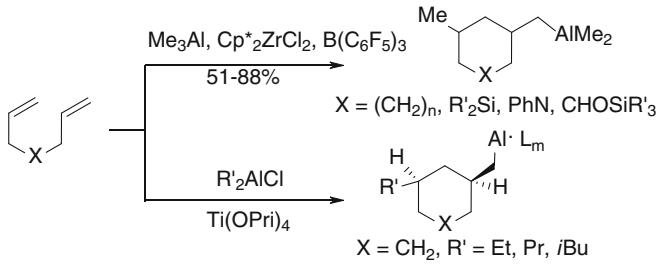


Scheme 14 Highly chemoselective carboalumination of olefins

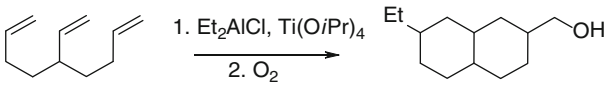
Unlike terminal olefins, α,ω-dienes (1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, and their N-, O-, and Si-containing derivatives) react, as a rule, with trialkyl alanes [84] or dialkylhaloalanes [85] in the presence of Zr- or Ti-containing complex catalysts to give cycloalkyl- or cycloheteroalkyl alanes (Scheme 15).

Negishi et al. [85] used $Ti(OiPr)_4$ as a catalyst to perform cascade carboalumination of α,ω-dienes and trienes with Et_2AlCl (Scheme 16).

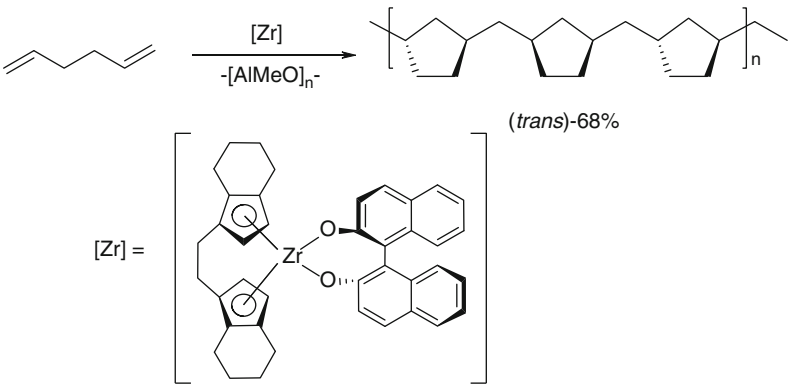
It is notable that catalytic carboalumination of α,ω-dienes was advantageously utilized to provide diastereo- and enantioselective cyclopolymerization of 1,5-hexadiene by Zr complexes. For example, in the presence of Cp_2ZrX_2 or $Cp_2{}^*ZrX_2$ (X = Cl, Me)



Scheme 15 Zr-Catalyzed carboalumination of α,ω-dienes



Scheme 16 Zr-Catalyzed cascade carboalumination of α,ω-dienes

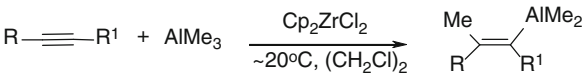


Scheme 17 Zr-Catalyzed cyclopolymerization of 1,5-hexadiene

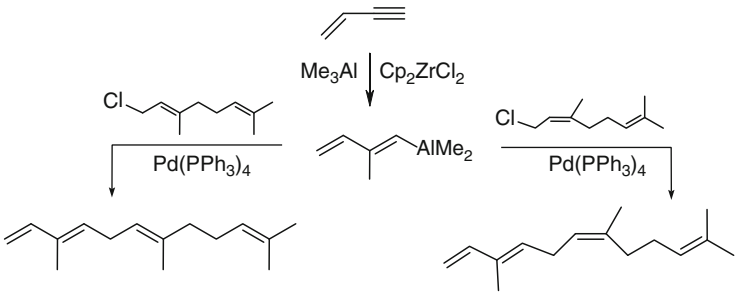
and methylalumoxane [-Al(CH_3)O-]$_n$, cyclopolymerization of 1,5-hexadiene yields polymer. The diastereoselectivity of the reaction depends on the initial catalyst. The application of Cp_2ZrMe_2 as a catalyst at −78°C produces the *trans*-polymer in 91% yield, while in the presence of Cp_2*$ZrCl_2$ at −25°C, the yield of the *trans*-polymer is 14% [86]. Cyclopolymerization of 1,5-hexadiene involving chiral zirconium catalyst and methylalumoxane affords optically active polymer [87, 88] (Scheme 17).

3.2 Carboalumination of Alkynes and Enynes

A most popular and widely used example of carboalumination of acetylene hydrocarbons with OACs is the reaction of gaseous acetylene with trialkyl alanes,



Scheme 18 Catalytic carboalumination of alkynes in the presence of Cp_2ZrCl_2



Scheme 19 Carboalumination of enynes in the synthesis of linear isoprene trimers

resulting in *Z*-alkenyldialkylalanes, which are formed with high stereoselectivity under mild conditions (40–60°C) [58, 89]. The thermal carboalumination of acetylenes with trialkylalanes is the subject of extensive literature [9].

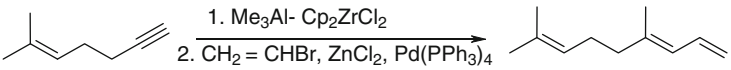
An example of significant advances in the field of acetylene carboalumination is the Negishi reaction [90, 91], which with Me_3Al represents a strictly regioselective Cp_2ZrCl_2-catalyzed 1,2-carboalumination of disubstituted acetylenes with Me_3Al (Scheme 18).

The Negishi reaction was used to prepare a large number of useful and practically valuable organoaluminum reagents and compounds. For example, an elegant method for the synthesis of linear isoprene trimers by stereo- and regiospecific cross-coupling of geranyl and neryl chlorides with alkadienyl aluminum, which was prepared by carboalumination of vinylacetylene with Me_3Al in the presence of catalytic amount of Cp_2ZrCl_2, was proposed [179] (Scheme 19).

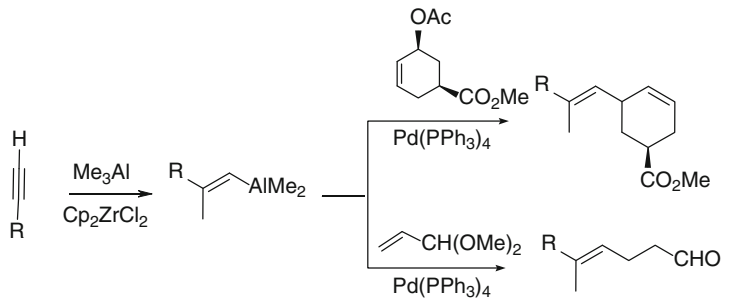
The approach including the catalytic carboalumination of terminal acetylenes with Me_3Al and the subsequent functionalization of the resulting alkenyl alanes was used to prepare natural isoprenoids, for example, geraniol [92], monocyclofarnesol [93], and farnesol [94]. Alkenylalanes and catalytic amounts of Ni or Pd phosphine complexes served for the development of an efficient method for the synthesis of polyene hydrocarbons of various structures, in particular, those containing a conjugated system of double bonds [95] (Scheme 20).

A similar approach was used in the synthesis of cyclic and acyclic functionally substituted unsaturated compounds [96, 97] (Scheme 21).

In recent years, catalytic carboalumination of acetylenes has found use in the synthesis of cycloalkenes [98–101], trisubstituted olefins, homoallyl alcohols, α,β-unsaturated esters, 1,3-enyne-1,4-disilanes [102–105], α,β-unsaturated organoboron or zirconium compounds, and also natural and biologically active compounds. For example, key synthons for the preparation of prostaglandins [86,



Scheme 20 Preparation analogs of natural isoprenoids by carboalumination



Scheme 21 Carboalumination applied to acyclic functionalized compounds

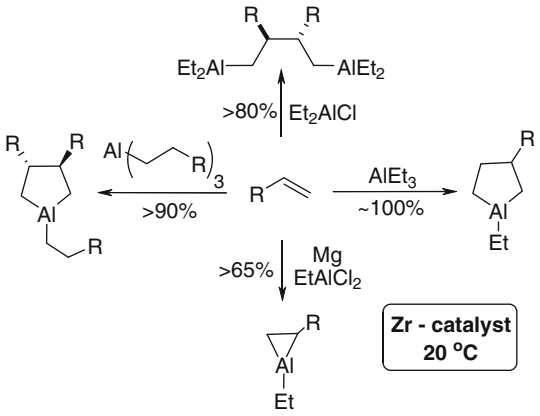
106], brassinolide [107], brassinosteroids [108], milbemycin [109, 110], zoapatanol [111–113], dendrolasin and mokupalide [114], verrucarin [115, 116], and many other products.

4 Catalytic Cycloalumination of Unsaturated Compounds

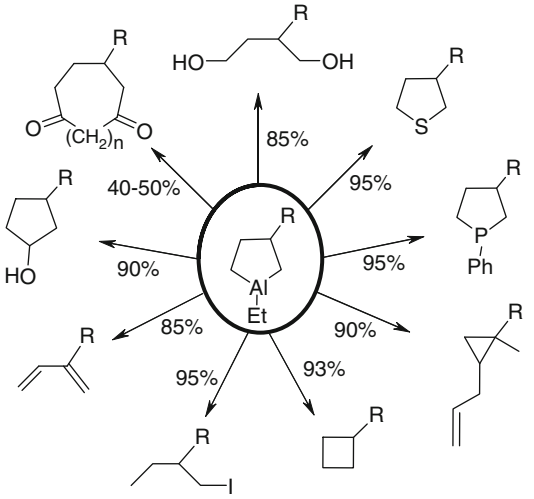
Unlike the carboalumination, catalytic cycloalumination of unsaturated compounds [2–6] bears a much higher synthetic potential, as it leads to the preparation of cyclic OACs containing both a new carbon–carbon bond and two highly reactive Al–carbon bonds (Scheme 1). This provides wide scope for one-pot syntheses of a broad range of carbo- and heterocyclic and bifunctional compounds of specified structures starting from simple olefins, acetylenes, allenes, and alkyl alanes.

The first data on the possibility of preparative synthesis of aluminacyclopentanes by catalytic reaction between α-olefins and Et_3Al catalyzed by Cp_2ZrCl_2 were published in 1989 [117], although as noted by the authors, these results were obtained back in 1985 [118]. Detailed investigation of the scope of this reaction and the main kinetic parameters affecting the yield and the selectivity of formation of novel classes of aluminacarbocycles culminated in the development of preparation methods for previously unknown three- and five-membered cyclic OACs and 1,4-dialuminum compounds [180, 181] (Scheme 22).

It was shown [119–132] that three-substituted aluminacyclopentanes are highly reactive toward nucleophilic and electrophilic reagents and cross-coupling, demetallation, and carbocyclization reactions. As a result, effective one-pot methods for the synthesis of carbo- and heterocyclic and bifunctional acyclic compounds were elaborated (Scheme 23).



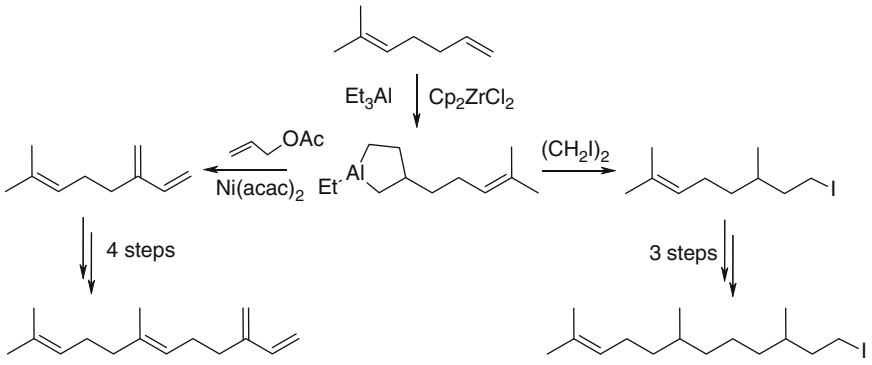
Scheme 22 Cycloalumination of α-olefins in the presence of Cp_2ZrCl_2



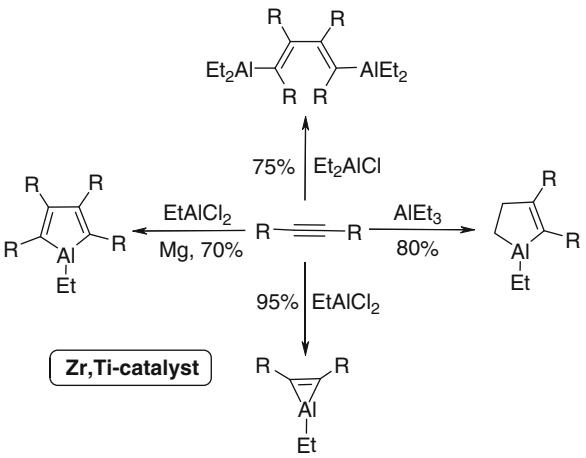
Scheme 23 Some transformations of substituted aluminacyclopentanes

In addition, the developed reactions are suitable for the design of linear E-isoprenoids with a specified number of C_5 moieties (Scheme 24) and can also be used in the synthesis of biologically active compounds, for example, in pheromones of the conifer sawfly, German cockroach, and the confused and red flour beetles [133–136].

The above-described transformations of five-membered aluminacarbocycles indicate that the catalytic cycloalumination of olefins discovered by the authors of works [2–8] has a broad synthetic potential; however, it remained unclear whether this reaction is typical only of olefins or it can be extended to other classes of unsaturated compounds, for example, allenes and acetylenes. This would allow the

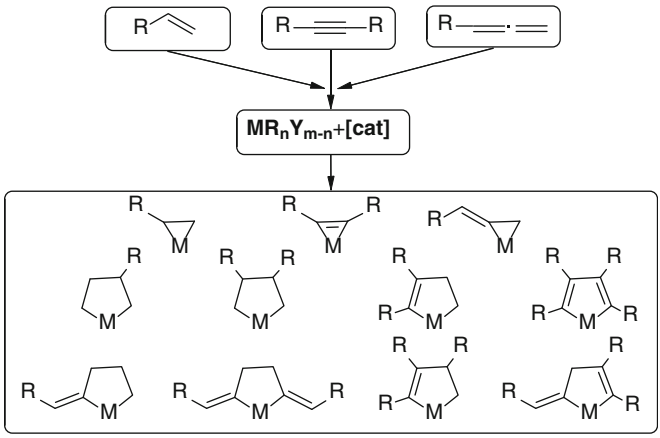


Scheme 24 Catalytic cycloalumination of olefins in the synthesis of *E*-isoprenoids



Scheme 25 Zr- and Ti-catalyzed cycloalumination of alkynes

preparation of the main group metal derivatives, e.g., aluminacarbocycles such as previously unknown alkylidenealuminacyclopropanes, aluminacyclopentanes, aluminacyclopropenes, aluminacyclopentenes, aluminacyclopentadienes, and similar metallacarbocycles of other main group metals and their acyclic analogs provided that they are thermodynamically stable. By practical implementation of the ideas put forward concerning the synthesis of cyclic and acyclic organoaluminum compounds, the authors succeeded in the preparation of aluminacyclopropanes [137, 138], aluminacyclopropenes, aluminacyclopentanes, aluminacyclopentenes, aluminacyclopentadienes and 1,2-dialuminioethylenes, studied their physicochemical properties [139–141] (Scheme 25), and also developed preparative methods for the synthesis of these classes of OACs. It was found that these OACs are stable under inert conditions and can undergo, most often, all of the reactions described for acyclic organoaluminum compounds.

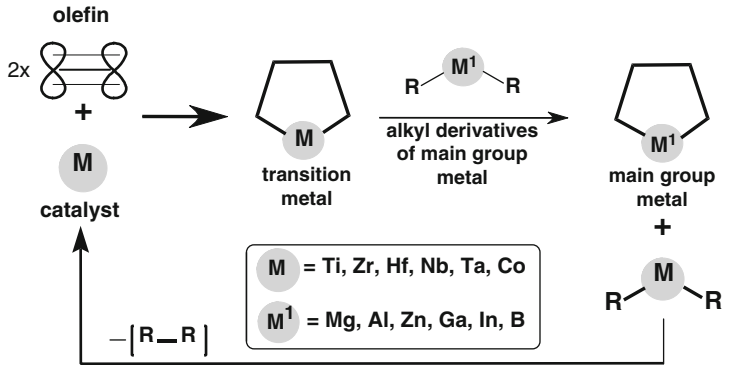


Scheme 26 Catalytic cyclometallation of unsaturated compounds in the synthesis of three- and five-membered metallacarbocycles of main group metals

Upon comprehensive investigation of the scope of catalytic cycloalumination of unsaturated compounds discovered by Dzhemilev et al. [5], the reaction was extended to other main group metals (Mg, Zn, In, B) (Scheme 26). The discovered family of organic and organometallic reactions can be used to synthesize organometallic compounds with small, medium, and large rings, bifunctional monomers with specified configuration of substituents, heterocycles, and other useful synthons in one preparative step starting from simple olefins, acetylenes, and organometallic reagents [2–8].

Fundamental studies into the organometallic chemistry of main group metals (Mg, Zn, Al, In, Ga, B) with participation of metal complex catalysts enabled the development of versatile catalytic ethylmagnesation [142–145], cyclomagnesation [146–159], and cycloalumination [2–8] reactions, which have become named reactions and are referred to in the modern literature as the *Dzhemilev reaction* [5, 73, 160]. Active research in this area of chemistry and study of the behavior of the above-indicated metallacarbocycles resulted in the development of original one-pot methods for the synthesis of a broad range of previously difficult to access metalla-, carbo-, hetero-, and macrocarbocycles of desired structure, and the study of the mechanisms of these reactions led to the discovery of the catalytic replacement of transition metal atoms (Zr, Ti, Co) in metallacarbocycles by non-transition metal (Al, Mg, Zn, Ga, In, B) to yield cyclic organometallic compounds of main group metals (Scheme 27).

As regards the catalytic cyclometallation mechanism, it was studied in detail by dynamic NMR spectroscopy [3, 4] in relation to the cycloalumination of olefins with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2. The authors identified

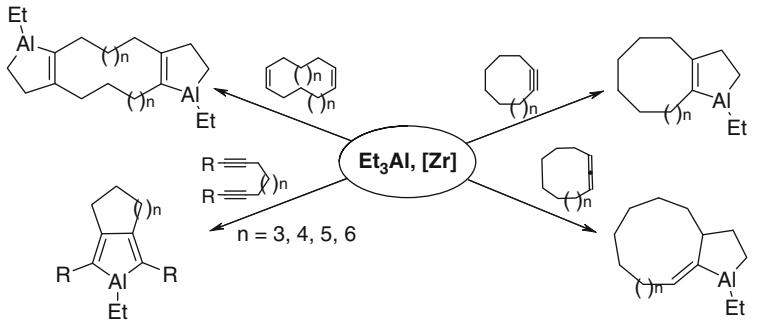


Scheme 27 Scheme of the catalytic replacement of transition metal atoms by main group metal atoms in metallacarbocycles

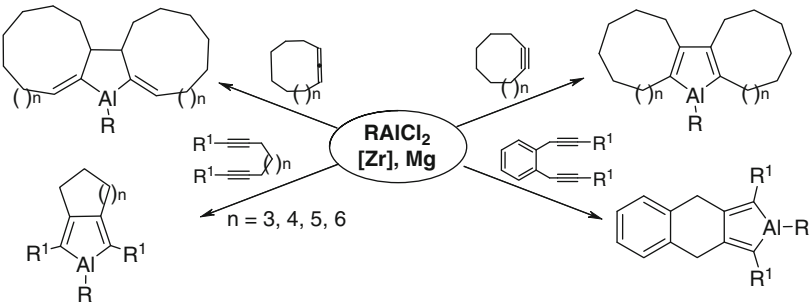
the intermediate bimetallic Zr–Al complexes responsible for the formation of target aluminacyclopentanes. The rate constants for the formation of intermediate complexes and target metallacarbocycles were measured experimentally and calculated by quantum chemical methods.

The history of discovery of the catalytic cyclometallation of unsaturated compounds, its application to the synthesis of three- and five-membered and macro carbocycles based on main group metals (Al, Mg, Zn, Ga, In, B), and their transformations to previously poorly accessible carbo- and heterocyclic compounds have been discussed in some monographs [5, 73] and reviews [2–4, 7, 142]. Therefore, in this chapter we present the achievements made in this rapidly developing area of organic and organometallic chemistry in the last 3–5 years, in particular, the application of catalytic cyclometallation in the synthesis of strained spiro compounds and polyfunctional macrocarbocycles and new approaches to the construction of metallacycles of a specified structure based on intermolecular cross cycloalumination of cyclic allenes and acetylenes with olefins, 1,2-dienes, and disubstituted alkynes. It is known from the above-presented published data that catalytic cycloalumination of aliphatic and aromatic olefins, allenes, and acetylenes, mainly acyclic has been extensively studied. In addition, some unsaturated compounds such as alkenes, alkynes, cumulated and conjugated dienes of cyclic structure, and methylidenecycloalkanes were considered to be inert in cycloalumination or were not used in this reaction. Recent studies filled this gap by the development of a number of original one-pot methods for the construction of polyfunctional macrocarbocycles, strained spiro compounds, and previously poorly accessible carbo- and heterocycles of a specified composition.

For example, the reactions of cyclic 1,2-dienes, alkynes, and alkadiynes with Et_3Al (1:3) in the presence of Zr complexes (5 mol% Cp_2ZrCl_2, hexane, 6 h, r.t.) were utilized to develop synthetic routes to previously unknown bis- and tricyclic OACs in 65–95% yields [161–164] (Scheme 28). As a development of studies on intermolecular cycloalumination of unsaturated compounds, cyclic allenes and



Scheme 28 Cp_2ZrCl_2-Catalyzed cycloalumination of cyclic allenes and mono- and diacetylenes with Et_3Al



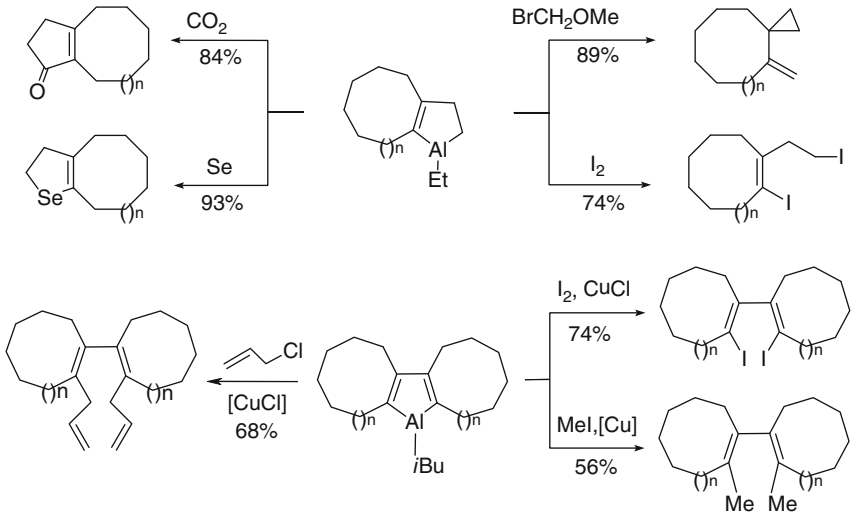
Scheme 29 Intra- and intermolecular cycloalumination of allenes and acetylenes involving alkylhaloalanes in the presence of Zr complexes

acetylenes and also α,ω-diacetylenes were made to react with $RAlCl_2$ (R = Et, *i*Bu, MeO, BuO, Pr_2N) in the presence of Cp_2ZrCl_2 catalysts to give novel bi- and tricyclic OAC [161, 163, 165, 166] (Scheme 29).

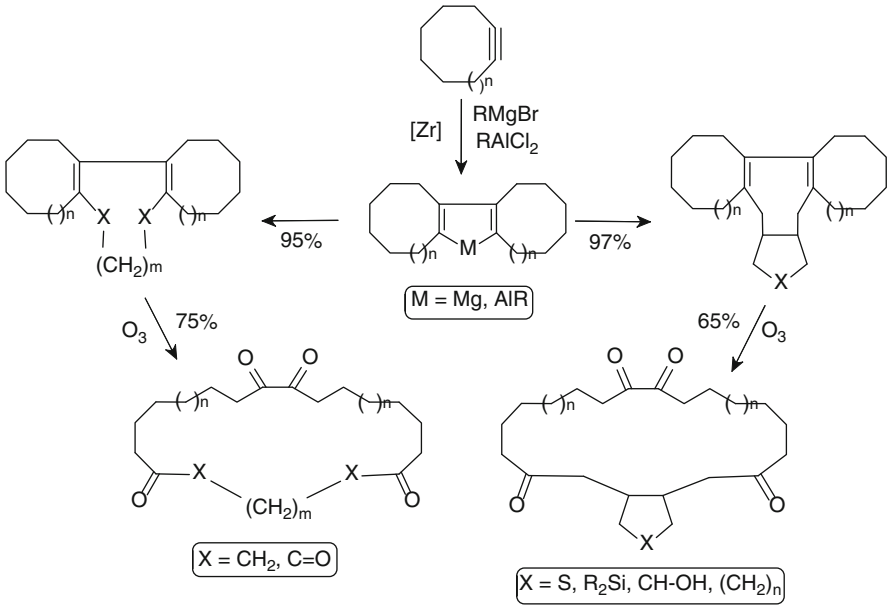
These novel classes of unsaturated cyclic OACs indicated above were used to develop effective one-pot methods for the synthesis of bifunctional and carbo- and heterocyclic compounds, in particular, spiro compounds [164, 165] (Scheme 30).

The above-described original approaches to the preparation of tricyclic alumina- and magnesacarbocycles were used [165, 167] to develop new effective methods for the synthesis of macrocyclic C_{20}–C_{28} polyketones, the methods comprising successive Cp_2ZrCl_2-catalyzed intermolecular cyclometallation of cycloalkynes with $RMgR^1$ and R_nAlCl_{3-n}, cross-coupling and oxidative cleavage of the double bonds in the resulting tri- and tetracyclic unsaturated compounds (Scheme 31) [168].

The above investigations allowed the authors [164] to develop practically impotent synthetic routes to important fragrance compounds, Muscone and Exaltone, based on bicyclo[10.3.0]pentadec-1(12)-en-13-one where catalytic cycloalumination of cyclododecyne was the key step (Scheme 32).

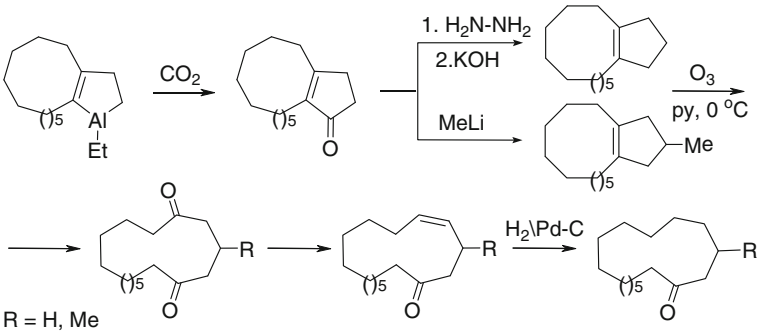


Scheme 30 Some transformations of novel bi- and tricyclic OACs

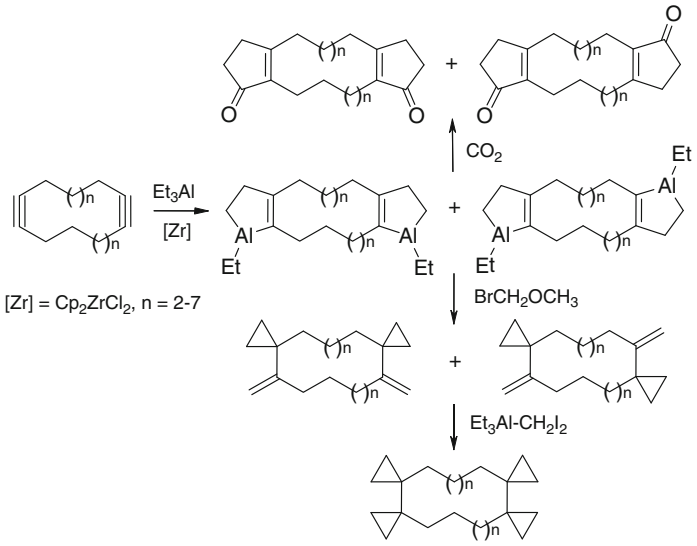


Scheme 31 Tricyclic OACs in the synthesis of macrocyclic polyketones

Cycloalumination of cyclic diacetylenes served for the development of synthetic methods for the preparation of practically important bis-cyclopentenones [169]; it was also used in the synthesis of macrocycles with spirocyclopropane moieties by carbocyclization of new tricyclic OACs obtained in situ by the reaction of the



Scheme 32 Cycloalumination of cyclododecyne in the synthesis of Muscone and Exaltone

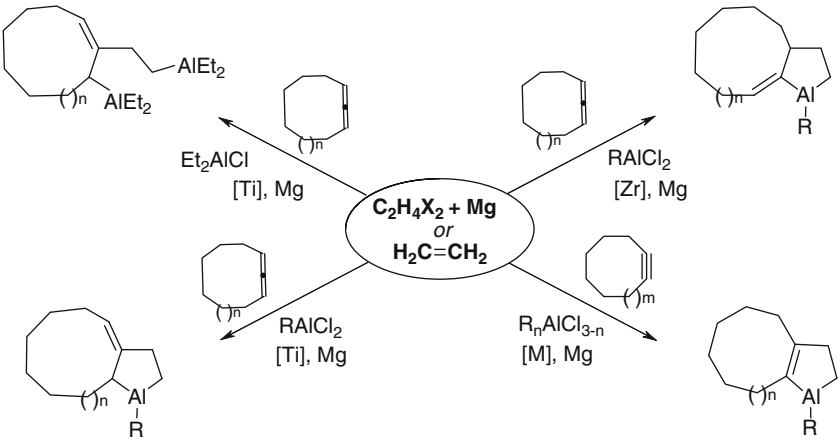


Scheme 33 Novel tricyclic dialuminum compounds in the synthesis of macrocyclic bis-cyclopentenones, di- and tetraspirocyclopropane compounds

appropriate cyclic diacetylenes with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 [170, 171] (Scheme 33).

Major progress was achieved [172] by implementing the idea of constructing aluminacarbocycles by cross cyclometallation of a mixture of two unsaturated compounds under conditions of homo-cycloalumination of unsaturated compounds with alkylhaloalanes catalyzed by Ti and Zr complexes. The studies resulted in joint cycloalumination of cyclic 1,2-dienes (cyclonona-1,2-diene, cyclotrideca-1,2-diene) or cycloalkynes (cyclooctyne, cyclodecyne, cyclotridecyne) and ethylene with $EtAlCl_2$ in the presence of Mg metal and the Cp_2ZrCl_2 catalyst, giving rise to bicyclic OACs in up to 85% yield (Scheme 34).

It was found that in addition to $EtAlCl_2$ or Et_2AlCl, the above reactions can be performed by means of various dihaloalanes of the type $RAlCl_2$



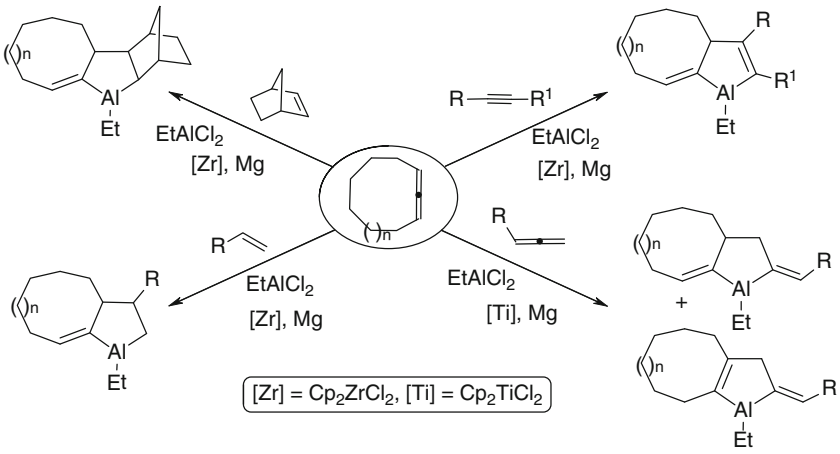
Scheme 34 Cross cycloalumination of cyclic allenes and acetylenes with ethylene with R_nAlCl_{3-n} in the presence of Ti and Zr complexes

(R = MeO, BuO, iPr$_2$N) in 40–81% yields. Ethylene was either supplied to the reaction mixture as the gas or generated in situ from 1,2-dihaloethane and magnesium. The cross intermolecular cycloalumination of cyclic 1,2-dienes or alkynes and ethylene with aluminum alkyl halide derivatives in the presence of Zr and Ti complexes furnishes unsaturated bicyclic aluminacyclopentanes or aluminacyclopentenes as well as the corresponding 1,4-dialuminum compounds in fairly high yields (Scheme 34).

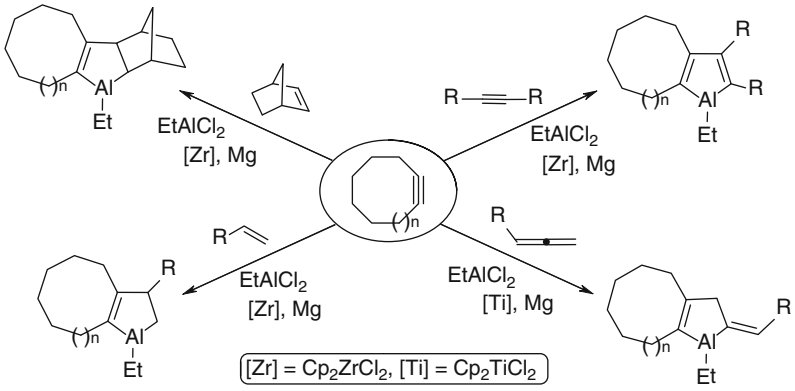
Relying on the successfully implemented idea of synthesizing bicyclic OACs using joint intermolecular cycloalumination of cyclic 1,2-dienes or alkynes and ethylene with R_nAlCl_{3-n} in the presence of Ti and Zr complex, the cross cycloalumination of cyclic allenes with unsaturated compounds (α-olefins, norbornenes, disubstituted acetylenes and terminal 1,2-dienes) was used to develop effective methods for the preparation of novel classes of unsaturated bicyclic aluminacyclopentanes, aluminacyclopentenes, and aluminacyclopentadienes of specified structure [173, 174] (Scheme 35).

By analogy with the above-presented schemes of the synthesis of bi- and tricyclic OACs, intermolecular cycloalumination of cycloalkynes with α-olefins, disubstituted acetylenes, and 1,2-dienes of various structure was carried out to give novel classes of OACs: bi- and polycyclic aluminacyclopenta-2,4-dienes [165] (Scheme 36).

For a long period of time after the discovery of catalytic cycloalumination of unsaturated compounds, 1,1-disubstituted olefins were considered to be nonreactive in these reactions. It was suggested [175] that unlike acyclic olefins with low-reactivity 1,1-disubstituted double bonds, strained cyclic unsaturated compounds with an activated methylidene bond, for example, methylidene cyclobutanes or methylidene cyclopropanes, would react with Et_3Al in the presence of transition



Scheme 35 Cross cycloalumination of cyclic allenes with olefins, 1,2-dienes, and acetylenes

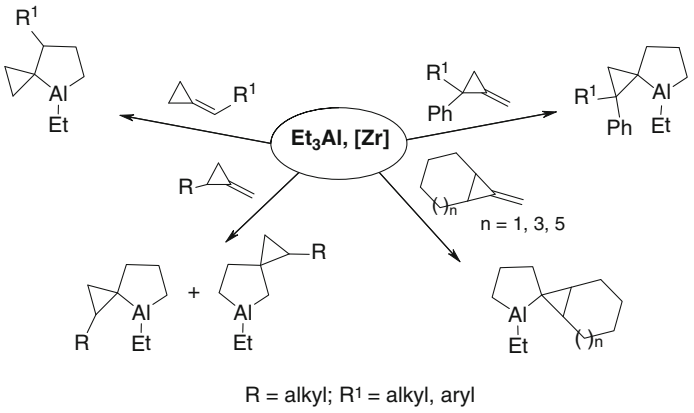


Scheme 36 Cross cycloalumination of cycloalkynes with olefins, 1,2-dienes, and acetylenes

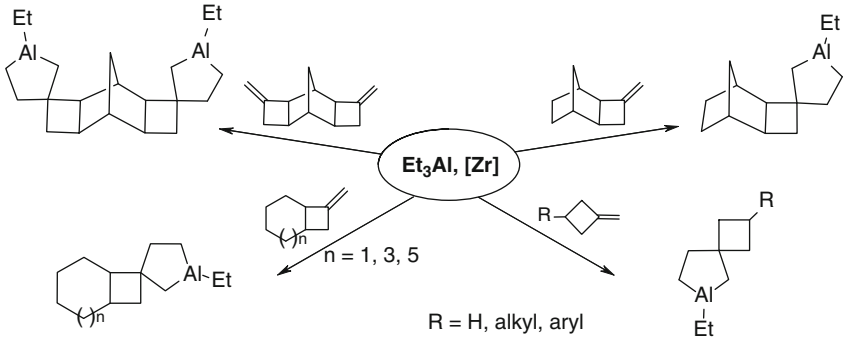
metal complexes as catalysts to give the corresponding spiro-type OACs. Studies carried out along this line showed that the cycloalumination of methylidene- and alkylidene cyclopropanes with Et_3Al catalyzed by Cp_2ZrCl_2 affords spiro-type OACs not described previously, namely, substituted aluminaspiro[2.4]octanes in high yields of 95% [176] (Scheme 37).

Similarly, methylidene cyclobutanes undergo cycloalumination with Et_3Al in the presence of Cp_2ZrCl_2 to give substituted 6-ethyl-6-aluminaspiro[3.4]octanes in high yields [175, 177] (Scheme 38). The metallacarbocycles thus obtained can be converted without isolation to spiro carbo- and heterocyclic compounds and bifunctional hydrocarbons containing a cyclobutane moiety [132, 175] (Scheme 39).

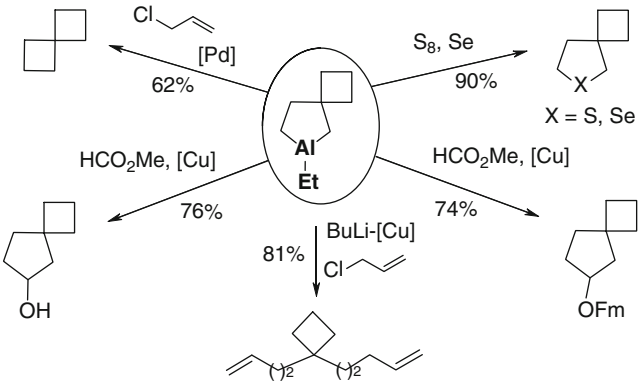
The catalytic cycloalumination reactions developed for strained methylidene cycloalkanes were employed for the development of a general one-pot method



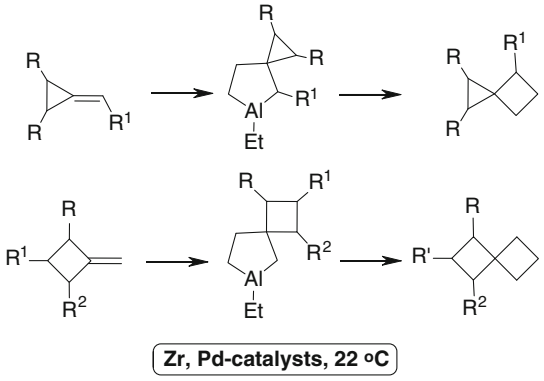
Scheme 37 Catalytic cycloalumination of methylidene and alkylidene cyclopropanes



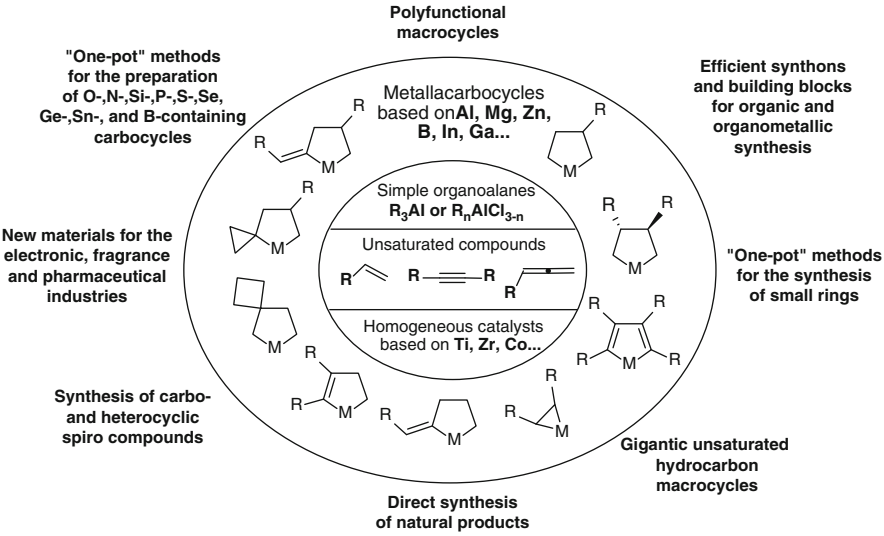
Scheme 38 Zr-Catalyzed cycloalumination of methylidene cyclobutanes



Scheme 39 Novel spiro OACs in the synthesis of spiro carbo- and heterocycles



Scheme 40 Catalytic cycloalumination of strained methylidene cycloalkanes in the synthesis of spiro[2.3]hexanes and spiro[3.3]heptanes



Scheme 41 Key applications of cyclometallation reaction (Dzhemilev reaction)

for the preparation of substituted spiro[2.3]hexanes and spiro[3.3]heptanes [170] (Scheme 40).

The results presented in this section of the review indicate that during the last 10–15 years, a new research area appeared in the organometallic chemistry of main group metals (Mg, Zn, Al, In, Ga, B), namely, the chemistry of small-, medium-, and macrocyclic metallacarbocycles. This line of research is being successfully developed extending both the scope of applicability of the new reactions and original reagents and the application of these methods in the synthesis of practically valuable compounds (Scheme 41). One can say without exaggeration that a new

ideology and strategy was developed in organic and organometallic synthesis that provides one-pot synthetic routes to structurally complex cyclic and acyclic compounds starting from simple olefins, acetylenes, and allenes involving trialky lalanes or alkylhaloalanes and Zr- and Ti-containing metal complex catalysts. In the near future this line of research may be expected to provide a variety of surprising results.

5 Conclusion

The data presented in this review reflect the modern achievements in hydro-, carbo-, and cycloalumination of olefins, acetylenes, and allenes catalyzed by metal complexes. The fundamental and applied research in this area has been carried out at laboratories, scientific centers, and companies all over the world, but in particular in Russia, and these have largely determined the strategy of development of organic and organometallic synthesis and created a solid basis for the elaboration of modern chemical engineering processes for the manufacture of a broad range of valuable products and materials.

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Organoaluminum Couplings to Carbonyls, Imines, and Halides

Andreas Kolb and Paultheo von Zezschwitz

Abstract While the stereoselective addition of zinc organyls to carbonyl compounds is nowadays an established synthetic method, the use of aluminum reagents is less common, even though they offer distinct advantages. This chapter presents an overview of the current status of catalytic asymmetric additions to aldehydes, ketones, and imines, as well as the difficulties and the limitations of such transformations, respectively. Certain combinations of substrate types and carbon nucleophiles were so far only achieved using stoichiometric systems under substrate or auxiliary control. These examples are also included, as well as aspects of cross-coupling reactions of aluminum organyls with organic halides.

Keywords Asymmetric addition · Carbonyls · Cross-coupling · Imines · Triorganoaluminum reagents

Contents

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1 Introduction

Among C,C-bond forming reactions, the addition of carbon nucleophiles to C,O- and related C,N-double bonds is one of the most fundamental transformations. The thus formed alcohols and amines typically contain a new stereogenic center, which has led to tremendous efforts to control the stereochemistry of these additions [1–7]. The classic reagents for racemic reactions (i.e., lithium and magnesium organyls) [3] are less suitable for this purpose because of their high (background) reactivities. In contrast, zinc organyls typically do not react with aldehydes in the absence of a catalyst, which makes them the standard reagents for asymmetrically catalyzed additions to carbonyls [1, 5]. However, zinc reagents are economically less attractive, and a special problem is caused by the notoriously low reactivity of $ZnMe_2$, which hampers the synthetically important introduction of methyl groups [8, 9]. The reactivity of aluminum organyls ranges in between these two groups of organometallic reagents as, on one hand, trialkyl alanes slowly react with carbonyls [10, 11]. On the other hand, they show a higher functional group tolerance than lithium and magnesium organyls, which allows for additions to aldehydes in the presence of, e.g., nitro, ester, and lactone moieties [12–15]. Additional advantages include the low price of unfunctionalized trialkyl alanes (AlR_3, R = Me, Et, *n*Pr, *n*Bu, *i*Bu), which are produced on an industrial scale, and the ready availability of specialized reagents by metathesis of lithium organyls with aluminum halides or by metalation of terminal alkynes with trialkyl alanes [16, 17]. Another attractive avenue is offered by hydroalumination or carboalumination of unsaturated C,C-bonds, which provides both stereochemically defined alkenyl- and alkyl alanes [11, 18–20].

Moreover, the reactivity of aluminum organyls is not only "in-between" the properties of magnesium and zinc reagents but is significantly different because of their diminished Brønsted-basic character and the strong Lewis acidity of the metal center [10]. Thus, trialkyl alanes have been used for additions to base-sensitive carbonyls [21], and the stereochemical course of their additions to chiral substrates can be opposite to that of other organometallics because of differences in the precoordination of Lewis-basic groups: the addition of $ZnEt_2$ to the atropisomeric 2-formyl arylamide **1** furnished the *syn*-diastereomer, whereas $AlEt_3$ led to predominant formation of the *anti*-isomer and EtMgBr added unselectively (Fig. 1) [22]. In the case of the chiral sulfoxide **2**, addition of MeMgBr or $ZnMe_2$ occurred on the *si*-face, whereas $AlMe_3$ furnished the other diastereomer through attack on the *re*-face, all with excellent diastereoselectivity [23]. Further possibilities arise from the fine-tuning of the Lewis acidity of alanes. This can be accomplished by switching from a non-coordinating solvent to a coordinating one, by the use of Lewis bases as additives, or by starting from isolable Lewis acid–base pairs, such as the intramolecularly stabilized alanes **3**, introduced by Blum, Schumann, et al. [24–26].

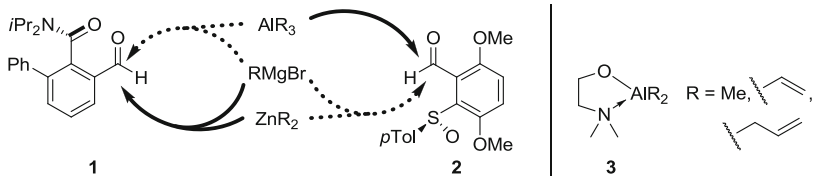


Fig. 1 Stereodivergent additions to chiral aldehydes; modified aluminum organyls

Mechanistically, the addition of aluminum organyls to carbonyls starts with the formation of a 1:1 complex when equimolar amounts of reactants are mixed at low temperature (−78 °C). Upon warming the reaction mixture, this complex decomposes to the addition product through a four-membered transition state **4** (Fig. 2). An excess of alane, however, enables the much faster formation of product through a six-membered transition state **5**. This was beautifully confirmed by Maruoka et al. using a bis(dimethylaluminum) reagent, which, via the transition state **6**, underwent smooth addition to aldehydes even at low temperature [27]. Ashby et al. showed in seminal publications that the type of transition state even influences the diastereoselectivity of such reactions. Use of 1.0 equiv. of $AlMe_3$ in the addition to 4-*tert*-butylcyclohexanone led to a 76:24 ratio of the *cis*- and *trans*-diastereomer, whereas a 12:88 ratio was observed with 3.0 equiv. of the same reagent [28]. On the basis of the transition states **4** and **5** for uncatalyzed alane additions, two possibilities were proposed for the role of chiral catalysts in stereoselective additions: In contrast to transition state **7**, in which the catalyst with a Lewis-basic group X plays the role of the second equivalent of alane, no direct interaction of catalyst and alane occurs in transition state **8** [29]. Additionally, a transannular interaction of aluminum and oxygen (arrow) can lead to an "open-book-like" conformation of the six-membered ring **7**. As a third possibility in catalytic additions, the aluminum organyl could deliver a carbon nucleophile to the catalyst by transmetalation and not interact with the carbonyl group; however, this should only happen in special cases due to the strong Lewis acidity and oxophilicity of alanes.

In this chapter, we will present the current status of stereoselective additions of aluminum organyls to carbonyls and imines, organized primarily by the type of substrate and secondarily by the applied process. We will focus on the methods of

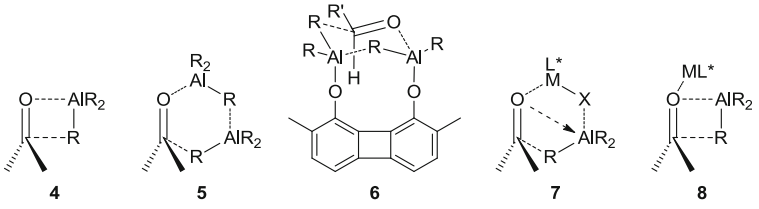


Fig. 2 Putative transition states for additions to carbonyls

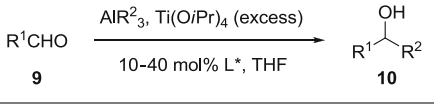
asymmetric catalysis because these are generally seen as the most elegant kind of stereoselective syntheses, and we will only cover stoichiometric systems using substrate or auxiliary control as long as no catalytic method is known. Moreover, we will briefly present recent research on cross-coupling reactions of aluminum organyls with organic halides, the main advantages of which are again the special reactivity and the good availability of this class of organometallics.

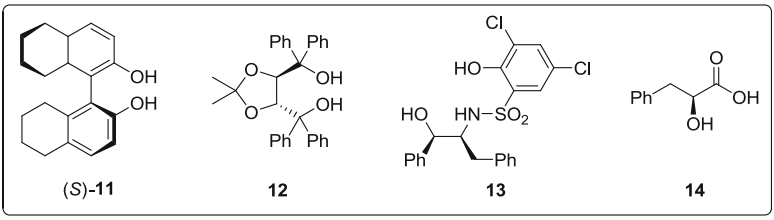
2 Stereoselective Additions to Aldehydes

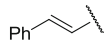
In general, the stereodifferentiation of the enantiotopic faces of aldehydes is comparably easy because of the different steric demands of hydrogen and the organic substituent at the carbonyl moiety. Typically, aromatic substrates are the first to be tested in new catalytic systems because they are not prone to undergo side reactions through formation of the respective enolates. Compared to the well-established organozinc reagents, the use of aluminum compounds is more difficult because of significant background reactivity. This is especially true for the addition of aryl groups because unsaturated residues are more readily transferred from aluminum. However, this fact enables the use of mixed alanes of the type $AlArAlkyl_2$ in such reactions. While the addition of zinc reagents is typically catalyzed by either numerous aminoalcohols, diols, or amines alone or by sulfonamides or diols in the presence of an excess of $Ti(OiPr)_4$ [1, 5, 30, 31], two methods exist for the asymmetric addition of their aluminum counterparts: either a titanium-mediated process or a nickel-catalyzed reaction.

2.1 Titanium-Mediated Addition of Alkyl and Aryl Groups

The first enantioselective addition of alkyl groups to aromatic aldehydes was reported in 1997 by Chan et al. using $AlEt_3$ and a chiral Ti-complex [32]. In this comparative study, the partially hydrogenated H_8-BINOL **11** proved to be superior to its parent compound BINOL, furnishing consistently higher ee's between 90% and 96% (Scheme 1). However, only moderate ee's of up to 53% were achieved in reactions with $AlMe_3$, and the use of $Al(iBu)_3$ solely afforded the reduction products. Gau et al. utilized the TADDOL ligand **12** under otherwise essentially the same reaction conditions and noticed a strong influence of the solvent and the quantities of $Ti(OiPr)_4$ and $AlEt_3$ on the selectivity [33]. The best results were achieved with 2.5 equiv. of each in THF; contrary to the addition of zinc organyls, non-coordinating solvents led to the isolation of racemic material. Nevertheless, the enantioselectivities were mostly inferior to those obtained using ligand **11**. An improved procedure was published shortly afterwards, which makes use of *N*-sulfonylated amino alcohols as ligands [34]. From various structural variations, compound **13** with two stereogenic centers emerged as the most effective one. Very high ee's were achieved in the





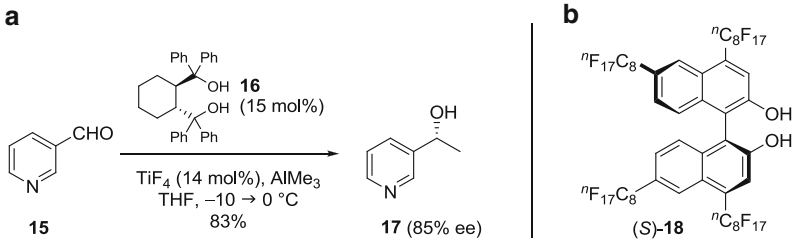
Entry	R^1	**11** (R^2 = Et) convers. / ee	**12** (R^2 = Et) yield[a] / ee	**13** (R^2 = Et) yield / ee	**13** (R^2 = Me) yield / ee	**14** (R^2 = Et) yield[b] / ee
1	Ph	100 / 96	94 / 84	98 / 96	100 / 98	96 / 90
2	2-ClC_6H_4	96 / 91	98 / 99	-	-	92 / 85
3	4-ClC_6H_4	59 / 90	99 / 79	100 / 94	-	85 / 89
4	2-$MeOC_6H_4$	93 / 94	97 / 43	-	-	85 / 89
5	4-$MeOC_6H_4$	98 / 93	91 / 79	-	-	90 / 66
6		-	100 / 78	100 / 88	99 / >99	80 / 63
7	*c*Hex	-	-	54 / 91	100 / 91	82 / 83

Scheme 1 Titanium-mediated addition of trialkyl alanes to aldehydes. All values indicate percentages; yields were: [a]determined by ^{1}H NMR, [b]isolated yields

addition of $AlEt_3$, not only to aromatic aldehydes but also to the aliphatic cyclohexanecarboxaldehyde and the α,β-unsaturated cinnamaldehyde. Beyond that, this catalytic system also proved suitable for the highly enantioselective transfer of a methyl or an allyl group from $AlMe_3$ or $AlAllylEt_2$, respectively. Gau et al. ascribe this superior performance to the phenoxide moiety in ligand **13**, which, enhanced by the electron-withdrawing chloro substituents, may increase the Lewis acidity at the titanium center. Additionally, it may provide conformational rigidity for a better stereoinduction.

α-Hydroxycarboxylic acids, which are readily available via diazotization of the respective amino acids, were investigated as inexpensive chiral ligands by Bauer and Gajewiak, and the higher homologue **14** of (*S*)-mandelic acid arose as the most promising derivative out of eight tested compounds [35]. The enantioselectivities are slightly lower than those with the ligands **11** and **13** (e.g., 90% vs. 96% ee for the addition to benzaldehyde), but interestingly, they are higher than those obtained using $ZnEt_2$ [36]. Additionally, the transformation of *n*-hexanal to (*S*)-octan-3-ol (with 77% ee using this ligand) is the first example of a linear aliphatic aldehyde in an asymmetrically catalyzed addition of an alane.

All these transformations are closely related to the respective additions of zinc reagents, which can also be mediated by a catalytic amount of the same chiral ligands and an excess of titanium alkoxides. The mechanism of the latter



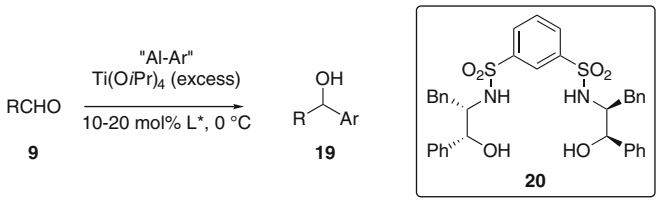
Scheme 2 (**a**) Titanium-catalyzed addition of $AlMe_3$. (**b**) Ligand for a fluorous biphasic system for the addition of $AlEt_3$. Conditions: 1.4 equiv. $Ti(OiPr)_4$, 20 mol% **18**, 3.0 equiv. $AlEt_3$, perfluoro (methyldecalin)/hexane, 53 °C

reactions has been elucidated, and a high amount of $Ti(OR)_4$ is necessary to (1) transform unreactive complexes of the type $[TiL^*(OR)_2]_2$ (L^* = chiral diolate) into catalytically active heterodinuclear complexes $[L^*Ti(OR)_2•Ti(OR)_4]$, (2) to undergo transmetalation with the zinc reagents leading to the formation of species $R'Ti(OR)_3$, and (3) to remove the formed addition products from the catalyst [37, 38]. However, a few dissimilarities exist in the addition of aluminum reagents because the preferred solvent is THF instead of toluene [33–35], and there can be a strong dependence of the enantioselectivity on the precise type of titanium alkoxide and the order of addition of titanium and aluminum reagent [35].

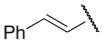
Interestingly, Carreira et al. were able to perform the addition of $AlMe_3$ to aldehydes with only catalytic amounts of TiF_4 [39]. Using the chiral diol **16**, additions occurred with up to 85% ee to a set of aromatic and two α,β-unsaturated aldehydes (Scheme 2a). However, in the addition of $AlEt_3$ stoichiometric amounts of the complex were needed in order to achieve high enantioselectivities. Although these results are striking from a mechanistic point of view, the economic benefit of being catalytic in titanium is overcompensated by the higher price of TiF_4.

Moreover, Chan et al. prepared several BINOL derivatives bearing long perfluoroalkyl chains as recyclable ligands for fluorous biphasic catalysis [40], and compound **18** with 68 fluorine atoms proved to have a sufficient partition coefficient of 53:1 in perfluoro(methyldecalin)/hexane (Scheme 2b) [41]. Even though a temperature of 53 °C was necessary to homogenize the reaction mixture, 77–82% ee was achieved over five runs in the addition of $AlEt_3$ to benzaldehyde, which favorably compares with 81% ee in the same reaction catalyzed by BINOL itself at 0 °C [32]. Thus, the ligand can easily be separated from the product mixture and only fresh $Ti(OiPr)_4$ has to be added for every catalytic cycle.

Apart from alkyl groups, the addition of aryl groups is also well elaborated, and suitable reagents such as $AlAr_3(THF)$ can conveniently be prepared by the addition of $AlCl_3$ to 3 equiv. of the respective Grignard reagent in THF [42, 43]. On the basis of the mechanistic insights discussed above, Gau et al. directly employed 10 mol% of the precatalyst $[Ti(H_8\text{-BINOLate})(OiPr)_2]_x$ together with 1.25 equiv. of $Ti(OiPr)_4$ and performed highly enantioselective additions to a very broad scope of substrates (Scheme 3) [44]. Various kinds of aromatic, α,β-unsaturated, as well as



9 **19** **20**

Entry	R	Ar	$AlAr_3$(THF)/**11** yield/ee	$AlPh_3$(THF)/**20** yield/ee	$AlArEt_2$(THF)/**11** yield/ee	Ar/Et ratio
1	4-ClC_6H_4	Ph	92 / 95	96 / 96	93 / 92	>99:1
2	2-$MeOC_6H_4$	Ph	96 / 95	95 / 96	90 / 74	>99:1
3	4-$MeOC_6H_4$	Ph	96 / 97	98 / 95	86 / 87	90:10
4	4-$F_3CC_6H_4$	Ph	94 / 96	97 / 96	93 / 90	>99:1
5	1-naphthyl	Ph	90 / 96	96 / 95	93 / 98	>99:1
6	2-naphthyl	Ph	92 / 94	97 / 96	85 / 83	87:13
7	2-furyl	Ph	89 / 94	97 / 95	-	-
8		Ph	95 / 91	93 / 85	93 / 91	>99:1
9	*n*Bu	Ph	90 / 91	90 / 87	-	-
10	*t*Bu	Ph	70 / 99	95 / 99	90 / 94	>99:1
11	Ph	4-$MeOC_6H_4$	80 / 90	-	85 / 62	90:10
12	Ph	1-naphthyl	52 / 72	-	-	-
13	Ph	2-naphthyl	90 / 92	-	-	-

Scheme 3 Titanium-mediated additions of aryl groups to aldehydes. All values indicate percentages

aliphatic aldehydes furnished yields and ee's exceeding 90%, and the transfer of different aryl groups onto benzaldehyde was also possible with only 1.2 equiv. of the aluminum reagent. All reactions proceeded in less than 10 min in THF at 0 °C, and the observed ee's are even more remarkable given that the uncatalyzed addition of $AlPh_3$(THF) to 2-chlorobenzaldehyde delivers 73% of the racemic secondary alcohol within the same reaction time. To obtain a deeper understanding of the reaction mechanism, an experiment was conducted with a stoichiometric amount of $PhTi(OiPr)_3$ [45] instead of the aluminum reagent and the product was formed with 96% ee. Therefore, a mechanism was suggested involving transmetalation of the aryl group from aluminum to titanium. In subsequent work, Gau et al. exchanged ligand **11** for the bis(*N*-sulfonylaminoalcohol) **20** which was originally designed to afford a synergetic bimetallic catalyst. Yet, results from the addition of $ZnEt_2$ indicate formation of two independent active centers [46]. Again, excellent enantioselectivities and almost quantitative yields were achieved for the addition of $AlPh_3$(THF) to a large variety of aromatic and aliphatic aldehydes [47]. In comparison with the use of H_8-BINOL (**11**), however, this method requires a higher catalyst loading, larger excesses of aluminum and titanium reagent, as well as longer reaction times.

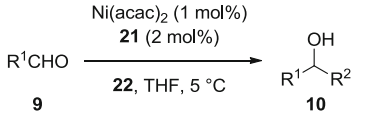
With the aim of improving the atom economy, Gau et al. also examined the catalytic asymmetric addition of reagents of type $AlArEt_2$(THF) to aldehydes and ketones (cf. Sect. 3.1) [48]. These compounds are available through either

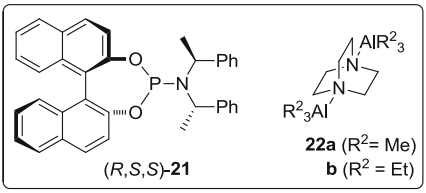
metathesis from $AlEt_2Br(THF)$ and ArMgBr or synproportionation of 1 equiv. of $AlAr_3(THF)$ with 2 equiv. of $AlEt_3(THF)$ and actually exist in solution as a mixture of four different species assigned as $AlAr_xEt_{3-x}(THF)$ with $x = 0$–3. Again, 10 mol% of the catalyst precursor $[Ti(H_8\text{-BINOLate})(OiPr)_2]_x$ together with an excess of $Ti(OiPr)_4$ induced enantioselectivities in the range of 62–98% ee (Scheme 3). The reaction was slightly slower when the catalyst was prepared in situ from **11** and $Ti(OiPr)_4$, but it furnished the same ee's. The selectivity of aryl vs. ethyl transfer significantly depended on the amount of alane, and the best results were achieved using 1.4–1.6 equiv. It is also notable that these reactions were performed in toluene, but some THF is of course introduced with the aluminum reagent. Gau et al. also described the synthesis and crystallographic characterization of arylaluminum reagents $AlPh_3(L)$ stabilized by different Lewis bases (L = Et_2O, $OPPh_3$, DMAP) [49]. Employed in additions to 2-chlorobenzaldehyde catalyzed by a titanium complex of an *N*-sulfonylated aminoalcohol, adducts of the strongly Lewis-basic $OPPh_3$ and DMAP showed no reactivity at all, while the Et_2O adduct afforded only 9% ee.

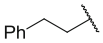
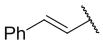
2.2 Nickel-Catalyzed Addition of Alkyl Groups

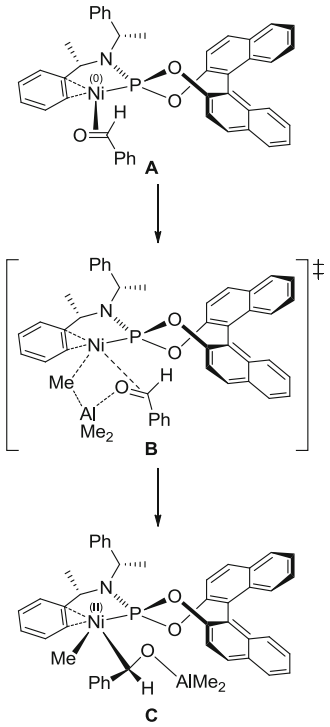
Aside from the titanium-mediated process described above, the asymmetric addition of alkyl groups to aldehydes can also be performed by nickel catalysts. This traces back to seminal work of Fujisawa et al. who had found that the addition of $AlMe_3$ to aldehydes can be catalyzed by $Ni(acac)_2$ and is strongly accelerated by phosphines and phosphites [50]. Racemic additions to aromatic and aliphatic aldehydes thus occurred in good yields with as little as 0.1 mol% of nickel. Interestingly, the reaction with $AlEt_3$ and $Al(iBu)_3$ predominantly led to the respective addition products with only small amounts of the reduced primary alcohols. This is in contrast to the nickel-catalyzed 1,4-addition of higher aluminum trialkyls to enones, in which the rate of β-hydride elimination surpasses that of 1,4-addition [51].

Subsequently, Woodward et al. pursued an asymmetric variant and achieved excellent enantioselectivities with 1 mol% catalyst loading using the Feringa-type phosphoramidite (*R*,*S*,*S*)-**21** (Scheme 4) [52, 53]. Furthermore, they were the first to use the Lewis acid–base complex **22a** (DABAL-Me_3) [54] for synthetic purposes. This $AlMe_3$ surrogate is an air-stable solid which is either commercially available or readily prepared from DABCO and 2 equiv. of $AlMe_3$ [55]. It can be stored in standard glassware and handled on the bench, and it is thus even more easily utilizable than the stabilized $AlMe_3$ analogue **3** of Blum, Schumann, et al. [26]. Interestingly, employment of **22a** led to higher enantioselectivities in the transformations of aromatic aldehydes than the use of free $AlMe_3$, and almost no β-hydride elimination was observed with the ethyl analogue **22b** (DABAL-Et_3); however, this latter reagent is less stable and has to be generated in situ (Entry 1). On the contrary, the uncomplexed alanes furnished better results in the case of enolizable acyclic aldehydes because the DABCO adducts led to enhanced





Entry	R^1	22a yield / ee	22b yield / ee
1	Ph	92 / 91	95 / 86
		(60 / 85)	(95 / 83)
2	4-BrC_6H_4	98 / 93	91 / 89
3	4-$CF_3C_6H_4$	58 / 94	90 / 95
4	4-*t*BuC_6H_4	91 / 94	-
5	3-$CF_3C_6H_4$	93 / 93	-
6	2-MeC_6H_4	78 / 90	-
7	3-$MeOC_6H_4$	58 / 89	-
8	*c*Hex	80 / 94	60 / 91
9		(99 / 89)	-
10		(60 / 95)	(72 / 48)
11		94 / 66	-



Scheme 4 Nickel-catalyzed addition of alkyl groups to aldehydes. All values indicate percentages; values in *brackets* were achieved using free $AlMe_3$ or $AlEt_3$ at −25 °C

α-deprotonation and side reactions (Entries 9,10). As another potential drawback, the modified reagents **22** obviously lead to a moderate catalyst deactivation, as higher TON and TOF can be achieved using the free alanes [56]. Nevertheless, the DABAL reagents overcome the potential risks resulting from the pyrophoric character of trialkyl alanes, which surely has deterred chemists from using organoaluminum reagents.

Mechanistically, the reaction might proceed through a complex **A**, in which nickel coordinates the ligand in a (*P,C=C*) mode and the aldehyde in a η^2-manner [56, 57]. Oxidative addition then furnishes the nickel(II) complex **C** through transition state **B**, and finally, reductive elimination delivers the product and the active catalyst. This explains very well the following limitations of the method: (1) bulky aldehydes (e.g., 2-naphthylcarboxaldehyde) or trialkyl alanes [e.g., $Al(iBu)_3$] are not tolerated due to steric crowding, (2) substrates with alkene moieties (e.g., cinnamaldehyde, entry 11) tend to react with lower ee's because π-bonding of the C,O- and the C,C-double bonds might compete with each other, (3) electron-rich aromatic substrates such as 2- or

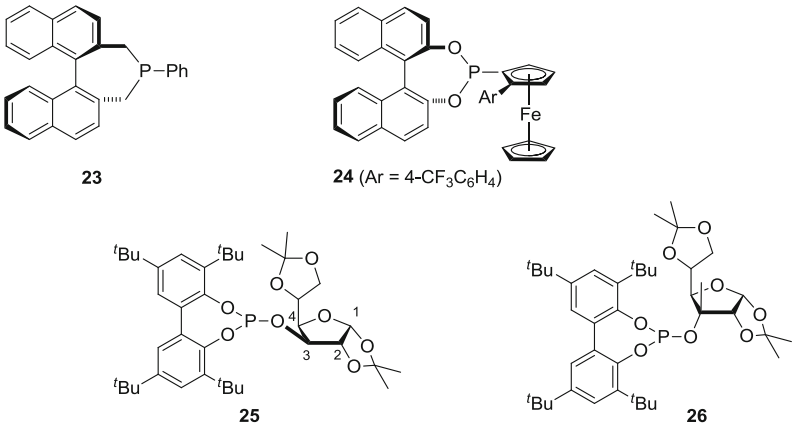


Fig. 3 Ligands for Nickel-catalyzed asymmetric additions

4-methoxybenzaldehyde react almost racemically because of the smooth formation of benzyl cations, whereas 89% and 90% ee were achieved with 3-methoxy- and 4-acetoxybenzaldehyde, respectively, and (4) substrates such as 2-pyridyl- or 2-thiophenecarboxaldehyde are also not suitable because they might coordinate with the catalyst in a η^1-manner via the lone pairs at the oxygen.

Although the original catalyst system is already used in the synthesis of target structures [58], considerable effort was spent on the optimization of the chiral ligand. The phosphine **23** proved of value in the addition to cinnamaldehyde (80% ee instead of 66%) [56]; the "ferrophite" ligand **24**, however, furnished a lower 77% ee in addition to benzaldehyde (Fig. 3) [59]. This type of ligand was designed to mimic the putative Ni,C=C contacts in the active catalyst, yet the stereoinduction might be lower due to a longer and thus weaker binding mode. Another interesting development is the use of sugars as chiral ligand backbones because they are economically attractive and offer a vast structural diversity that allows for broad screenings and optimizations for the desired application [60]. Diéguez, Pàmies, and Woodward prepared several sugar-based ligand libraries, and the glucofuranoside-phosphite **25** was identified as the most suitable ligand for the asymmetric addition. Bulky substituents in the ortho and para positions of the biaryl moiety turned out to be necessary for high yields and enantioselectivities, respectively, and lower ee's were observed in the case of pyranoside derivatives or furanosides with inverted configuration at C-3 or C-4. Thus, transformations of aromatic aldehydes were comparably or even more stereoselective than using the phosphoramidite **21**, and remarkably, even 4-methoxybenzaldehyde underwent the reaction with an excellent ee [61]. In contrast, ligand **25** is not suitable for additions to aliphatic aldehydes and typically delivers higher selectivities when using the uncomplexed free trialkyl alanes. In addition, the allofuranoside ligand **26** is noteworthy because it enables 84% ee in transformations of 2-naphthylcarboxaldehyde and at least 46% ee with 2-methoxybenzaldehyde,

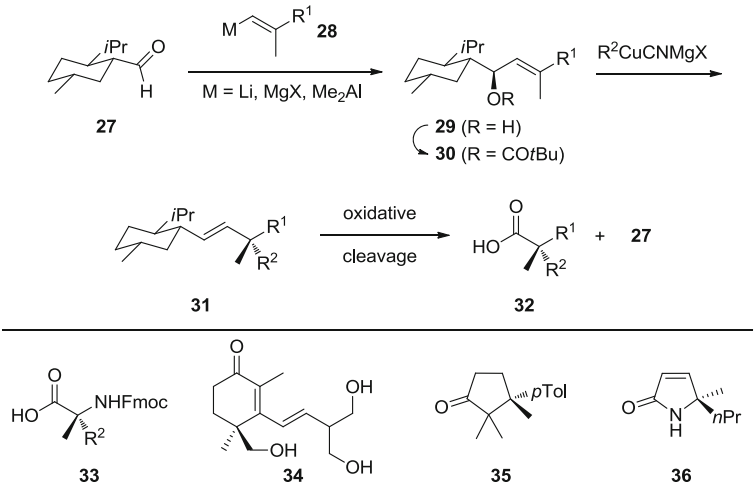
both substrates reacting almost racemically with the original catalyst system [62]. These ligands are therefore not just substitutes for the phosphoramidite **21** in complexes **A–C** shown in Scheme 4, but lead to significantly different characteristics of the catalytic process.

Despite further investigations [63–65], no other sugar- or glucosamine-based ligand has so far outperformed the glucose-derived compound **25**. Keeping in mind that the high number of Lewis-basic, oxygen-containing functional groups in these structures offers multiple coordination sites for trialkyl alanes, it is not surprising that optimization is a nontrivial pursuit. Anyway, this research is very important and worthwhile because the highly selective addition of cheap aluminum reagents catalyzed by low amounts of inexpensive nickel and abundantly available chiral ligands is surely a dream reaction in organic synthesis.

2.3 Substrate Controlled Addition of Allyl, Alkenyl, and Alkynyl Groups

In contrast to alkyl and aryl groups, the stereoselective addition of allyl, alkenyl, and alkynyl groups is still in its infancy. This might partially be due to the high reactivity of the respective aluminum reagents because these unsaturated residues, similar to aryl groups, are more easily transferred than alkyl groups. Moreover, the addition products, especially in the case of allylic and propargylic alcohols, are typically rather sensitive toward (Lewis) acidic conditions, which can conflict with the use of alanes. Yet, as their facile preparation is one of the main advantages of aluminum reagents compared to other organometallics, such stereoselective reactions are particularly valuable.

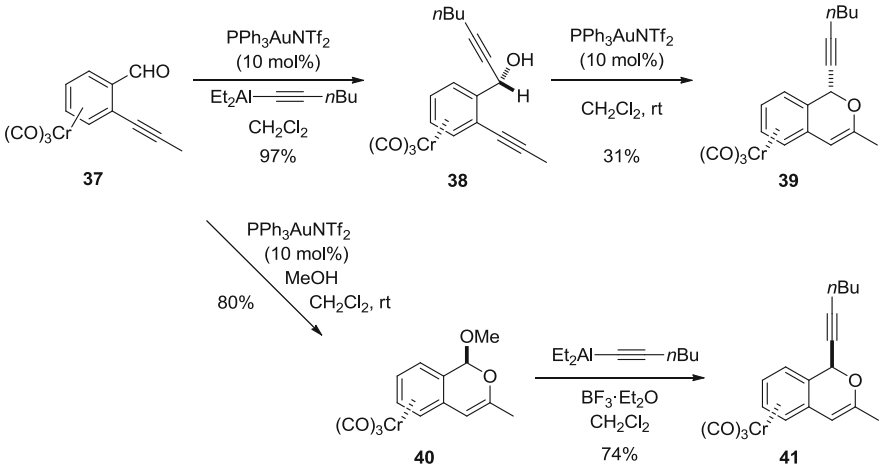
The catalytic asymmetric allylation of aldehydes was so far only reported by Gau et al. using $AlAllylEt_2$, 10 mol% of ligand **13**, and an excess of $Ti(OiPr)_4$ (cf. Sect. 2.1) [34]. Thus, benzaldehyde and 2-naphthylcarboxaldehyde were transformed in quantitative yields with 90% and 96% ee, respectively. Based on the considerations discussed above, the reaction might proceed through in situ formation of $(Allyl)_xTi(OiPr)_{4-x}$ species as the final allylating reagents, but the mechanistic details and the synthetic potential of this reaction were not further studied. However, the attractiveness of allyl aluminum reagents was recently also illustrated in racemic transformations. Yao et al. studied the addition of a reagent described as "$AlAllyl_3$" to aldehydes and obtained high yields even when using only 0.4 equiv. at temperatures of −78 °C to 0 °C [66]. Additions to sterically crowded ketones such as 2-adamantanone and di-*tert*-butyl ketone occurred in yields exceeding 90% if 0.7 equiv. reagent was used at 20 °C. The formation of this "$AlAllyl_3$" was performed by oxidative addition of allyl bromide to metallic aluminum in the presence of catalytic amounts of $HgCl_2$, which, however, should furnish the mixed compound $Al_2Allyl_3Br_3$ [67, 68]. Regardless of the actual species, the aluminum reagent is highly reactive and can transfer all three allyl



Scheme 5 Diastereoselective addition of alkenyl alanes and subsequent formation of quaternary carbon centers

groups. This type of aluminum sesquihalides was lately obtained by Knochel et al. starting from either allylic halides in the presence of $InCl_3$ or propargylic bromides in the presence of $PbCl_2$ [69, 70]. The approach tolerates the presence of functionalities such as ester or cyano groups in the organic residues, and the thus formed aluminum reagents undergo diastereoselective additions to aldehydes and ketones, presumably via six-membered transition states. Evidently, an asymmetric variant of this procedure would be highly interesting, and it is noteworthy in this regard that the enantioselective addition of AlAllyl(iBu)$_2$ to various aldehydes was already reported in 1986 by Mukaiyama et al. using stoichiometric amounts of $Sn(OTf)_2$ and a proline-derived chiral diamine [71, 72].

Catalytic asymmetric additions of alkenyl alanes to aldehydes have so far not been reported at all (for asymmetric addition to ketones, cf. Sect. 3.1), although such reagents can easily be obtained by hydroalumination or carboalumination of terminal alkynes with just diisobutylaluminum hydride (DIBAH) or $AlMe_3$ in the presence of Cp_2ZrCl_2, respectively [20]. Yet, a synthetically very useful diastereoselective addition to the menthone-derived aldehyde **27** was reported by Spino et al. (Scheme 5). While the addition of alkenylmagnesium and alkenyllithium species **28** occurred with a low 2:1 selectivity, application of the crude products from carboalumination of various alkynes furnished the adducts **29** in high yields and with diastereomeric ratios of up to 20:1 [73]. This increased Cram-selectivity was studied in detail [74], and excess $AlMe_3$ from the carboalumination turned out to be the crucial factor. Thus, even higher diastereoselectivities were achieved from the addition of alkenyllithium reagents in the presence of 2.5 equiv. of $AlMe_3$. This is presumably not due to the formation and addition of lithium alanates of type Li[AlAlkenylMe_3] but to coordination of the Lewis-acidic alane to the carbonyl moiety [75]. After formation of the pivalate esters **30**, treatment with cuprates gave



Scheme 6 Stereodivergent synthesis of isochromene chromium complexes

rise to S_N2' reactions, resulting in the stereoselective formation of allylic quaternary carbon centers. Finally, oxidative cleavage of the C,C-double bond led to the α-quaternary carboxylic acids **32** together with recovery of the chiral auxiliary **27** [73]. Depending on the group R^1 in the starting alkyne, this method was also used for the formation of α-quaternary amino acids **33** [76] or intermediates for the total synthesis of the natural product (+)-Cassiol **34** [77]. Moreover, allylic alcohols **29** can undergo Claisen rearrangements after transformation into allyl,vinyl ethers which was applied to the total synthesis of (+)-Cuparenone **35** [77], and they provide access to enantiopure allylic amines via sigmatropic rearrangements of the derived cyanates or azides, which was applied to the formation of the pyrrolone **36** [78, 79].

Similar to alkenyl derivatives, catalytic asymmetric additions of alkynyl alanes to aldehydes (or ketones) are unknown. Such reagents are readily obtained by metalation of terminal alkynes with DIBAH or $AlMe_3$ in the presence of catalytic amounts of NEt_3 or $MeN(SiMe_3)_2$, as recently shown by Micouin et al. [16, 17], and therefore their application in enantioselective additions to carbonyls would be extremely useful. In lieu of such transformations, a recent application of alkynyl alanes in a stereodivergent synthesis of isochromene chromium complexes is presented. Starting from the chromium-complexed benzaldehyde **37**, Uemura et al. first performed a gold-catalyzed diastereoselective addition of a hexynyl alane, and the product **38** was then cyclized with the same catalyst to yield the *syn*-isomer **39** (Scheme 6). Alternatively, the same starting material **37** was first cyclized with methanol as the entering nucleophile, and the acetal **40** was then treated with the aluminum reagent in the presence of a Lewis acid to yield the *anti*-isomer **41** [80].

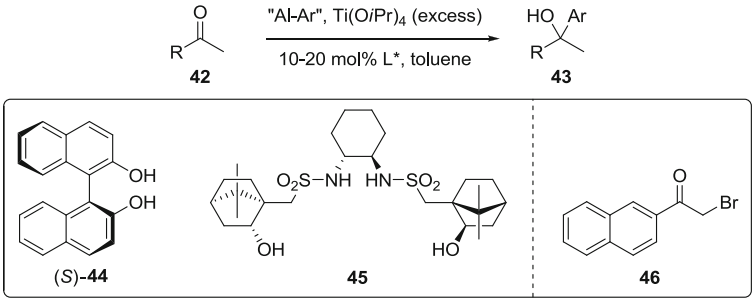
3 Stereoselective Additions to Ketones

In general, the construction of quaternary carbon centers is an important task in synthetic organic chemistry and catalysis research directed thereupon [81]. Optically active tertiary alcohols, as a special example, occur in many bioactive compounds, but are still challenging key-motifs. As opposed to their secondary counterparts, they cannot be prepared via stereoselective reduction of a carbonyl group, and the addition of carbon nucleophiles is much more complicated in the case of ketones than for aldehydes. This is due to the more demanding differentiation of the enantiotopic faces and the lower electrophilicity of the carbonyl group. Thus, there must be a fair balance between reactivity and selectivity in effective catalytic systems, and only limited examples were reported using organozinc, -tin, -silicon, -boron, and -aluminum reagents [82, 83].

3.1 Titanium-Mediated Addition of Aryl- and Alkenyl Groups

Parallel to the transformation of aldehydes (cf. Scheme 3), Gau et al. examined the addition of aryl alanes to ketones. Using $AlAr_3$(THF) and almost the same titanium alkoxide-based system with just BINOL **44** instead of H_8-BINOL **11**, very good results were achieved with a wide range of aryl,methyl and three examples of alkenyl,methyl ketones (up to 97% ee and 98% yield, Scheme 7) [84]. 2-Methoxyacetophenone turned out to be an exception, delivering only 30% ee, because its ability to chelate the titanium center might lower the stereoinduction. In contrast to aldehydes, the smaller dihedral angle of BINOL **44** compared to H_8-BINOL **11** [38] might now be advantageous because it should lead to a larger binding pocket for the bulkier ketones. Notably, toluene was employed as solvent whereas CH_2Cl_2 and THF furnished low yields. This can be explained by the higher reactivity and Lewis acidity of alanes in non-coordinating solvents, which are obviously necessary to overcome the lower electrophilicity of ketones.

trans-1,2-Bis(hydroxycamphorsulfonylamino)cyclohexane **45**, a ligand previously introduced by Walsh et al. and Yus et al. for enantioselective additions of $ZnPh_2$ to ketones [85–89], was also investigated by Gau et al. in the respective transformation with $AlAr_3$(THF) [90]. While the reaction proceeded only sluggishly under the conditions optimized for ligand **44**, a substoichiometric amount of $MgBr_2$ was found to promote high yields of up to 99% as well as enantiomeric excesses of up to 98%, the results of which favorably compare with the results using $ZnPh_2$. A particularly good improvement was achieved in the case of aliphatic ketones, but 6 equiv. of the aluminum reagent, 10 equiv. of Ti(O*i*Pr)$_4$, and 20 mol% of **45** were required. In analogy to aldehydes (cf. Sect. 2.1), mechanistic experiments were conducted using stoichiometric amounts of PhTi(O*i*Pr)$_3$ instead of the alane in order to clarify whether a transmetalation takes place within the catalytic cycle. With ketones, however, the titanium organyl led to inferior enantioselectivities, which conflicts with the hypothesis of involvement of an aryltitanium species.



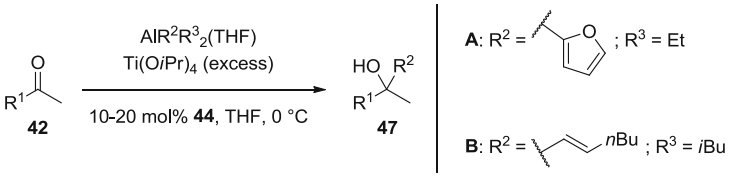
Entry	R	Ar	$AlAr_3(THF)$ / **44** yield / ee	$AlAr_3(THF)$ / **45**[a] yield / ee	$AlArEt_2(THF)$ / **44** yield / ee
1	2-naphthyl	Ph	85 / 93	99 / 92	87 / 90
2	2-BrC_6H_4	Ph	50 / 97	87 / 98	49 / 93
3	2-$MeOC_6H_4$	Ph	98 / 30	99 / 18	96 / 29
4	3-$MeOC_6H_4$	Ph	74 / 77	99 / 92	77 / 72
5	**46**	Ph	90 / 82	-	93 / 77
6	2-naphthyl	4-MeC_6H_4	94 / 91	97 / 90	93 / 91
7	Ph	4-$TMSC_6H_4$	91 / 93	83 / 81	77 / 91
8	Ph	4-$MeOC_6H_4$	87 / 78	-	89 / 93
9	*n*Bu	Ph	67 / 19	97 / 52	60 / 15
10	*i*Pr	Ph	37 / 33	82 / 83	38 / 48

Scheme 7 Titanium-mediated additions of aryl groups to ketones. All values indicate percentages. – [a]Plus 48 mol% $MgBr_2$

The same research group also used $AlArEt_2(THF)$ reagents for the addition to ketones [48]. The results were slightly inferior to those obtained using $AlAr_3(THF)$, but contrary to the reaction of aldehydes, no competing ethyl transfer was observed. This might be the consequence of the less electrophilic carbonyl group in ketones paired with a lower transferability of alkyl groups. Nevertheless, this procedure allows for significantly higher atom economy, which is particularly important for the addition of valuable functionalized aryl groups.

The same type of reagent was also used by Gau et al. for the transfer of 2-furyl groups (Scheme 8, conditions **A**) [91]. Al(2-furyl)Et_2(THF) was prepared from the respective lithium compound and $AlEt_2Cl$, and it again formed a mixture of different species in solution. Interestingly, an inverted order of addition was beneficial; the substrate was added first and the alane was added second to the Ti(O*i*Pr)$_4$/BINOL mixture. In this manner, a range of aryl, methyl ketones was screened and furnished the respective chiral tertiary alcohols in up to 94% yield and generally >90% ee. Contrary to the above-mentioned phenyl-derived aluminum reagents, additions of the furyl group proceeded smoothly in THF.

Very similar reaction conditions also allowed for the enantioselective introduction of *E*-configured alkenyl moieties (Scheme 8, conditions **B**) [92]. As little as 1.6 equiv. of Al**Alkenyl**(*i*Bu)$_2$(THF) proved to be sufficient to achieve yields of the allylic

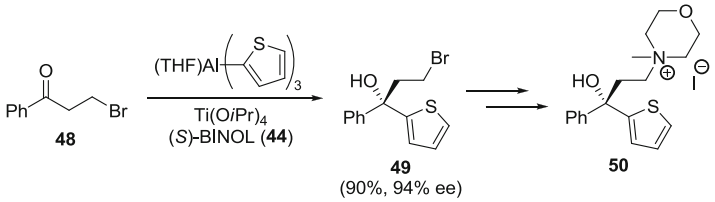


Entry	R^1	A yield / ee	B yield / ee
1	Ph	90 / 93	91 / 92
2	2-naphthyl	94 / 90	92 / 92
3	2-ClC_6H_4	70 / 92	85 / 90
4	4-ClC_6H_4	86 / 91	90 / 97
5	2-$MeOC_6H_4$	-	87 / 86
6	4-$MeOC_6H_4$	74 / 92	93 / 87

Scheme 8 Addition of furyl and alkenyl groups to aryl,methyl ketones

alcohols exceeding 80% with ee's ranging between 81% and 98%. Interestingly, even the problematic 2-methoxyacetophenone reacted highly selectively, and in addition to (*E*)-hexenyl groups, residues stemming from hydroalumination of 6-chloro-1-hexyne, 3-phenyl-1-propyne, 1-ethynylcyclohexene, and 1-ethynylcyclohexane were successfully added.

Enantiomerically enriched, tertiary alcohols could also be constructed by addition of Al(2-thienyl)$_3$(THF), mediated by the same catalyst system [93]. Several aryl,methyl ketones and an enone could frequently be transformed in almost quantitative yields and with ee's exceeding 90%. Again, 2-methoxyacetophenone furnished only a moderate ee of 45%, and unfortunately, alkyl,methyl ketones (alkyl = *n*Pr, *i*Pr, *n*Bu) were transformed all in 96% yield but with less than 17% ee. Conducting the reactions in toluene led to better results than in THF, and the optimized conditions allowed the stereoselective total synthesis of the anticholinergic/spasmolytic drug tiemonium iodide (**50**) in 84% yield over three steps from **48** (Scheme 9).

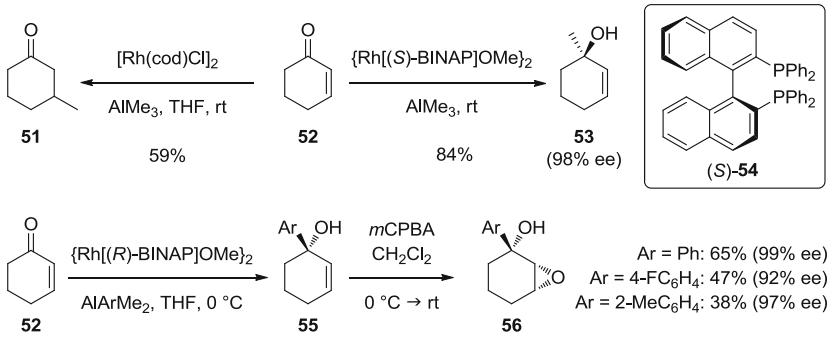


Scheme 9 Asymmetric synthesis of (*S*)-tiemonium iodide via 2-thienyl addition. Conditions: 2.0 equiv. Ti(O*i*Pr)$_4$, 10 mol% **44**, 1.7 equiv. alane, toluene, 0 °C, 24 h

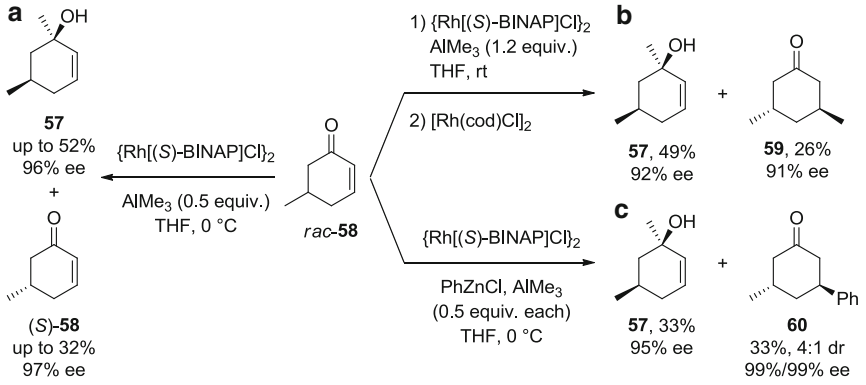
3.2 *Rhodium-Catalyzed 1,2-Additions to Cyclic Enones*

Among the examples of titanium-mediated additions of alanes to ketones, there is only a very scarce number of additions to α,β-unsaturated (acyclic) ketones (cf. Sect. 3.1). Indeed, while cycloalk-2-enones are the standard model substrates for enantioselective 1,4-additions, differentiation of their enantiotopic faces is much more complicated in the case of 1,2-additions. Therefore, highly enantioselective 1,2-additions of zinc reagents were only reported for 2-substituted derivatives [94, 95]. Initially intending to develop an asymmetric conjugate addition analogous to the Hayashi-Miyaura reaction [96, 97], the author's group studied the rhodium(I)-catalyzed transformation of alanes with cyclohexenone. The expected 1,4-addition of $AlMe_3$ only took place using the achiral $[Rh(cod)Cl]_2$ complex (cod = cycloocta-1,5-diene), whereas in situ generated Rh(I)/BINAP (**54**) complexes led to an unprecedented 1,2-addition furnishing the allylic alcohol **53** in a very high yield and with almost perfect enantioselectivity (Scheme 10) [98]. This also held true for cycloheptenone and several substituted cyclohexenones, but cyclopentenones afforded low yields due to both decomposition of the initially formed aluminum alkoxides and the consumption of the starting material in oligomerizing Michael additions. The same protocol also allowed for the highly stereoselective addition of different aryl groups starting from mixed alanes of the type $AlArMe_2$, which were prepared from $AlMe_2Cl$ and the respective Grignard reagent. The resulting 1-arylcyclohexenols **55** were directly transformed into diastereomerically pure epoxides **56** because of their low stability.

Moreover, kinetic resolutions of racemic 5-substituted cyclohexenones were performed using 0.5 equiv. of $AlMe_3$ or DABAL-Me_3 (**22a**) (Scheme 11, path a) [99]. *cis*-Configured allylic alcohols **57** were thus obtained in excellent yields and ee's of up to 96% together with pure leftover enantiomers of the starting material **58**. Furthermore, new concepts were presented for regiodivergent reactions on racemic mixtures (RRM) [99, 100]. In a sequential regiodivergent RRM, the reaction started with kinetic resolution by 1,2-addition of $AlMe_3$ to (*R*)-**58** catalyzed by $[Rh(BINAP)Cl]_2$. After a time delay, additional $[Rh(cod)Cl]_2$ was added, which



Scheme 10 Rhodium-catalyzed additions of alanes to cyclohexenone

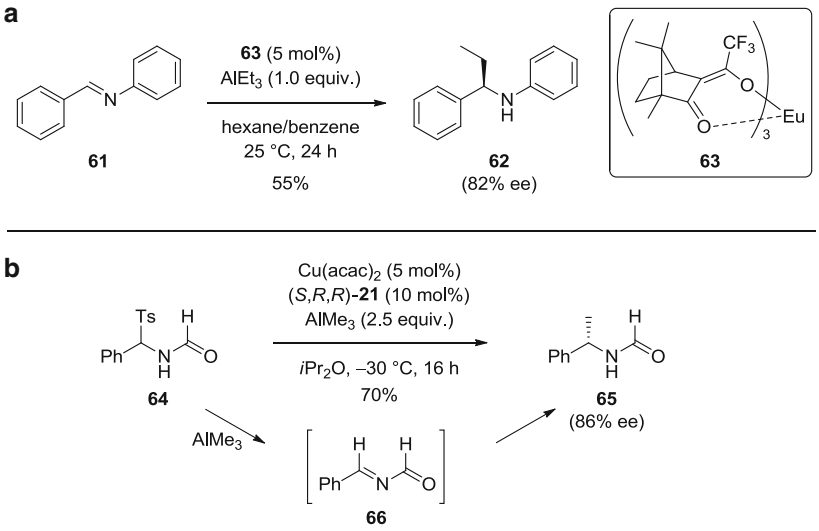


Scheme 11 Various resolutions of racemic 5-methylcyclohexenone. (**a**) Classic kinetic resolution. (**b**) Sequential regiodivergent RRM: one organometallic compound – two different catalysts. (**c**) Parallel kinetic resolution (PKR): one precatalyst – two different organometallic compounds

enabled a *trans*-selective 1,4-addition of excessive $AlMe_3$ to the enriched (*S*)-enone in the same reaction vessel (Scheme 11, path b). Under optimized conditions, a 75% combined yield of 1,2-adduct **57** and 1,4-adduct **59**, both with >90% ee, was achieved. Another special type of regiodivergent RRM is made possible because the facial selectivities of the rhodium-catalyzed 1,2-addition of alanes [98] and 1,4-addition of arylzinc chlorides [101] are reversed: a parallel kinetic resolution (PKR) with the same chiral precatalyst but two different organometallic reagents (Scheme 11, path c). Although both addition reactions must proceed through entirely different mechanisms, and thus dissimilar catalytic species, they could be performed in parallel. Both, product **57** from 1,2-addition of $AlMe_3$ and **60** from conjugate addition of PhZnCl were formed in 33% yield each and with enantiomeric excesses ≥95%.

4 Stereoselective Additions to Imines

α-Chiral amines appear as substructures in numerous natural products and synthetic drugs, and they are commonly used as ligands and auxiliaries for asymmetric synthesis or for chiral resolutions [102]. The asymmetric addition of carbon nucleophiles to imines represents one of the most efficient approaches for their preparation [103, 104], despite several obstacles in comparison to the corresponding transformations of carbonyls (cf. Sects. 2 and 3). Imines typically exist as mixtures of (*E*)/(*Z*)-isomers, and additionally, they show a lower electrophilicity. Therefore, more powerful nucleophiles are required for addition reactions, which, on one hand, can cause deprotonation and thus formation of azaenolates, and on the other hand, lead to even higher requirements regarding stereoinduction by the chiral catalysts.



Scheme 12 Transition metal-catalyzed additions of trialkyl alanes to imines. (**a**) Lanthanide catalysis. (**b**) Addition to an *N*-formylimine

Transition metal-catalyzed additions of organoaluminum reagents to aldimines have been known since the pioneering work of Fujisawa et al. [50], who obtained the desired racemic amine by addition of $AlMe_3$ to *N*-tosylbenzalimine. No background reaction was observed in the absence of $Ni(acac)_2$, thus leaving room for stereoselective modifications by means of chiral ligands.

Although Fujisawa failed to run additions to electronically unactivated Schiff bases, Molander, Blum, et al. managed to perform this challenging conversion: under lanthanide catalysis, $AlMe_3$ and $AlEt_3$ were added to *N*-arylimines derived from different aromatic aldehydes [105]. No competing reduction of the imines was observed upon ethylation, and in one example, an optically enriched amine was produced in 55% yield with 82% ee using the chiral shift reagent (+)-$Eu(tfc)_3$ (**63**, tfc = tris[3-(trifluoromethylhydroxymethylene)-camphorate]) as catalyst (Scheme 12a). The reaction worked best in benzene; no conversion took place in THF. Attempts to replace the lanthanide complex with standard Lewis acids almost completely shut down the reaction, thus suggesting a transmetalation mechanism. Blum et al. later found that the racemic addition of $AlEt_3$ to Schiff bases is also promoted by substoichiometric amounts of cerium(IV) compounds [106]. They obtained up to 99% yield in the reaction of various benzylidene *N*-arylamines with 3 equiv. of $AlEt_3$ and 0.75 equiv. of ceric ammonium nitrate (CAN) in benzene at room temperature. Despite these promising results, the enantioselective addition was not further pursued.

Minnaard, Feringa, et al. described asymmetric additions to in situ formed *N*-formyl imines **66**, the resulting amines **65** being easily deprotected under mild conditions (Scheme 12b) [107]. This is the copper/phosphoramidite-catalyzed

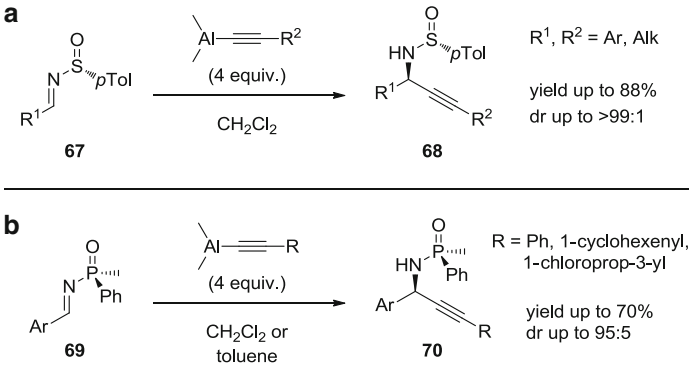
variant of a reaction previously published by Mecozzi and Petrini [108], who used organolithium and -magnesium reagents rather than zinc or aluminum organyls. The imines of type **66** were liberated from α-amidosulfones **64** with the help of the organometallic reagent, and excellent yields exceeding 92% and enantiomeric excesses exceeding 88% were reported for additions of $ZnEt_2$, $Zn(i\text{Pr})_2$, and $Zn(n\text{Bu})_2$. $ZnMe_2$ furnished the desired product with only 10% ee, and thus, $AlMe_3$ came into play, delivering **65** in 70% yield with 86% ee (interestingly of the opposite configuration).

In attempts to recover the chiral ligand **21**, the analogous oxidized phosphoric amide was also isolated. This compound is formed by a copper-catalyzed side-reaction with sulfinate as oxidant and actually works as a cocatalyst that significantly increases the enantioselectivity of the $AlMe_3$ addition. A similar effect was achieved applying a combination of **21** and hexamethylphosphoric triamide (HMPA), and thus, the improved stereoselectivity was suggested to arise from strong coordination effects.

Although the above-mentioned references are the only ones that describe catalytic asymmetric additions of alanes to imines, approaches based on chiral auxiliaries are more common. For the preparation of chiral allyl amines, Wipf et al. performed additions to enantiopure *N*-sulfinylimines using alkenyldimethyl alanes, which were generated by carboalumination of terminal alkynes [109]. This class of activated imines was established by Davis [110, 111] and Ellman [112] and is synthetically attractive because of the relatively mild conditions for the deprotection of the resulting amides. Additions to *p*-tolylsulfinylimines furnished the allylic amides in 60–85% yield with diastereomeric ratios of up to 95:5. Even higher selectivities of up to 99:1 were achieved with *tert*-butylsulfinylimines, but this went along with significantly lower yields (20–67%). The scope of the reaction includes differently substituted terminal alkynes [*n*Hex, *t*Bu, Ph, $(CH_2)_3OSi(i\text{Pr})_3$] and imines derived from aromatic aldehydes, cinnamaldehyde, and cyclohexanecarboxaldehyde. Interestingly, the (*E*)-selectivity in the final products exceeded that of the alkenyl alanes, which was attributed to a lower reactivity of (*Z*)-alkenyl alanes. For this reason, internal alkynes are not suitable for this procedure.

Analogously, Royer et al. investigated the addition of aluminum acetylides to *p*-tolylsulfinylimines **67** (Scheme 13) [113]. Under optimized conditions (4 equiv. alane, CH_2Cl_2, 0 °C), the respective propargylic amides **68** were obtained in high yields and up to >99:1 diastereomeric ratio. Again, the selectivity was not only much higher than employing Grignard or organolithium reagents but also reversed (cf. Fig. 1). While the $AlMe_3$-promoted addition of lithium acetylides might proceed through a chair-like transition state such as that proposed by Ellman et al. [112, 114], the additions of alkynyl alanes presumably take place through acyclic transition states of the substrate, which is activated by coordination of two separate aluminum species to both the nitrogen and the oxygen of the functional group.

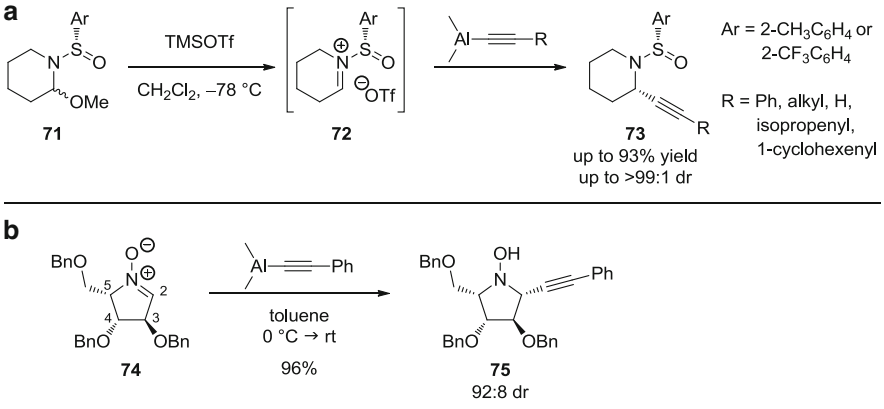
Moreover, Royer et al. were the first to expand such diastereoselective additions to enantiopure *N*-(*P*-methyl-*P*-phenylphosphinoyl)imines **69**. Good yields and high



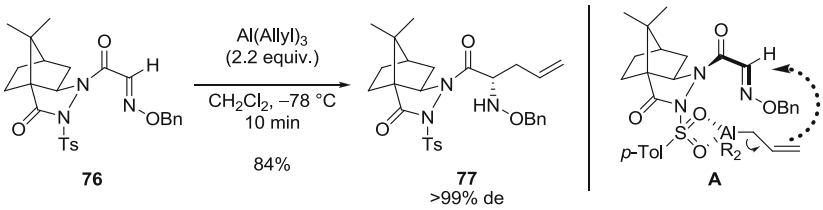
Scheme 13 Alkynyl addition to (**a**) sulfinyl and (**b**) phosphinoyl imines

selectivities were achieved, which are, however, slightly inferior compared with those obtained using sulfinylimines **67** (Scheme 13b) [115]. Nevertheless, this new type of chiral auxiliary is very promising, and aluminum reagents appear to be optimal for this transformation because no conversion occurred with lithium acetylides, and magnesium acetylides added unselectively. In this context, it is notable that Wipf et al. have performed microwave-accelerated additions of alkenyl alanes to achiral *N*-diphenylphosphinoylimines [116], and Bräse et al. reported additions of $AlMe_3$ and $AlEt_3$ to the corresponding ketimines partly in quantitative yields [117].

Cyclic *N*-sulfinyliminium salts **72** are another new type of highly activated substrates for aluminum acetylide additions and were also introduced by Royer



Scheme 14 Conversion of cyclic substrates: (**a**) sulfinyliminium salts and (**b**) carbohydrate-derived nitrones



Scheme 15 Diastereoselective allylation of glyoxylic oxime ethers

et al. (Scheme 14a) [118]. They were generated in situ from α-methoxy-*N*-sulfinylpiperidines **71** and underwent additions of differently substituted aluminum acetylides. The yields were mostly very good and o-tolyl or even better o-trifluoromethylphenyl as substituent on the sulfur induced high diastereoselectivities. In contrast, zinc acetylides produced substantial amounts of enamides due to their higher Brønsted basicity.

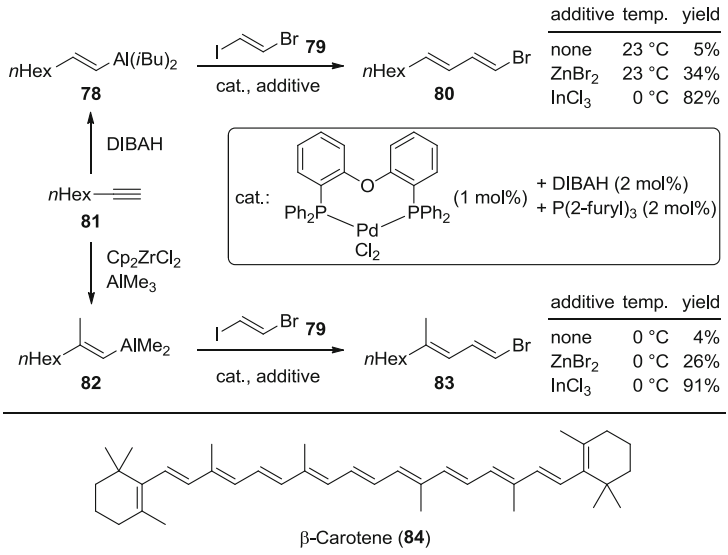
Influenced by the $ZnMe_2$-assisted addition of terminal alkynes to nitrones developed by Chavant et al. [119, 120], Micouin et al. performed the same type of reaction using $AlMe_3$ and obtained several propargylic hydroxylamines [121]. For a stereoselective variant, Desvergnes, Py, et al. prepared the carbohydrate-derived nitrone **74**, but only achieved high diastereoselectivities in the addition of phenylacetylene (Scheme 14b) [122]. Moreover, the preformed alkynyl alane had to be used because in situ formation from $AlMe_3$ and the alkyne predominantly led to methyl addition. From the reaction of stereoisomeric nitrones of the type **74**, it was concluded that the diastereoselectivity solely depended on the configuration at C-3.

Szymoniak et al. reported on a completely different type of addition to aldimines: a zirconium-catalyzed transformation of trialkyl alanes [123]. Using 5 mol% of Cp_2ZrCl_2, ethyl and *n*-butyl groups could be introduced to *N*-aryl and *N*-alkyl imines derived from aromatic and heteroaromatic aldehydes in 67–95% yield. $Al(nBu)_3$ furnished lower yields than $AlEt_3$ due to concomitant reduction, but these results are still very interesting, because the related addition of Grignard reagents is limited to ethyl groups. The potential of chiral auxiliaries in this transformation was clearly shown by employing an *N*-[(*R*)-2-hydroxy-1-phenylethyl]imine, which induced an impressive d.r. of >97:3 with 92% yield. No conversion occurred with $AlMe_3$, and it is thus very likely that the reaction proceeds through formation of azazirconacycles.

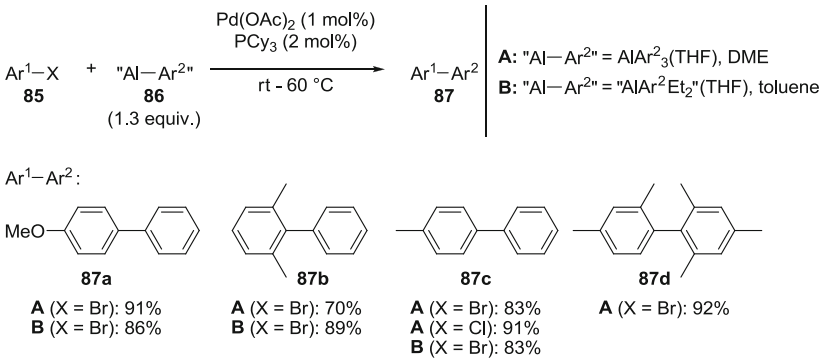
The only example of stereoselective allylations by an alane is a study by Chen et al., which also allows for a direct comparison to the use of allyltributylstannane in the presence of $Sn(OTf)_2$ [124]. A range of glyoxylic oximes was tested with chiral auxiliaries mainly derived from terpenes, and substrate **76** turned out the best (Scheme 15). The tosyl group of this camphorpyrazolidinone is believed to coordinate with triallylaluminum (transition state **A**), thus directing its attack to the *si*-side of the oxime ether. The tin reagent furnished a slightly higher yield with this substrate, and very good results were also obtained with (−)-borneol or (−)-pinanediol as auxiliary.

5 Cross-Coupling Reactions of Aluminum Organyls with Organic Halides

Since long before the 2010 Nobel prize in chemistry was awarded to pioneers of Pd-catalyzed cross-coupling reactions, these C,C-bond forming transformations belonged to the most studied and applied group of reactions in organic chemistry. Organometallic reagents of boron, tin, and zinc are the most commonly used, but it is frequently overlooked that cross-couplings using alkenyl alanes were reported even earlier [125, 126], and they are also classified as "Negishi couplings" [127]. Their lack of toxicity distinguishes them from tin reagents, and it is again mainly their ease of preparation that makes them attractive compounds. Moreover, their strong Lewis acidity is a distinctive feature that can lead to conversion of even poorly reactive substrates. As early as 1978, Negishi et al. reported on the tremendous acceleration of alkenyl alane–alkenyl halide couplings in the presence of zinc salts [128], and some years ago an even more pronounced effect was observed with $InCl_3$: alkenyl alanes **78** and **82**, stemming from the hydro- and carboalumination of octyne **81**, underwent cross-couplings with 1-bromo-2-iodoethene (**79**) with marked differences which depended on the presence and the type of additive (Scheme 16) [129]. The total synthesis of β-carotene (**84**), comprising four alkenyl alane–alkenyl halide couplings, is an instructive example for the effectiveness of these transformations [130]. In this section, some recent developments of cross-couplings involving alanes will be highlighted, especially those using the novel reagents already mentioned in the sections on addition reactions. For more detailed



Scheme 16 Palladium-catalyzed alkenyl alane–alkenyl halide couplings

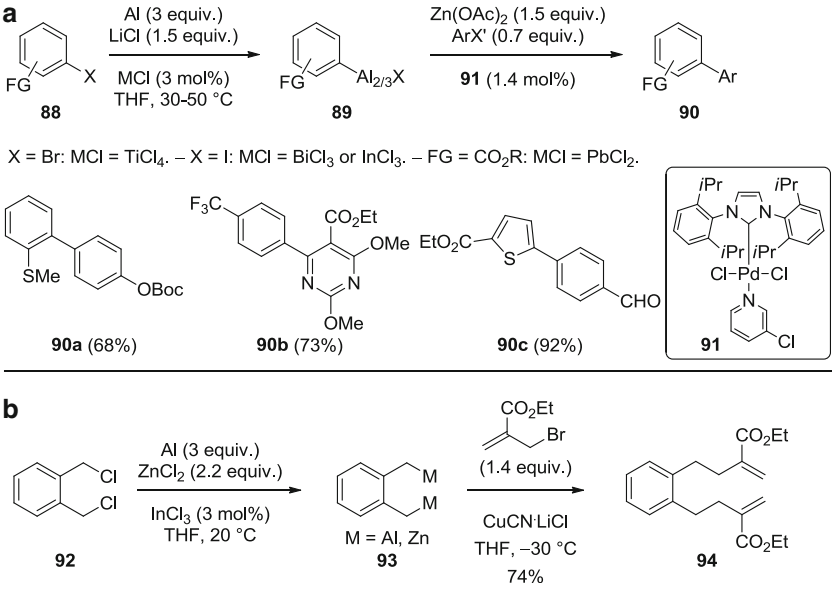


Scheme 17 Preparation of biaryls by palladium-catalyzed cross-couplings

information, the reader is referred to several excellent reviews and book chapters on this topic [11, 131, 132].

Besides additions to carbonyls, Gau et al. also used alanes of type $AlAr_3(THF)$ for aryl–aryl couplings, thus obtaining the interesting biaryl structural motif (Scheme 17) [133]. A rather simple catalyst consisting of $Pd(OAc)_2$ and tri(cyclohexyl)phosphine (PCy_3) proved suitable and delivered very good yields with electron-poor, electron-rich, and also sterically very hindered aryl bromides (biaryl **87b**). Cross-couplings with aryl chlorides were also possible (biaryl **87c**), but required an elevated reaction temperature of 60 °C. Beyond phenyl groups, substituted aryl rings, including 2,4,6-trimethylphenyl groups, could be transferred from aluminum (biaryl **87d**). These reactions were performed in toluene, and the active catalyst was preformed by heating the palladium salt, the phosphine, and the alane for 1 h to 100 °C. To overcome the drawback that only one aryl group in each $AlAr_3(THF)$ is consumed, the same research group also employed $AlArEt_2(THF)$ alanes in these transformations [134]. In fact, yields of biaryls were partially even better and no coupling of ethyl groups was observed. The employment of these more atom-efficient alanes, however, precludes the use of aryl chlorides because the transmetalation to palladium is obviously slower than in the case of $AlAr_3(THF)$ alanes.

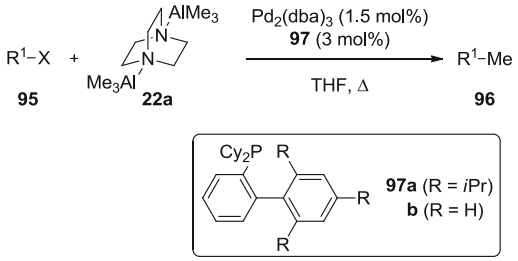
Even more economic is the use of aluminum sesquihalides $Al_2R_3X_3$, also written as $RAl_{2/3}X$, which have been used by Knochel et al. for additions to aldehydes and ketones in case of allyl, propargyl, and allenyl residues (cf. Sect. 2.3). The respective aryl compounds **89** can be prepared by oxidative addition in the presence of LiCl and catalytic amounts of either $TiCl_4$ for aryl bromides, $InCl_3$ or $BiCl_3$ for aryl iodides, or $PbCl_2$ for compounds **88** with ester or amide groups (Scheme 18a) [135]. After transmetalation with a zinc salt, these reagents undergo smooth Pd-catalyzed cross-coupling reactions with various aromatic and heteroaromatic bromides and iodides to form biaryls **90**. Apart from economic considerations, these transformations are highly interesting because of the chemoselectivity of the aluminum reagents, which tolerates the presence of sensitive functionalities such as ester, nitro, and formyl groups as well as a broad range of heteroaromatic rings as exemplified by products **90a–c**. The same also holds true



Scheme 18 Preparation of aryl and benzyl aluminum reagents through oxidative addition and subsequent cross-coupling reactions

for the preparation and cross-coupling reactions of the corresponding benzyl derivatives, the oxidative addition now being most efficiently catalyzed by $InCl_3$ [136]. For secondary benzyl chlorides or those bearing ester or nitrile groups on the aromatic ring, yields were improved if transmetalation with $ZnCl_2$ already occurred during the initial metalation, and a range of diarylmethanes was obtained after subsequent cross-couplings with aryl bromides and iodides. Moreover, Cu-catalyzed allylations could be performed, including the twofold metalation and allylation of dichloride **92** to furnish product **94** in a marvelous 74% yield (Scheme 18b).

Cross-coupling reactions of alkyl metals are equally important, and the special reactivity of trialkyl alanes has been used for a long time, e.g., for transformations of ketone-derived enol phosphates [137, 138]. In order to reduce the pyrophoric character and to increase nucleophilicity, the modified reagents **3** were employed by Blum, Schumann, et al. for reactions with aryl and alkenyl halides [139, 140], and recently, Woodward et al. demonstrated that the more easily available DABCO adducts **22** are also very suitable for this purpose (Scheme 19). Preliminarily results were obtained by employing $[Pd(PPh_3)_4]$ as catalyst [56], which were later on improved by use of the electron-rich ligand **97a**. A wide range of aryl bromides, chlorides, and triflates as well as alkenyl triflates and benzyl bromide were successfully converted [55, 141]. For the selective methylation of a C,Br-bond next to a C,Cl-bond, ligand **97b** furnished better results, and functional groups including aldehydes, alcohols, and nitriles were tolerated. This method is, however, less suitable for pyridines and substrates bearing



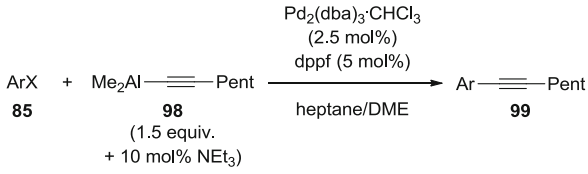
95	yield
4-NCC_6H_4-Cl	95%
4-MeC_6H_4-Cl	99%
4-ClC_6H_4-Br	96%
4-$(CHO)C_6H_4$-Br	88%
4-$NO_2C_6H_4$-Cl	81%
Bn-Br	72%
cyclohexenyl triflate	>99%

Scheme 19 Methylation of organic halides with DABAL-Me_3

enolizable carbonyl moieties. Use of DABAL-Et_3 (**22b**) also allowed for ethylations with only trace amounts of reduced products stemming from β-hydride elimination, and most notably, the transformation is very robust, permitting aerobic conditions and the use of undried THF. Promising results were also achieved in biphasic mixtures of organic solvents and ionic liquids, which enable rapid isolation of the cross-coupled products and recycling of the catalyst [142].

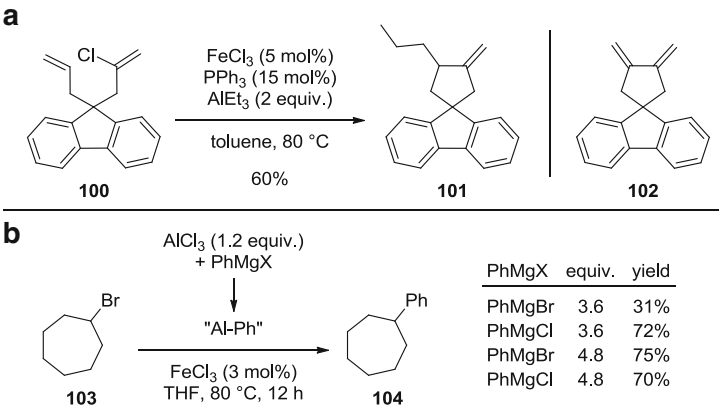
Inspired by the ability to obtain dialkylalkynyl alanes **98** from NEt_3-catalyzed deprotonation of terminal alkynes with $AlMe_3$ [17], Micouin et al. performed cross-coupling reactions with aryl halides (Scheme 20) [143]. Such alkyne–aryl couplings are typically considered to be in the domain of the Sonogashira protocol, i.e., the continuous formation of copper acetylides during the cross-coupling process, but alkyne homodimerization is occasionally a problem, which can be solved by the use of preformed metal acetylides [144, 145]. The best results were achieved with bis(diphenylphosphino)ferrocene (dppf) as the ligand on palladium and 1,2-dimethoxyethane (DME) as the cosolvent, thus leading to efficient couplings of electron-rich and electron-poor aryl halides with both the heptyne- and the phenylacetylene-derived alane. On the basis of the respective phenyl derivatives, the yields strongly depended on the leaving group X, and only the particularly reactive 2-chloropyridine allowed for cross-couplings involving C,Cl-bonds.

This protocol recently rose in appeal by the observation of Gau et al. that 4 mol% of cheap $[NiCl_2(PPh_3)_2]$ catalyzes such aryl–alkyne couplings with an even higher efficiency [146]. Moreover, various benzyl bromides as well as bromomethyl-substituted heteroarenes were alkynylated in yields exceeding 90% when diethyl ether was used as the solvent. These nickel-catalyzed benzyl–alkynyl couplings



ArX	temp.	yield
PhI	25 °C	>99%
PhBr	85 °C	87%
PhOTf	85 °C	62%
PhCl	85 °C	0%

Scheme 20 Aryl–alkynyl couplings employing alanes



Scheme 21 Iron-catalyzed cross-coupling reactions of aluminum reagents

thus add to the seminal work of Lipshutz and Negishi on the related couplings of alkenyl alanes and their use in the syntheses of Coenzymes Q [147–149].

The use of iron catalysts for cross-coupling reactions is even more attractive and intensively studied; however, little is known about the application to alanes [150]. An interesting transformation, an alkylative cyclization, was recently found by serendipity. Planning to reduce an iron catalyst with $AlEt_3$ and then perform a Heck-type cyclization of the 2-chlorohepta-1,6-diene **100**, Kotora et al. obtained the alkylated product **101** instead of the expected **102** (Scheme 21a) [151, 152]. The same reaction also occurred with $AlMe_3$, and a catalytic cycle was proposed in which an alkyl iron species first undergoes carboferration of the unfunctionalized C,C-double bond, followed by carboferration of the chloro-substituted one, and finally a β-chloride elimination. Moreover, Nakamura et al. studied iron-catalyzed cross-couplings of alkyl halides with aryl aluminum reagents and noticed astonishing effects [153]. While no cross-coupling product **104** was obtained using salt-free $AlPh_3$(THF), the best results were achieved when the aluminum reagent was formed from $AlCl_3$ and 3 equiv. of PhMgCl (but not PhMgBr) or 4 equiv. of either Grignard reagent (Scheme 21b). Thus, the active compound is clearly a magnesium alanate, and it was established that such alanates are even formed upon using a 3:1 ratio of Grignard reagent and $AlCl_3$ and not just the expected neutral $AlPh_3 \bullet 3\ MgX_2$. After optimization of the iron catalyst, this method proved suitable for cross-coupling of different aryl groups with primary and secondary alkyl bromides and chlorides.

6 Conclusion

Although much less studied, the application of aluminum reagents in catalytic asymmetric additions to C,O-double bonds provides excellent results that are not outranked by those obtained from employing zinc reagents. Of particular efficiency

is the nickel-catalyzed addition of trialkyl alanes or their DABCO adducts to aldehydes, whereas aryl groups can be introduced by the titanium-mediated process. Clearly, it would be very interesting to expand these reactions to be able to employ readily available alkenyl and alkynyl alanes or sesquihalides $Al_2R_3X_3$ (R = allyl, propargyl, allenyl, benzyl, or aryl), which are easily obtained by oxidative addition of organic halides to aluminum powder. However, this requires modulation of their high inherent reactivity in order to suppress pronounced background reactivity. Moreover, aluminum reagents are well suited for the transformation of ketones into enantiopure tertiary alcohols because the lower electrophilicity of these substrates can be compensated for by the high reactivity of alanes. Notably, the titanium-mediated process is already applicable to not only aryl but also alkenyl additions, and the unique feature of the rhodium-catalyzed addition of $AlMe_3$ and aryl alanes is the perfect stereocontrol in the case of plain cyclic enones. However, the synthetic scope is still quite limited and it would be important to either increase the turnover number or substitute the expensive rhodium by a cheaper transition metal in order to make this method more cost-effective.

Unfortunately, catalytic asymmetric additions of organic alanes to imines are almost unknown, and admittedly, zinc reagents are better applicable for this purpose. But the characteristics of aluminum organyls reveal their potential: the high Lewis acidity should enable activation of the rather unreactive C,N-double bonds and the low Brønsted basicity should preclude deprotonation and formation of the respective azaenolates. Because chiral α-tertiary and α-secondary amines are ubiquitous structural motifs in natural products and synthetic bioactive compounds, exploration of alane additions is highly relevant.

Finally, cross-coupling reactions involving aluminum reagents have primarily been used for alkenyl transfers from the carbo- and hydroalumination products of terminal alkynes. A number of interesting results were published in recent years and will surely broaden the application of alanes and aluminum sesquihalides to these C,C-bond forming reactions.

All in all, the authors are convinced that research in the field of organoaluminum reagents and their catalytic transformations will continue to be highly rewarding and will certainly make them realize their full potential.

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Conjugate Addition of Organoaluminum Species to Michael Acceptors and Related Processes

Oscar Pàmies and Montserrat Diéguez

Abstract Over the last decade much effort has been devoted to develop new methodologies to expand the conjugate addition and related processes to the use of triorganoaluminum reagents. This chapter covers the recent literature reports (ca. 2003 onward) on asymmetric conjugate addition of triorganoaluminum reagents to a range of Michael acceptors and also mechanistically closely related allylic alkylation of allylic substrates. It also includes cascade processes where the intermediate enolates (conjugate addition) and alkenes (allylic alkylation) are used for the synthesis of more complex molecules (including natural products and pharmaceutical targets).

Keywords Allylic alkylation · Asymmetric catalysis · Conjugate addition · Michael acceptors · Triorganoaluminum regents

Contents

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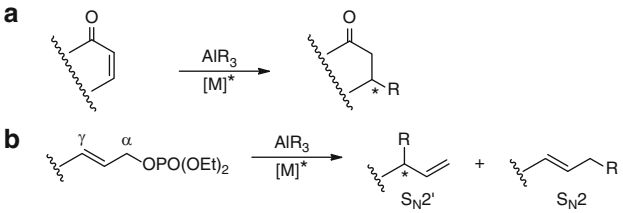
1 Introduction

Metal-catalyzed conjugate addition and allylic alkylation of Michael acceptors with organometallic reagents are two of the most powerful carbon–carbon bond forming processes [1–17]. For a long time, these transformations were performed with diorganozinc or Grignard reagents, and the use of triorganoaluminum reagents was less studied [1–17]. The main reason may be that triorganoaluminum reagents are regarded as hazardous reagents due to their vigorous reactions with water and air. This pyrophoric character is a problem for low molecular weight alanes. However, this pyrophoric character is drastically reduced either by using diluted solutions in hydrocarbons or by complexation with Lewis basic groups (i.e., DABAL-Me_3) [18]. On the other hand, the use of triorganoaluminum reagents is very attractive because they can be easily prepared on an industrial scale using several methodologies such as hydro- and carbo-alumination. Moreover, in contrast to other organometallic reagents, aluminum has a high Lewis acidity and oxophilicity, which diminishes the nucleophilicity of the organic residues and can enrich the scope of the reactions [15].

In the last years most of the efforts has been devoted to their asymmetric versions with the aim to easily build up enantio-enriched synthons for biological active and natural compounds [4–7]. Significant advantages of these processes are the high compatibility with many functional groups, low cost of the metals used (typically copper and nickel), and the often high regio- and enantioselectivities. In the metal-catalyzed asymmetric conjugate addition an α,β-unsaturated compound is attacked by a nonstabilized carbon nucleophile (Scheme 1a) to form a new stereogenic carbon center. In the metal-catalyzed asymmetric allylic substitution, the new stereogenic carbon center is formed by the attack of a nonstabilized carbon nucleophile to an allylic substrate (Scheme 1b). In this reaction the control of the regioselectivity is one of the major issues, because the displacement of an allylic leaving group can occur in two different ways. The first one is the direct attack on the carbon bearing the leaving group at α-position, formally known as S_N2 reaction. The second γ-substitution, also referred to as S_N2', displaces the leaving group while involving an allylic shift of the double bond.

In the past few years impressive results have been obtained in the development of highly efficient new metal catalytic systems by exploring several ligand types, metal sources, and reaction conditions. Remarkable efforts have been made to enlarge the scope of substrates and nucleophiles increasing the possibilities for their use in the synthesis of more complex chiral organic molecules.

This chapter covers the recent literature reports (ca. 2003 onward) on asymmetric conjugate addition of triorganoaluminum reagents to enones, α,β-unsaturated systems, nitroalkenes and also mechanistically closely related allylic alkylation of allylic phosphonates. It also includes cascade processes where the intermediate enolates (conjugate addition) and alkenes (allylic alkylation) are used for the synthesis of more complex molecules. This chapter is organized as follows. In Sect. 2 we present the results in the asymmetric conjugate addition. In this part, the



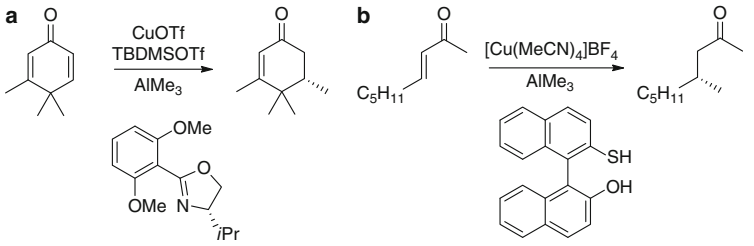
Scheme 1 Typical examples of enantioselective metal-catalyzed conjugated addition (**a**) and allylic alkylation reactions (**b**). R = alkyl, vinyl, aryl, or alkynyl

catalytic data are grouped according to the type of Michael acceptor and nature of the triorganoaluminum reagent. In Sect. 3 the results obtained in asymmetric allylic substitution reaction are covered. For each reaction we also discuss their application to organic synthesis.

2 Asymmetric Conjugate Addition Reactions

The renaissance on the use of trialkylaluminum as alternatives to diorganozinc and Grignard reagents for this transformation appeared in the late 1990s mainly because they are readily available and they offer additional hydro- and carboalumination possibilities for their preparation [19]. Moreover, their higher reactivity, due to the stronger Lewis acidity, allows the Cu-catalyzed 1,4-addition of very challenging sterically hindered substrates (i.e., β,β′-trisubstituted enones), which, at that time, were inert to organozinc and Grignard methodologies.

Most of the successful asymmetric versions of this chemistry have made use of trialkylaluminum reagents, a trend started by the groups of Iwata and Woodward (Scheme 2). Thus, Iwata and coworkers reported the Cu-catalyzed 1,4-addition of $AlMe_3$ using 2-aryloxazolines as ligands [20]. They found that the presence of Lewis acids, such as *tert*-butyldimethylsilyl triflate, is crucial if good yields and enantioselectivites have to be achieved (Scheme 2a). On the other hand, Woodward and coworkers avoided the need for the addition of a Lewis acid by using binaphthol heterodonor S, O ligands [21]. These ligands contain both *hard* and *soft* donors groups to easily accommodate bimetallic aluminum-cuprate species, which are responsible for the catalytic activity (Scheme 2b). In the last decade a large plethora of chiral ligands, including homodonor (phosphite, phosphoroamidite, *N*-phosphine, and carbene) and heterodonor (P–O, P–P′ and P–N), have been applied to this process. Among them, the use of biaryl-based phosphoroamidites, diaryl *N*-phosphines, and chiral *N*-heterocyclic carbenes has shown to provide the best enantioselectivities in this process (Fig. 1).



Scheme 2 Pioneering work on the asymmetric conjugate addition using trialkylaluminum reagents

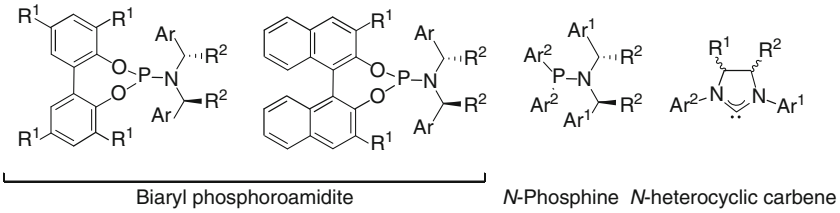


Fig. 1 Most representative ligand types

2.1 Cyclic Enones as Michael Acceptors

Cyclic Michael acceptors are the most popular substrates because their use overcomes the problem of s-*cis* and s-*trans* conformational interconversion of acyclic substrates. Among the cyclic substrates, cyclohexenone has become the model substrate for testing new catalytic systems. The special reactivity of the cyclopentenone and of the large macrocyles, such as cyclopentadecenone, should be pointed out. Cyclopentenone is the most reactive substrate, and the resulting enolate is reactive enough to undergo Michael addition to unreacted cyclopentenone, thus lowering the isolated yield of the reaction. The other problem with this substrate is the flatness of the molecule, which is less sensitive to the steric requirements of the chiral ligand. On the other hand, large macrocycles, i.e., cyclopentadecenone, are large enough ring to allow s-*cis* and s-*trans* conformational interconversion, and so they behave like acyclic Michael acceptors.

2.1.1 Using Trialkylaluminum Reagents

For unsubstituted cyclic enones, 4,4-substituted and 2-substituted cyclic enones, the use of Cu-precursors modified with biaryl phosphoroamidite ligands has been widely studied (Fig. 1). In general, two sets of conditions have been found to be optimal for the 1,4-addition of trialkylaluminum reagents, the choice of which depends on the solvent and the copper source used. Thus, while copper thiophene

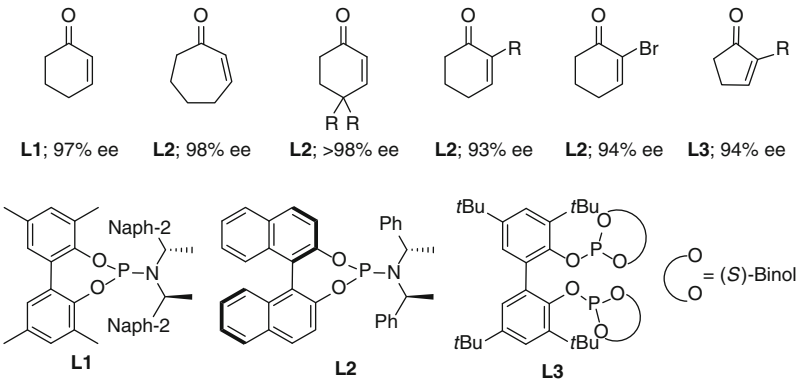


Fig. 2 Representative results in the 1,4-addition of trialkylaluminum reagents to unsubstituted, 4,4-substituted and 2-substituted cyclic enones

carboxylate (CuTC) was best using diethyl ether as solvent, THF was better with the precursor $[Cu(CH_3CN)_4]BF_4$, developed by Kubas. Under optimized conditions, excellent enantioselectivities have been obtained in the addition of trialkylaluminum species to a range of 6- and 7-membered ring cyclic enones (Fig. 2) [22]. These results are comparable with those obtained using other organometallic reagents [14]. However, while the use of Cu-phosphoroamidite catalytic systems only provided low-to-moderate enantioselectivities for 2-cyclopentenone and 2-alkyl cyclopentenone derivatives [23], the use of biaryl-based diphosphite ligands provided excellent enantioselectivities for this substrate classes (i.e., up to 94% for 2-cyclopentenone [24] and up to 72% for 2-methyl-2-cyclopentenone [24]). The Cu-phosphoroamidite methodology has also been extended to carbamate protected α,β-unsaturated lactams with less success [25]. (The use of diorganozinc reagents led to much higher enantioselectivities.) More recently, on the other hand, trialkylaluminum reagents have been successfully used in the conjugate addition of α-halogenated cyclic enones (Fig. 2) [26]. This substrate class is very attractive because the resulting chiral α-halo ketones are valuable intermediates for the synthesis of high-value chemicals [27–31].

As previously stated the use of trialkylaluminum reagents is of great importance for the synthesis of chiral quaternary carbon centers. Thus, due to their stronger Lewis acidity, a better activation of the substrates is reached overcoming the steric hindrance of trisubstituted α,β-unsaturated ketones. (Recently the use of chiral bidentate *N*-heterocyclic carbenes has allowed the conjugate addition of diorganozinc and Grignard reagents to β,β′-trisubstituted enones. See, for instance [32].) For this substrate class, the use of biaryl-based phosphoroamidite, *N*-phosphine (SimplePhos), and *N*-heterocyclic carbene ligands has been the most successful ones. Thus, a wide range of trisubstituted substrates and trialkylaluminum reagents has been explored.

Biaryl-based phosphoroamidite ligands provide optimum results (conversions and enantioselectivities) for the less hindered 6- and 7-membered substrates (i.e., R^1 = Me or Et; Fig. 3) and less hindered triorganoaluminum reagents (i.e., $AlMe_3$

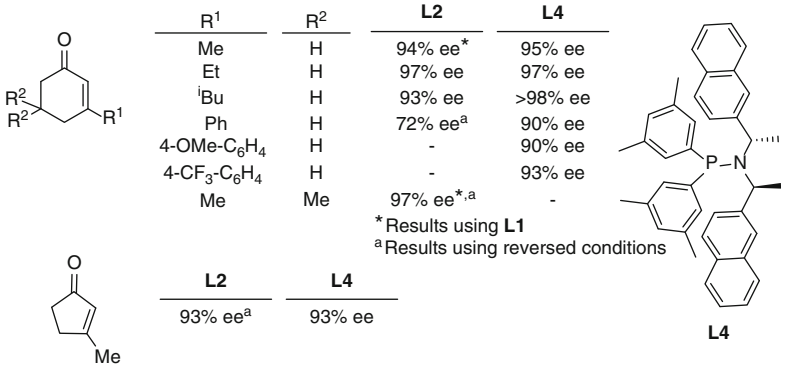


Fig. 3 Representative results for the addition of trialkylaluminum reagents to trisubstituted cyclic enones using biaryl-based phosphoroamidite and *N*-phosphine ligands

and $AlEt_3$) under similar reaction conditions than those used for disubstituted ones (Fig. 3) [33]. However, for more challenging 5-membered ring systems and bulky 5,5′-dialkyl substituted and 3-aryl-substituted cyclohexenones, special reaction conditions (reversed addition, i.e., the trialkylaluminum reagent is slowly added over the enone and catalyst solution) were developed for high enantioselectivities [33].

N-phosphine (SimplePhos) ligands provide similar levels of enantioselectivity than those observed with phosphoroamidite ligands for simple trisubstituted enones [23, 34, 35]. However, the scope of this type of ligands is higher, because they also facilitate the highly enantioselective 1,4-addition of trialkylaluminum species to more challenging hindered substrates (i.e. $R^1 = i$Bu; Fig. 3) and 3-aryl-cyclohexenones (R^1 = aryl; Fig. 3) [35]. In addition, SimplePhos ligands are very efficient in the addition of Al*n*Pr$_3$ and Al*n*Bu$_3$ reagents to bulky trisubstituted cyclohexenones [35], clearly better than phosphoroamidite-type ligands which proceed with low conversions [33].

More recently, *N*-heterocyclic carbenes have also been successfully applied in the conjugate addition of trisubstituted enones using trialkylaluminum reagents. In general, the conjugate addition of trisubstituted 5-membered cyclic enones using *N*-heterocyclic carbenes proceeds with higher enantioselectivities than those using previously mentioned P-donor ligands (**L1**–**L4**) (Fig. 4) (for a recent review, see [36]). This excellent performance also extends to the conjugate addition of enones containing bulky substituents (i.e., *i*Bu, Ph) and also to 6- and 7-membered cyclic enones.

2.1.2 Using Arylaluminum Reagents

For many years the introduction of an aryl group to an unsaturated enone has been dominated by the Rh-catalyzed addition of arylboronic acids (for a recent review,

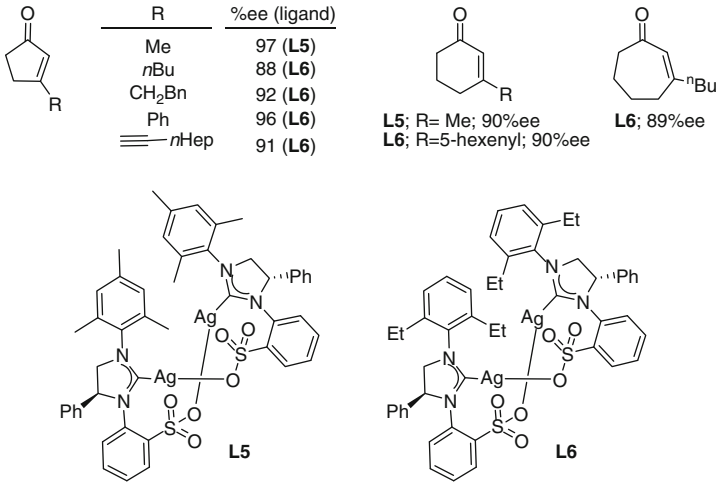
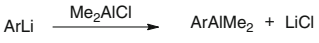


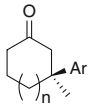
Fig. 4 Representative results for the addition of trialkylaluminum reagents to trisubstituted cyclic enones using *N*-heterocyclic carbene ligands

see [36]). However, most of the reports deal with the use of disubstituted substrates. The development of methods for the construction of chiral quaternary centers bearing an aryl group is still therefore of great importance. Conjugate addition of organometallic species has recently appeared as a new methodology for the preparation of chiral quaternary centers. Despite this, only few reports have been published. Most of the examples make use of substrates in which the aryl group is present (i.e., 3-aryl-substituted enones) [13, 35, 37]. In the last years there have been few reports on the conjugate addition of aryl-zinc species and Grignard reagents using Cu–*N*-heterocyclic carbene catalytic systems. However, most of the examples are limited to the addition of phenyl and *para*-anisyl groups [38, 39] or deal with the use of highly activated substrates. (Recently the use of chiral bidentate *N*-heterocyclic carbenes has allowed the conjugate addition of diorganozinc and Grignard reagents to β,β′-trisubstituted enones. See, for instance [32]; see also [40].)

An important breakthrough in this field appeared in 2008 when the groups of Hoveyda and Alexakis independently discovered that in situ formed dialkylarylaluminum species efficiently transfers the aryl group to the product using Cu–*N*-heterocyclic carbenes (Hoveyda) [37] and Cu–phosphoroamidite and Cu–*N*-phosphine catalytic systems (Alexakis) [41]. Hoveyda and coworkers developed a protocol in which dimethylarylaluminum species, which are formed from transmetalation of ArLi using Me_2AlCl in pentane, were used in the Cu-conjugate addition of methyl-substituted 5- and 6-membered cyclic enones using a specially designed carbene ligand **L7** [37]. Excellent enantioselectivities were obtained when *ortho*-substituted aryl groups were used (Fig. 5).

Alexakis and coworkers, on the other hand, found that the selection of reagents and experimental conditions for the preparation of dialkylarylaluminum species is





Ar	n	% ee
C_6H_5	0	72
2-Me-C_6H_4	0	98
2-OMe-C_6H_4	0	95
4-OMe-C_6H_4	0	71
C_6H_5	1	90
2-Me-C_6H_4	1	96
2-OMe-C_6H_4	1	83
4-OMe-C_6H_4	1	84
4-CF_3-C_6H_4	1	86

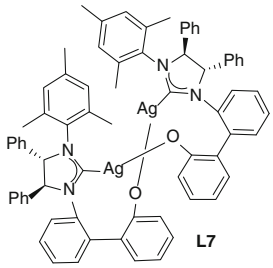
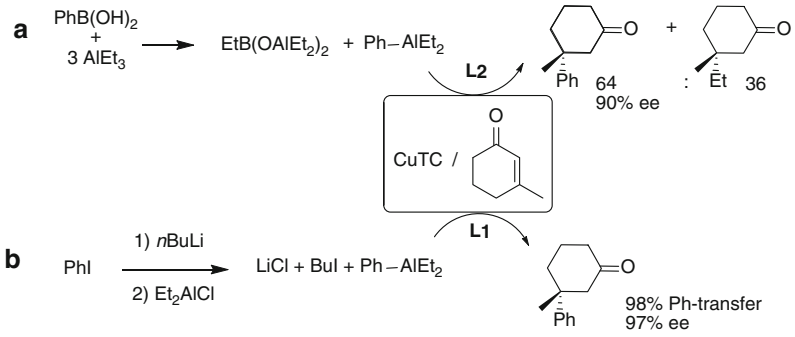


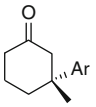
Fig. 5 Representative results for the addition of aryldimethylaluminum reagents to trisubstituted cyclic enones using *N*-heterocyclic carbene ligand **L7**



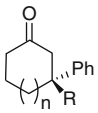
Scheme 3 Conjugate addition of diethyl phenyl aluminum prepared by: (**a**) transmetalation of phenyl boronic acid and (**b**) halogen/lithium exchange followed by transmetalation

crucial (Scheme 3) [41]. Thus, while the use of $PhEt_2Al$ prepared by transmetalation of phenyl boronic acid using $AlEt_3$ leads to the formation of 36% of undesired by-product from the ethyl transfer to the substrate (Scheme 3a), the use of diethylarylaluminum species formed by halogen/lithium exchange using *n*BuLi followed by Li/Al-transmetalation using Et_2AlCl almost exclusively transfers the aryl group (Scheme 3b). Moreover, they found that Et_2AlCl is a better transmetalation agent than Me_2AlCl (previously used by Hoveyda) and iBu_2AlCl. It should be pointed out that tedious salt removal is not necessary for the latter case, since their presence does not affect the product outcome of the reaction.

Using this methodology a broad range of aryl groups with different electronic and steric properties was introduced in a range of trisubstituted cyclic enones (Fig. 6). Again, phosphoroamidite **L1** and *N*-phosphine **L4** ligands provided similar high enantioselectivities (up to 98.6% ee). Interestingly, the product outcome is not affected by the electronic nature of the aryl group to be transferred. Thus, several *para*- and *meta*-substituted aryl groups are useful in this reaction providing excellent enantioselectivities. Nevertheless for sterically hindered aryl groups



Ar	% ee (ligand)
C_6H_5	97 (**L1**)
2-Me-C_6H_4	84.6 (**L4**)
3-Me-C_6H_4	97.8 (**L1**)
4-Me-C_6H_4	96.3 (**L1**)
3-OMe-C_6H_4	98 (**L1**)
4-OMe-C_6H_4	97.2 (**L1**)
4-CF_3-C_6H_4	98.4 (**L1**)
2-naphthyl	98.6 (**L1**)



R	n	% ee (ligand)
Et	1	95 (**L1**)
^{i}Bu	1	98.6 (**L4**)
Me	2	96.5 (**L4**)
Me	0	77.5 (**L4**)

Fig. 6 Representative results for the addition of aryldiethylaluminum reagents to trisubstituted cyclic enones using biaryl-based phosphoroamidite and *N*-phosphine ligands

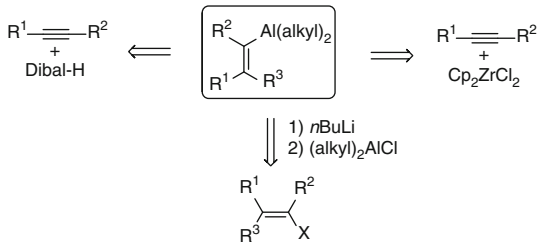
(substituted at 2 position) and for substrates containing bulkier substituents (i.e., *i*Bu), the use of *N*-phosphine ligand **L4** is preferred over the phosphoroamidite ligands [41]. Similar behavior has been observed in the conjugate addition of trisubstituted enones using trialkylaluminum reagents (see above).

2.1.3 Using Vinylaluminum Reagents

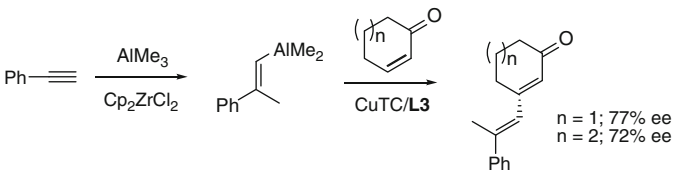
As for the transfer of aryl groups to enones, the Cu-catalyzed conjugate addition of vinylaluminum reagents represents a valuable alternative to the well-established Rh-catalyzed addition of vinylboron species for the formation of chiral quaternary centers. (There are few examples on the creation of quaternary stereogenic centers using Rh-catalyzed addition of alkenylboronic reagents, and those that do are limited to highly activated substrates. See, for instance [42].) To this respect mixed vinyldialkylaluminum species combine strong nucleophilicity as well as electrophilic activation via complexation of the carbonyl moiety and thus allow the addition of various vinyl groups to trisubstituted ketones. It is well known that these species transfers the substituents with sp^2-carbon centers attached to aluminum much faster than substituents bearing sp^3-carbon centers [15, 43, 44]. In most cases, the alkyl groups therefore are only transferred in small amounts if any.

Mixed vinyldialkylaluminum can be prepared by carboalumination, hydroalumination, or halogen/Li-exchange-Li/Al-transmetalation sequence (Scheme 4). Interestingly, all these procedures have shown to be compatible with the Cu-catalyzed conjugate addition and therefore can be used in a *tandem* process without the need of isolating the vinyldialkylaluminum species. Not surprisingly the bulk of the examples are limited to the use of the most effective ligands for the Cu-conjugate addition, i.e., biaryl phosphoroamidite, *N*-phosphine, and *N*-heterocyclic carbene ligands.

The first example on enantioselective addition of vinyl species to enones was reported in 2005 by the groups of Woodward and Alexakis using Cu-phosphoroamidite catalytic systems (Scheme 5) [22]. They used the carboalumination of phenylacetylene, using Cp_2ZrCl_2 in dichloromethane, to form the corresponding vinyldimethylaluminum species. After solvent exchange (from CH_2Cl_2 to Et_2O), this species was successfully used in the conjugate addition of



Scheme 4 Methodologies developed for the preparation of vinyldialkylaluminum reagents

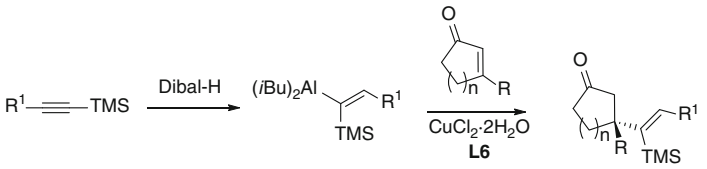


Scheme 5 *Tandem* carbometalation/conjugate addition

cyclohexenone and cycloheptenone catalyzed by Cu/**L2** catalytic system, affording enantioselectivities up to 77%. It should be pointed out that the conjugate addition is highly tolerant to the presence of Cp_2ZrCl_2.

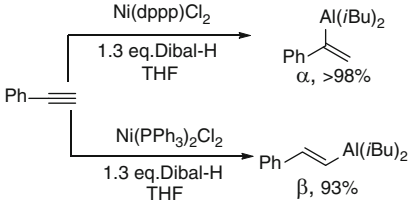
Despite the hydroalumination of terminal alkynes is known since 1960 [45], vinyldialkylaluminum reagents, formed via hydroalumination, have been scarcely used in Cu-catalyzed conjugated addition [44]. (To our knowledge there are only two early reports dealing with racemic conjugate addition reaction, see [46].) The use of these nucleophiles is hampered by the concomitant formation of Al-acetylides. These acetylides can act as competing ligands in the presence of copper complex and therefore lead to undesired side reactions and low activities. To circumvent this problem several alternatives have been developed, such as using lower amounts of vinylaluminums. (The use of lower amounts of vinylaluminums leads to higher enantioselectivities, see [47].) A more general alternative, however, is the use of Si-protected alkynes, which makes impossible the alkyne deprotonation. In this respect Hoveyda and coworkers have shown that a wide range of Si-substituted vinylaluminum reagents can be efficiently added to several trisubstituted cyclic substrates using carbene ligand **L6** [48]. Thus, both β-alkyl-substituted cyclopentenones and cyclohexenones and a range of alkyl- as well as aryl-substituted 1-trimethylsilyl aluminums undergo asymmetric conjugate addition efficiently (full conversions in less than 30 min) and with high enantioselectivity (Scheme 6).

Another methodology developed to circumvent the formation of Al-acetylides and their deleterious effect on conjugate additions is the selective Ni-catalyzed hydroalumination of alkynes [49]. Thus, by varying the Ni-catalysts high levels of α- or β-selectivity can be obtained and more important with very low levels of (<2%) of Al-acetylide formation (Scheme 7). This methodology has been used to



n	R	R^1	% ee	n	R	R^1	% ee
1	Me	*n*Pr	86	2	Me	*n*Pr	94
1	Me	$(CH_2)_4O$*t*Bu	85	2	Me	$(CH_2)_4O$*t*Bu	92
1	Me	Ph	90	2	Me	Ph	97

Scheme 6 Selected results for the *tandem* hydroalumination of silylacetylenes/conjugate addition using *N*-heterocyclic carbenes



Scheme 7 Selective preparation of α- or β-vinylaluminum species using Ni-catalysts

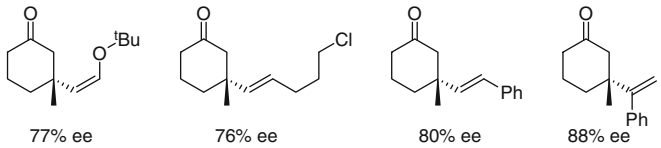
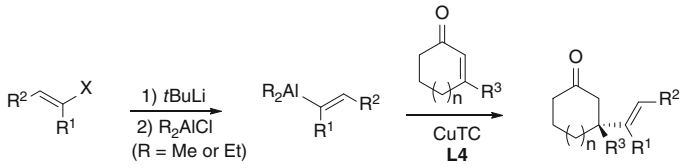


Fig. 7 Representative results for the *tandem* hydroalumination/conjugate addition using *N*-phosphine ligands

extend the nucleophile scope (Fig. 7) in the Cu-catalyzed conjugate addition of trisubstituted cyclohexenones using SimplePhos ligand **L4**. (The use of lower amounts of vinylaluminums leads to higher enantioselectivities, see: [47].)

Mixed vinyldialkylaluminum can also be prepared by halogen/Li-exchange-Li/Al-transmetalation sequence. This method, already used for the preparation of dialkylarylaluminum reagents (see above), makes use of commercially available or easily accessible alkenylhalides [41]. An important feature of this methodology is the fact that the formation of deleterious Al-acetylides is not possible. However, the atom economy of the process, which involves the formation of high amounts of salts, needs to be improved for scale up applications. Alexakis and coworkers have demonstrated the effectiveness of the *tandem* formation of vinyldialkylaluminum/conjugate addition using CuTC/**L4** catalytic system for the synthesis of alkenyl containing quaternary stereocenters (Scheme 8) [41, 50].



n	R^1	R^2	R^3	% ee
1	Me	H	Me	91
1	H	Ph	Me	91
1	H	4-Cl-C_6H_4	Me	96
1	Ph	H	Me	94
1	Me	H	Ph	43
1	Me	H	*i*Bu	83
2	Me	H	Me	48

Scheme 8 Representative results for the *tandem* halogen/Li-exchange-Li/Al-transmetalation sequence/conjugate addition using *N*-phosphine ligands

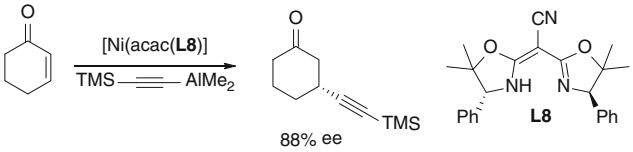
2.1.4 Using Alkynyl Aluminum Reagents

The conjugate addition of alkynyl groups to unsaturated enones represents one more important synthetic challenge. In contrast to other organometallic reagents, the use of copper-based catalytic systems needs to be avoided because of the inertness that arises from the strong binding of the alkynyl ligand to copper [51]. Instead of copper catalysts, early reports indicate that Ni(I) catalysts, generated from $Ni(acac)_2$ by in situ reduction with Dibal-H, can promote this reaction using organoaluminum acetylines [52, 53]. Despite this, there are only two recent reports on the conjugate addition of alkynyl aluminum reagents to enones. The first one disclosed the first example of enantioselective conjugate addition of an alkynyl group to a cyclic enone [54]. Corey and coworker discovered that specially designed Ni/cyanobisoxazoline (**L8**) catalysts are able to perform conjugate addition of dimethylalumino TMS-acetylide to 2-cyclohexenone under carefully controlled conditions (Scheme 9).

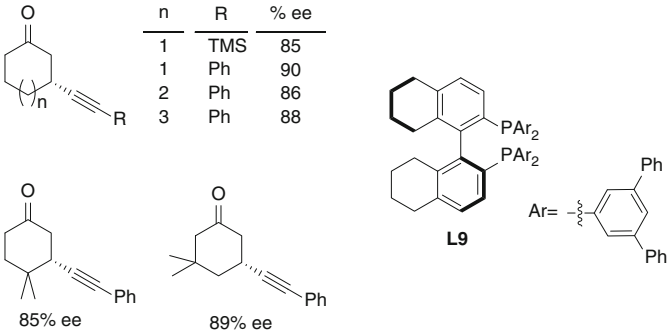
More recently, the same group found that alkynyl aluminum reagents undergo conjugate addition to cyclic enones in the presence of chiral Ni–bisphosphine complexes [55]. They found that the use of binol-based phosphine **L9** provides high yields and enantioselectivities (up to 90% ee) for a broad range of cyclic enones. Interestingly the scope of the reaction is not limited to TMS-protected acetylides but it can be extended to aryl-acetylides (Scheme 10).

2.2 Linear Enones as Michael Acceptors

Because of the s-*cis* and s-*trans* conformational interconversion, enantiofacial selectivity of the enone is more difficult and therefore linear enones are more demanding substrates than the cyclic ones. In general, they need different ligands



Scheme 9 First enantioselective conjugate addition of alkynyl aluminum reagents

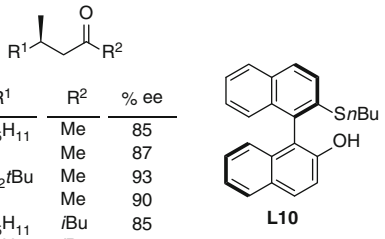


Scheme 10 Representative results for the conjugate addition of alkynyl aluminum reagents using bisphosphine ligands

than those required for cyclic enones. The most studied substrates have been chalcone and benzylidene acetone, with alkyl-substituted enones being less studied. For chalcone and benzylideneacetone, valuable ligand classes affording high levels of enantioselectivity have been developed using other organometallic reagents than triorganoaluminum [14]. On the other hand, the use of triorganoaluminum reagents in the conjugate addition of alkyl-substituted linear enones has also shown to be very useful to achieve high levels of enantioselectivity. (For successful applications using other organometallic reagents, see for instance: [56]. For successful applications using other organometallic reagents see also: [57].)

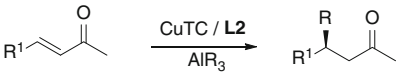
In this context, an important breakthrough came with the work of Woodward and coworkers. They extensively studied the enantioselective conjugate addition of alkyl-substituted linear enones using trialkylaluminum reagents [21, 58–61]. For this purpose they used a large library of binaphthol heterodonor S, O ligands. The sulfur moiety in these ligands can be either thiol, thioether, or thiourethane. Nevertheless, the best results were obtained for the Cu-catalyzed trimethyl aluminum addition to alkyl-substituted linear enones using the thioether-hydroxyl ligand **L10** (Fig. 8) [61].

Another of the most studied ligand's classes is the previously mentioned biaryl-phosphoroamidite ligands. Again, the selection of the copper source, solvent, and ligand was crucial for high yields and enantioselectivities. The best results were obtained using CuTC and phosphoroamidite ligand **L2** in diethyl ether as solvent. Under these conditions, a range of aliphatic enones provided high yields and



R^1	R^2	% ee
nC_5H_{11}	Me	85
*i*Bu	Me	87
CH_2tBu	Me	93
*i*Pr	Me	90
nC_5H_{11}	*i*Bu	85
nC_5H_{11}	*i*Pr	76

Fig. 8 Representative results for the conjugate addition of trimethylaluminum to alkyl-substituted linear enones using heterodonor ligand **L10**



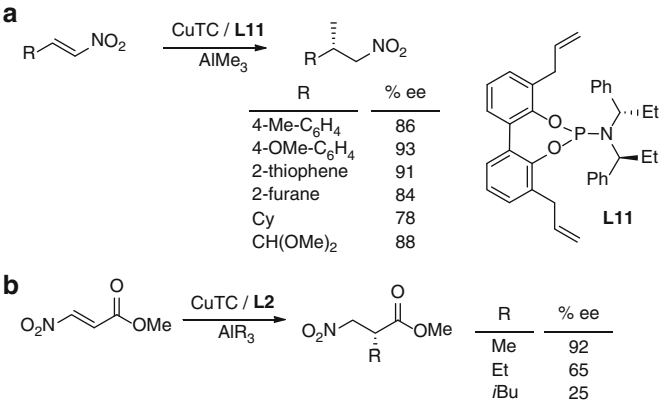
R^1	R	% ee
Cy	Et	86
*t*Bu	Et	84
*i*Pr	Et	90
nC_6H_{13}	Me	72
nC_5H_{11}	Me	70
*n*Bu	Me	70
*i*Pr	Me	96
Cy	Me	96

Scheme 11 Representative results for the conjugate addition of trialkylaluminum to alkyl-substituted linear enones using phosphoroamidite ligand **L2**

enantioselectivities, although longer reaction times than with 2-cyclohexenone were necessary in all cases (Scheme 11) [22]. The only exception can be found in the trimethyl aluminum addition of non-branched aliphatic substrates which provided moderate enantioselectivities (up to 72% ee). However, the use of α-branching substituents in those substrates increased the selectivity considerably (ee's up to 96%). It should be mentioned that these phosphoroamidite ligands induce higher levels of enantioselectivities when trialkylaluminum reagents are used than with diorganozinc reagents. Thus, for instance, the replacement of diethyl zinc by triethyl aluminum increases enantioselectivity from 80% to 90% in the conjugate addition of *trans* 5-methyl-3-hexen-2-one using phosphoroamidite ligand **L2**. More recently, this methodology has also been extended to linear dienones [62] and linear *N*-acyl-2-pyrrolidinones [63]. Although, the enantioselectivities achieved in the conjugate addition to dienones using trialkyl aluminum reagents (up to 96% ee) were slightly higher than in diorganozinc reagents, the low chemical yields (typically 15–20%) hampers their potential utility.

2.3 Other Michael Acceptors

Other Michael acceptors have also been tested in the enantioselective conjugate addition of triorganoaluminum reagents. These mainly include activated substrates such as nitro-olefins and nitro-acrylates, 1,1′-dicarbonyl enones and

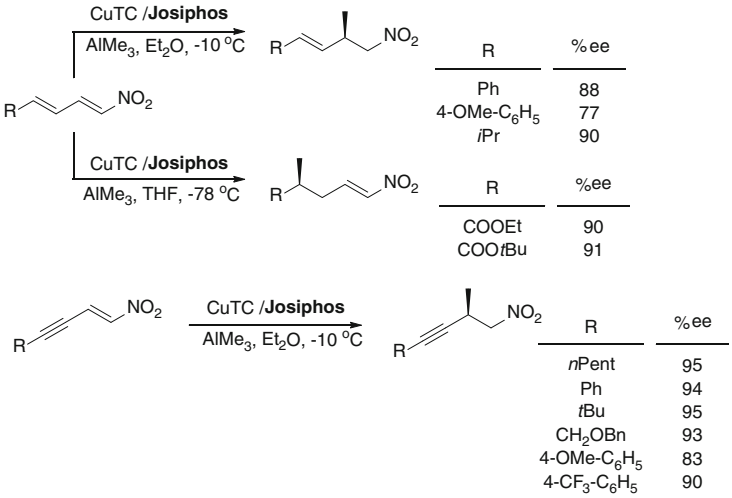


Scheme 12 Representative results for the conjugate addition of trialkylaluminum to (**a**) nitroalkenes and (**b**) nitro-acrylates using phosphoroamidite ligands

2,3-dicarboxylates. Nitroalkenes are among the most reactive Michael acceptors. Their adducts are one of the more useful intermediates for the preparation of valuable organic compounds [9]. Significant results on the conjugate addition of trialkylaluminum have been achieved for a range of nitroalkenes. Thus, for instance, it has been shown that trialkylaluminum reagents could advantageously replace diorganozinc in the Cu-catalyzed conjugate addition to a wide range of nitroalkenes using phosphoroamidite type ligands (Scheme 12a) [64] Similarly, Cu–phosphoroamidite ligands have also been successfully used in the conjugate addition of doubly activated nitro-acrylates [65]. Enantioselectivities up to 92% have been achieved using Cu/**L2** catalyst precursor (Scheme 12b).

More recently, an enantioselective and regiovergent conjugate addition of trialkylaluminum reagents to nitrodienes and nitroenynes has been described [66]. By appropriate fine-tuning of the reaction conditions, it is possible to selectively form the 1,4- or 1,6-adduct using CuTC as copper source and the diphosphine Josiphos as ligand. Thus, if the reaction is carried out in diethyl ether at −10°C, the 1,4-adduct exclusively formed in high enantioselectivities, while the formation of the 1,6-adduct is favored by using THF as solvent at −78°C (Scheme 13). It should be pointed out that enantioselectivity is highly affected by the source of trialkylaluminum reagent. Thus, the highest enantioselectivities were achieved using $AlMe_3$, while the use of bulky trialkylaluminum reagents led to almost a complete loss of enantioselectivity.

Other important classes of activated substrates that have been recently used in the asymmetric conjugated addition of triorganometallic reagents are the difunctionalized 1,1′-dicarbonyl enones (i.e., 2-acyl-cyclohex-2-enones and coumarin derivatives) [67] (high enantioselectivities have also been obtained using diorganozinc reagents, see: [68]; for other successful applications using diorganozinc reagents, see: [69]) and 2,3-dicarboxylates [70]. A common feature of the asymmetric conjugate addition of these substrates is that it proceeds with the



Scheme 13 Regiovergent and enantioselective conjugate of nitrodienes and nitroenynes

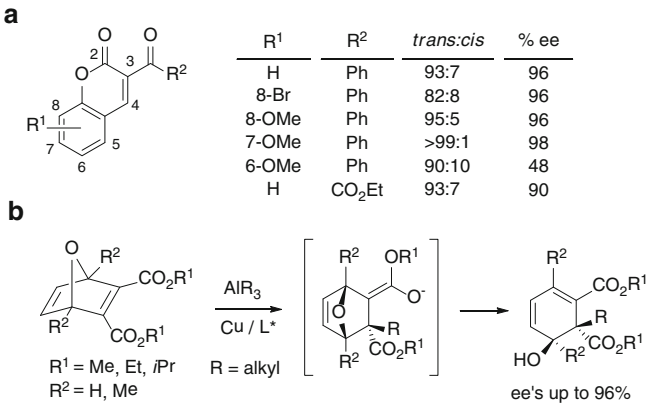


Fig. 9 Representative results for the Cu–phosphoroamidite-catalyzed conjugate addition of trialkylaluminum to: (a) coumarin derivatives and (b) oxabicyclo[2.2.1]alkene 1,2-carboxylates

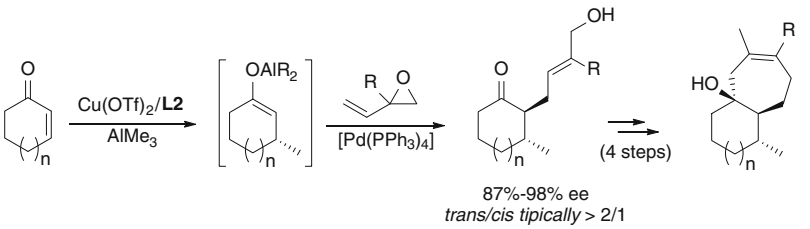
simultaneous creation of at least two stereocenters. For these transformations, the use of biaryl-phosphoroamidite has shown to proceed with high selectivities (Fig. 9). Thus, the addition of trialkylaluminum reagents for a range of 3-acylcoumarins proceeds with 85–98% ee and *trans*:*cis* ~90:10 (Fig. 9a) [67]. However, coumarins substituted at position 6 and 2-acyl-cyclohexenones proceeds with lower enantioselectivities [67]. On the other hand, the conjugate addition of trialkylaluminum to oxabicyclo[2.2.1]alkene 1,2-carboxylates proceeds with concomitant elimination, which lead to the ring-opening of the oxacycle [70]. The *syn* relationship of the incoming alkyl group and the hydroxy moiety clearly rules out

the involvement of an allylic substitution mechanism because the latter will lead to an opposite stereochemical relationship. (In the literature there are other examples of asymmetric copper-catalyzed ring-opening of oxabicycles, which proceeds through a S_N2' allylic substitution process; see Sect. 3.2.) This methodology therefore allows the generation of two or more stereocenters, one of which is quaternary, in one step in high selectivity (Fig. 9b) [70].

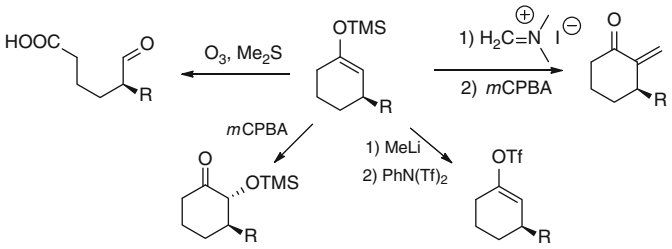
2.4 *Reactivity of Aluminum Enolates and Application in Organic Synthesis*

The asymmetric conjugate addition is a methodology not only limited to the selective introduction of a carbon nucleophile into the β-position, but the nucleophilicity of the resulting metal enolate intermediate allows the reaction with a range of electrophiles. This allows the modification at both α- and β-position of enones and therefore provides a powerful tool for the preparation of more complex molecules. An important feature of the aluminum enolates is that they are more stable than zinc enolates. (The high stability of the aluminum enolates allowed the isolation of several of them. For pioneering work in this area, see: [71].) This behavior is probably due to the "strong" bond between the aluminum and the oxygen atoms. However, this high stability hampers their potential utility. Thus, for instance, aluminum enolates are almost inert toward its reactivity with diethylcarbonate and several allylating reagents under numerous experimental conditions [33]. On the other hand, the use of aluminum enolates for an aldol reaction is known since the middle 1970s [72]. A more recent example of direct reactivity of in situ formed aluminum enolates can be found in their reactivity toward vinyl oxiranes [73]. Thus, a range of allylic alcohols have been prepared through a *tandem* reaction involving enantioselective conjugate addition and Pd-catalyzed allylic substitution reaction (Scheme 14). This reaction proceeds with moderate-to-good diasteroselectivity, and the resulting allylic alcohols were then used to form [6,7]bicyclic adducts and in a formal synthesis of the anticancer agent *clabularin B* [74].

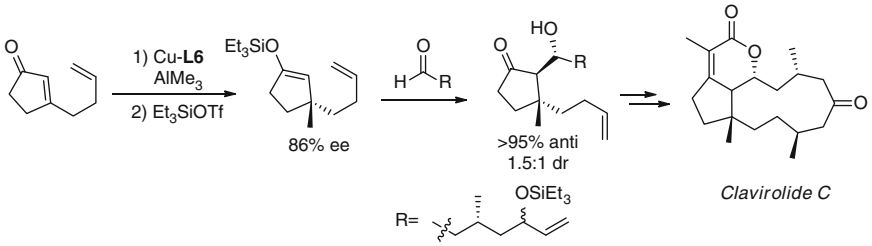
To overcome the limitation of the high stability of the aluminum enolates, the oxygen atom has been transformed to silyl enol ethers, enol acetates, and allyl enol carbonates. Silyl enol ethers and enol acetates are precursors to lithium enolates. Enol acetates and allyl enol carbonates are precursors of α-allylated adducts via the Tsuji-Trost rearrangement [75–77]. The silylation of aluminum enolates using TMSOTf is well established [78], although in some cases the isolation is difficult [33]. Silyl enol ethers allow further modification to be performed as they behave as lithium enolates (Scheme 15). A recent application can be found in the silylation of the conjugate addition adduct (*R*)-((3-(but-3-en-1-yl)-3-methylcyclopent-1-en-1-yl)oxy)triethylsilane which allows aldol condensation to form an intermediate in the synthesis of *Clavirolide C* [79], a diterpene with a *trans*-bicyclo[9.3.0] tetradecane structure (Scheme 16) [80].



Scheme 14 Vinyl oxirane ring-opening using aluminum enolates from asymmetric conjugate addition. Application to the synthesis of [6,7]bicyclic adducts



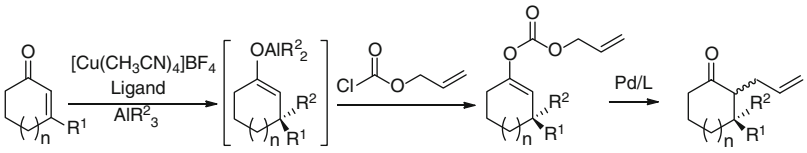
Scheme 15 Possible transformations of enol silanes



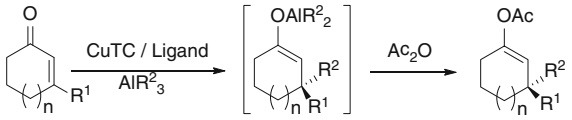
Scheme 16 Aldol condensation of silyl enol ethers

The transformation of the aluminum enolate to the allyl enol carbonate as precursors for α-allylated adducts has also been explored. An important feature of this transformation is that diethyl ether inhibits the carbonate formation. Therefore, the combination of THF as solvent and $[Cu(CH_3CN)_4]BF_4$ as copper source needs to be used (Scheme 17) [33].

In recent years more effort has been devoted to study the possibilities offered by the trapping of the aluminum enolate in the form of enol acetates (Scheme 18). As for silyl enol ethers, both cyclic and linear aluminum enolates can be easily transformed. For the linear enolates both *E*- and *Z*-isomers can be formed. Interestingly the use of aluminum enolates favors the formation of *Z*-enolates [81]. The main advantages of this methodology to the previous ones are that: (a) *O*-acylation can usually be achieved using diethyl ether as solvent of choice, which corresponds appreciably to the most general experimental conjugate addition conditions;



Scheme 17 *Tandem* copper-catalyzed conjugate addition of triorganoaluminum-allyl enol carbonate formation. The formation of α-allylated adducts is also shown



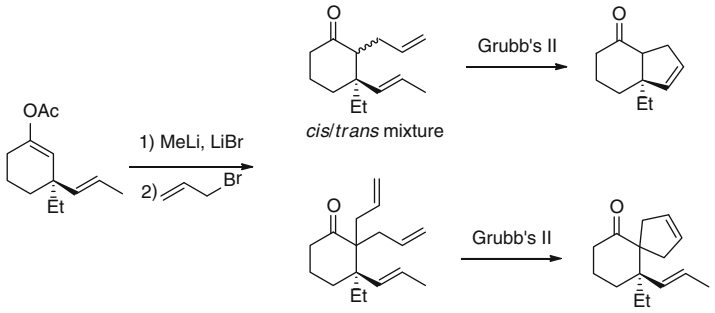
Scheme 18 *Tandem* copper-catalyzed conjugate addition of triorganoaluminum-allyl enol acetate formation

(b) cheap acetic anhydride can be used. Moreover, the use of freshly distilled Ac_2O is not necessary since the enolate reactivity is higher toward acetic anhydride than the residual acetic acid; and (c) enol acetates are more stable that silyl enol ethers and if necessary they can usually be isolated in high yields [81]. The only limitation of using the *tandem* trialkylaluminum conjugate addition-*O*-acylation process can be found in the fact that acetic anhydride cannot be added in the beginning of the reaction. In contrast to the use of diorganozinc reagents, the trialkylaluminum species attacks the acetic anhydride, which results in low yields due to the lack of reagent for the conjugate addition [81].

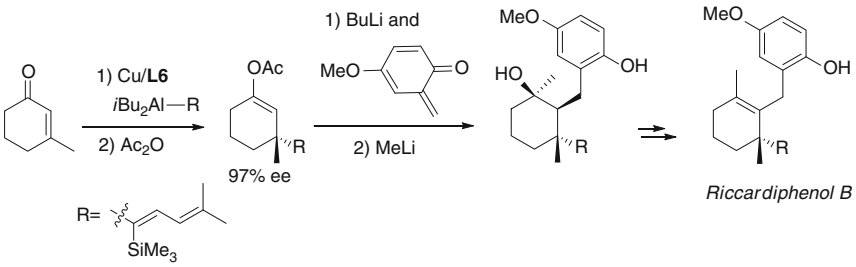
Enol acetates have a large number of synthetic uses. The major one, however, is as a regiospecific enolate equivalent. The lithium enolate can be quantitatively generated with no loss of enantioselectivity following the procedures described by House [82] and Posner [83]. The main drawback of this method is the generation of lithium *tert*-butoxide, which can act as a base. This disadvantage can be overcome by adding one equivalent of potassium *tert*-butoxide [84, 85]. A recent example that takes advantage of the large plethora of possible reactions that can be performed with lithium enolates is the α-allylation of (*R*,*E*)-3-ethyl-3-(prop-1-en-1-yl) cyclohex-1-en-1-yl acetate (Scheme 19) [86]. Upon allylation a 3:1 mixture of monoallylated and biallylated adduct was observed. Both compounds undergo easily ring-closing methathesis to form the [5,6]-bicyclic compound and the spirocycle, respectively. Note that by adding of an excess of allyl bromide the formation of gem-bisallylated compound is favored.

Another recent application involving the formation of the lithium enolate is the α-benzoylation using an excess of *o*-quinone methide. This transformation has been used for the preparation of the natural product *Riccardiphenol B* (Scheme 20) [48].

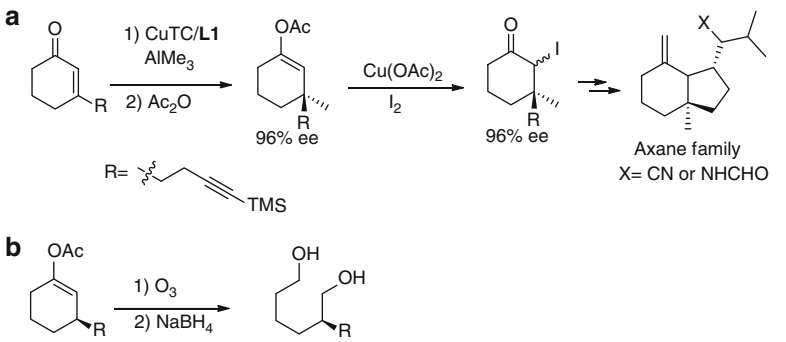
Other typical examples of the reactivity of enol acetates are: (a) the copper-catalyzed α-iodination (Scheme 21a) and (b) the reductive ozonolysis (Scheme 21b). These methodologies have been recently used for the synthesis of several natural products of the axane family [35] and chiral diols, respectively [59].



Scheme 19 Allylation-ring-closing metathesis reaction

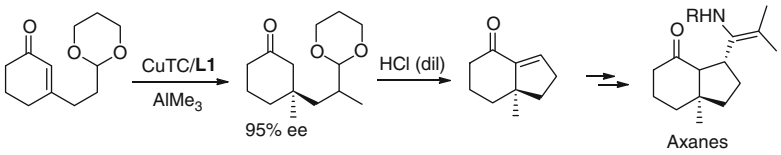


Scheme 20 Lithium enolate-α-benzoylation reaction. Application to the synthesis of *Riccardiphenol B*

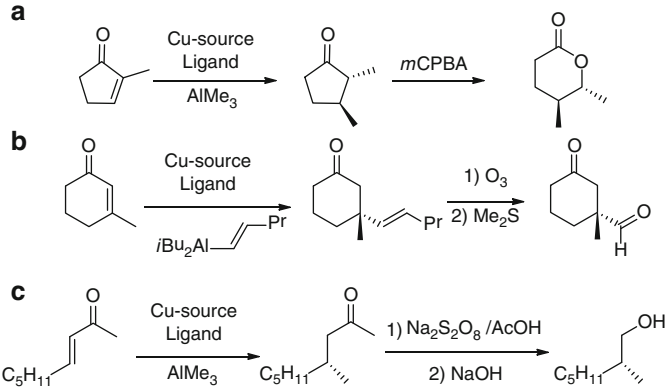


Scheme 21 (**a**) Lithium enolate-α-iodonization reaction. (**b**) Reductive ozonolysis reaction

One should keep in mind that further functionalization can also be built-in function on the substrate itself. Thus, for instance, acetals upon acidic hydrolysis allow an intramolecular aldolization–crotonization. This transformation produces chiral bicyclic α,β-unsaturated compounds. These compounds are important intermediates for the synthesis of sesquiterpene derivatives. For instance, this procedure has been recently used in the alternative synthesis of axane derivatives [87] isolated from the marine sponge *Axinella cannabia* (Scheme 22) [33].



Scheme 22 Aldolization–cyclization of acetals

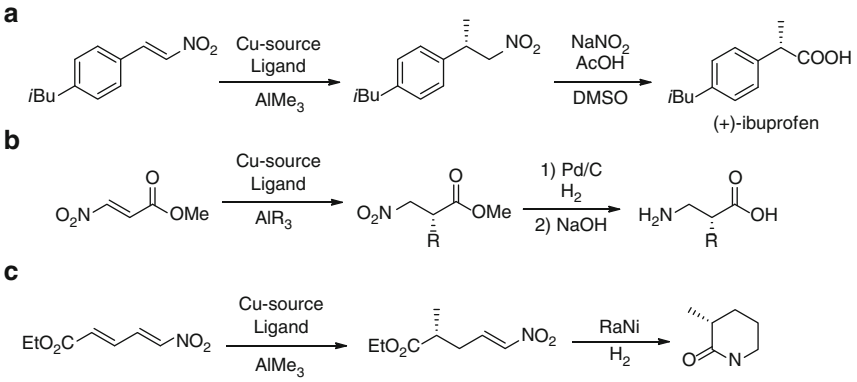


Scheme 23 (**a**) Baeyer–Villiger oxidation. (**b**) Oxidative ozonolysis. (**c**) Ketone reduction

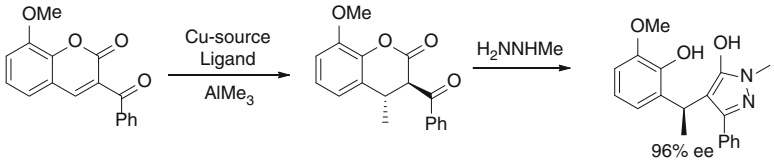
There are other simple transformations that can be performed on the hydrolyzed ketone adduct. One of them is the regioselective Baeyer–Villiger oxidation (Scheme 23a) [23, 33]. This methodology gives access to chiral lactones, which are key intermediates in the preparation of valuable intermediates. Another one is the oxidative ozonolysis (Scheme 23b), which gives access to chiral aldehydes [33]. Finally, there is also the ketone reduction to a primary alcohol (Scheme 23c) [59].

Other simple transformations that have been applied takes advantage of the special reactivity of the nitro group, which can be easily transformed to a wide range of compounds (i.e., aldehydes, carboxylic acid, nitriles, etc.) [9]. Thus, for instance, the sequence asymmetric triorganoaluminum conjugate addition to nitroalkenes coupled with the oxidative transformation of the nitro group gives access to aryl propionic acids, which are important nonsteroidal anti-inflammatory drugs (Scheme 24a) [64]. Another transformation of this group includes the formation of unnatural β-amino acids via conjugate addition of AlR_3 to nitro-acrylates followed by catalytic hydrogenation/saponification sequence (Scheme 24b) [65]. More recently, the product formed from the 1,6-addition to nitrodienoate has been subjected to a *tandem* reduction/cyclization reactions leading to the formation of a chiral lactam (Scheme 24c) [66].

Finally, there is a considerable interest in small heterocyclic species in medicinal chemistry. Thus, for instance, 3-hydroxypyrazoles have shown interesting antihyperglycaemic, angiotensin II antagonist, and phytotoxic properties [88–91]. This compounds' class can be easily obtained from the coumarin conjugate addition adducts by simple reflux with ethanolic H_2NNHMe (Scheme 25) [67].



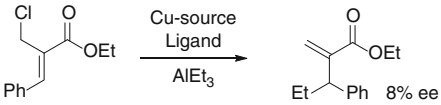
Scheme 24 Transformation of the nitro group after conjugate addition



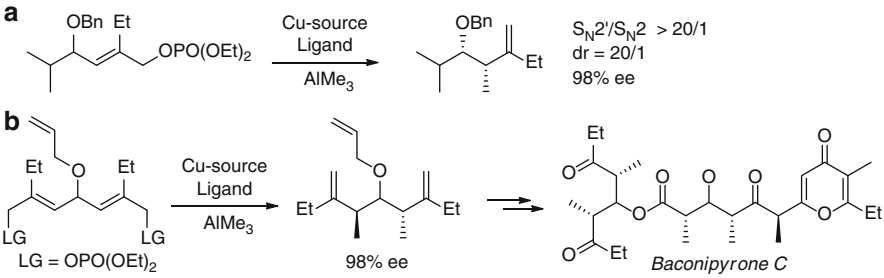
Scheme 25 Enantioselective synthesis of 3-hydroxypyrazoles

3 Asymmetric Allyllic Alkylation Reactions

Asymmetric allylic substitution is also a potentially powerful transformation for creating new chiral C–C bonds from readily available starting materials. Great efforts have been made to control the chemo-, regio-, and enantioselectivities of the reaction products. Most of the metals, including palladium the most widely used, allow the use of stabilized nucleophiles (such as malonates and amines) [92–101]. Complementary to these, copper allows the use of nonstabilized nucleophiles such as small alkyl, vinyl, or alkynyl groups in the form of organometallic species [7, 14, 16]. The first successful attempts were made with a chiral leaving group and a stoichometric organocopper reagent. It was only in the middle of 1990s that the first catalytic process was disclosed by Bäckvall and van Koten using Grignard reagents [102–104]. Since then, the scope of organometallic species has been extended to diorganozinc and triorganoaluminum reagents. In contrast to the conjugate addition, there are many parameters that dictate the regioisomeric outcome of the reaction, such as the substrate, leaving group, solvent, temperature, organometallic source, and speed of addition of the reagents. Thus, regioselectivity can be controlled at will by fine-tuning of these conditions.



Scheme 26 Allylic substitution of Baylis–Hillman substrates



Scheme 27 Allylic substitution of allylic phosphonates using trialkylaluminum reagents

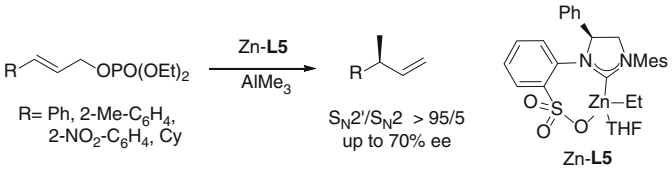
3.1 Asymmetric S_N2' Substitutions

As for the conjugate addition, pioneering work on the use of triorganoaluminum reagents for the allylic substitution came with the work of Woodward and coworkers in 2000 [105]. However, the use of binaphthyl thioether-hydroxyl ligands led to poor regio- and enantioselectivities in the allylic alkylation of Baylis–Hillman-derived allylic substrates using triethylaluminum (Scheme 26). Regio- and enantioselectivies for this type of substrates have been recently improved by using Ni-phosphonite catalysts (regioselectivity up to 86% and ee's up to 94%) [106].

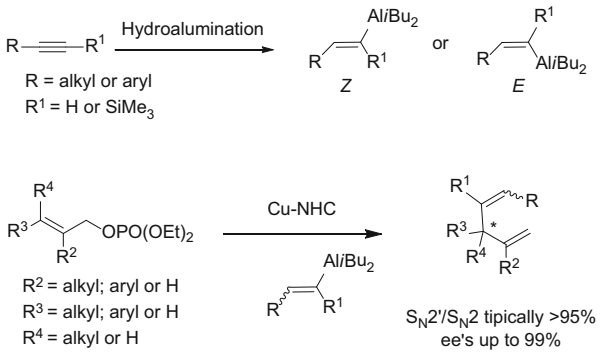
In contrast to the early use of diorganozinc and Grignard reagents, the first successful application of triorganoaluminum reagents was disclosed very recently (2007) by Hoveyda and coworkers. They found out that the use of phosphonate as leaving group in combination with the (*S*)-binol version of *N*-heterocyclic carbene ligand **L7** afforded high regio-, diastereo-, and enantioselectivities (Scheme 27a) [107]. It should be mentioned that under the same reaction conditions, the related bis-allylic diphosphate afforded an analogous high diastereo- and enantioselectivity (Scheme 27b) [107]. The formed adduct was further used as building block for the synthesis of the metabolite *Baconipyrone C*.

More recently, the same authors found out that the Zn–**L5** complexes promote the allylic alkylation in the *absence* of Cu salt. Thus, a range of aryl- and alkyl allylic phosphonates was alkylated using trimethylaluminum in high regioselectivities (typically >95%) and good enantioselectivities (up to 70%) (Scheme 28) [108].

Hoveyda and coworkers have also demonstrated that the sulfonated *N*-heterocyclic carbenes **L5** and **L6** can be efficiently used in the Cu-catalyzed allylic alkylation with vinylaluminum reagents (generated in situ by non-catalyzed and Ni-catalyzed



Scheme 28 Allylic alkylation of allylic phosphonates with $AlMe_3$ using Zn–**L5** catalyst precursor

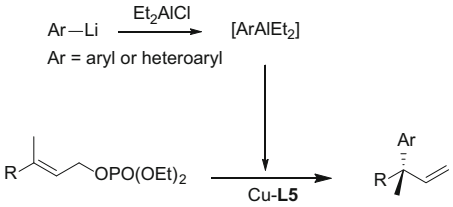


Scheme 29 *Tandem* hydroalumination/allylic substitution of vinylaluminum reagents

hydroalumination) [49, 109–111]. Using this *tandem* methodology a wide range of β- and γ-substituted allylic phosphonates has been successfully alkylated with *E*- and *Z*-vinyl aluminum reagents (Scheme 29). This has led to the enantioselective formation of dienes containing *E*- and *Z*-alkenes with tertiary or quaternary chiral centers. The utility of these protocols is demonstrated though a concise enantioselective synthesis of some natural products (i.e., nyasol [110] and bakuchiol [111]) and the possibilities for further functionalization of the double bonds [i.e., ring-closing metathesis (one-pot asymmetric allylic substitution/cross- or ring-closing metathesis has been recently disclosed by Alexakis et al. using Grignard reagents as nucleophiles; see for instance [112]).]

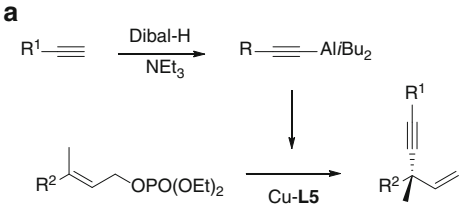
Hoveyda and coworkers also coupled the above-mentioned protocol for the preparation of diethylarylaluminum species (formed from transmetalation of ArLi using Et_2AlCl) with the Cu-allylic alkylation of γ-/γ′-disubstituted allylic phosphonates (Scheme 30) [113]. Interestingly this methodology also proved to be valid for a range of heteroarylaluminum reagents. Thus, this *tandem* protocol gives access to numerous molecules, containing aryl- or heteroaryl-substituted quaternary stereocenters which cannot be easily prepared by other methodologies. (Ni-catalyzed reactions of styrenes with ethylene furnish enantiomerically enriched products with a benzylic vinyl unit at an all-carbon quaternary stereogenic center. See [114] and references therein.)

Interestingly, and in contrast to the conjugated additions, the use of Cu-**L5** catalytic systems has recently allowed the enantioselective synthesis of alkyne-substituted

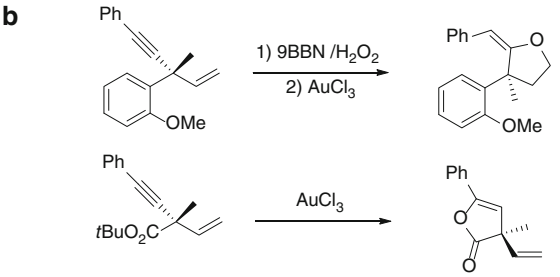


R	Ar	S_N2'/S_N2	%ee
CO_2tBu	Ph	>98:2	82
$SiMe_2Ph$	Ph	>98:2	92
Ph	2-furyl	>98:2	>96
2-Me-C_6H_4	2-furyl	>98:2	>96
4-NO_2-C_6H_4	2-furyl	>98:2	>96
Ph	2-thienyl	>98:2	92
Ph	3-thienyl	>98:2	88

Scheme 30 Representative results for the *tandem* transmetallation/allylic substitution of arylaluminum reagents

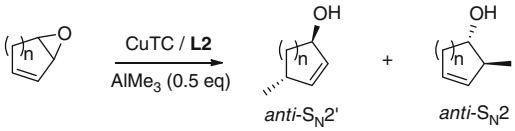


R^2	R^1	S_N2'/S_N2	%ee
CO_2tBu	Ph	>98:2	96
$SiMe_2Ph$	Ph	>98:2	92
Ph	Ph	>98:2	90
2-OMe-C_6H_4	Ph	>98:2	>99
4-NO_2-C_6H_4	Ph	>98:2	86
Cy	Ph	>98:2	88
Ph	*n*Hex	>98:2	92
4-Cl-C_6H_4	Cy	>98:2	92



Scheme 31 (**a**) Representative results for the *tandem* hydroalumination/allylic substitution of alkynyl aluminum reagent. (**b**) Au-catalyzed conversion to furanes and lactones

quaternary stereocenters through allylic substitution with alkynyl aluminum reagents (Scheme 31a) [115]. Alkynyl aluminum reagents were prepared from Dibal-H in the presence of an excess of triethylamine [116, 117]. The potential of the alkylation adducts is shown through their use in the Au-catalyzed cyclization (Scheme 31b) [115].



n	S_N2': S_N2	%ee
1	61:39	87
2	94:6	82
4	58:42	93

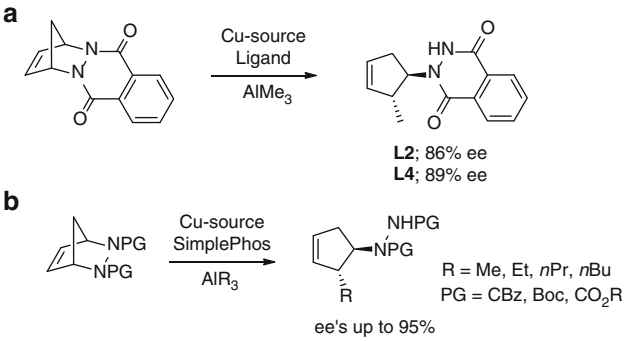
Scheme 32 Kinetic resolution of allylic epoxides

3.2 *Ring-Opening of Allylic Oxiranes*

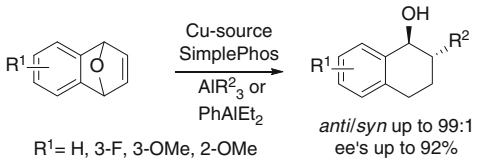
Allylic monoepoxide can be used as substrates for chiral organocopper reagents. Thus, for instance, a racemic mixture of cyclic allylic epoxides can react kinetically with half an equivalent of organometallic reagent, thus enriching the optical purity of starting material. This principle was first illustrated by Feringa et al. using diorganozinc reagents in the late 1990s [118]. More recently, Alexakis and coworkers demonstrated that the triorganoaluminum reagents can efficiently deracemize cyclic allylic epoxides (Scheme 32) [125]. Thus, by using Cu/**L2** catalytic system both chiral allylic and homo-allylic alcohols were obtained in high enantioselectivities (up to 93% and 99%, respectively). However, regioselectivities in favor of the S_N2' adduct were not optimal for each ring-size.

Desymmetrization of *meso* bicyclic compounds is also a simple valuable transformation that can occur via a S_N2' displacement because it allows the selective formation of several stereocenters in a single step. The ring-opening using an organometallic can proceed with two different mechanisms leading to diastereoisomeric products. The *anti* product is obtained in the Cu-catalyzed reaction via a pure S_N2', while the *syn* adduct is obtained via carbometallation. Pineschi et al. were the first to publish the desymmetrization of polycyclic hydrazines using trimethylaluminum reagents affording ee's up to 86% (Scheme 33a) [119]. Shortly after, Alexakis and coworkers disclosed that enantioselectivities can be improved (ee's up to 96%) by using *N*-phosphine (SimplePhos) ligands (Scheme 33a) [34, 120, 121]. More recently, the same authors have shown that Cu-SimplePhos catalytic precursors can be efficiently used for a range of trialkylaluminum reagents regardless the hydrazine protecting group (Scheme 33b) [122].

N-SimplePhos ligands have also been successfully applied in the desymmetrization of oxabenzonorbornadienes with triorganoaluminum reagents (Scheme 34) [123, 124]. The corresponding homoallylic alcohols are obtained in high yields and selectivities. Interestingly, *tandem* lithium/aluminum exchange to form $PhEt_2Al$ followed by desymmetrization reaction can also be used to incorporate aryl substituents. However, and in contrast to the conjugate addition, the ethyl substituent is also transferred.



Scheme 33 Desymmetrization of *meso* polycyclic hydrazines



Scheme 34 Desymmetrization of *meso* oxabenzonorbornadienes

4 Conclusions

Metal-catalyzed conjugate addition and allylic alkylation of Michael acceptors with organometallic reagents represent powerful tools for the construction of new C–C bonds. In particular, the enantioselective variants have become reliable and convenient methods for synthesizing chiral stereocenters, with high selectivities. In this respect, triorganoaluminum reagents have been recently appeared as an interesting alternative to organozinc and Grignard reagents since the potential exists to more easily extend their range by technically simple hydro- and carboalumination reactions. Today, a wide range of alkyl-, aryl-, vinyl-, and alkynyl aluminum reagents can be successfully used in the metal-catalyzed conjugate addition and allylic alkylation reactions. In addition, the range of potential Michael acceptors has also been expanded. Moreover, reaction intermediate enolates (conjugate addition) and alkenes (allylic alkylation) can be used in cascade processes, allowing the synthesis of more complex molecules.

All these advances provide a basis for further research. For instance, the possibilities offered in the allylic alkylation reactions need to be therefore further exploited (there are only few publications on this topic). Thus, for instance the expansion toward the use of other leaving groups rather than phosphonates would be welcome. With regard to the conjugate addition of (hetero)aryl- and alkynyl aluminum reagents very few examples have been reported. Consequently, these areas are open to further development, and this will provide interesting findings that

will benefit organic synthesis. It is also clear that research on the development of new catalytic systems with improved characteristics would be crucial for these purposes.

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