9.06
Aluminum

S Saito, Nagoya University, Nagoya, Japan

9.06.1 Introduction

Modern aluminum organometallic chemistry began in earnest with the pioneering work of Ziegler in the 1950s.[1] He was the first to synthesize alkylaluminum reagents directly from aluminum metal, olefins, and hydrogen. With only modest changes, this reaction is still used industrially to manufacture detergents. Ziegler also discovered that the "ate complex" lithium tetraethylaluminate ($Et_3Al + EtLi$) was an active catalyst for the oligomerization of ethylene, and shortly thereafter he realized that titanium dramatically accelerated the reaction and produced polyethylene. The astonishing discoveries that the ate complex showed potential reactivity, and especially, that alkylaluminums could activate transition metals for the polymerization of olefins, revolutionized polymer chemistry and made researchers around the world suddenly aware of the utility and potential importance of organoaluminums. In fact, subsequent studies disclosed that aluminum alkyls are highly reactive with a variety of simple molecules including oxygen, water, carbon dioxide, hydrogen, and alkenes.[2–5] Very recently, it was shown that even carbon monoxide inserted into Bu^t–Al bonds at $20\,°C$[6] (Equation (1)) on the basis of the earlier observation that increased Me_3Al monomer concentration resulted in increased formation of the $Me_3Al\cdots(O{=}C)$ complex at 15–35 K.[7] Investigation of the fundamental reactivity has led to the development of commercially important aluminum alkyl catalysts and co-catalysts for polymerization of higher olefins,[8,9] dienes,[10] epoxides,[11,12] as well as for the production of linear terminal alkenes and alcohols.[2–5,13]

$$2Bu^t_3Al \ + \ 2CO \ \xrightarrow[\substack{62\%}]{\substack{\text{hexane} \\ 20\,°C}} \quad (1)$$
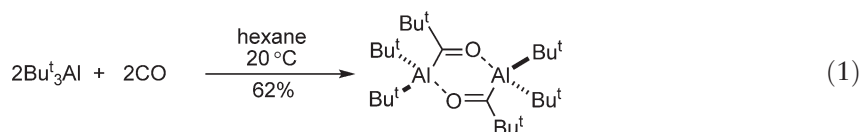
In view of the established technology base concerning aluminum alkyls and the state-of-the-art of aluminum reagents in organic and polymerization processes, organoaluminum compounds have undoubtedly been among the most thoroughly investigated organometallics, in turn expanding their scope in catalytic applications and even in material science[14–19] over only a few decades. A recent SciFinder search of "organoaluminum" since 1993 produced more than 6500 citations of new publications. This number includes more than 4500 patents issued since then and 1800 scientific publications from academia and this result clearly forecasts organoaluminum significance in industry due to commercial availability as bulk chemicals. Alkylaluminum reagents are readily prepared from oil byproducts and are generally inexpensive, serving as polymerization catalysts, ceramic precursors, and specialty chemicals in electronic device fabrication. By 1967, organoaluminum compounds were available in 100 000 lb lots at a cost of $1 per pound. It is therefore not surprising that both general and specialized interests in organoaluminums will continue to experience growth in the next half century in both industry and academia, as well as much further research to establish the fundamentals regarding their chemical and physical properties. The major advances made in organoaluminum chemistry until ∼2000 have been well summarized in several reviews and monographs. Some cover the more synthetic aspects of utilizing aluminum reagents in organic synthesis,[20–27] and an extremely broad range of the structural and coordinative properties of aluminum species has been accumulated.[28–32] In particular, Professor Eisch's contributions made in the previous COMC (1982) and COMC (1995)[3–5] are deserving of appreciation. It is strongly recommended that readers refer back to those clear-cut outlines which cover the historical, more fundamental, and even advanced aspects of organoaluminum chemistry under scrutiny from the 1950s to 1993.

A number of scientific and industrial works have been dealing with the research and development (R & D) of polymerization technology and material applications in the field of aluminum chemistry, the details of which are excluded as much as possible unless otherwise notable features are found. These came out during the period 1993–2004, encompassing more than 3000 patents and papers. Recent developments in this area, especially during this period, constitute the main focus of this chapter. Over 300 scientific papers are surveyed, chosen carefully from more than 1800 scientific papers, which the author considered to be deserving of particular mention due to their presentation of the most valuable issues. Emphasis is placed more on applied aspects, rather than fundamentals. These include the specialized topics that are notable for novelty and significance in: the bonding and structural features of the aluminum atom in relation to its catalytic activity, the mechanism of formation and reaction of organoaluminum species, and those properties applied in organic and polymer synthesis.

It is highly likely that the three broad areas of improved aluminum chemistry, that is, novel catalysis, functional materials, and biological studies, will see substantial activity in the future. This will be the result of a further understanding of organoaluminum chemistry, not only from an advanced synthesis perspective in conjunction with elucidation of reactivity, structural, and physical features, but also against the environmentally and biologically important practice of the scattering of inorganic aluminum wastes, which has been receiving significant attention of late.[29]

9.06.2 Basic Bond Properties of Organoaluminum Compounds

9.06.2.1 Aluminum–Carbon Covalent and Non-covalent Bonds

9.06.2.1.1 Aluminum(III)–carbon interactions

Progress in the theoretical and experimental chemistry of organoaluminum compounds requires knowledge of their physiochemical properties, which is based either on reliable experimental data or on empirical relationships. The characteristic features of aluminum(III) reagents are generally derived from the high Lewis acidity of organoaluminum monomers, which feasibly leads to the dimeric, trimeric, and even higher oligomeric structures. Heteroatom-containing solvents such as Et_2O and THF coordinate to an aluminum atom, allowing preferential formation of the monomeric tetracoordinate aluminum complex. The formation of higher coordinates (penta-, hexa-, and even higher coordinates) also results in special cases. In contrast, in hydrocarbon solvents, coordination of solvent is minimal and self-association of the organoaluminums is more significant.

The temperature- and solvent-dependent reactivity of organoaluminum compounds has been described in detail,[33] where the association behavior of Me_3Al in toluene at variable temperatures was illustrated. At $-55\,^\circ$C, the ratio between bridged methyl and terminal methyl was found to be 1:2, that is, most of the Me_3Al has the dimeric structure. With an increase in temperature, the methyl groups start rapidly exchanging and the NMR signals randomize, while the two distinct resonance peaks of the methyl groups are maintained. At $-35\,^\circ$C, the set of signals coalesced into a single broad peak and were no longer distinguishable at higher temperatures. Even at room temperature (RT), the vacant p-orbital of an aluminum atom may be occupied and relatively unavailable for reaction. Unlike most aluminum alkyls for which dimerization is strongly favored, t-Bu_3Al is a monomer even at RT (Figure 1).[34] Recent ebullioscopic studies of Me_3Al and Et_3Al clearly showed that these compounds are associated even in vapor. Up to 60% of Me_3Al is associated at 413 K, and 12% of Et_3Al, at 423 K.[35] Another study showed that upon heating of dimeric Me_3Al at 573 K, a 200:1 ratio of monomer to dimer resulted in the deposited matrix.[7] The stability of the dimer Al_2Me_6 was even measured in the gas phase, with an enthalpy of approximately 20 kcal mol^{-1} in favor of the dimeric form.[2] The degree of association of trialkylaluminums in vapor sharply decreases with increasing alkyl chain length. At low pressure and high temperature, the monomeric form predominates.[2] Additional thermodynamic and thermochemistry investigations thoroughly checked the accuracy and reliability of previous data on the vaporization of organoaluminum compounds, and estimated the dissociation energies of Al–R covalent bonds ($E_g = 288.6$ (Al–Me); 272.5 (Al–Et); 273.1 (Al–Pr); 280.3 (Al–Bu) kJ mol^{-1}).[36]

Analogous to Al–Me–Al bonding, Al–Me–M-type bonding (M = Sm,[37] Zr,[38] Y[39]) is commonly seen in a number of the XRD structures of the corresponding heterobimetallic compounds (Figure 2). The Al–Me–Ti bond in Cp_2TiCl_2–Me_3Al (μ-chlorobis(cyclopentadienyl)(dimethylaluminum)-μ-methylenetitanium)[40,41] is well known to easily decompose into an Al–(CH_2)–Ti species, and further into the CH_2=$TiCp_2$ formation (Figure 3). Those reactivity properties have been well featured in the synthetic application of the Tebbe reagent, which was originally devised for the
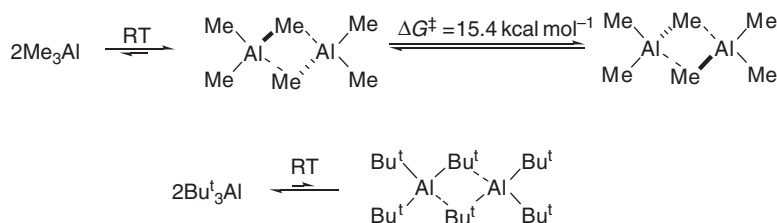

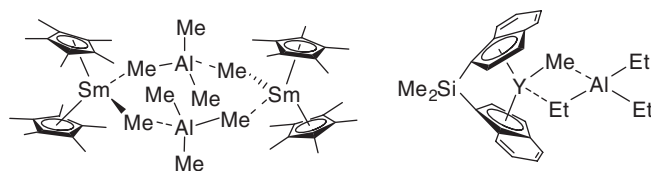**Figure 1** Equilibrium between trialkylaluminum monomer and dimer.
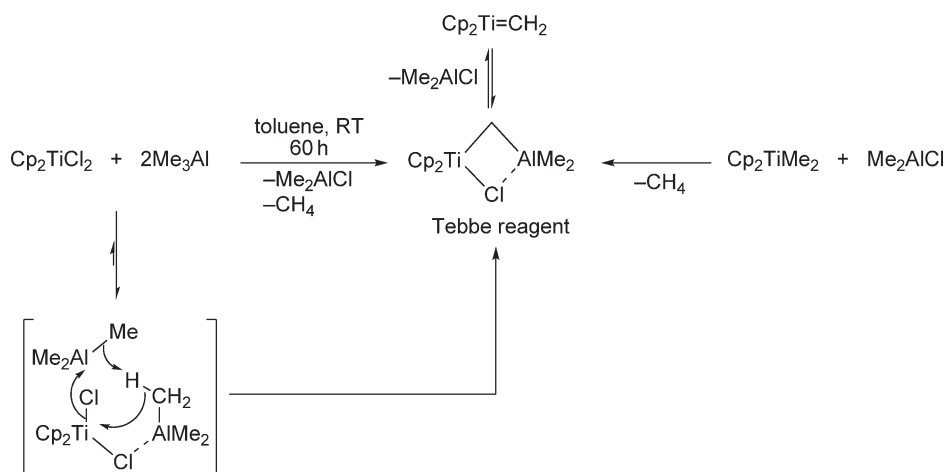

Figure 2 Al–Me–M (M = Sm, Y) bonds.

Figure 3 Synthesis of the Tebbe reagent.

metathesis of terminal olefins and the olefination of carbonyl (C=O) groups, and which recently found expanded scope in the metathesis of P=O, S=O, and Se=O groups (Figure 4).[42] Hence the Tebbe reagent is often represented as a "protected" alkylidene complex, that is, a weak complex between ClAlMe$_2$ and Cp$_2$Ti=CH$_2$, such as in **1** (Figure 5). However, ^{1}H NMR results are more suggestive of a cyclic structure **2**. A structural model for the Tebbe reagent, ClAlH$_2$/H$_2$Ti=CH$_2$, has been calculated theoretically and shows the Lewis acid ClAlH$_2$ to be strongly bound to the titanium alkylidene, rather than, as often represented, only weakly associated.[43] A similar cyclic structure was found in a related compound consisting of a methylalumoxane (MAO) and *ansa*-titanocene complex (Figure 6).[44]

Although carbenes and their transition metal complexes, as well as their bonding properties, have attracted considerable attention recently,[45] there are few reports of 13-group adducts of carbenes involving characteristic
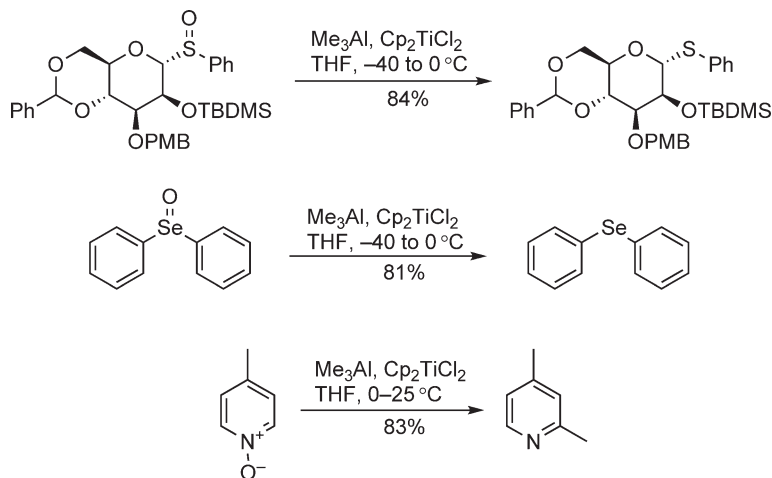

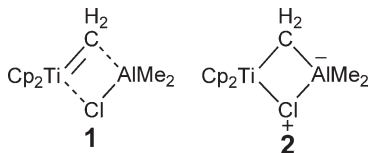**Figure 4** Tebbe reagent in deoxygenation reactions.

Figure 5 Two different candidates for the structures of the Tebbe reagent.
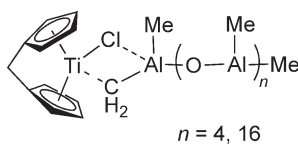
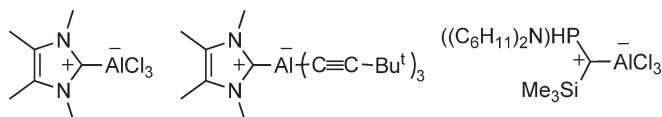**Figure 6** MAO–*ansa*-titanocene complex.

Figure 7 Aluminum–carbene complexes.

Al–C bonds. A preliminary high-yield synthesis and characterization of a stable *N*-heterocyclic carbene bound to an aluminum atom was accomplished in 1992.[46] The aluminum carbene adduct 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene–AlH$_3$ **3** was obtained by treatment of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene with Me$_3$N·AlH$_3$ in toluene (Equation (2)). Thus, carbene adduct **3** is more stable than the corresponding Me$_3$N adduct. The ^{13}C NMR signal for the C$_2$ of **3** appears at δ 175.3, substantially upfield from the free carbene (δ 219.7 ppm). The ^{27}Al NMR resonance of δ 107 for **3** is typical of four-coordinate aluminum species. These resonances suggest an electronic structure for the imidazole fragment, which is intermediate between the free carbene and the fully delocalized imidazolium ion. The C(carbene)–Al distance is 2.034(3) Å, which is slightly longer than the Al–C(terminal) distance of 1.958 Å observed for AlPh$_3$. Roesky[47,48] and Bertrand[49] recently reported the carbene adducts of AlCl$_3$ and Al(C≡CBu^t)$_3$ (Figure 7). The former has an Al–C(carbene) distance of 2.009(5) Å, which is slightly shorter than the 2.051(2) Å of the latter.

$$(2)$$
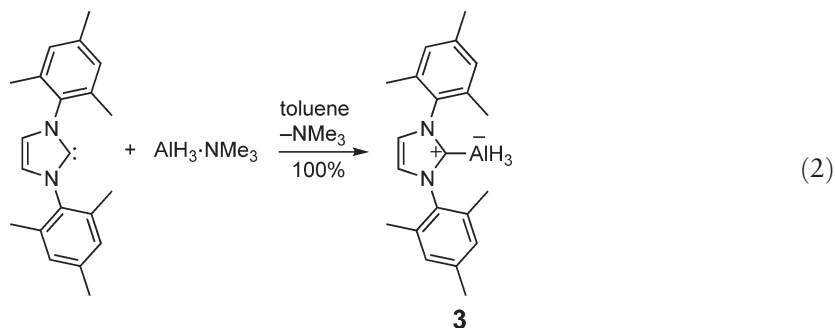
Roesky studied in depth the properties of Al–alkynyl covalent bonds using the XRD structures of several alkynylaluminum compounds.[48] In the IR spectra of all alkynylaluminum compounds, a sharp absorption band was observed around 2100 cm^{-1}, which can be ascribed to the ν(C≡C) stretching frequency. Of particular interest is the fact that the geometry of the aluminum atom varies from tetrahedral to trigonal bipyramidal by simply changing one of the three alkynyl substituents on aluminum to a more electron-withdrawing bromo group (Figure 8). In contrast with the previously reported π-complex dimer[50] or oligomer[51] of the alkynylaluminum complex (Figure 8),
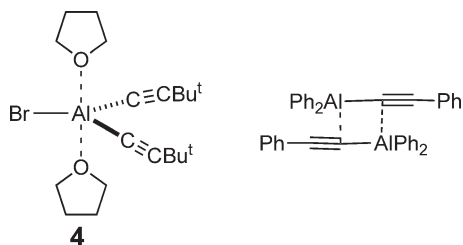

Figure 8 Aluminum–alkyne σ and π bonds.

noncovalent interaction of THF, dioxane, or Me$_3$N with an aluminum atom allowed isolation of monomeric structures such as **4**. Al–alkenyl bonds have been synthesized extensively through carboalumination and hydro-alumination processes and ^{13}C NMR data of the corresponding alkenylaluminum compounds have accumulated in the recent literature.[52]

9.06.2.1.2   Al(0)– or Al(ɪ)–carbon interactions

The absorption of unsaturated organic molecules such as benzene or olefins on Al metal surface has become the subject of intense scrutiny because of the growing technological importance of a microscopic understanding of the interactions and bonding mechanisms in organic substrate–metal interfaces. In addition, fundamental investigations of the relatively weak interaction between Al$^+$ and hydrocarbons could predict the potential reactivity of the more positive aluminum species, and could provide insight into how they could be utilized in the activation of organic molecules, which definitely provides a new avenue to organic synthesis.

   The structure and bond-dissociation energies (BDEs) for Al(methane)$^+$, Al(acetylene)$^+$, Al(ethene)$^+$, and Al(ethane)$^+$ have been determined using both the *ab initio* calculations using post-HF methods MP2, MP4, and QCISD(T) with polarization and diffuse functions and Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry.[53] The *ab initio* results indicate the following 300 K data: BDE(Al$^+$–methane) = 5.2, BDE(Al$^+$–acetylene) = 13.2, BDE(Al$^+$–ethene) = 13.6, BDE(Al$^+$–ethane) = 8.4 (end-on), and BDE(Al$^+$–ethane) = 8.5 kcal mol^{-1} (side-on). According to the results of the FTICR experiments, the Al$^+$–ligand BDE values increase in the following order: Al$^+$–CH$_4$ < Al$^+$–C$_2$H$_6$ < Al$^+$–C$_2$H$_4$ < Al$^+$–C$_2$H$_2$. Compared to the literature data of several transition metal ion (e.g., M$^+$ = Co$^+$, Fe$^+$, Zr$^+$, Nb$^+$) complexes (ca. 15–22 kcal mol^{-1} for M$^+$–CH$_4$; ca. 57–59 kcal mol^{-1} for M$^+$–C$_2$H$_2$; 15–28 kcal mol^{-1} for M$^+$–C$_2$H$_6$), the BDE values for the aluminum ions are lower in general. Two effects are considered to be responsible for the difference between these absolute BDE data. One is that the classical π-MO backdonation from Al$^+$ to the empty antibonding (σ^*-) orbitals of each hydrocarbon ligand does not exist due to the unoccupied π-orbital of Al$^+$. The second effect results from the Pauli repulsion due to the filled Al$^+$ s-orbital, resulting in an increased Al$^+$–hydrocarbon distance and a less efficient overlap of bonding orbitals. Although the slight discrepancy of the BDE ordering with regard to Al$^+$–ethane and Al$^+$–acetylene was also obtained in other theoretical studies,[54] the experimental results are, in general, comparable to the theoretical. The bonding, structure, and vibrational properties of the Al–C$_2$H$_4$ complex (Al(C$_2$H$_4$)) have also been investigated theoretically by Bouteiller using a DFT approach.[55] It has been found that this complex is π-bonded in its ground state, with ^{2}B$_2$ electronic symmetry and C_{2v}-structure, in which the ethane geometry is largely altered. From topological charge density studies, it was proposed, on the one hand, that the bonding between Al and C$_2$H$_4$ belongs to the unshared electron interaction and therefore corresponds to a mostly electrostatic interaction and, on the other hand, that the electron density in the valence shell of the aluminum region is pushed away from C$_2$H$_4$. As for Al(C$_2$H$_4$), several bonding schemes are suggested by Kasai (Figures 9(a)–9(d)),[56] Manceron (9(b), 9(c), and 9(e)),[57] and Bouteiller.[55] The difference in bonding properties between Al(C$_2$H$_4$) and Al(C$_2$H$_4$)$^+$ was reinvestigated more recently.[58] The binding in Al(C$_2$H$_4$)$^+$ is due to a σ-bond between the ethylene π-bond and an empty 3p-orbital on aluminum (Figure 9(f)). In Al(C$_2$H$_4$), the dominant interaction is due to the same σ-bond with an additional contribution from a singly occupied π-bond formed between the occupied aluminum 3p-orbital and the ethane π^*-orbital (Figure 9(g)). The weakness of the bonding interaction of the Al–unsaturated hydrocarbon, compared to the bonding with transition metals, was similarly demonstrated by another experiment along with theoretical studies, in which the adsorption behavior of benzene
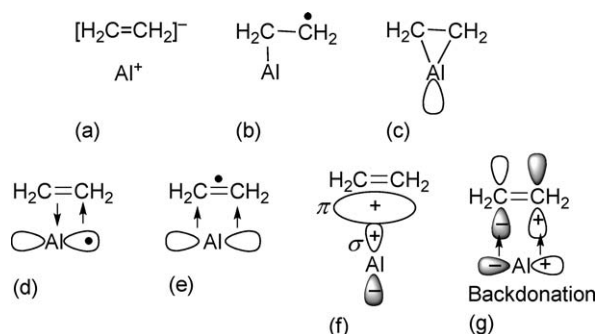

Figure 9   Possible variation in Al(0)– and Al(ɪ)–ethylene interactions.
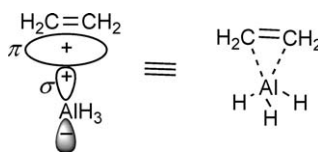
Figure 10 Al(III)–ethylene interaction.

on an Al(111) surface was evaluated using angle-resolved ultraviolet photoelectron, high resolution electron energy loss, thermal desorption spectroscopies, and work function measurements, as well as DFT calculations.[59] The experimental observation that only small changes in electronic and vibrational structure of benzene occur on adsorption was supported by DFT calculations. It was also strongly suggested that the aromatic ring is oriented parallel to the Al surface, but the main bonding mechanism is the mutual polarization of adsorbate and substrate. The adsorption of isolated C_2H_4 molecules onto Al(100) was calculated in a different way, but no chemical binding was observed although physisorption was predicted. The addition of an aluminum atom (Al(0)) to an ethene[60] or an allene compound[61] was investigated using ESR and EPR techniques. In addition to the theoretical studies on the interactions of Al(0) or Al(I) species with olefins, *ab initio* calculations were used to characterize the validity of π-complexes formed between trivalent aluminum (Al(III)) species and alkenes[62,63] (Figure 10) or alkynes.[64] Features of the interactions of Al(III) in the formation of π-allylaluminum hydrides were substantiated using EPR studies.[65]

9.06.2.2 Aluminum–Halogen Covalent and Non-covalent Bonds

Al–halogen covalent bond energy decreases in the order Al–F > Al–Cl > Al–Br > Al–I.[66] Of the halides, the bonding properties of weak non-covalent interactions in organoaluminum chloride dimers have been the most widely investigated. Alkylaluminum chlorides are dimeric in vapor and in liquid. Al–Et–Al bridging bonds in Et_3Al are weaker than similar bonds in alkylaluminum chlorides: E_g(Al–Et–Al) (33.1 kJ mol^{-1}) < E_g (Al–Cl–Al) (58.6 kJ mol^{-1}) (the latter value was taken as being equal to the dissociation energy of the $AlCl_3$ dimer (117.2 kJ mol^{-1})).[67] In addition, the bonding and structural features of organoaluminum(halide) complexes were investigated by experimental far-infrared spectroscopy, combined with quantum simulations.[68] The experimental and calculated far-infrared spectra agree very well, holding promise for the far-infrared/quantum simulation approach employed to reveal more detail on the catalytically active site in Ziegler–Natta catalysis. Hartree–Fock calculations support the previous conclusions that the dimer of $Me_{n-3}AlCl_n$ ($n = 1-3$) is consistently more stable than the corresponding monomers by 18.6 kcal mol^{-1} (78 kJ mol^{-1}) for $MeAlCl_2$, 19.2 kcal mol^{-1} for Me_2AlCl, and 18.3 kcal mol^{-1} for $AlCl_3$. Participation of two chloro groups in the bridging events significantly stabilizes the dimeric structure, while bridging by a methyl group reduces the stability (Figure 11). If both methyl groups take part in the self-bridging of $2MeAlCl_2$, destabilization by 1.2 kcal mol^{-1} occurs as compared to the separated monomers.

The Al–F covalent and dative bonds were thoroughly investigated by Roesky through their synthesis, and their versatile bonding features were highlighted in his excellent review.[69,70] Recent theoretical methods revealed that peroxo compounds of aluminum, such as $F_2Al(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)AlF_2$, are stabilized by covalent Al–F bonds (Figure 12).[71] Organoaluminum complexes comprising Al–F—Zr^+ dative bonds are particularly intriguing subjects for the study of the molecular basis of polymerization catalysis (Equation (3)).[72] Tertiary alkyl fluorides are likely to be activated
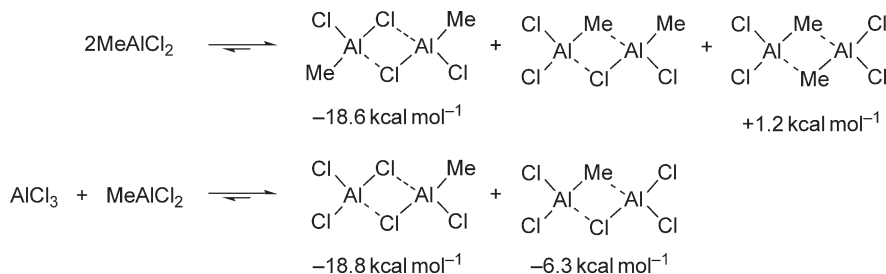

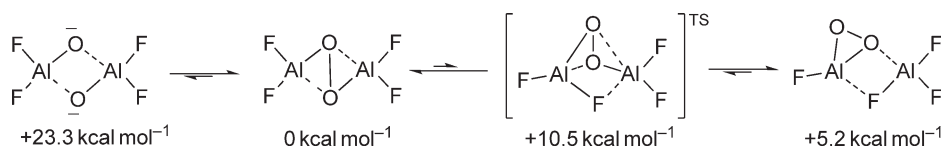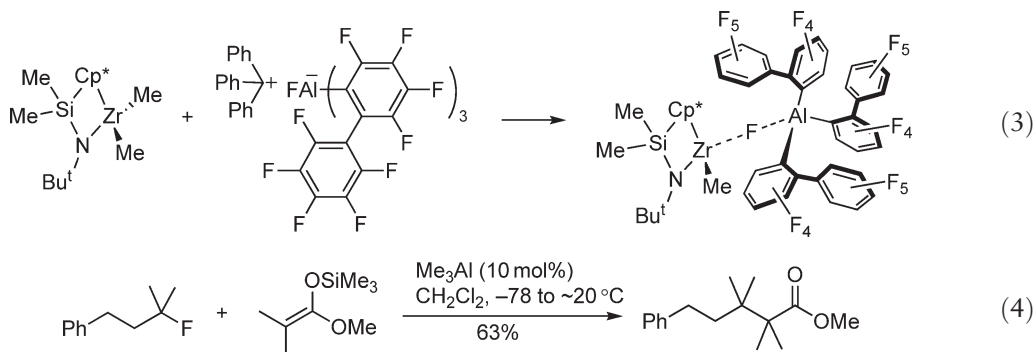**Figure 11** Al–Cl bonds in alkylaluminum chlorides.

Figure 12 Peroxoaluminum compounds stabilized by Al–F bonds.

upon coordination of both stoichiometric and catalytic amounts of alkylaluminum compounds, as evidenced by the substitution reaction with several nucleophiles (Equation (4)).[73]

(3)

(4)

9.06.2.3 Aluminum(III)–Oxygen Covalent and Non-covalent Bonds

It has been well recognized that a combination of Al–O covalent and non-covalent interactions leads to extremely complex molecular aggregates of aluminum alkoxide species.[74–79] These aggregates provide structural diversity and disproportionation dynamics, in which it is difficult to identify and predict the most stable structure. Raman spectroscopy was used to determine the dominant structure of a sequential family of organo(alkoxy)aluminum compounds.[80] A series of samples varying in ligand composition and location, prepared via a redistribution reaction between different ratios of tri-t-butoxyaluminum and Me_3Al, was surveyed (Figure 13). An average structure of the general formula $Al_2(OBu^t)_n Me_{6-n}$ ($n = 1-5$) was correlated with the typical signals (904 cm^{-1} peak from the stretching of terminal Bu^{t}O groups; 921 cm^{-1} peak from the stretching of bridging OBu^t groups, etc.)

Although this type of complex aggregates fulfills the vacant p-orbital of aluminum, thereby significantly reducing its Lewis-acidic character, intramolecularly oxygen-stabilized organoaluminum is monomeric, frequently adopting pentacoordinate structure with respect to the aluminum atom (Figure 14),[81,82] and thus it could be a strong catalyst candidate. In conjunction with the development of efficient co-catalysts for Ziegler–Natta olefin polymerization, a series of this class of organoaluminum compounds was synthesized and applied in $TiCl_4$-catalyzed ethylene polymerization.[82] The incorporation of coordinating oxygen functionalities into the ligand systems of the organoaluminum complexes
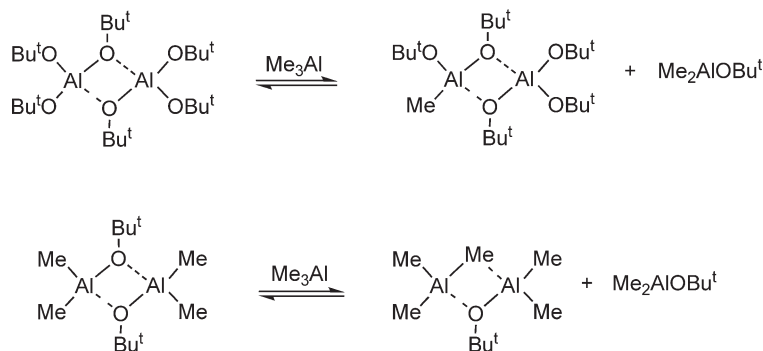

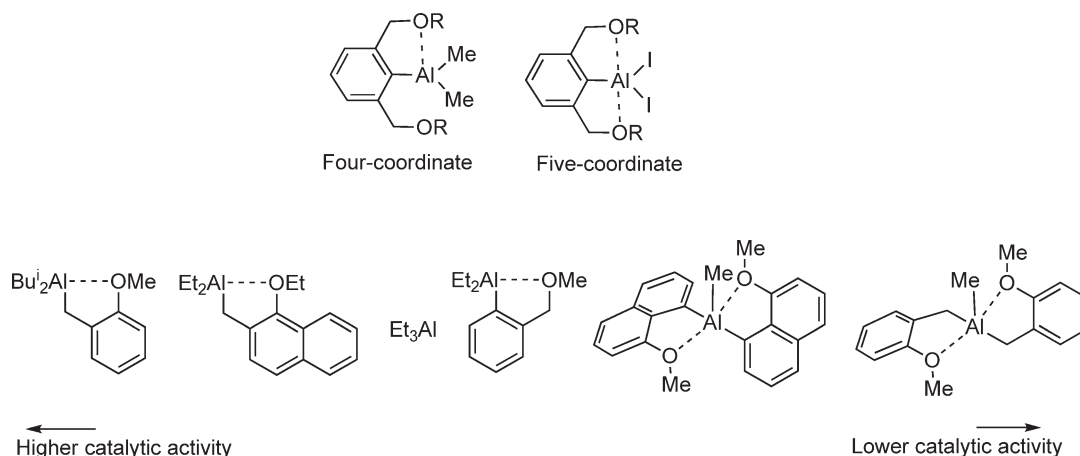**Figure 13** Al–O covalent and dative bonds in alkoxyaluminum dimers.

Figure 14 Intramolecular Al–O dative bonds and their influence on the order of catalytic activity.

causes a significant increase in co-catalytic activity (Figure 14). Some of these, in which the oxygen atom is directly bound to an aromatic ring system, showed an activity even higher than that of Et$_3$Al. Modifications of the donor groups yield an expected trend: the oxygen atom of aryl ethers provides weaker binding than alkyl ethers in Al···O dative bonds. It is thus reasonable to ascribe the highest reactivity to the electronic environment of aluminum, where the oxygen atom is most weakly bound to the aluminum atom. This might allow for an alternative route to either tetra- or pentacoordinate complex. In the case of propene polymerization using the MgCl$_2$/TiCl$_4$ catalyst system, the most active co-catalyst (Figure 14) showed results comparable to those obtained by Et$_3$Al.[83]

Alternating covalent and non-covalent bonds as seen in the Al–O···Al unit constitute the basic components of methylalumoxane (MAO) and other alkylalumoxane derivatives. The general scope of their preparation, as well as the basic aspects and the rich variety of dynamic behavior of Al–O···Al linkages, have been well summarized in COMC (1995). Despite the great importance of MAO as co-catalyst for olefin polymerization, its structure is essentially elusive.[84,85] Although the identification of a structural and reactivity relationship between MAO and much simpler alkylalumoxane derivatives[86] has been a concern for over 30 years, many unsolved problems still remain. Recent results from Barron's group published in 1995[87] (preliminarily in 1993[88] and 1994[89]) on the structure of oligomers of tetra-t-butyldialumoxane and t-butylalumoxanes are probably best viewed in this light. Using ^{1}H NMR measurements, structure **5** was proposed to be formed when [(Bu^t)Al(μ_3-O)]$_6$ and Cp$_2$ZrMe$_2$ were mixed in a 1:1 ratio (Equation (5)). Unlike [(Bu^t)$_2$Al{μ-OAl(Bu^t)$_2$}]$_2$, [(Bu^t)Al(μ_3-O)]$_7$ **6** and [(Bu^t)Al(μ_3-O)]$_9$ **7** are also active co-catalysts for the polymerization of ethylene (Figure 15). In this view, the terminal unit of the alumoxane, and even that of MAO, might be responsible for the co-catalytic activity. However, except for the [(Bu^t)Al(μ_3-O)]$_6$ species forming **5**, it was impossible to characterize any compounds, formed from the interaction with Cp$_2$ZrMe$_2$. The formation of an alumoxane cage structure is highly dependent upon reaction conditions: when trioxane structure **8** is heated in boiling hexane on a small scale (1.5 g), it yields three compounds **6, 7, and 9**. The latent catalytic activity underlying the compound diversity is obvious, but what the electronic basis would be for the actual catalytic unit in those alkylalumoxanes remains totally unclear. Structure **10** was proposed to be most responsible for the substantial reactivity of MAO.[90,90a] The alumoxane hydroxides **11** represent the first structural characterization of an alkylalumoxane, in which all the aluminum centers adopt a distorted five-coordinate geometry.[91]

$$(5)$$
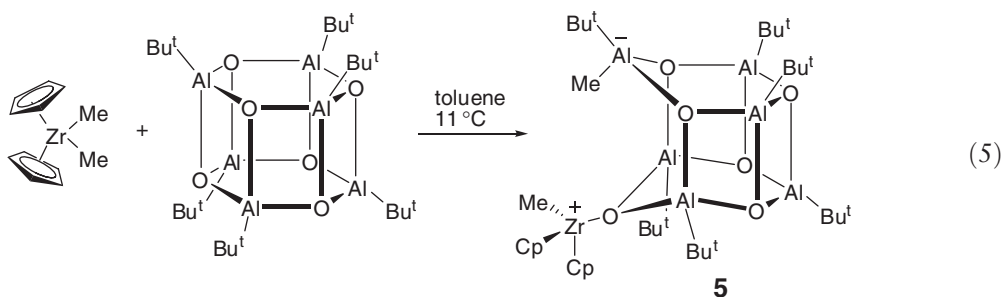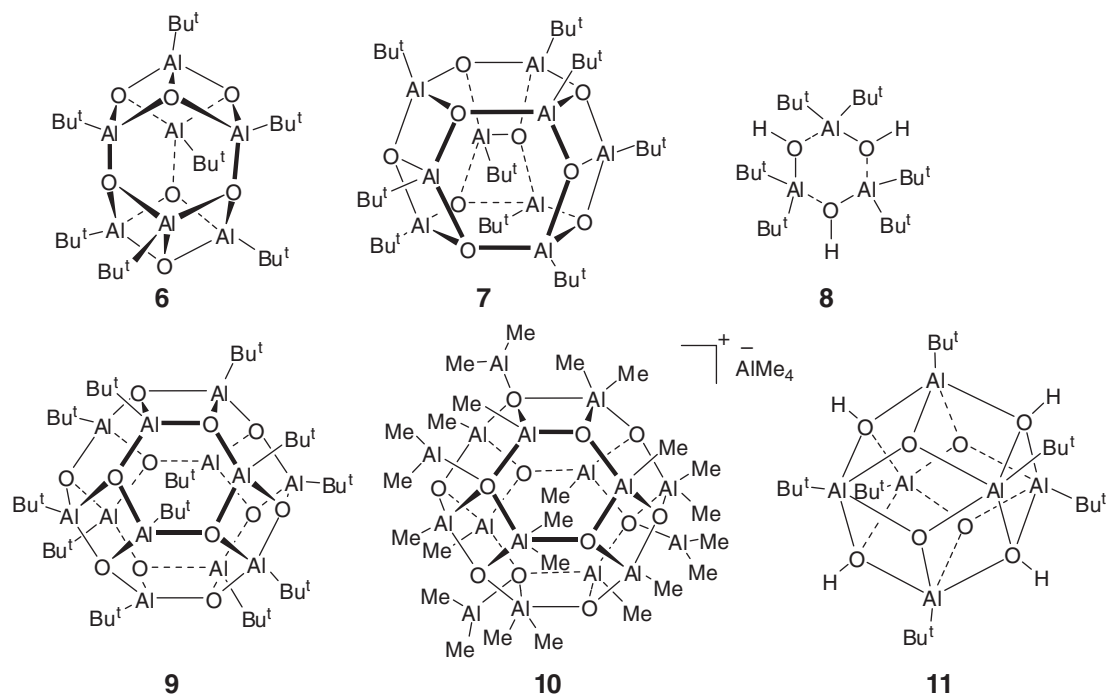
Figure 15   Various structures of MAO.

Unlike the unpredictable structural diversity in complex aggregates of alumoxanes and relatively small organo-aluminum alkoxides, bulky aluminum aryloxides tend to form monomeric structures even in solution and in the solid state. For example, monomeric methylaluminum bis(2,6-di-*t*-butyl-4-methylphenoxide) (MAD)[92] (Equation (6)) and aluminum tris(2,6-diphenylphenoxide) (ATPH)[93] (Equation (7)) were isolated as pale yellow solids from hydrocarbon solvents. These reagents are readily prepared by treatment of Me_3Al with 2 and 3 equiv. of the corresponding phenol, respectively. In contrast, the steric requirement of methylaluminum bis(2,6-diphenylphenoxide) (MAPH)[94] does not allow for persistence of the monomeric structure, so that this organoaluminum compound is in equilibrium with the dimethylaluminum phenoxide species and ATPH. This disproportionation process, which has been well investigated by Barron,[75] is ascribed to self-association occurring between two or multiple MAPH molecules. The extremely bulky aluminum tris(2,6-di-*t*-butyl-4-methylphenoxide)[95] was also synthesized but through a separate pathway, involving the stepwise reactions of two distinct aluminum hydrides (Equation (8)).

$$ (6) $$

$$ (7) $$

$$(8)$$
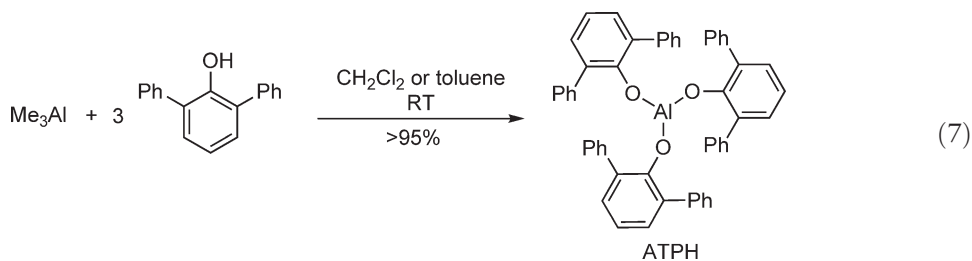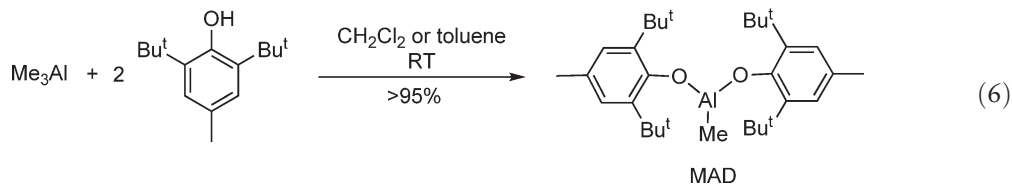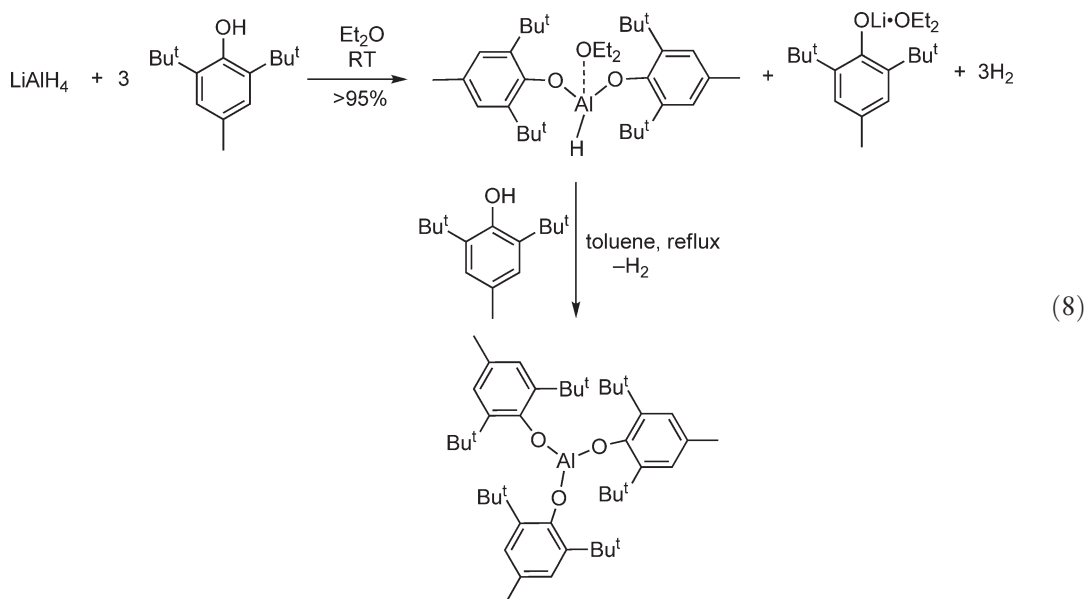
The use of these monomeric species is advantageous for organic synthesis because the vacant p-orbital is not occupied with any undesirable base components and barely exposed prior to the activation of heteroatom-containing reactants. The Lewis acidity of these reagents might decrease with covalent Al–O bond formation, especially in cases where the π-bonding between the aryloxy lone pairs and the empty $3p$ of Al is involved.[96,97] However, this π-bonding seems unlikely in most cases, as discussed by Eisch in COMC (1995). In addition, loosening of the aggregation can compensate for the assumed decrease in reactivity, and thus high oxophilicity is preserved. In fact, the MAD complexes of carbonyl compounds such as benzophenone,[96] acetophenone,[97] a camphor derivative,[98] and ethyl and methyl benzoates[75] were relatively stable and have structures determined by XRD. The ATPH complexes of DMF,[99] benzaldehyde,[100] benzoyl chloride,[100] α,β-unsaturated aldehydes,[101] ketones,[101] and esters[101] were also verified. ATPH has found broad utility in obtaining unprecedented reactivity and selectivity in organic synthesis: for example, conjugate addition to α,β-unsaturated aldehydes[99] and ketones,[102] vinylogous aldol reaction,[103–105] alkylation at the more substituted α-site of unsymmetrical ketones,[106] and dearomatic functionalization of aromatic carbonyl compounds (Figure 16).[100] The exceptional reaction behavior can be ascribed mainly to the steric influence of these aluminum reagents.

9.06.2.4 Aluminum(III)–Nitrogen Covalent and Non-covalent Bonds

Both Al–N covalent and non-covalent bonds are the basic components of the well-organized aggregates of aluminum amides or imides, yielding aluminazene,[107] a cubane-like tetramer, or hexagonal cage hexamer (Equation (9)).[108] Al–N covalent bonds are frequently so labile that this nature has been successfully applied in organic synthesis including the carbon–nitrogen bond formation via novel alumino-nitrogenation of terminal alkynes (Equation (10)),[109] as well as deprotonation of carbonyl[20] and imino[110] compounds that generates the aluminum enolate equivalents in the Fischer indole synthesis (Equation (11)).[110]

$$(9)$$
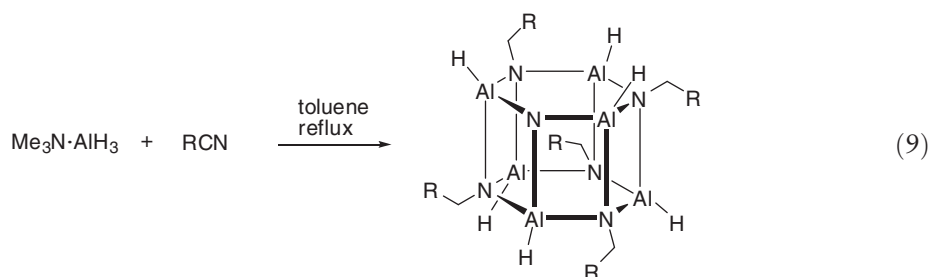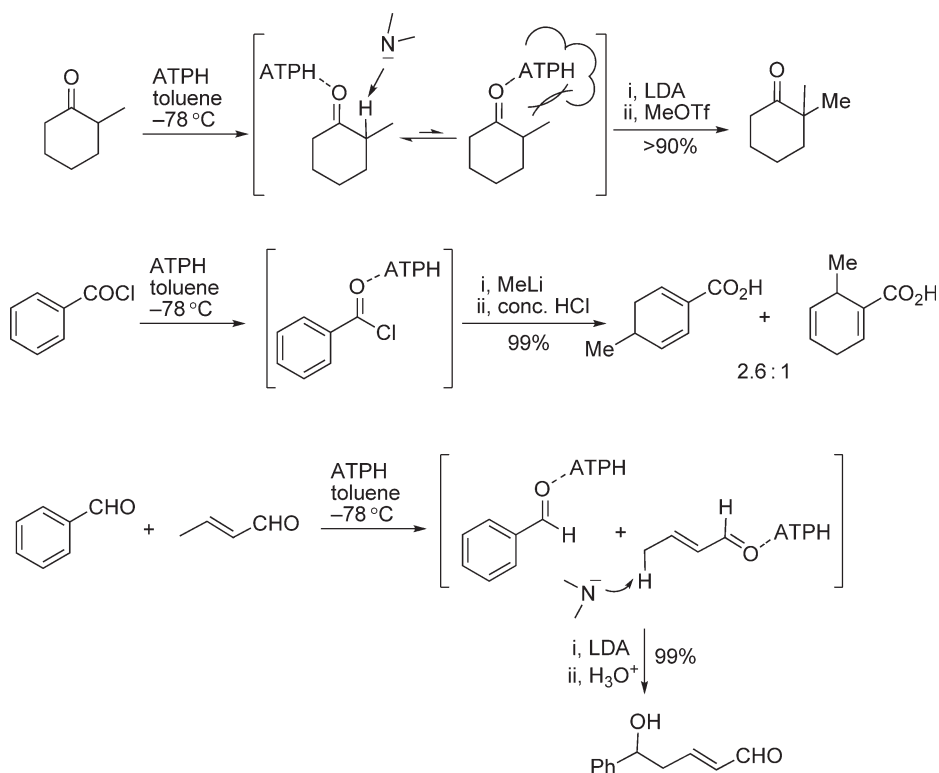
Figure 16 ATPH in organic synthesis.

(10)

(11)
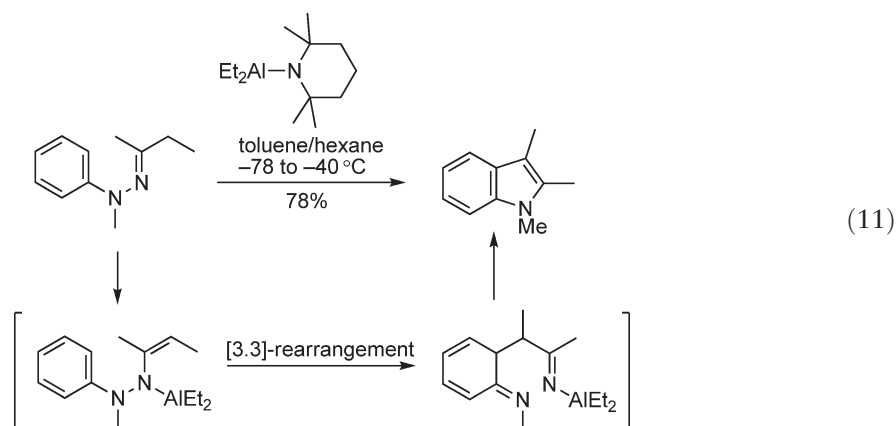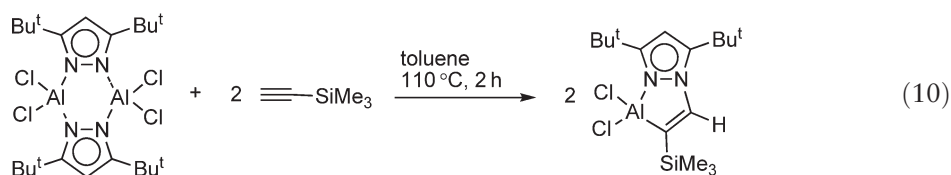
In contrast to the oligomers formed by intermolecularly connected Al$\cdots$N dative bonds, a series of monomeric metallacycles was synthesized and their XRD structures were determined (Figure 17).[111–119] Several five-membered structures are comprised of one Al–C covalent and one Al$\cdots$N dative bond provided by the bidentate ligand conformation. Their potential ability as candidates for co-catalysts in MgCl$_2$/TiCl$_4$-mediated polymerization was also demonstrated (Figure 17).[83] For the propene polymerization, all co-catalysts reach activities in the range of Et$_3$Al
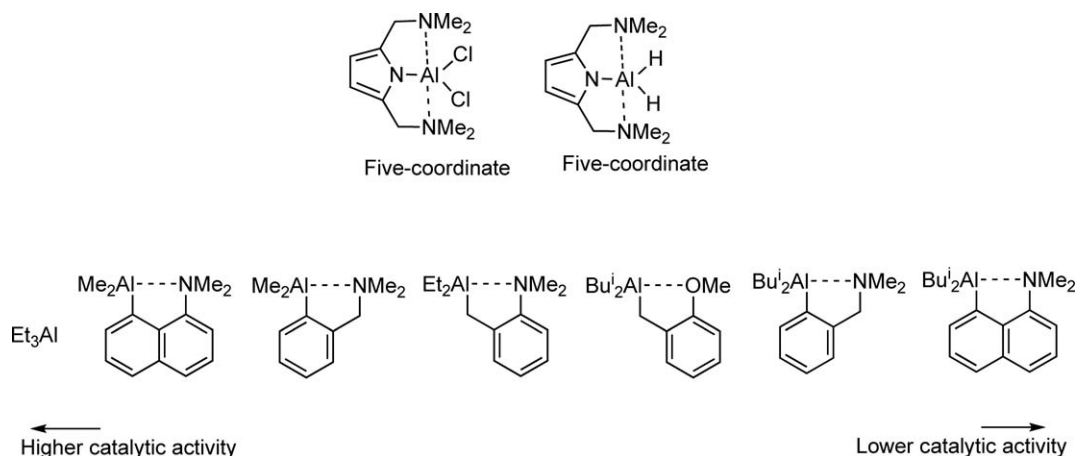
Figure 17 Intramolecular Al–N dative bonds and their influence on the order of catalytic activity.
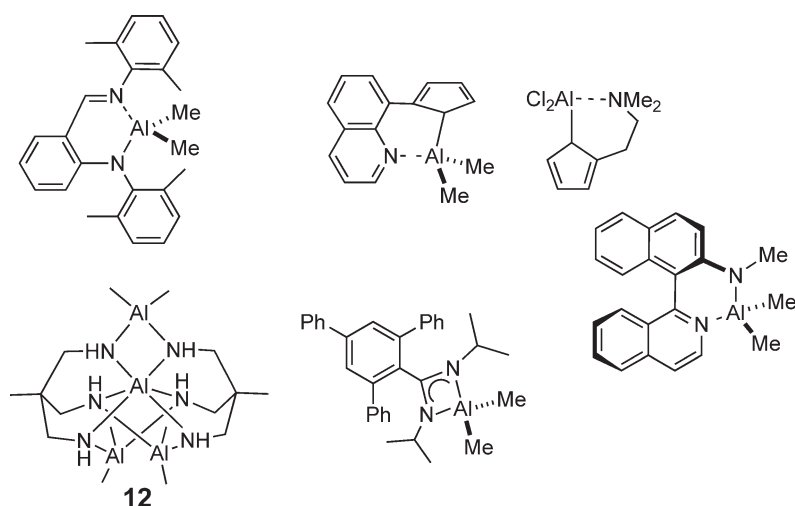
Figure 18 Structure diversity imposed by Al–N bonds.

and some of those exceed the results of Et$_3$Al in ethylene–propene co-polymerization. Intriguing and complicated chelation structures involving aluminum amide or imide compounds are frequently found in the literature (Figure 18).[111–119] Both four- and six-coordinated Al atoms were observed with a tripodal ligand, in which three NH groups serve as both chelating and bridging units to give **12**. Some of these are strong candidates for aluminum cations, as shown later in the chapter.

9.06.2.5   Aluminum(III)–Sulfur–Selenium and –Tellurium Covalent and Non-covalent Bonds

Similarly, small organoaluminum thiolates tend to make the dimer, trimer, or highly oligomeric structure (Figure 19).[120] A series of intramolecularly sulfur-stabilized monomeric organoaluminum compounds has also been reported (Figure 20).[121] Unusual structural geometry, where a dinuclear aluminum compound adopts a five- and four-coordinate geometry at once, has been verified in the structure of organoaluminum complexes in N$_2$S and N=S coordination environments (Figure 20).[122] Cubic clusters, the composite elements of which are Al and Se, or Al and Te, have been prepared by treatment of **13** with an excess of elemental selenium or tellurium (Equation (12)).[123] The reaction proceeded smoothly at elevated temperature to give iterative units of aluminum selenide or aluminum
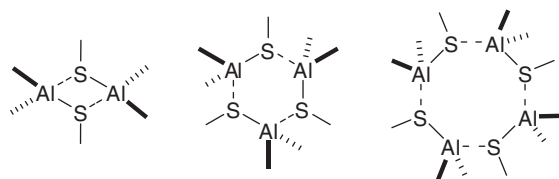
Figure 19   Variation in oligomeric structures involving Al–S bonds.
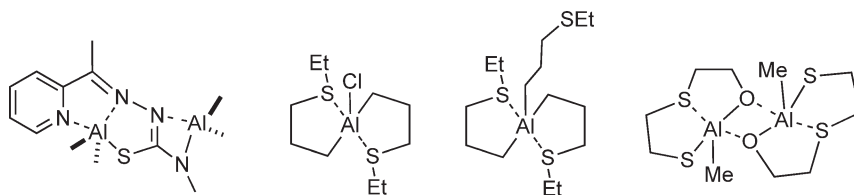
Figure 20   Structure diversity structures imposed by Al–S bonds.

telluride, in good yields. This reaction and those reported by other groups[124] represent new and facile routes to organoaluminum chalcogenides.

$$4(Me_3Si)_3CAlH_2 \cdot THF \quad + \quad 8/x \; E_x \quad \xrightarrow[\;83\%\;]{\substack{toluene \\ RT-100\,^\circ C}} \quad (12)$$

13   E = Se, Te
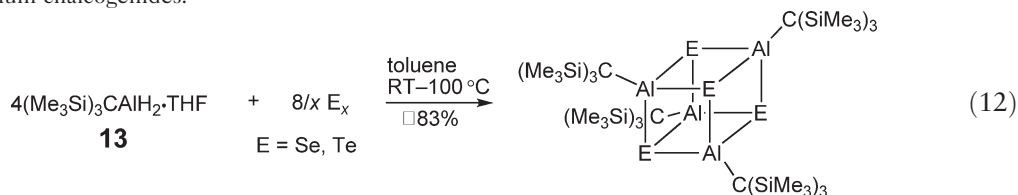
9.06.2.6   Mixed Covalent and Non-covalent Bonding Systems Involving Aluminum(III)–Oxygen, –Nitrogen, and –Sulfur Bonds

Further systematic studies enabled direct comparison among a series of non-covalent (dative) bond properties in the solid-state structure of organoaluminum alkoxides, in which additional amines, oxygen, or sulfur are incorporated into the alkoxide tethers.[125] Five-membered metallacycles were formed with bidentate O–R^1–Y-type ligands (Y = NR$_2$, OR, SR), most of which imposed again the five-coordinate geometry onto the aluminum center (Figure 21).[125–131] Bond distance of Al$\cdots$Y decreases in the order of Al$\cdots$N < Al$\cdots$O < Al$\cdots$S. Concerning the donor strength of different elements, the data are consistent with the usually assumed sequence N > O > S (Figure 22).[126] Temperature-dependent lengthening of these dative bonds in the solid state was interpreted as a consequence of thermal excitation rather than the effect of liberation.

X = NMe$_2$, OR, SMe
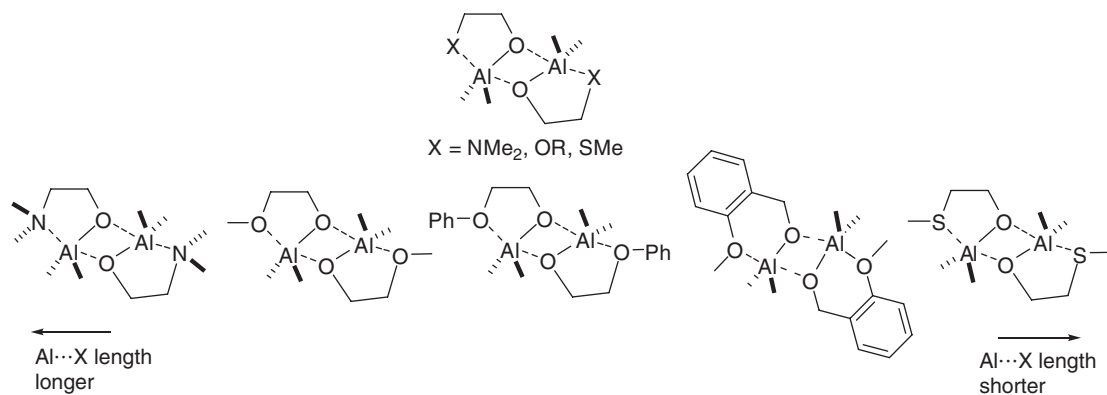
Figure 21   Difference in bond length in the aluminum complexes containing heteroatoms.
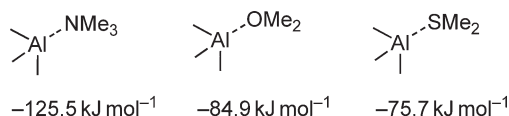
Figure 22 Stability of Al–X (X = N, O, S) dative bonds.

Four-coordinate   Five-coordinate

$K_{eq} = 0.456$ $K_{eq} = 0.275$ $K_{eq} = 0.179$
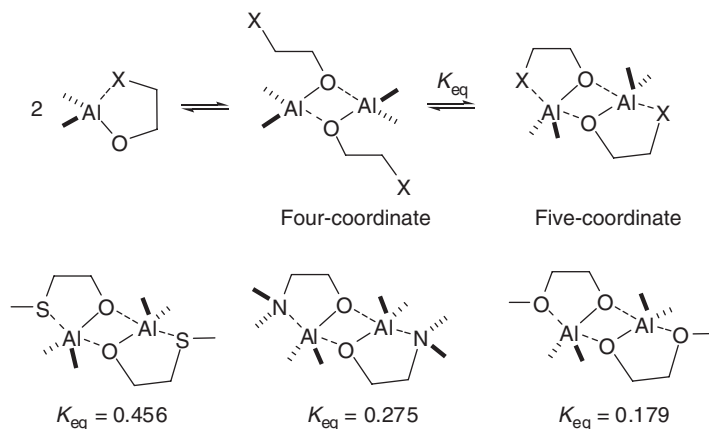
Figure 23 Equilibrium constants of intramolecular association–dissociation dynamics.

It should be noted, however, that a different sequence of bond strength was proposed for this type of compound (Figure 23).[126] Organoaluminums that contain these bidentate ligands exhibit unpredictable geometry and Lewis acid–base interactions dependent upon steric factors and elements embedded in their ligating groups. A three-way equilibrium was proposed in order to shed light on one of the complex dynamic behaviors of the compounds. The equilibrium constant K_{eq} was measured for a set of $[R_2Al(\mu\text{-}OR^1)]_2$ (R = Me, Et, Bu^t; R^1 = Me, Bu^t) compounds. Steric constraint with R groups affected the length of Al···O or Al···N dative bonds: the more increased the steric hindrance of R, the longer the Al···N or Al···O distance.

Development of a more profound understanding of the geometry factors that control the extent of oligomerization and coordination number at the aluminum center should be the subject of future research. The elucidation of structural and dynamic behavior is of great importance for gaining control of the coordination and geometric properties that lead to the fine-tuning of the reactivity of aluminum(III) species in the discovery of latent catalysts or co-catalysts in the future. This control in a diverse group of heteroatom-containing organoaluminum compounds has been the subject of many reports, but it still appears to be difficult to reach a definite, reliable conclusion that clearly explains all of the scattering observations.

9.06.2.7 Aluminum(III)–Phosphine Covalent and Non-covalent Bonds

Simple AlCl$_3$ or R$_3$Al adducts of small phospines tend to generate four-[132] or five-coordinate species,[133] and consistently favor monomeric, dimeric, or higher oligomeric structures,[132] depending on reaction conditions, including stoichiometry of reagents (Equations (13) and (14)).[134] A multiple[135] or mixed[136] donor system of tridentate ligand reinforced the five-coordinate, monomeric aluminum species, which could serve as the precursors of organo-aluminum cations (Figure 24).

$$Et_2AlCl \ + \ 2LiP(SiMe_3)_2 \ \longrightarrow \ \tag{13}$$

$$2Et_2AlCl \ + \ P(SiMe_3)_3 \ \longrightarrow \ + \ Et_3Al \tag{14}$$
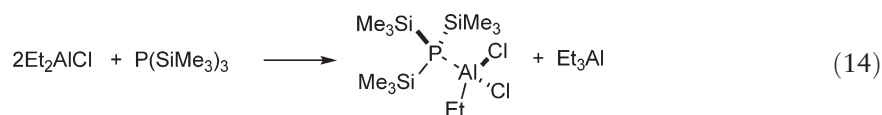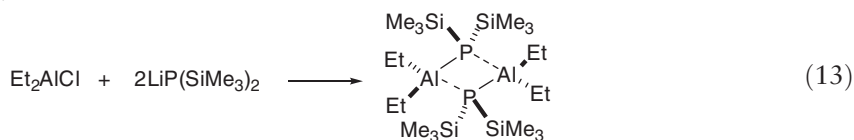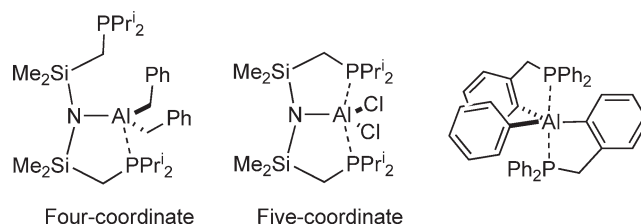
Figure 24   Structure diversity of the aluminum–phosphine complexes.

   These fundamental investigations strongly support the strong capability of the aluminum atom for making coordination bonds with the unoccupied lone pairs of halogens, oxygen, nitrogen, sulfur, other chalcogen elements, phosphines, and even with hydrocarbons. Despite the importance of the electronic nature of each element, obviously steric factors sometimes prevail over electronic factors in dynamic behavior, and the preference for some specific interactions and structures, as well as the formation and reaction of heteroatom-containing organoaluminum compounds, is shown.
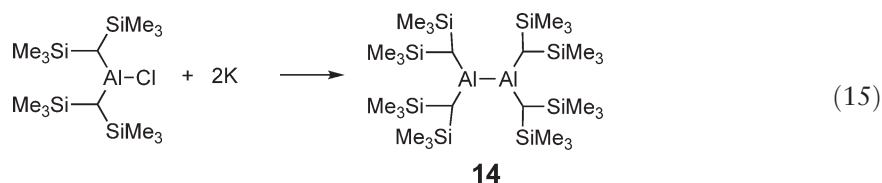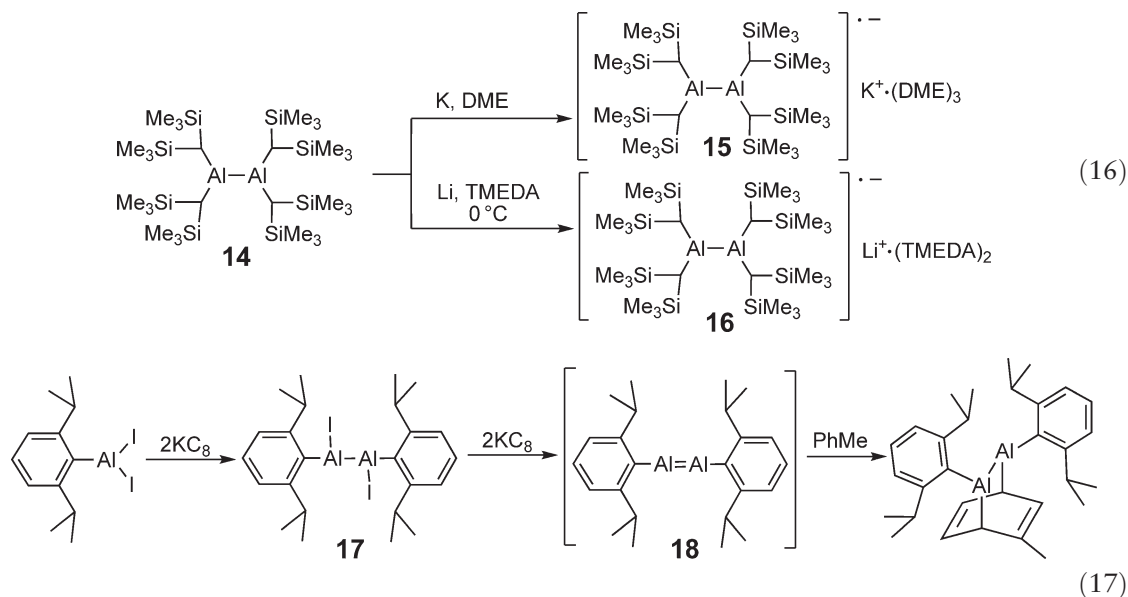
9.06.2.8   Bonds in Organoaluminum(ɪɪ) Compounds: Al–Al Bonds

It is interesting that the first compounds containing Al–Al bonds are a relatively recent development in organo-metallic chemistry.[137] While efforts purporting the synthesis of Al–Al may be traced back to the 1960s–1970s,[138,139] these reports presented neither compelling nor spectroscopic data supporting such a metal–metal interaction. Uhl is credited with unambiguously reporting the first compound **14** containing an Al–Al bond in 1988 (Equation (15)).[140] The tris(trimethylsilyl)methyl group (trisyl group) and 2,4,6-tri-i-propylphenyl group are frequently used as a particularly convenient masking group to protect, and for isolation of, relatively unstable aluminum species. The Al–Al bond distance of 2.660(1) Å serves as a benchmark in this field of chemistry. The aluminum atoms in **14** reside in trigonal-planar geometry. An "electronic system delocalized over the Al–Al bond" was suggested as a factor for the planar C_2Al–AlC_2 core. The possibility of π-bonding participating in Al–Al bonds was examined through alkali metal reduction of **14**, which gave dark blue and black-violet radical monoanions **15 and 16**, respectively (Equation (16)).[141–143] This π-radical was characterized spectroscopically (ESR, UV–VIS, and IR) and suggests Al–Al one-electron π-bonds. The Al–Al bond distance in the radical anion of 2.53(1)Å is substantially shorter than that observed for the neutral dialane, and this shortening of 0.13 Å was claimed to be the result of an "Al–Al π-bond of partial multiple bond character". It was revealed that mixed valence isomers of dialanes, viz. RAl–AlR_3, might be capable of existence if the appropriate substituents were employed. In fact, DFT calculations[144,145] on the proto-typical dialane H_2Al–AlH_2 revealed that the valence isomer HAl–AlH_3 is less stable than H_2Al–AlH_2 by 9.17 kcal mol^{-1}.[146] However, replacement of one of the dialane hydride substituents by cyclopentadiene inverted this order and $(\eta^5$-$C_5H_5)Al$–AlH_3 is more stable than the dialane $(\eta^5$-$C_5H_5)AlH$–AlH_2 by 10.79 kcal mol^{-1}.[146] In contrast to the authenticated structures containing Al–Al bonds, clear evidence for the existence of Al≡Al double bonds has not been documented thus far. However, "dialuminene", HAl≡AlH, was predicted to have a stronger Al≡Al bond (ca. 10 kcal mol^{-1}) than its heavier congeners involving Ga≡Ga or In≡In bonds (ca. 3 kcal mol^{-1}).[147–149] The Al≡Al bond distance was calculated to be 2.613 Å, which is shorter than most Al–Al single bonds in dialanes. Power recently showed that reaction of $ArAlI_2$ with KC_8 afforded the 1,2-diiodoalane **17** and probably, the aluminene **18**, which was subsequently trapped by toluene to give the [4+2]-addition product (Equation (17)).[150] This result is strongly suggestive of the transient nature of **18**, even though it was not isolated in pure form.

$$\tag{15}$$

14

$$(16)$$

$$(17)$$

9.06.2.9   Bonds in Organoaluminum(I) Compounds: Al–Al Bonds

Since aluminum diiodides are susceptible to reduction upon treatment with alkali metals, the reductive dehalogenation of [(trisyl)AlI$_2$·THF] with Na/K alloy gave a novel tetrahedral structure [Al(trisyl)]$_4$ as orange platelets (Equation (18)).[151] Similarly, an [(η^5-C$_5$Me$_5$)Al]$_4$ tetrahedron was synthesized in 1991,[152] which is extremely thermally stable and decomposes at 205 °C, turning to a brown solid. Several additional synthetic routes to this aluminum tetrahedron have been screened (Figure 25).[153] [Cp*Al]$_4$ was able to be converted into [(η^5-C$_5$Me$_5$)Al]–Al(C$_6$F$_5$)$_3$, consisting of both strong electron-donating and -accepting aluminum components (Equation (19)).[146] Indeed, the Al–Al bond distance (2.591(3) Å) is shorter than those in typical dialanes (2,4,6-i-Pr$_3$C$_6$H$_2$)Al$_2$ (2.647(3) Å),[143] and (t-Bu$_3$Si)$_4$Al$_2$ (2.751(2) Å),[154] but comparable to that in [RIAl–AlClR] (R = [(Me$_3$Si)$_2$-PhC(Me$_3$Si)N], 2.593(3) Å; Figure 26).[155] Exclusively, N-based[156] and Si-based[157] tetrameric aluminum(I) compounds **19** and **20** have been characterized by XRD (Figure 26).
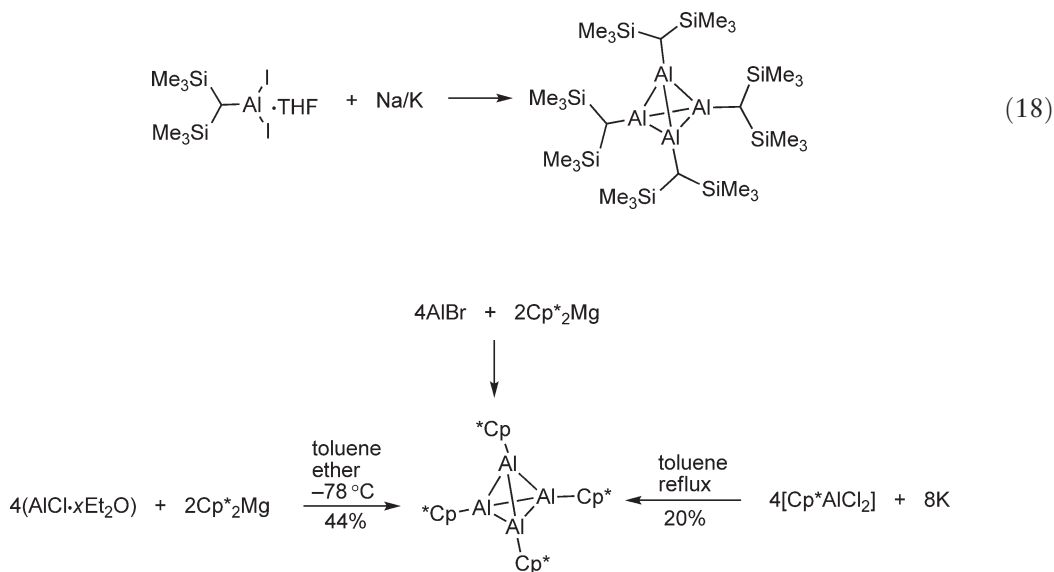

$$(18)$$

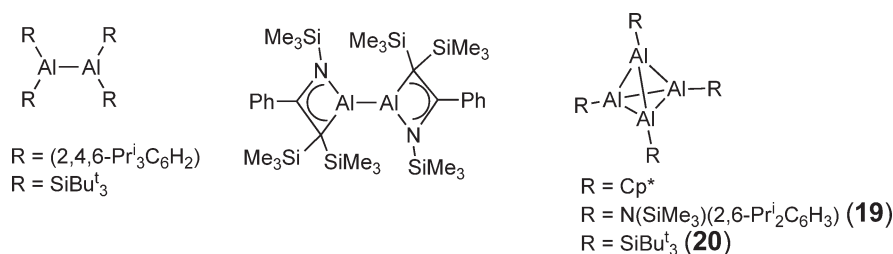**Figure 25**   Synthesis of the Al(I) tetrahedron.

Figure 26   Al(ii)–Al(ii) and Al(i)–Al(i) bonds.

(19)
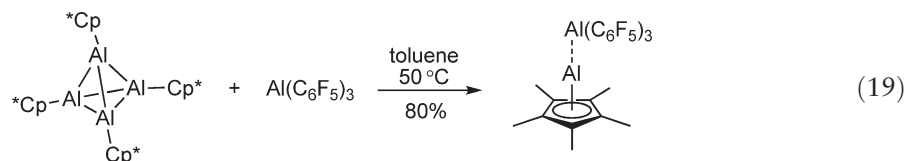
The aluminum(i) tetrahedra are easily synthesized following simple synthetic steps, one of which involves reduction of Al(iii). The tetrameric interaction in [Cp*Al]$_4$ is allowed to dissociate in solution by adjustment of the elevated temperature, and in the gas phase, eventually into monomeric form. The tetramerization energy was estimated to be about −150 kJ mol^{-1},[158] and the molecular structure of the monomer was studied using gas-phase electron diffraction.[159] The photoinduced reaction of the Cp*Al monomer with H$_2$ in an Ar matrix at 12 K was followed by IR spectroscopy.[160] The Cp*Al monomer is less stable than its tetramer, so it cannot be kept for more than a few hours at 100 °C. The physical properties of monomeric CpAl and Cp*Al were also examined in quantum-chemical studies, which suggested that the negative pole is apparently located at the Al center and that there is a significant amount of π-backdonation from Cp to Al.[161] The more kinetically and thermodynamically stable mono-meric Al(i) species **21** was first synthesized using a bulky protecting group to ensure kinetic stability as had been done to isolate Al–Al species (Equation (20)).[162]

(20)

21
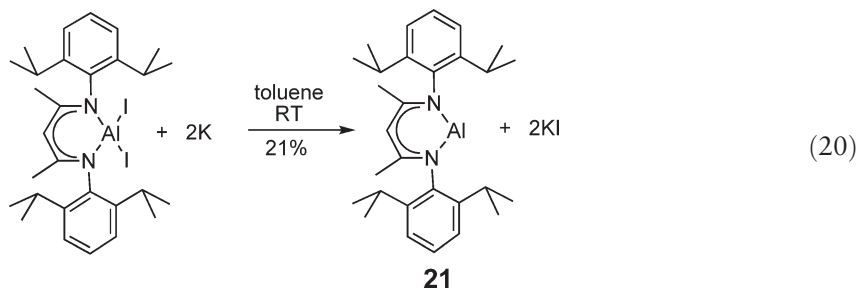
A notable structural aspect of **21** is the coordination number of 2 at the Al center. The lengthening of the N–Al bonds and the nearly 90° acute N–Al–N angle indicate that two 3p-orbitals on the Al center are essentially involved in the bonding to the two N atoms. A preliminary insight into the peculiarities of the aluminum-containing metallacycle was gained from *ab initio* calculations by analyzing the Laplacian of electron density. A lone pair of electrons is accommodated on the metal atom and arranged outside of the metallacycle in a quasi-trigonal-planar manner. This non-bonded lone pair also implies a singlet carbene character of the Al atom. These properties allow the argument that the electrons originating from an s^2-configuration of the Al(i) center are stereochemically active, leading to an sp-like hybrid. In this conjecture, the "off-cycle" side of the Al(i) atom could be considered as a Lewis base. At the same time, the charge depletion close to the Al atom in the semiplane of the metallacycle can be described as Lewis acid-type behavior.

The reactivity of such bulky monomeric Al(i) species has been further surveyed.[163] The reaction was carried out with diazobenzene (Equation (21)),[164] phenyl azide derivatives,[165] trimethylsilyl azide (Equation (22)),[166] alkynes (Equation (23)),[167] P$_4$ (Equation (24)),[168] and carbenes.[169]

(21)

(22)

(23)

(24)
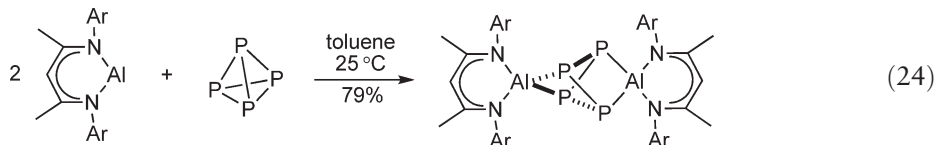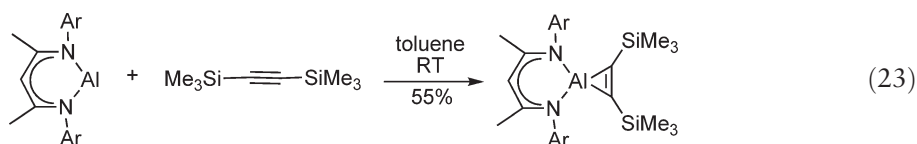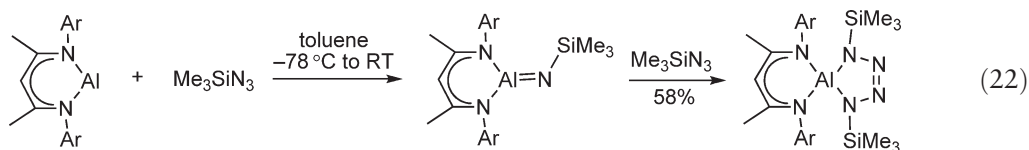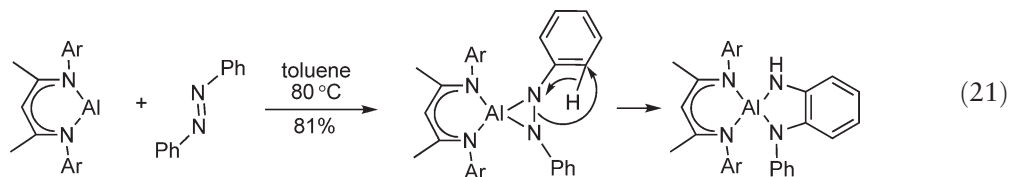
9.06.2.10   Aluminum(I)–Boron Bonds

The aluminum–boron bond is rarely found in the literature (see one example noted in COMC (1995)) but can be synthesized following a procedure analogous to the mixing of electron-donor Al(I) and -acceptor Al(III) components used to generate $[(\eta^5\text{-}C_5Me_5)Al]\text{–}Al(C_6F_5)_3$. When the low-valent aluminum(I) compound $[Cp^*Al]_4$ was mixed with electron-deficient boron(III) species, novel Al–B bonds were easily formed (Equation (25)).[170] In fact, theoretical studies indicate that the most significant contribution for a bonding interaction involves mixing of the 9-borafluorene LUMO with the CpAl HOMO. Cubic clusters comprising Se and Te were also synthesized from the aluminum(I) tetrahedron (Equation (26)).[153]

(25)

(26)
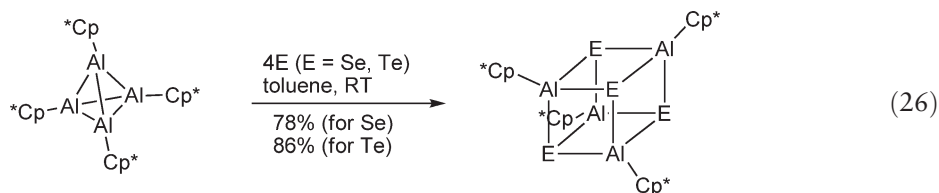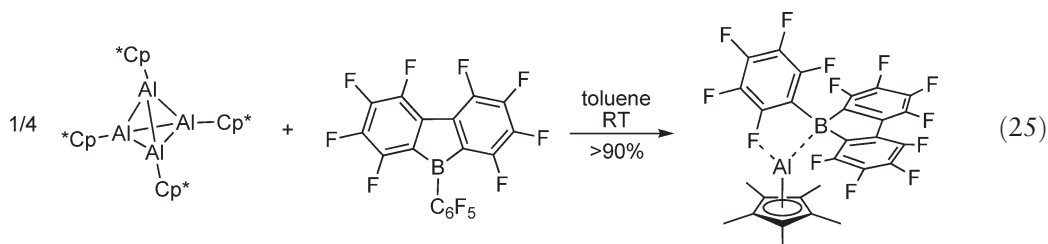
9.06.2.11   Aluminum–Transition Metal Bonds

There are only a few examples reported for Al–M (transition metal) bonds. The first Al–M bond was featured in the synthesis, structure, and bonding of $[(\eta^5\text{-}C_5Me_5)Al\text{-}Fe(CO)_4]$ (Equation (27)).[171]

$$[(Cp^*AlCl_2)_2] \ + \ 2K_2[Fe(CO)_4] \ \xrightarrow[10\text{--}20\%]{\text{toluene}} \ 2[Cp^*Al\text{-}Fe(CO)_4] \ + \ 4KCl \tag{27}$$
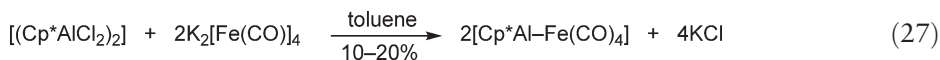
The AlX fragments bonded to transition metals in compounds of the general formula $[(CO)_5M\text{-}AlXL_2]$ (M = Cr, Mo, W; X = H, Cl, alkyl) were extensively investigated both experimentally and theoretically. The electronic structure was analyzed using the natural bond orbital (NBO) analysis, and metal–ligand interactions were characterized with the help of charge-decomposition analysis (CDA).[172] The differences in optimized geometry and electronic distribution in bonding between base-free complexes $(CO)_5W\text{-}AlX$ and base-ligated complexes $(CO)_5W\text{-}[Al(NH_3)_2X]$ (X = H, Cl) were compared, and there were several characteristic features worth mentioning. The bond energies of the base-free complexes are >30 kcal mol^{-1} lower than those calculated for the base-ligated complexes. The aluminum lone pair orbitals of AlH and AlCl have a much higher percent s-character (91.5% and 93.8%, respectively) than those of $Al(NH_3)_2H$ and $Al(NH_3)_2Cl$ (77.5% and 84%). These Al$\cdots$NH$_3$ bonds are clearly stronger (64.0–65.1 kcal mol^{-1} for the two NH$_3$) than in the free ligands $AlH(NH_3)_2$ (33.1 kcal mol^{-1}) and $AlCl(NH_3)_2$ (30.5 kcal mol^{-1}). These results are all due to electron donation from the Al lone pair orbital to the $W(CO)_5$ fragment. The W–Al bond is further investigated using topological analysis of the electron density distribution. The AlH fragment alone clearly shows an area of electron concentration at Al, which represents the lone pair electrons of Al. In contrast, the base-free complex $(CO)_5W\text{-}AlH$ has a large area of electron density in the area of the W–Al π-bonding, which suggests stronger W-to-Al backdonation in $(CO)_5W\text{-}AlH$ than in $(CO)_5W\text{-}[Al(NH_3)_2H]$. CDA was used to estimate the relative donor and acceptor strength of ligands more quantitatively. In base-ligated complexes $(CO)_5W\text{-}[Al(NH_3)_2X]$, Al-to-W donation is more significant than in $(CO)_5W\text{-}AlX$, which strongly supports the previous arguments. The calculated donation and backdonation indicate that AlH and AlCl are stronger acceptors than $Al[(NH_3)_2H]$ and $Al[(NH_3)_2Cl]$, which is reasonable. The calculated Al-to-N backdonation is negligible in comparison to the N-to-Al donation.

The bond formation between iridium(III) and Al(III) was also reported recently.[173] The synthesis of monomeric $[Cp^*(PMe_3)IrH_2](AlPh_3)$ was achieved by simply mixing $[Cp^*(PMe_3)IrH_2]$ and Ph_3Al (Equation (28)), while the dimeric structure predominates in the corresponding complex of Et_3Al. Compared with the W–Al distance of 3.110(3) Å in $Cp_2WH_2AlMe_3$,[174] which predominates in the η^1-H-type structure (Figure 27), the Ir–AlPh$_3$ distance of 2.684(2) Å proved to be much shorter. The Ir–AlPh$_3$ bond is stronger than Ir–AlEt$_3$ bond. Ni and Al atoms are connected by two-center two-electron bonds in the $(CpNi)_2\text{-}(Cp^*Al)_2$ complex, derived by treatment of Cp^*Al with $[CpNi(CO)]_2$ (Equation (29)).[175] A series of unusual Co–Al cluster complexes[176,177] and Cr–Al(I) bonds[178] was also recently reported (Equations (30) and (31)).

$$\text{AlPh}_3 \ + \ [Cp^*Ir(PMe_3)H_2] \ \xrightarrow[74\%]{\substack{\text{toluene} \\ \text{reflux}}} \tag{28}$$

$$[(Cp^*Al)_4] \ + \ [(Cp_2Ni)] \ \xrightarrow[72\%]{\substack{\text{toluene} \\ 50\,^\circ C}} \tag{29}$$
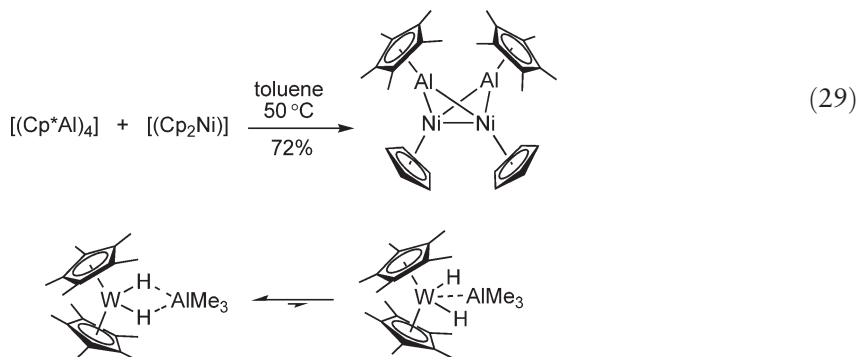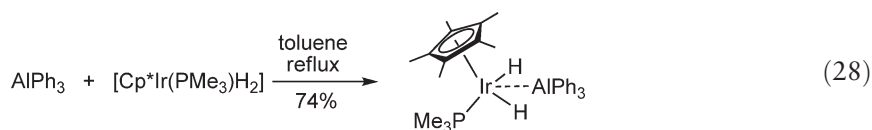
Figure 27   Equilibrium between W–H–Al and W–Al bonding species.

$$(30)$$

$$(31)$$
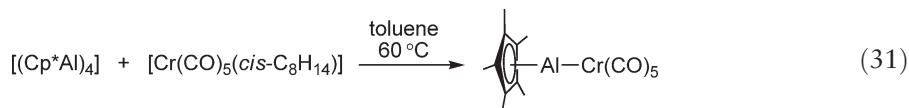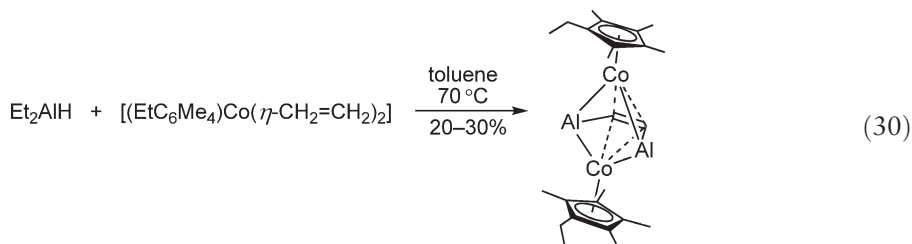
9.06.3 New Aspects in the Synthesis of Organoaluminum Compounds

Early synthetic experiments demonstrated that organoaluminum complexes could be made from aluminum metal. Ethylaluminum sesquiiodide ($EtAlI_2 + Et_2AlI$) was prepared by Hallwachs and Schafarik in 1859 upon combining ethyl iodide with aluminum metal.[28] In 1865, Buckton and Odling prepared aluminum alkyls from mercury alkyls and aluminum metal.[28] Since these milestones concerning organoaluminum syntheses, essentially nothing was improved upon in this area for nearly a century. From 1950 to 1970s, headed by Ziegler's pioneering "synthesis from aluminum metal, olefin, and hydrogen", several other basic syntheses of organoaluminums were established, and the concept-based procedures are summarized in detail in COMC (1982)[3] and COMC (1995),[4,5] among others.[24] The preparation methods developed so far can be roughly classified into seven types: (i) reduction of organoaluminum halides by alkali metals; (ii) hydroalumination; (iii) carboalumination; (iv) direct alumination of carbon acids, including acetylene derivatives; (v) transmetallation from organotin, -magnesium, -lithium, and -boron compounds; (vi) via tetraorganoaluminates; and (vii) homologation of diazoalkanes. Through these procedures, higher organoaluminums with elongated carbon chains or bearing more functional carbons are made accessible. This chapter is limited only to notable improvements accomplished recently along these lines.

9.06.3.1 Aluminum–Metal Exchange

9.06.3.1.1 Aluminum(III)–tin exchange

Early studies of the organotin–chloroaluminum exchange process were carried out by Neumann et al.[179] Although aryl–alkyl metathesis between tin and aluminum still remains a possible side-process, this method provides an effective route to unsolvated organoaluminum compounds and is frequently employed because organotin compounds are generally air and moisture stable, and halogenated aluminum compounds constitute good commercial resources. Recent work by Eisch[180] and others[181] has demonstrated the broad applicability of this method for the preparation of a range of organoaluminum compounds bearing allyl-, benzyl-, alkenyl-, alkynyl-, and arylaluminum bonds (Equations (32)–(37)). The work also describes their potential utility as co-catalysts for titanocene-mediated ethylene polymerization.

$$(32)$$

$$(33)$$

$$(34)$$

$$\text{PhCH}_2\text{SnMe}_3 \quad + \quad \text{MeAlCl}_2 \xrightarrow[\sim 90\%]{\substack{\text{mesitylene}\\ \text{hexane} \\ 20\text{–}110\,^\circ\text{C}}} \text{PhCH}_2\text{AlCl}_2 \quad + \quad \text{Me}_4\text{Sn} \tag{35}$$

$$\text{o-C}_6\text{H}_4(\text{SnMe}_3)_2 \quad + \quad \text{Me}_2\text{AlCl} \xrightarrow[89\%]{\substack{\text{heptane}\\ \text{RT}}} \text{o-C}_6\text{H}_4(\text{AlMe}_2)_2 \quad + \quad 2\text{Me}_3\text{SnCl} \tag{36}$$

$$\tag{37}$$
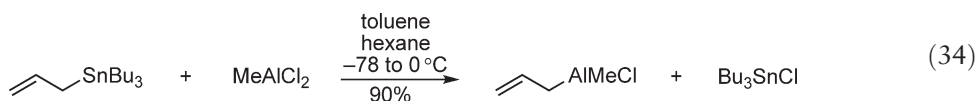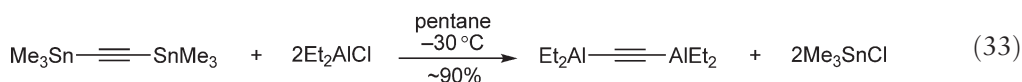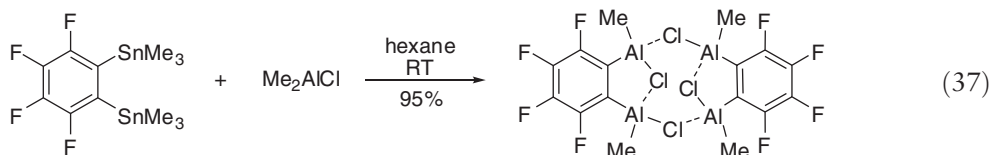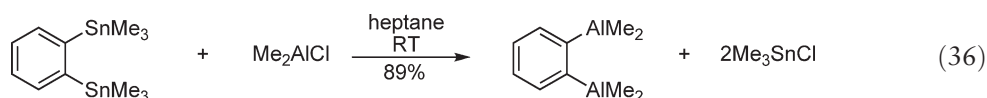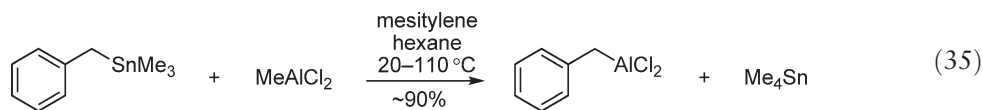
9.06.3.1.2 Aluminum(III)–boron exchange

Organoborons are regarded as soluble, relatively stable, and less toxic than organotin or -mercury compounds, so their usefulness in the preparation of organoaluminum compounds has been well discussed. The equilibrium and the exchange rate of organic groups between organoaluminum and -boron compounds depend strongly on the electronic and steric nature of both the 13-group elements. Me_3Al or Et_3Al is often employed so as to facilitate the spontaneous removal of the resulting volatile organoboron species (i.e., Me_3B or Et_3B; Equation (38)).[182]

$$\text{Me}_3\text{Al} \ + \ \text{B}(\text{C}_6\text{F}_5)_3 \xrightarrow[]{\substack{\text{toluene}\\ \text{RT}}} 0.5(\text{C}_6\text{F}_5)_2\text{Al}_2\text{Me}_4 \ + \ (\text{C}_6\text{F}_5)_2\text{BMe}$$

$$\rightleftharpoons 0.5(\text{C}_6\text{F}_5)_4\text{Al}_2\text{Me}_2 \ + \ (\text{C}_6\text{F}_5)\text{BMe}_2 \xrightarrow[83\%]{} (\text{C}_6\text{F}_5)_3\text{Al} \ + \ \text{BMe}_3\uparrow \tag{38}$$
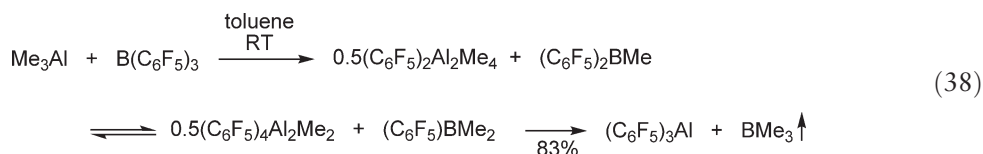
Exchange reactions sometimes suffer from undesirable elimination steps to give the corresponding alkenes, along with aluminum hydrides. This method recently offered a major advance in the synthesis of aluminum tris(pentafluorobenzene), ($Al(C_6F_5)_3$), which has found tremendous application as a co-catalyst in olefin polymerization (see also Section 5.2.1).[183] $Al(C_6F_5)_3$ is so extremely electrophilic that it can be isolated as the η^1,π-complex of the hydrocarbon upon exposure to toluene or benzene (Figure 28).[184] NMR studies indicated that the boron/aluminum stoichiometry and solvent used are critical factors in affording high purity $Al(C_6F_5)_3$.[185] It is worth mentioning that early studies on the synthesis of $Al(C_6F_5)_3$ via treatment of Et_3Al with $B(C_6F_5)_3$ without any solvent resulted in an explosion when the reaction temperature reached 70 °C, but at 50 °C no $Al(C_6F_5)_3$ was formed.[186,187] $Al(C_6F_5)_3$ and $B(C_6F_5)_3$ showed distinct reactivity upon treatment with the bis(imide) complex of group IV metals (Figure 29).[188] Trimethylaluminum reacts with $[CPh_3][B(C_6F_5)_3]$ at elevated temperature to give a mixture of $AlMe_{3-n}(C_6F_5)_n$ compounds, depending on Al/B ratio. $Al(Bu^i)_3$ undergoes β-hydride elimination significantly faster than Al/B exchange.

Hydroalumination of 1-alkynes generally proceeds without the aid of transition metal catalysts. However, the reaction sometimes suffers from undesirable side-processes, including the formation of alk-1-ynylalanes or protonolysis of the intermediate alk-1-enylalanes. In particular, these side-products increase significantly in the reaction of
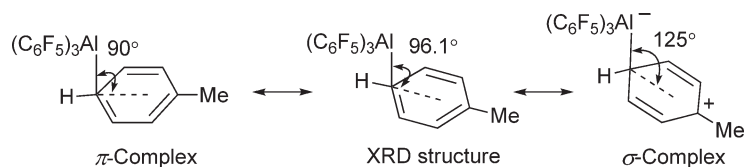
Figure 28 Al–arene σ and π complexes.
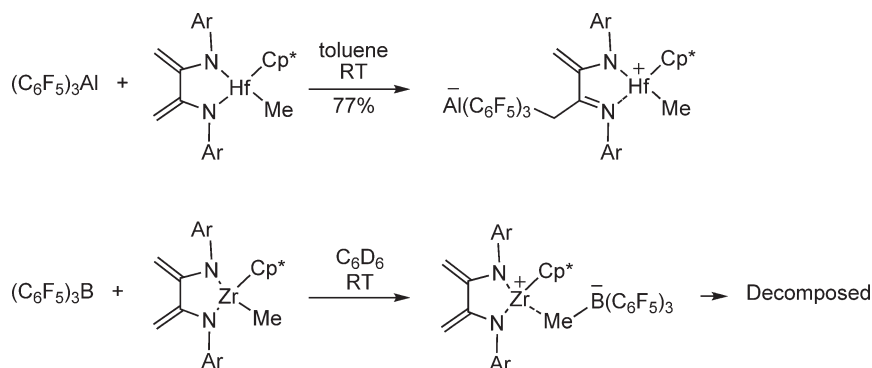
Figure 29   Different reactivity in the reaction of Al(C$_6$F$_5$)$_3$ and B(C$_6$F$_5$)$_3$.

conjugated alk-1-ynes. In contrast, treatment of (E)-1-alkenyldicyclohexylboranes with diisobutylaluminum hydride (Bu$^i_2$AlH) in the presence of 1-hexene resulted in transfer of the alkenyl group from boron to aluminum to give (E)-alkenyldiisobutylalanes in high yields with retention of configuration at the double bonds (Equation (39)).[189]

$$(39)$$
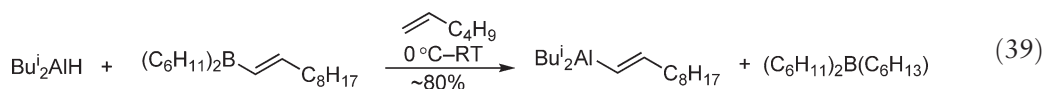
9.06.3.2   Direct Alumination of Aromatic Rings

Aromatic aluminum compounds are also available by direct alumination of multiply functionalized aromatic rings using aluminum amide ate complexes (Equation (40)).[190] The reaction tolerates various functional groups on an aromatic nucleus, such as bromine, alkoxy, amide, and cyano groups, and even heterocyclic aromatics, including indoles and pyridines, can participate successfully in this deprotonative procedure. Thus, an o-bromoaluminum benzene intermediate was stable enough at –78 °C but at RT underwent clean formation of the benzyne, which was subsequently trapped by an enenophile (Equation (41)).

$$(40)$$

$$(41)$$
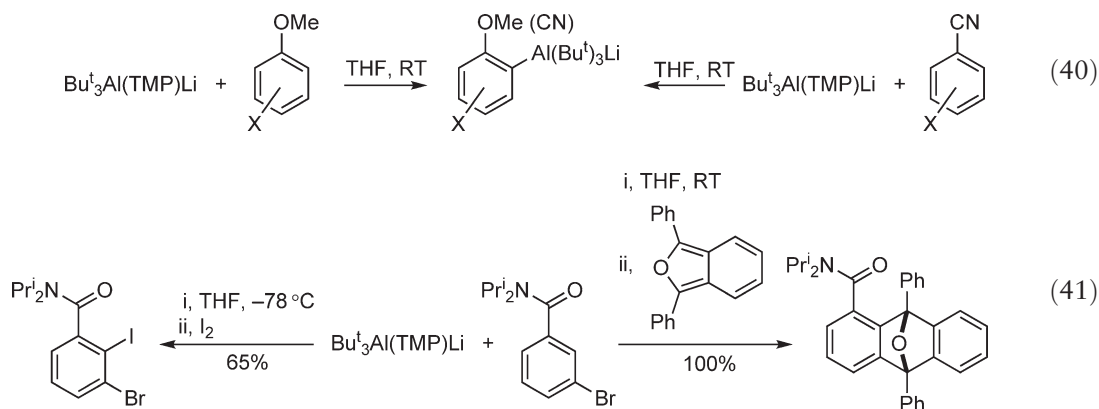
Aromatic carboxylic acids were obtained in good yield, essentially free of diaryl ketones by carboxylation of aromatics with a carbon dioxide–Al$_2$Cl$_6$/Al system at moderate temperature (20–80 °C).[191] It was not possible to distinguish between two possible mechanistic reaction pathways based on the experimental results. According to theoretical DFT calculations, one possible though unlikely pathway involves an initial complexation between benzene and Al$_2$Cl$_6$, with subsequent formation of organoaluminum intermediates (PhAlCl$_2$ and PhAl$_2$Cl$_6$) (Figure 30). A rather superelectrophilic aluminum chloride-activated carbon dioxide species, namely CO$_2$AlCl$_2^+$, seems to be involved in this typical electrophilic aromatic substitution pathway.
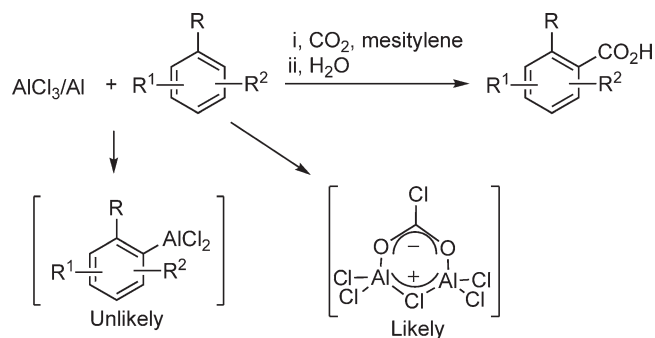
Figure 30 Reaction of arene ring and CO_2.

9.06.3.3 Carboalumination and Hydroalumination

The addition of aluminum hydride and alkyls to non-activated C–C multiple bonds (C≡C or C=C) is referred to as hydroaluminaton and carboalumination, respectively. The reactions involve metathesis of each C–C multiple bond with *Al–H* or *Al–C* bonds, giving an *Al–C=C–H* (or *Al–C–C–H*) or *Al–C=C–C* (or *Al–C–C–C*) structure, respectively. These methods are of broad utility in the construction of Al–C linkages, including Al–alkenyl and Al–alkyl bonds, which can be further converted into C–C bonds (Equations (42)–(45)).[192–196] Therefore, a great contribution has been made in synthetic applications, in addition to the mechanistic studies, of hydroalumination and carboalumination since 1993.[197–199]
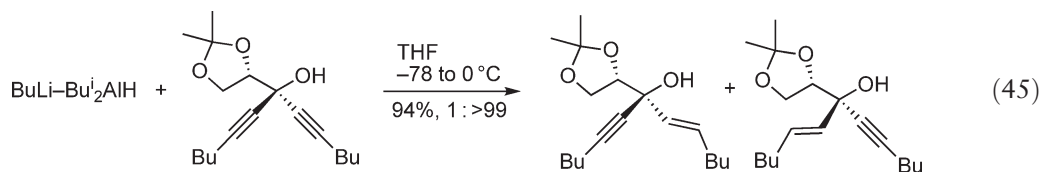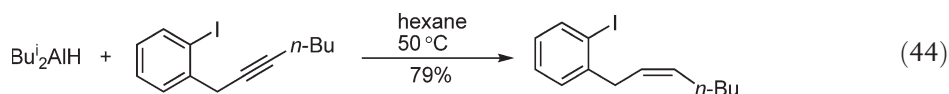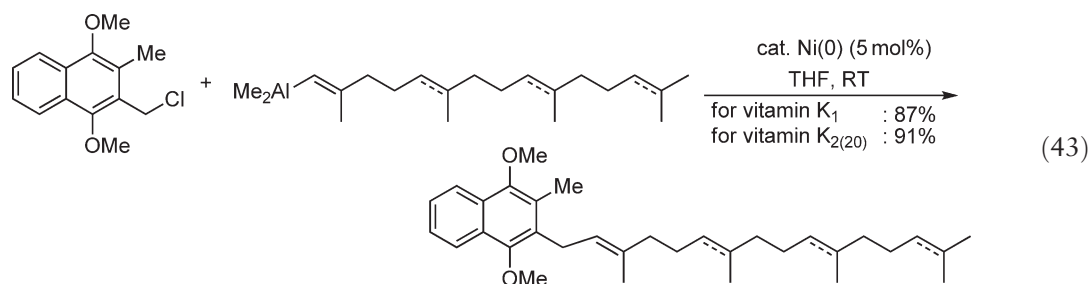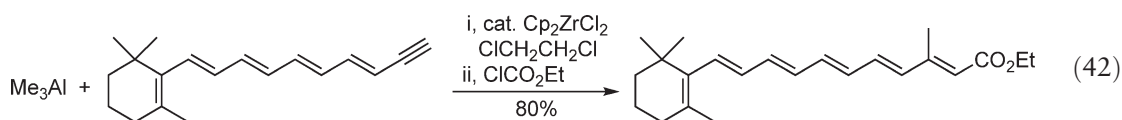
Carbo- and hydrometallation reactions are frequently catalyzed by group 4 metals (Ti, Zr) and are thus highly associated with the question of how the Ziegler–Natta polymerization or Tebbe processes should be controlled or

modified. While chiral Ni–BINAP catalysts were recently introduced into asymmetric hydroalumination (Equation (46)),[200–203] Cp_2TiCl_2 and Cp_2ZrCl_2 have been most profoundly investigated in the catalytic processes.

$$ (46) $$
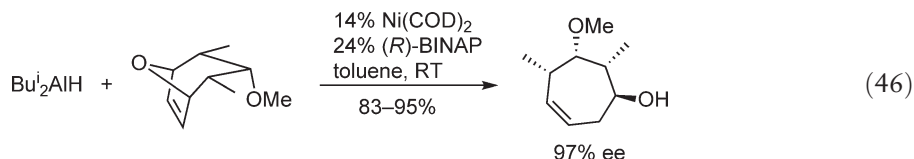
The mechanism of the carboalumination of alkenes falls into either of the following two classes depending on the unsaturated substrates used and the reaction conditions: (i) alkene insertion into a transition metal–carbon or aluminum–carbon bond and (ii) coupling of two alkenes with low-valent metal(II), leading to metallacyclopentanes or -propanes. Yoshida and Negishi have proposed[204] that Cp_2ZrCl_2-catalyzed carboalumination of alkynes involves methylation of Cp_2ZrCl_2 with Me_3Al to give $ZrCp_2Cl(Me)$ and Me_2AlCl. Subsequent carbozirconation of the alkyne yields the corresponding alkenylzirconium derivatives; their transmetallation with Me_2AlCl results in alkenyldi-methylalanes, accompanied by regeneration of the catalyst. The reaction mechanism likely involves the existence of a reversible process where the methyl group or methyl radical is transferred from the aluminum atom to the Zr atom, as evidenced by NMR measurements. However, further investigations[205,206] showed that this reaction involves direct carboalumination of alkynes by Me_2AlCl activated by $Cp_2ZrCl(Me)$ (Figure 31). When Et_3Al was used in place of Me_2AlCl, it was proposed that the Cp_2ZrCl_2-catalyzed cyclic carboalumination of alkynes proceeds via bimetallic C–H bond activation and gives 22, which rearranges to yield $Cp_2ZrEtCl$ and the aluminacyclopentene (Figure 32).[207] This mechanism is based on a series of earlier studies on the reaction of Et_3Al with Cp_2ZrCl_2 by Sinn[208] and Kaminsky[209] in the 1960s and 1970s, and is in good agreement with theoretical data obtained by PM3 calculations.[210]

Related to these metathesis processes, the first report of a regioselective synthesis of a previously unknown five-membered organoaluminum compound was published in 1989 (Equation (47)).[211] Later, it was found that this reaction is versatile and allows for a one-step synthesis of five-membered organoaluminums from Et_3Al and terminal alkenes in nearly quantitative yields.[212] This reaction is termed "catalytic cycloalumination"[213] or "cyclic carboalumination".[214] The synthesis of aluminocyclopentenes was achieved through intramolecular cycloalumina-tion of disubstituted acetylenes with Et_3Al in the presence of catalytic Cp_2ZrCl_2 without any solvents
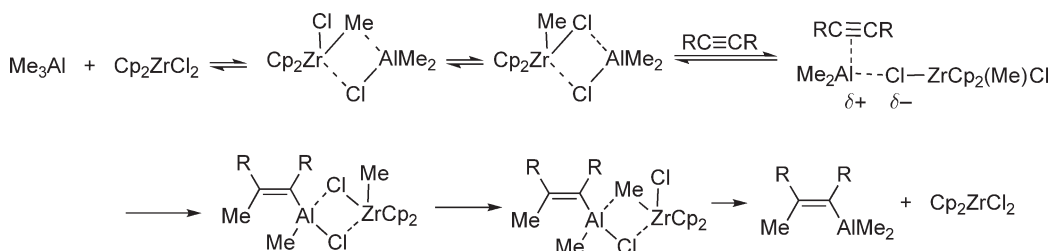
Figure 31 Proposed mechanism of the carboalumination promoted by Me_3Al and cat. Cp_2ZrCl_2.
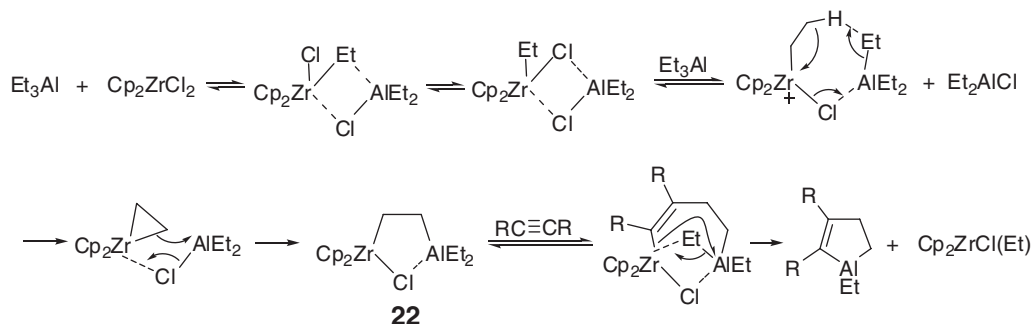
Figure 32 Proposed mechanism of the carboalumination promoted by Et_3Al and cat. Cp_2ZrCl_2.

(Equation (48)).[199] Increasing the internal alkynes by twice the amount and addition of Mg led to the alumino-cyclopentadiene (Equation (49)).[215] Dimerization of terminal alkenes involving an aluminum center resulted in the formation of aluminocyclopentane when the Zr catalyst and Mg used had the proper reaction conditions (Equation (50)).[216] In contrast, 1,4-dialuminobutane was readily formed using a twofold excess of R_2AlCl following a similar reductive process in THF (Equation (51)).[217] In 1997, Dzhemilev and co-workers developed a method for the synthesis of a class of metallacycles named "aluminocyclopropanes" (Equation (52)).[218] The reaction involves the use of alkylaluminum dichlorides ($RAlCl_2$), Mg, and catalytic Cp_2TiCl_2. Mg was used as well for reduction of Ti(IV) to generate low-valent titanium species. Similar adjustment of reaction conditions allowed for the synthesis of alumino-cycropropenes through cycloalumination of 1,2-disubstituted acetylenes using $RAlCl_2$, Mg, and catalytic Cp_2TiCl_2 (Equation (53)).[219] The nature of the solvent had great influence on the formation and reactivity of intermediary titanium- and zirconium-containing metallacycles, the common key species in the synthesis of aluminocycloalkanes and -alkenes.

$$Et_3Al \ + \ R^1 \diagdown\!\diagup \xrightarrow[98\%]{\substack{cat.\ Cp_2ZrCl_2 \\ 20\,^\circ C}} \quad \text{(47)}$$

$$Et_3Al \ + \ R^1C{\equiv}CR^1 \xrightarrow[75-90\%]{\substack{cat.\ Cp_2ZrCl_2 \\ 20\,^\circ C}} \quad \text{(48)}$$

$$RAlCl_2 \ + \ 2R^1C{\equiv}CR^1 \xrightarrow[>93\%]{\substack{cat.\ Cp_2ZrCl_2 \\ Mg,\ THF}} \quad \text{(49)}$$

$$RAlCl_2 \ + \ 2R^1 \diagdown\!\diagup \xrightarrow[70-90\%]{\substack{cat.\ Cp_2ZrCl_2 \\ Mg,\ THF,\ 20\,^\circ C}} \quad \text{(50)}$$

$$2R_2AlCl \ + \ R^1 \diagdown\!\diagup \xrightarrow[\sim75\%]{\substack{cat.\ Cp_2ZrCl_2 \\ Mg,\ THF,\ 20\,^\circ C}} \quad R_2Al{-}{\diagup}{\diagdown}{-}AlR_2 \quad \text{(51)}$$

$$RAlCl_2 \ + \ Ar \diagdown\!\diagup \xrightarrow[65-85\%]{\substack{cat.\ Cp_2TiCl_2 \\ Mg,\ THF,\ 20\,^\circ C}} \quad \text{(52)}$$

$$RAlCl_2 \ + \ R^1C{\equiv}CR^1 \xrightarrow[65-90\%]{\substack{cat.\ Cp_2TiCl_2 \\ Mg,\ THF,\ 20\,^\circ C}} \quad \text{(53)}$$
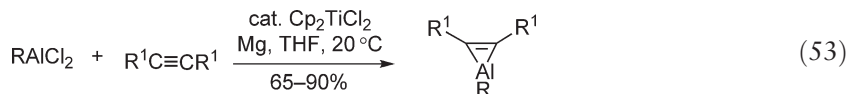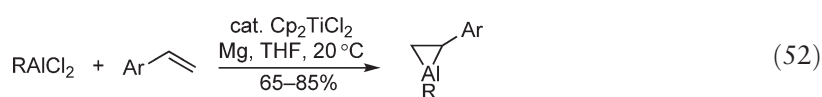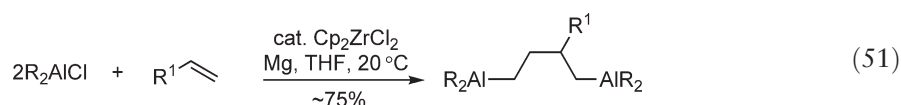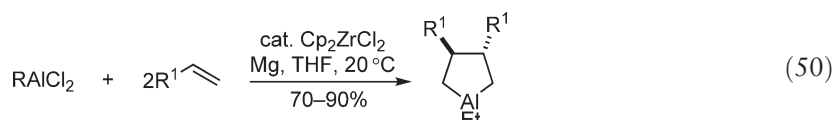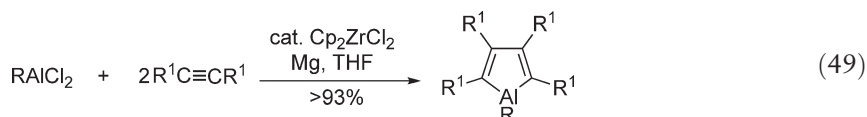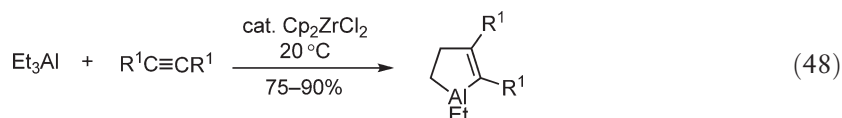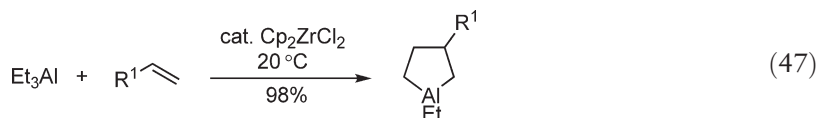
9.06.4   New Aspects in Reactivity of Organoaluminum Compounds

Organoaluminum(III) compounds can act not only as nucleophiles but also in the electrophilic adhesion and subsequent activation of heteroatom-containing substrates. The dual functions of organoaluminums recall a simplified mechanistic model working with acid–base-type interactions and reactions. The most common geometry around aluminum is tetrahedral, which accommodates typical reactive intermediates, and subsequently initiates coupling at the most electrophilic and nucleophilic intersections. In fact, upon formation of ate complexes with organometallic species (organolithium, organomagnesium, etc.) or coordination complexes with neutral Lewis bases (heteroatom-containing substrates such as carbonyl and imino compounds, ethers, and amines, etc.) (Figure 33), transfer of the alkyl group from aluminum atom begins in either an intra- or an intermolecular fashion. However, contrary to representative alkyl-transfer reactions, the organic chains attached to aluminum are almost inert, given the special
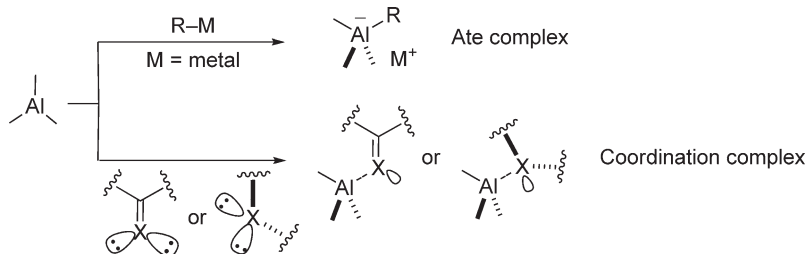
Figure 33 Aluminum ate complex and coordination complex in tetrahedral geometry.

arrangement with the coordination sphere of aluminum. In many cases, this nature could be applied to Lewis acid-promoted reactions, allowing a number of bimolecular and intramolecular carbon–carbon bond-forming reactions. The next section briefly describes some of the notable properties of the reactivity of organoaluminum compounds.

9.06.4.1 Tunable Reactivity of Methyl and Other Alkyl Groups on Aluminum(III)

Organoaluminum(III) reagents commonly have high oxophilicity. Trialkylaluminum compounds, especially Me_3Al and Et_3Al, ignite spontaneously in air at ambient temperature. Most aluminum alkyls react violently with water. Covalent bonds formed between aluminum and oxygen or halogen atoms are extremely strong – the energy of the Al–O bond is estimated to be $138 \, kcal \, mol^{-1}$. Special care must be taken with their handling; the precautions are explicitly indicated elsewhere. Increasing molecular weight by increasing the number of carbons in the aluminum alkyl chain reduces pyrophoric reactivity. Replacing alkyl groups by alkoxy or other heteroatoms including halogen atoms also reduces the reactivity, that is, the remaining alkyl groups bound to the aluminum(III) center lose their mobility comparatively.

9.06.4.1.1 Aluminum alkyls in reaction with protic groups

Since the most common carbon-bonded ligand for aluminum is the methyl group, it would be most appropriate to begin discussions regarding reactivity differences with various types of Al–Me bonds. For example, the (salen)Al–Me complex is a shelf stable compound (Figure 34). ("Salen" is the name that has historically been used to describe the entire class of such ligands possessing various diamino backbones; however, it is also the specific name of the ethylenediamine derivatives.)[220] The 5,10,15,20-tetraphenylporphyrinato (TPP)-based aluminum reagent (TPP)Al–SPh frequently has higher reactivity in initiating anionic polymerization than (TPP)Al–Me.[221] Me_3Al works as an effective methylating agent for carbonyls, imines, and epoxides, among others,[24] but MAD[92] does not.

In fact, the methyl group of MAD shows intriguing reactivity upon treatment with water.[222] The reaction of MAD with water is slow, and although CH_4 is formed, the primary product of hydrolysis is 2,6-di-t-butyl-4-methylphenol (Equation (54)). Before liberating the phenol, the aquo complex **23** was formed by treatment of 1.0 equiv. of H_2O with a THF solution of MAD. Complex **23** was stable at $-40\,°C$ but gradually decomposed at $5\,°C$ following first-order kinetics with $k_{obs} = 3.0 \times 10^{-4} \, s^{-1}$. This suggests that liberation of phenol overrides the general tendency that aluminum methyl rapidly reacts to enable the entropically favored pathway, that is, evolution of CH_4 gas. In contrast, a 1:1 complex of Me_3Al and H_2O was kept inert at $-70\,°C$, while at $-40\,°C$ it began decomposing, resulting primarily in $Me_2Al(OH)$.[223] The more inert nature of the Me group of $Me_2Al(OH)$ as opposed to that of Me_3Al is also

MAD   (salen)Al–Me   (TPP)AlMe
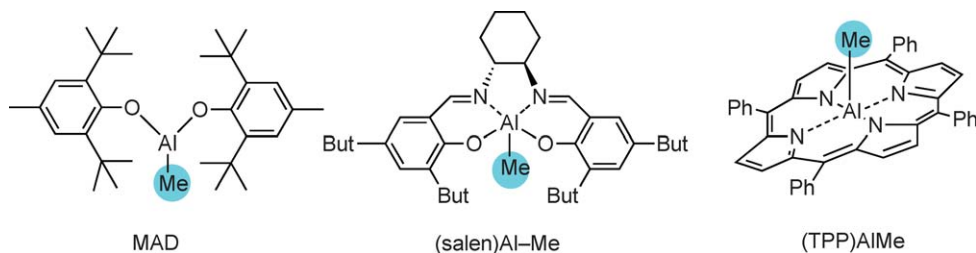
Figure 34 Al–Me bonds in various aluminum complexes.

demonstrated by an experiment employing a 2:1 mixture of Me_3Al and H_2O: a second liberation of methane to form $Me_2Al–O–AlMe_2$ starts above $-20\,°C$. Et_3Al was also examined along these lines and found to be consistently less reactive than Me_3Al. Compared with Me_3Al, however, Bu^i_3Al was more reactive and started decomposing at $-50\,°C$, but the second decomposition step was slower. The search for a partial decomposition of organoalanes by water merits identifying the formation mechanism of MAOs or other cage structures comprising repeated Al–O–Al linkages, which has attracted great attention from polymer scientists. Roesky recently reported time-dependent spectral data obtained during the hydrolysis of relatively bulky trialkylalanes and -galliums.[86,224] Bu^t_3Al is rather inert to amino alcohols, giving the hydrogen-bonded coordination complex **24** without formation of any covalent bonds and liberation of hydrocarbon gas (Equation (55)).[225] The thiomorphine complex **25** is stable at $25\,°C$ while gradually decomposing at higher temperatures, eventually forming homodimer **26** (Equation (56)).[226]

(54)

(55)

(56)
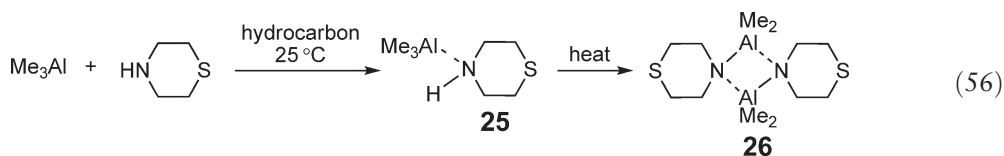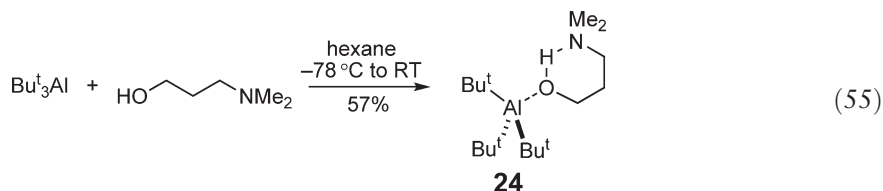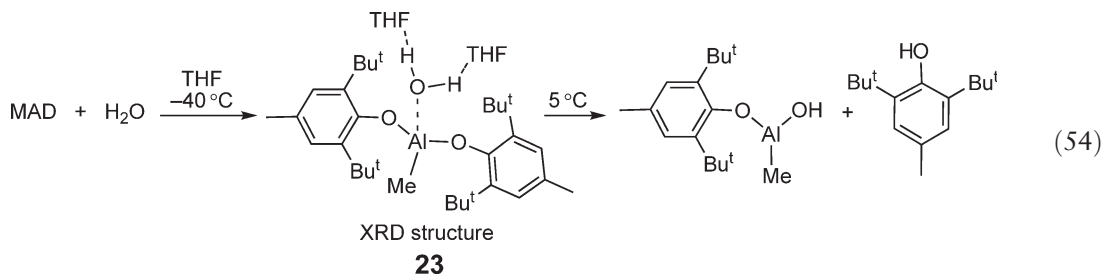
9.06.4.1.2   Aluminum alkyls in alkylation and deprotonation

The reactivity of Me_3Al can also be altered by coordination of solvent, and this treatment affects the addition mode of Me_3Al to carbonyl, imino, or olefinic substrates. This can be most typically seen in the case of solvated Me_3Al monomer giving axial alcohol predominantly, while the stereochemical reversal was observed in hydrocarbon solvents, in which the "closed" (homo)dimer (Me_6Al_2) predominates (Figures 35 and 36).
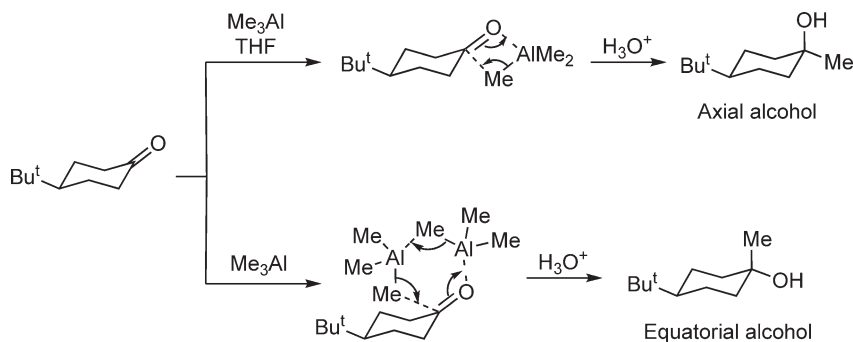
Figure 35   Different stereoselectivity controlled by Me_3Al dimer and monomer.
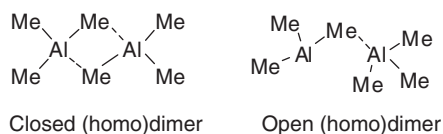
Figure 36 Closed dimer and open dimer of Me$_3$Al.
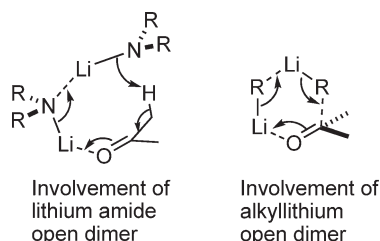
Figure 37 Involvement of open dimer in deprotonation and alkylation reactions.

The importance of the reagent on open dimers was also pointed out in the proposed mechanism of deprotonation by lithium amides and alkylation by organolithiums in carbonyl and imine chemistry (Figure 37).[227,228] This mechanistic basis was further extended to the catalyst-promoted addition of Et$_2$Zn[229] or BH$_3$[230] to carbonyl compounds. The involvement of "open" (homo)dimers overriding the monomer mechanism is now the general understanding, and a strong possibility. However, steric demands in a transition state ensemble sometimes favor a monomer pathway. It is reasonable to ascribe this exception to a decrease in steric congestion in the monomers relative to the open dimers. Although MAD alone apparently is not a promising methylating agent, combined use with MeLi or MeMgX (X = Cl, Br, I) affords effective methylation.[231] When a 1 : 1 toluene/Et$_2$O solution of MAD and MeLi (or MeMgX) was treated with the ketone, smooth addition to the carbonyl group took place with the formation of **27** or **28**, most likely via an open "hetero"-dimer pathway (Ashby transition state) (Figure 38). Thus, MAD might have a role in directing the methyl transfer through a relay mechanism.

The opposite sense of diastereoselectivity has been observed frequently, giving, for example, alcohol **29** or **30** exclusively in the MAD/MeM (M = Li, MgX) system (Equations (57) and (58)).[232,233] For the deprotonation events of the α-proton of ketones, a monomer pathway was proposed (Figure 39),[234] but the open dimer mechanism cannot be ruled out entirely. The relatively bulky aluminum phenoxide may be involved in the monomer pathway due to its
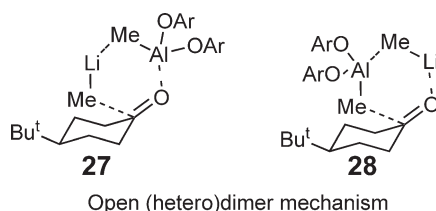
Figure 38 Two different open dimers in alkylation of 4-Bu^t-cyclohexan-1-one.
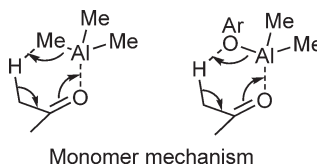
Figure 39 Me$_3$Al monomer mechanism in deprotonation of acetone.

steric effects.[235] Note that the phenoxy group is likely to be more susceptible to deprotonation and, hence, reacts faster than the alkyl groups but slower than the amide groups, both being attached to an aluminum center.

$$\text{PhS} \quad \xrightarrow[\text{80\%}]{\substack{\text{i, MAD, toluene} \\ \text{ii, MeLi, Et}_2\text{O} \\ -78\,°\text{C}}} \quad \text{PhS} \quad + \quad \text{PhS} \quad \mathbf{29} \quad 1:10.2 \tag{57}$$

$$\xrightarrow[\text{81\%}]{\substack{\text{i, MAD, toluene} \\ \text{ii, MeMgBr} \\ -78\,°\text{C}}} \quad + \quad \mathbf{30} \quad 5:95 \tag{58}$$
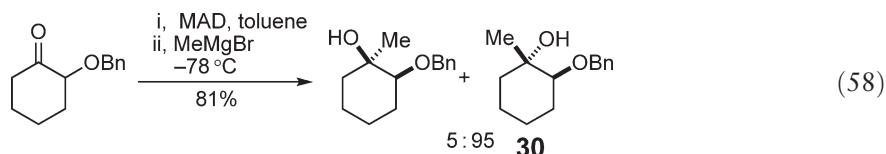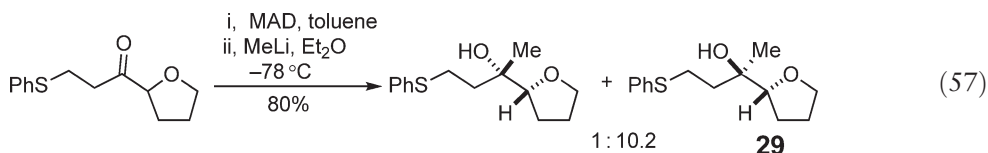
9.06.4.1.3 Aluminum alkyls in radical reaction

The methyl group of MAD shows another distinct behavior upon exposure to O_2: it works as a radical initiator, presumably through homolytic cleavage of the Me–Al bond. This reaction affords diastereoselective radical cyclization of chiral α,β-unsaturated esters (Equation (59)).[236] There exists rather old though subsequently growing evidence that many of the reactions of organoaluminums involve free-radical and/or peroxo intermediates upon UV or O_2 treatment,[5] one of which was isolated, and its structure was verified recently by XRD (Equation (60)).[237] However, ESR studies of MAD under an O_2 atmosphere revealed that homolytic cleavage of the aluminum–oxygen bond took place with the formation of two free radicals stable at RT. These are the only observable species: one is the phenoxy radical and the other is the more stable radical comprised of aluminum and the phenoxy group.[238] The peroxide–trialkylaluminum system is frequently used in industrial application for initiating radical co-polymerization of ethylene with vinyl acetate.[239]

$$\xrightarrow[\text{84\%}]{\substack{\text{MAD, Bu}_3\text{SnH} \\ \text{dry air, toluene} \\ -78\,°\text{C}}} \qquad \text{84\% de} \tag{59}$$

$$\xrightarrow[\substack{\text{toluene, } -15\,°\text{C} \\ 100\%}]{O_2} \tag{60}$$
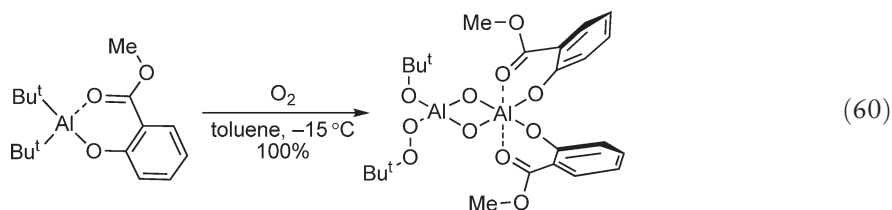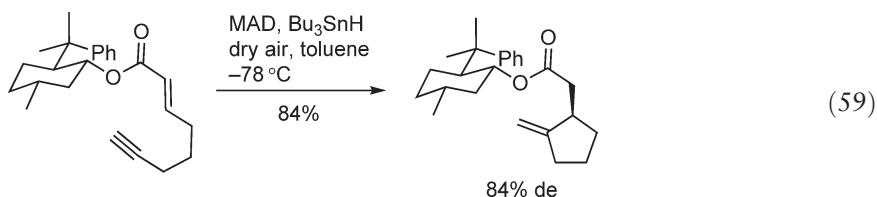
9.06.4.1.4 Aluminum alkyls in polymerization

The methyl group of (TPP)AlMe is also activated upon exposure to visible light (>350 nm), serving as a methylating agent for α,β-unsaturated esters.[240–242] This behavior was applied in the initiation of polymerization of methyl methacrylate (MMA) in the presence of MAD. The very high-speed chain process seems to start, upon light irradiation, with the conjugate addition of the Al–Me bond of (TPP)AlMe to a methacrylate activated by MAD and reach completion within 30 s (Figure 40). The resulting enolate might further react with a second methacylate activated by a (TPP)Al$^+$ species, or return to the (TPP)Al$^+$, generating a second (TPP)Al–enolate complex, followed by conjugate addition to a methacrylate. The Al–enolate complexes formed in each propagation step serve as the nucleophilic growing species, producing the repeating unit and eventually a polymer chain with a narrow molecular weight distribution (MWD ~ 1.1). (TPP)AlEt promotes CO_2 insertion into the Al–Et bond upon visible light irradiation in the presence of 1-methylimidazole.[242]
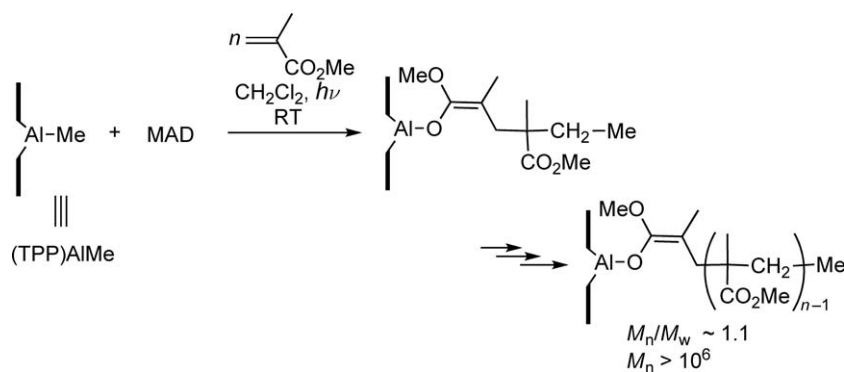
Figure 40 Schematic description of (TPP)AlMe-promoted polymerization of MMA.

A complex reaction mechanism that explains an abnormal feature of MAD, facilitating transfer of the methyl group on its own, was postulated.[243] The (salen)–AlMe complex **31** was used to initiate the polymerization of MMA in the presence of Ni(acac)$_2$ and MAD (Equation (61)). Without MAD, the conversion of the monomer is very low. MAD was suggested to play a dual role: it activates the MMA, and generates the active nickel catalyst responsible for enolate formation (Figure 41). The first step involves transfer of the methyl group of MAD to the Ni center. During the next step, the monomer MMA might insert into the Ni–Me bonds of **32**, generating the Ni–enolate complex **33**. Subsequent group exchange between **33** and the aluminum methyl of **31** gives **34**, which serves as the primary propagating anionic species, and Ni–Me catalyst **32** regenerates spontaneously. This is reminiscent of the "nickel effect", the basic nature of which has been well discussed in COMC (1995). In particular, the Me$_3$Al– and Et$_3$Al–Ni(acac)$_2$ catalytic system in conjugate addition events has been studied in detail in many works.[244] CIDNAP effects were analyzed recently in the reaction of Et$_3$Al with CHCl$_3$ in the presence of Ni(acac)$_2$.[245]

(61)
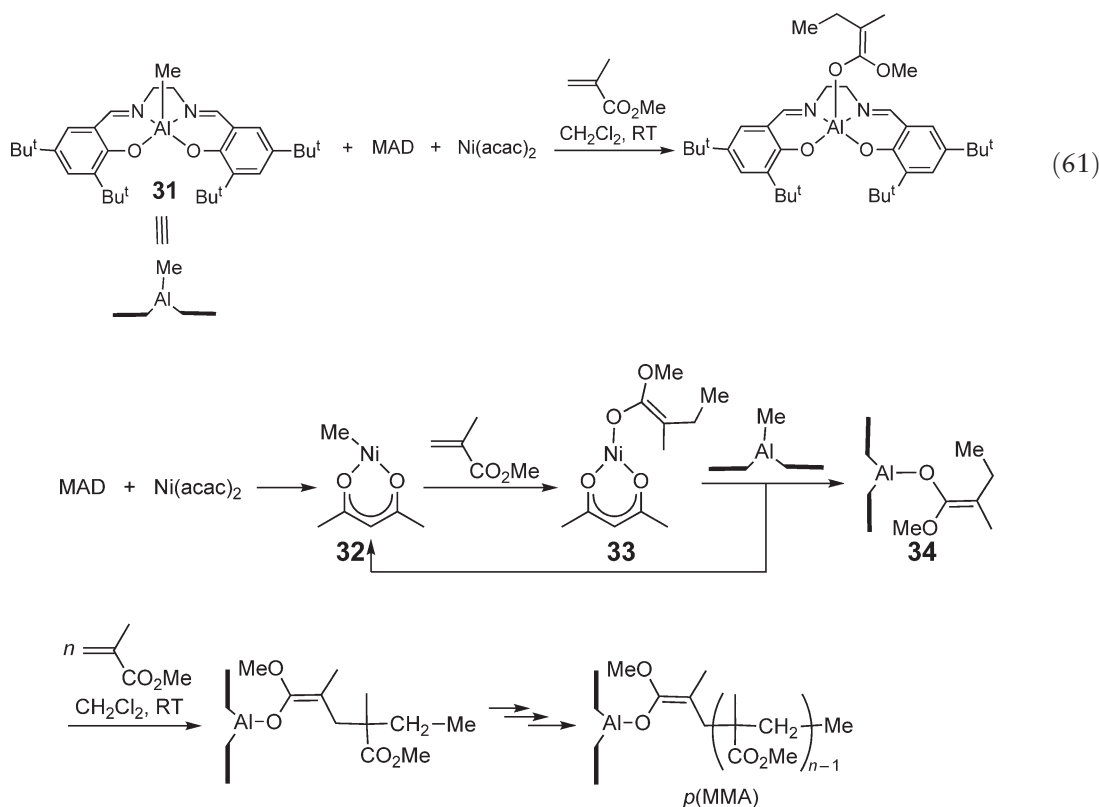
Figure 41 Proposed mechanism of MAD–Ni(acac)$_2$-mediated polymerization of MMA.
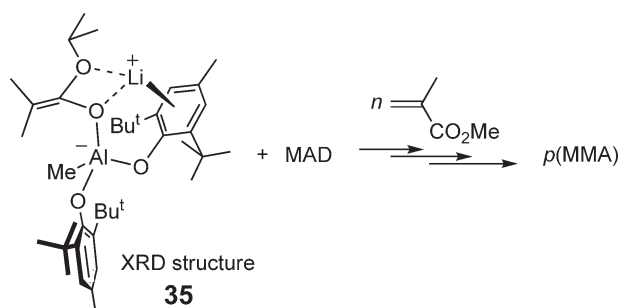
Figure 42 Possible reaction intermediate involved in polymerization of MMA promoted by MAD.
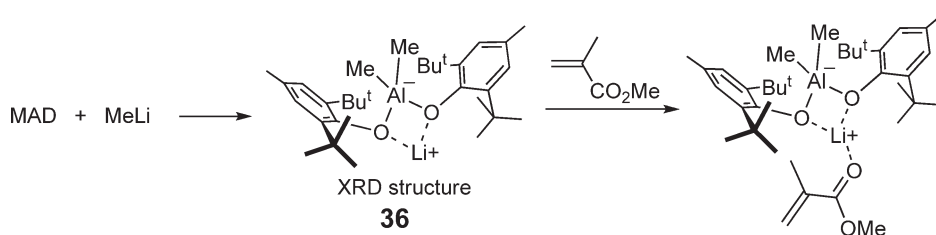
Figure 43 Possible reaction intermediate involved in polymerization of MMA promoted by MAD and cat. MeLi.

The MAD/RLi system and its variants are widely used in the polymerization of methacrylates or acrylates.[246] By taking into account the inertness of the methyl group of MAD, RLi serves as the initiator of polymerization like (TPP)AlMe. The MAD–Li-enolate complex **35**,[247] which might resemble the core structure of the propagating enolate species, was isolated and its structure was determined by XRD (Figure 42).[248] By performing kinetic studies using **35**, MAD, and the monomer MMA, it was suggested that the "single-site anionic propagating center" mechanism is operative, which compares well with the one proposed for the MAD/(TPP)AlMe system. Another mechanistic scenario that involves coordination of conjugated carbonyl compound at the Li+ of lithium dialkyl-aluminum bis(2,6-di-t-butyl-4-methylphenoxide) **36** was proposed based on XRD (Figure 43).[249] Note that activation of the monomer by MAD is a critical treatment in enabling the polymerization. MAD is also considered to be a nice scavenger of small amounts of H_2O and O_2,[250] which reside in the reaction mixture and possibly prevent high performance of the chain processes.

9.06.4.1.5 Aluminum alkyls in reactions with carbon–carbon multiple bonds, oxiranes, and other functional groups

Me_3Al and Et_3Al have been widely used for alkylation of various functional groups. Very recent examples include the ring-opening methylation of oxiranes (Equations (62) and (63)),[251–253] lactones[254] and aminoacetals (Equation (64)),[255] and the methylation of the anomeric position of sugar derivatives[256–258] (Equations (65) and (66)) and carbamates (Equation (67)).[259] A second alkylation was suppressed to yield ketones in the methylation of esters with Me_3Al/ethylenediamine system (Equation (68)).[260]

$$(62)$$

$$(63)$$

$4Me_3Al$ + [structure] $\xrightarrow[\text{95\%}]{\substack{\text{toluene} \\ 20\,°C}}$ [structure] >99% de (64)

$9Me_3Al$ + [structure] $\xrightarrow[\text{73\%}]{\substack{CH_2Cl_2 \\ 0\,°C}}$ [structure] (65)

$3Me_3Al$ + Bu^tMe_2SiO [structure] OBn $\xrightarrow[\text{46\%}]{\substack{\text{hexane} \\ \text{reflux}}}$ [structure] + [structure]   >90 : <10 (66)

$3Me_3Al$ + Bn [structure] OMe $\xrightarrow[\text{67\%}]{\substack{(CH_2Cl)_2 \\ 65\,°C}}$ Bn [structure] Me (67)

$3Me_3Al$ + [structure] OMe $\xrightarrow[\text{98\%}]{\substack{MeHN\text{---}NHMe \\ \text{toluene} \\ \text{reflux}}}$ [structure] Me (68)
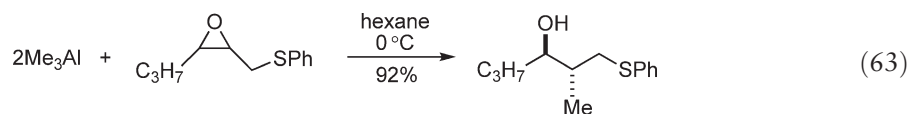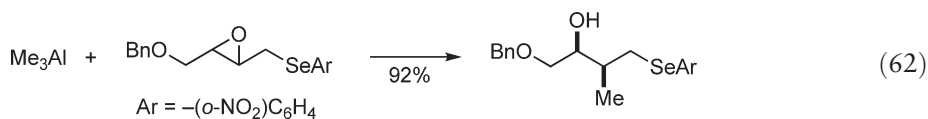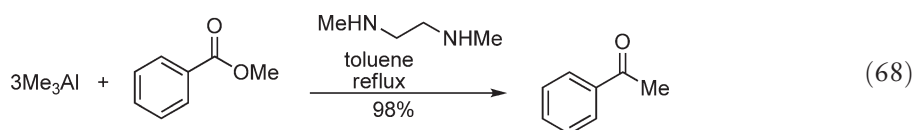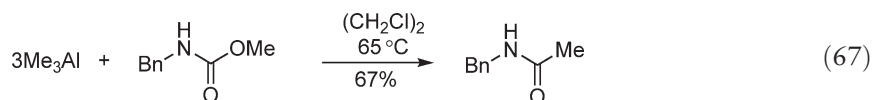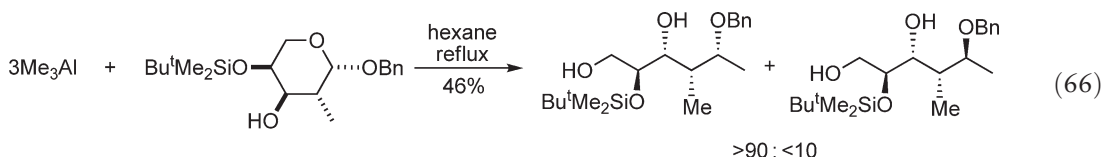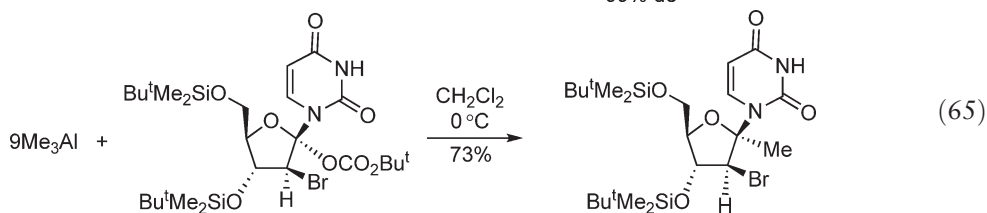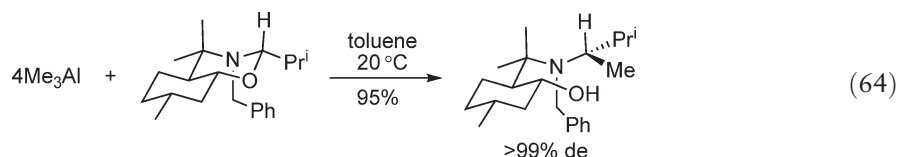
The use of Me_3Al is generally effective for the methylation of C=C (double) and C≡C (triple) bonds, being promoted by transition metals such as Ti, Zr, Cu, Pd, and Ni species. This rather old chemistry has been well established, achieving carbometallation and conjugate addition to α,β-unsaturated ketones and esters. Alkylation of allylic epoxides proceeded at the C=C double bonds, followed by simultaneous ring opening in the presence of the catalytic Cu–**37** species (Equation (69)).[261] It was subsequently found that the transfer of the methyl group from Al to the transition metal is facilitated, irrespective of whether the several heteroatoms are attached to Al covalently or non-covalently (Equations (70)–(72)).[262–265] Therefore, Me_3Al can be replaced by the more air and moisture insensitive derivatives **38–40**, which have found broader utility, due to their easier handling, in various methyl–aryl coupling and conjugate addition processes. It was also elucidated that a small amount of H_2O enhances the reaction rate of the methylalumination of terminal alkynes (Equation (73)).[266]

$2Me_3Al$ + [structure] $\xrightarrow[\text{45\%, 94:6}]{\substack{(S,S,S)\text{-}\mathbf{37}\ (2\ \text{mol\%}) \\ CuTC\ (1\ \text{mol\%}) \\ THF,\ -40\,°C}}$ [structure] OH 82% ee + [structure] OH (69)

(S,S,S)-**37**

$$(70)$$

38

$$(71)$$

39

$$(72)$$

40

$$(73)$$
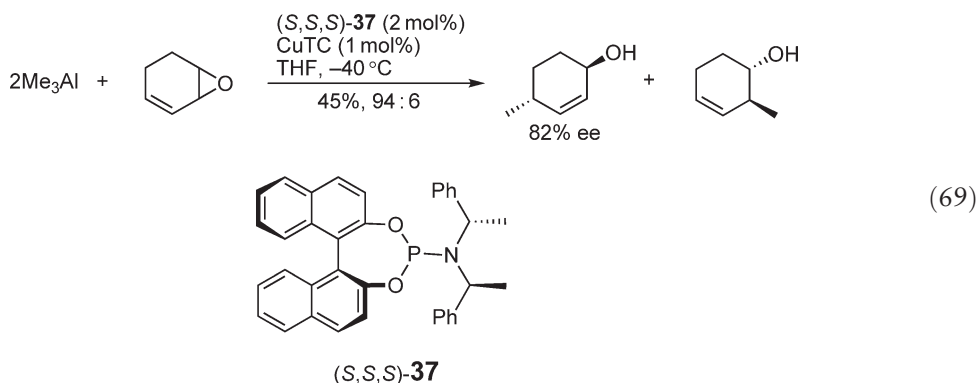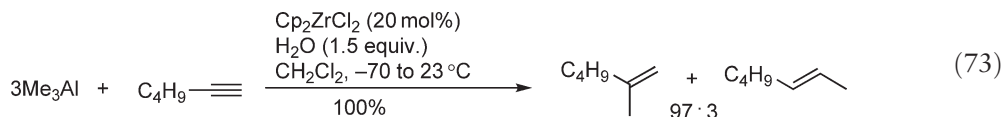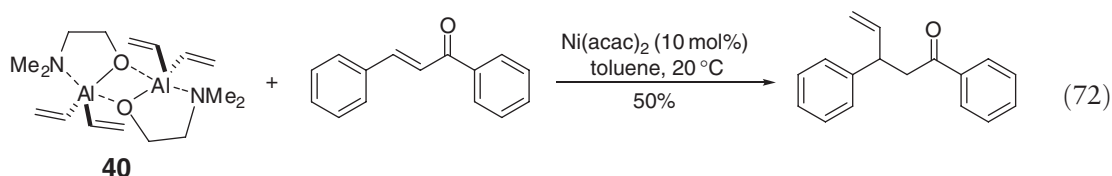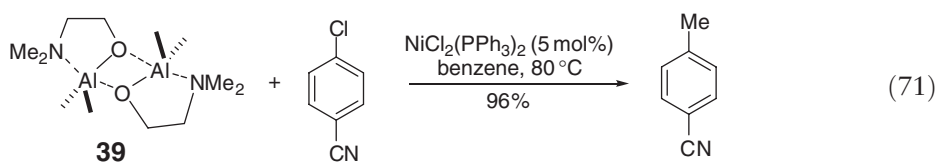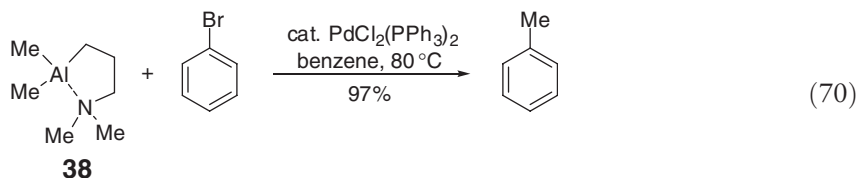
Et$_3$Al is sometimes a good ethylating agent with the aid of a transition metal catalyst;[267–271] however, β-hydride elimination frequently competes with ethylation, bringing about reductive processes such as reduction of vinyl phosphates[272] and hydroalumination of alkynes[273] in the presence of Pd(0) catalysts. The use of Ni(acac)$_2$ as a catalyst was shown to be limited to aluminum alkyls without β-hydrogen in the conjugate addition.[274] β-Hydride elimination/transfer is the side-process commonly observed with other organoaluminums incorporating higher alkyl chains. This hampers the synthetic scope of those organoaluminum reagents from further expansion, no matter how they are used, with or even without transition metal species. However, there is significant growing evidence that availability of those higher alkyls could be maintained by the proper choice of transition metal catalyst, ligand, substrates, and/or reaction conditions. The Ni-catalyzed aryl–ethyl coupling was indeed facilitated by Et$_3$Al in certain cases.[270,271] The Et, Pr, or even Bu^i groups of aluminum are transferable to α,β-enones in Cu(I)-catalyzed conjugate addition (Equation (74)).[267–269] The Zr-catalyzed ethylalumination of terminal alkynes proceeds readily at a low temperature, thereby suppressing the β-hydride elimination from proceeding significantly (Equations (75) and (76)). Negishi found effective methods for methyl-[275] and ethylalumination[276] of terminal olefins, which was further extended to the asymmetric version using a chiral zirconocene-type catalyst **41** (Figure 44).[277]

$$(74)$$

R = Me, Et, Pr, Bu^i

$$(75)$$
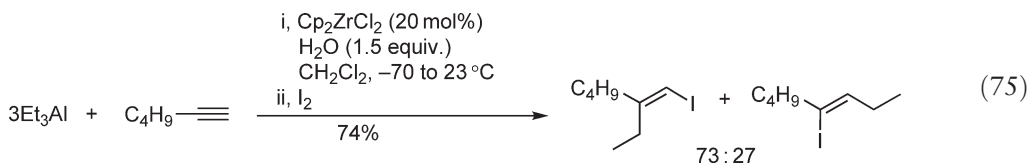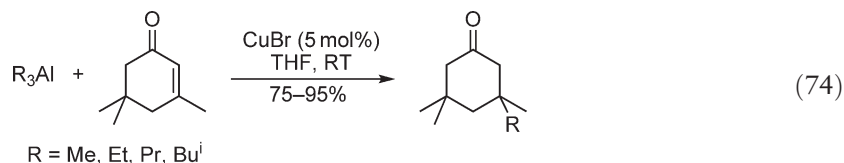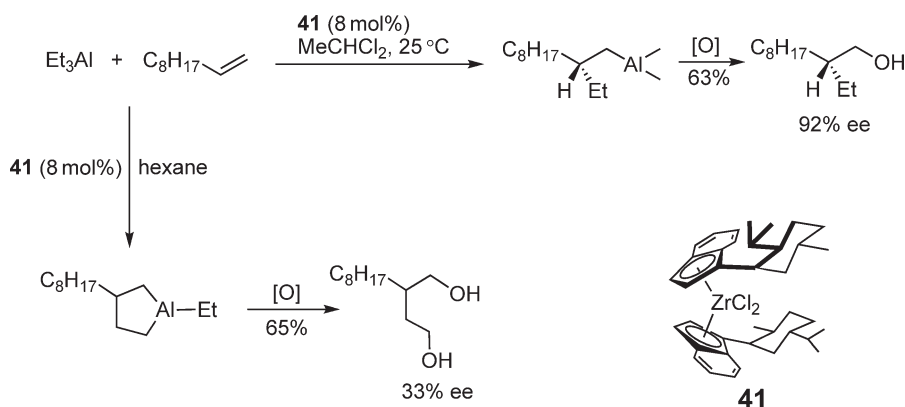
Figure 44 Solvent effects on product distribution in the asymmetric ethylalumination.

(76)
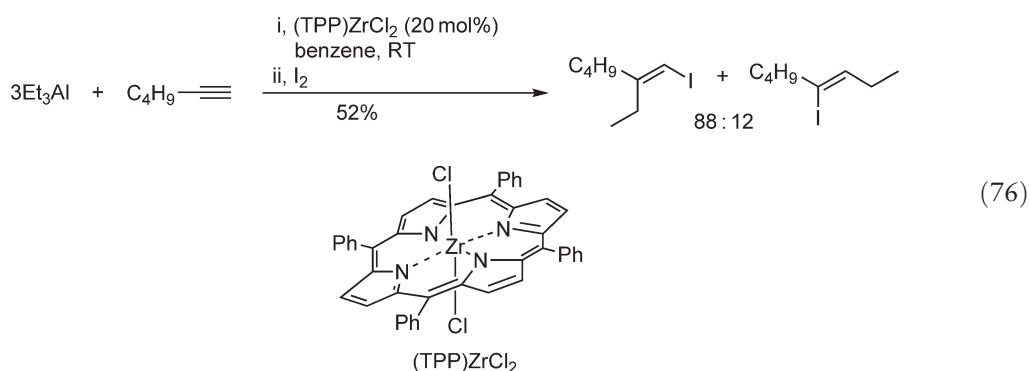
Although methyl and ethyl groups embedded into the elaborate coordination sphere of aluminum are certain to have potential reactivity, it is obvious that special treatment is necessary for promoting the alkyl transfer, which otherwise is difficult to achieve. Thus, MAD and other elaborate methylaluminum species are finding wider applicability as monomeric Lewis acid reagents in both polymerization and organic synthesis by taking advantages of this rather inert nature of the methyl group and high oxophilicity of the aluminum atom. Some of those catalytic properties will be clearly demonstrated in the forthcoming sections.

9.06.4.2 Organic Group-selective Transfer from Aluminum(III) Ate Complexes to Electrophiles

As mentioned above, most trivalent organoaluminum-mediated reactions are initiated by coordination of the substrate to an aluminum atom; thus, significant solvent effects are observed in many cases which affect the reaction rate, pattern, and selectivity. Similarly, the ate complexes of organoaluminum compounds, adopting tetracoordinate geometry, dramatically change the reactivity of the parent trivalent organoaluminums. The complex has already satisfied the octet rule and behaves as a nucleophile rather than a Lewis acid. If different organic groups (e.g., alkyl, alkenyl, alkynyl, or aryl groups) were attached at the same time to an aluminum atom, the question arises as to which organic group would be more reactive. Each covalent bond has discrete covalent nature, and their order of reactivity has been roughly estimated as hydride (H$^-$) > alkynyl (Csp) > alkenyl (Csp^2) > alkyl (Csp^3). For example, the ate complex of an alkynylaluminum species undergoes alkynyl coupling in the presence of an oxovanadium reagent. The reaction is intriguing in several ways. When the aluminum atom is simultaneously bound to alkynyl, alkenyl, and alkyl groups, the cross-coupling is accommodated with the first two of these groups after delivery to the vanadium center, and thereafter, undergoes reductive elimination (Equation (77)).[278] Neither alkynyl–alkynyl coupling nor alkenyl–alkenyl homo-coupling was detected. This group-selective process depends on the structural and electronic

features of the oxovanadium species and reaction conditions. Although the triorganoaluminum species is less reactive as a nucleophile than the corresponding ate complex, even the former neutral species are capable of cross-coupling under more drastic conditions. At higher temperatures, aryl(diethyl)aluminums undergo ethyl–aryl cross-coupling in the presence of $VO(OEt)Cl_2$.

(77)
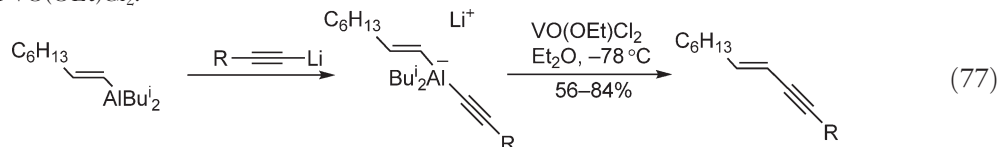
In another reaction, alkynyl groups were transferable in the presence of a catalytic amount of Me_3Al (Equation (78)).[279] Preference for the Ph group transfer has been well featured in the competitive alkyl transfer process leading to selective imine arylation (Equation (79)).[280,281] Higher organic chains such as ethyl and butyl are generally less reactive than a methyl group, as evidenced from the reaction of the corresponding aluminum ate complex hybridized with those different alkyl groups. This order of reactivity was validated by recent examples of oxirane ring opening[282] (Equation (80)) and Meerwein pinacol-type rearrangement (Equation (81)),[283] both of which are accompanied by subsequent methylation. A notable discrepancy is evident in light of the dissociation energy of Al–Me ($283.6\,kJ\,mol^{-1}$), Al–Et ($272.5\,kJ\,mol^{-1}$), Al–Pr ($273.1\,kJ\,mol^{-1}$), and Al–Bu ($280.3\,kJ\,mol^{-1}$).[36] The methylation proceeded with a stoichiometric amount of Me_3Al and a catalytic amount of BuLi. Note that the ethyl group seems to have higher mobility than the butyl group.[284]

(78)

(79)

(80)

(81)
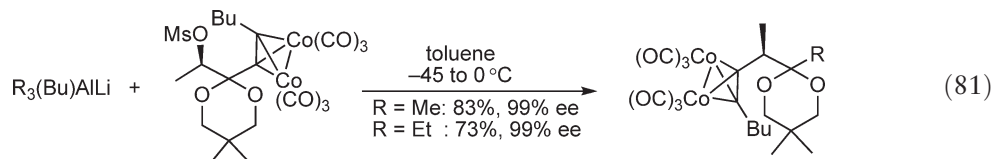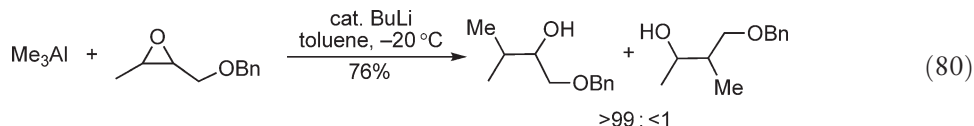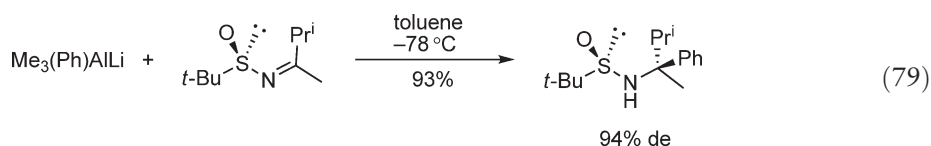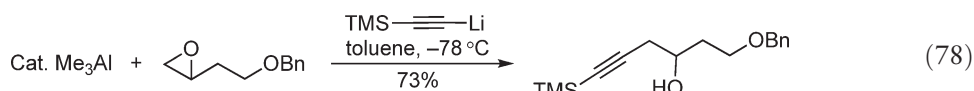
There exist many other examples that illustrate the reactivity of organic groups as well as hydrides bound to aluminum, which sometimes significantly affect the selectivity of the reaction. Notable results were found in older as well as recent literature, describing hydroaluminations (Equation (82)),[285] Beckmann rearrangements (Equation (83)),[286] and epoxide ring-opening alkylations (Equation (84)).[287]

(82)

Bu$^i_2$AlH
CH$_2$Cl$_2$
−78 to 0 °C
94–97%

99 : 1

C$_{11}$H$_{23}$

+

C$_{11}$H$_{23}$

(83)

LiAlH$_4$ + Me$_3$Al
THF, −78 to 0 °C
94–97%

5 : 95

3Me$_3$Al
CH$_2$Cl$_2$, 0 °C
87%

92 : 8 (R = Me)

R^{1}O

OH

R^1 = SiMe$_2$Bu^t

R^{1}O

OH

+

R^{1}O

OH

(84)

BuLi + 3R$_3$Al
CH$_2$Cl$_2$
−30 to 0 °C
92–93%

8 : 92–7 : 93
(R = Me, Et)
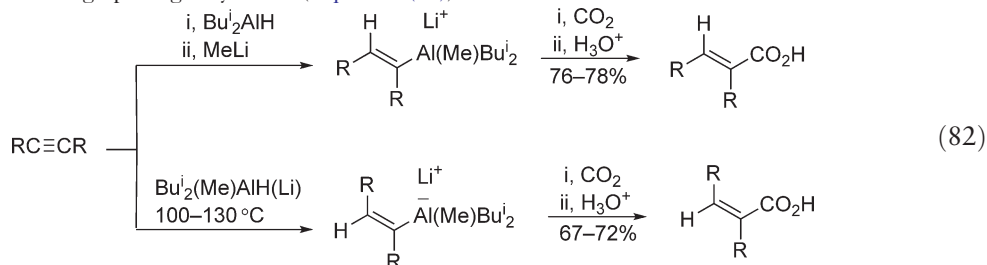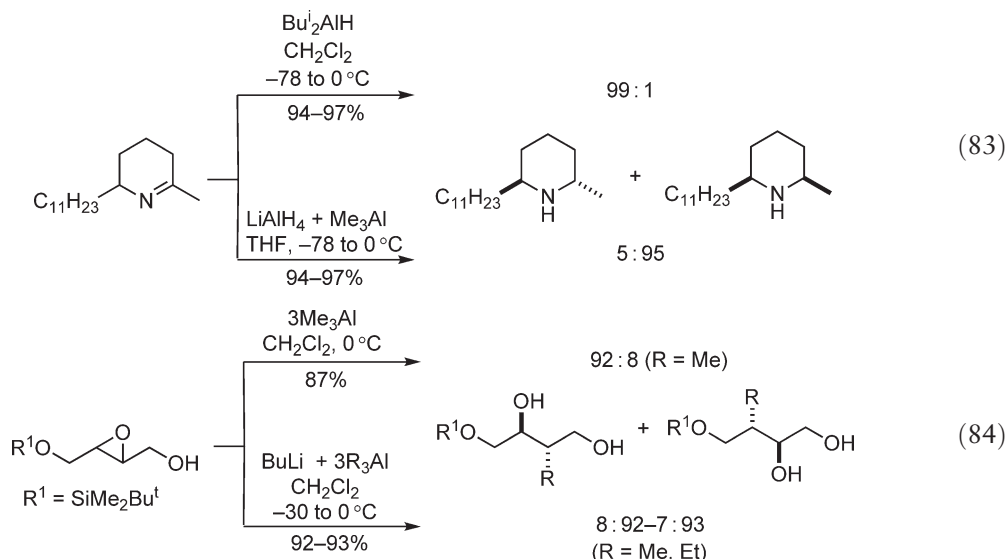
9.06.5 Specialized Topics – Recent Advances in Organoaluminum and Related Compounds as Lewis-Acidic Promoter for Organic Transformations

9.06.5.1 Ligand-induced Geometrical Diversity Affording New Reactivity of Organoaluminum(III) Compounds

Aluminum is most stable as a trivalent metal, adopting trigonal geometry with sp^2-hybridization. Upon coordination with a Lewis base, the geometry changes to sp^3-hybridization, with structures adopting tetrahedral geometry. The geometry of aluminum can, however, be altered significantly by the nature of the ligand attached to it, which sometimes is consistent with hybridization other than sp^2 or sp^3, even though d-orbital hybridization is highly unlikely. The XRD structures of various aluminum(III) complexes indeed support the properties of the geometry of aluminum. For instance, all the (salen)AlX species adopt a square-bipyramidal metal-centered geometry, but the potentially electrophilic nature of the complex is preserved, affording typical Lewis acid-promoted reactions. This and other numerical data are indicative of an available vacant orbital in either the equatorial or apical direction that recalls sp^3d^2, but, if not, that invokes an as yet unknown type of quasi-hybridization, presumably the sum of three independent p-orbitals ($p_x + p_y + p_z$), which can also provide octahedral geometry.

Therefore, it should be pointed out that the catalytic nature of aluminum varies substantially with subtle changes in aluminum geometry. Organoaluminum complexes adopting a higher-coordinate geometry, while retaining Lewis-acidic character, have found broad utility as structurally more stable catalysts or co-catalysts in organic and polymer synthesis. Nelson recently disclosed[288–291] that ligands **42 and 43** had entirely different effects not only on the structural geometry, but also on the carbonyl activation capacity of aluminum. The Lewis acidity of **44** and the distored metal coordination geometry were validated by the reactions, which the corresponding methylaluminum catalysts promoted, and by XRD (Figure 45). The geometry of **45** indicated that the expanded chelate size of the propylene triamine-derived ligand conferred sufficient conformational flexibility to enable the Al(III) ion to adopt a

R
N
NH HN
Tf   Tf
42

Me$_3$Al →

R
N
N–Al–N
Tf   Me   Tf
O
44
Catalytically
active

R
N
N–Al–N
Tf   O Me Tf
45
Catalytically
inactive

← Me$_3$Al

R
N
NH HN
Tf   Tf
43
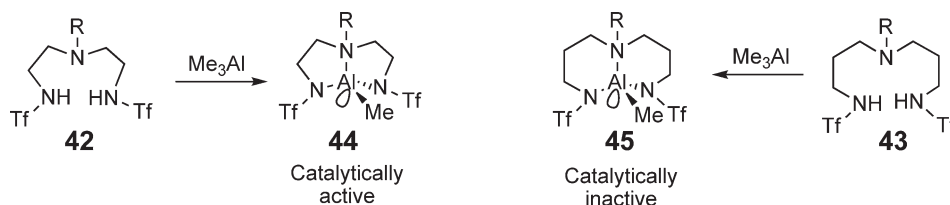
Figure 45 Difference in carbonyl activation capacity imposed by chelation ring size of aluminum reagents.
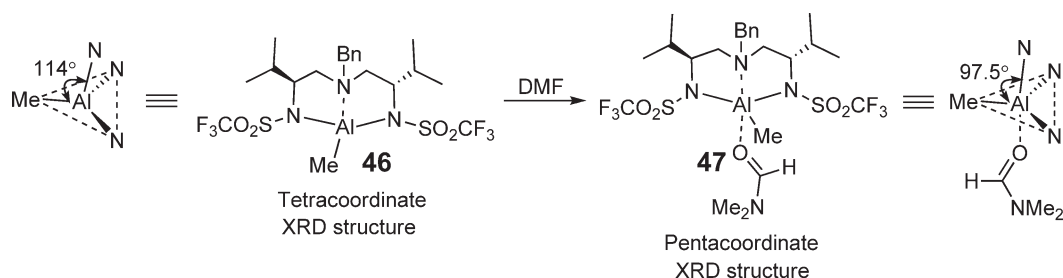
Figure 46 Trigonal bipyramidal geometry accommodated by the fused five-membered rings.
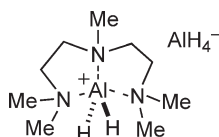
Figure 47 Polyamine-ligated aluminum cation accommodated by the fused five-membered rings.

low-energy, tetrahedral (sp^3-) coordination geometry. The author concluded that other than sp^3, presumably $sp^3 d$-Al(III) hybridization in **44** and **46** furnished a low-lying metal-centered LUMO, thus ideally disposing the Al(III) center to accommodate a fifth ligand in order to complete the trigonal-bipyramidal coordination geometry, and achieving a Lewis acid–base complex such as **47** (Figure 46). Conversely, the electron-rich, highly coordinated complex **45**, lacking any ligand-imposed coordinative distortion, has minimal Lewis-acidic character. Subsequent studies substantiated the catalytic versatility of this type of structure, for example, **48**, in a range of typical Lewis acid-catalyzed reactions (Equation (85)).[289–291] In fact, penta- and even hexacoordinate species, frequently found in organoaluminum complexes, are accommodated by at least one five-membered metallacycle produced from multidentate ligands. An earlier example of a polyamine-ligated aluminum cation represents a higher coordinate, similar to those generated by Nelson (Figure 47).[292]

$$(85)$$
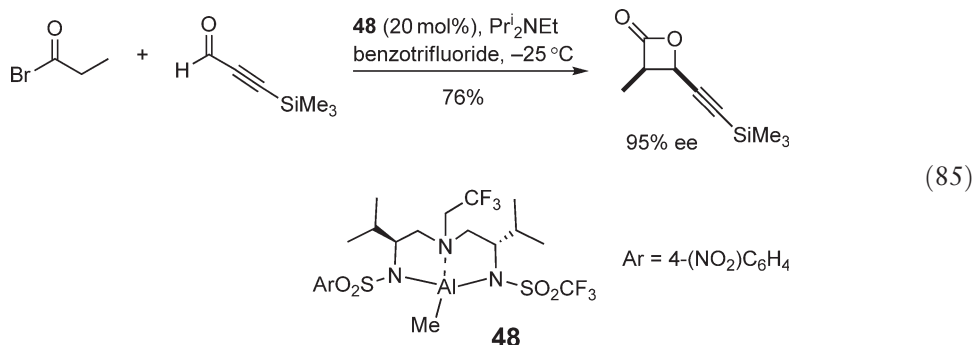
In contrast, such higher coordinates seem relatively unusual for a simple six-membered metallacycle, being liberated from a substantial distortion. In some cases, however, a ligand-imposed coordinative distortion arises, exposing an available vacant orbital for the six-membered metallacycle. For example, a 1:1 mixture of BnOH and the organoaluminum compound bearing amine bis(phenolate) proved to catalyze the living anionic polymerization of ε-caprolactone with narrow MWD (~1.1).[293] The XRD structure of **49** adopts a distored tetrahedral geometry corresponding to four coordinate; however, to keep the living polymerization nature, each aluminum alkoxide intermediate must accommodate the binding of an incoming substrate, adopting a consistent five-coordinate geometry in each propagation step (Figure 48). The aluminum-centered trigonal-bipyramidal geometry is also explicitly indicated in another example of a seven-membered metallacycle (Figures 49 and 50).[294] This higher-coordination geometry is not as distored as that attained by a five-membered ring; hence, one plausible explanation for the higher
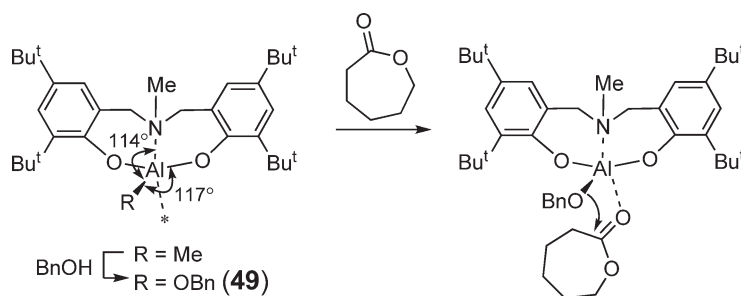
Figure 48 Trigonal bipyramidal geometry possibly accommodated by the strain of fused seven-membered rings.
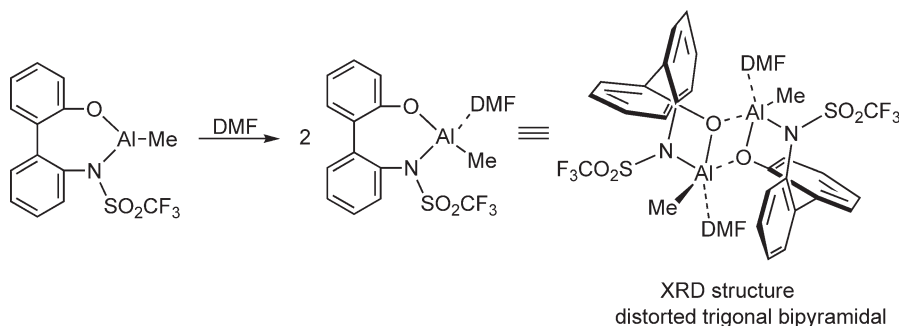
Figure 49 Trigonal bipyramidal geometry possibly accommodated by electron-withdrawing ligand.
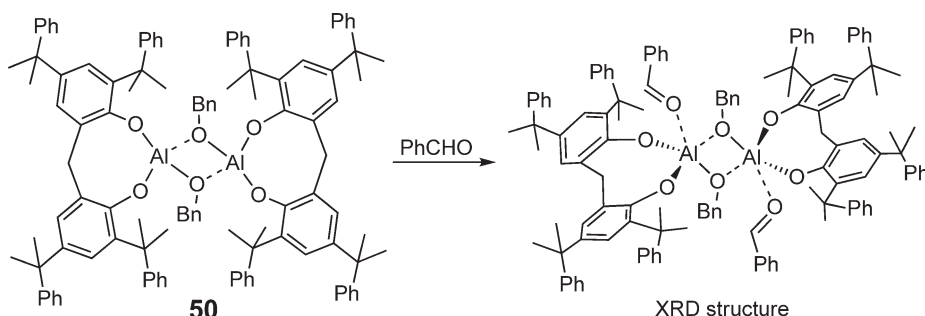
Figure 50 Trigonal bipyramidal geometry possibly accommodated by the strain due to steric bulk of the highly oxygenated seven-membered metallacycle.

coordinate is that it seems to be induced by the additional action of a strong electron-withdrawing ligand. It is well known that by lowering the metal-centered LUMO with more electronegative groups on the metal center, tin and silicon adopt higher-coordination geometry – penta- and hexacoordinates. Similarly, a newly available vacant orbital might be exposed on the aluminum center. According to a survey of the number of XRD structures of aluminum complexes, it would be reasonable to state that the more electronegative the group attached covalently to an aluminum center, the more feasible a higher coordination. The geometrical change from tetra- to pentacoordinate was indeed observed in another example of the highly oxygenated seven-membered metallacycle, upon coordination of benzaldehyde to the tetracoordinated dimer **50** (Figure 50).[295]

9.06.5.2 Cationic Organoaluminum Compounds

Neutral organoaluminum(III) compounds have broad applicability in organic synthesis as extremely strong Lewis-acidic reaction promoters. However, the exploration of increased reactivity in aluminum is a key subject for expanding their utility, especially in polymer synthesis and in the activation of relatively stable substrates

(e.g., CO and CO$_2$). One of the first cations structurally characterized and described in early literature were extraordinarily septacoordinate.[296] Multi-oxygen pentacoordinate crown ethers were also introduced.[297] Subsequently, four-coordinate cations started emerging in the literature (Equation (86)).[298–301] They were too reactive and labile to be used broadly in synthetic applications.

$$\text{Me}_2\text{AlBr} \ + \ 4\text{NH}_2\text{Bu}^t \ \xrightarrow{\text{toluene}} \ \overset{\displaystyle \text{Br}^-}{\underset{\displaystyle \underset{\text{Me}\quad\text{Me}}{\text{Al}}}{\text{Bu}^t\text{H}_2\text{N} \overset{+}{} \text{NH}_2\text{Bu}^t}} \tag{86}$$
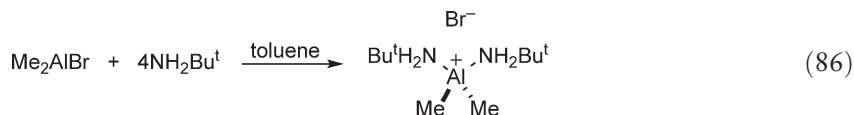
So far, cationic organoaluminum species are likely to be kept more stable if the following conditions are satisfied: (i) the electron richness around the aluminum atom is enhanced by multidentate ligand attachment, or especially by achieving higher coordination at aluminum; and (ii) a vacant aluminum orbital is superimposed on an expanded array of π-orbitals provided by the attachment of a bidentate ligand, where the metallacycle accommodates effective electron delocalization. The significant contribution of the latter criteria can be found in the following examples (Equations (87)–(90)). The imine fragment provides a cyclic π-conjugated system to enable electron delocalization that stabilizes the aluminum cation; otherwise, merely ligand exchange takes place (Equation (87)).[302,303]

$$\text{(structure)} + 1/3 \text{ B(C}_6\text{F}_5)_3 \xrightarrow[\text{reflux}]{\text{toluene}} \text{(structure)} + 1/3 \text{ BMe}_3 \uparrow \tag{87}$$

Ar = 2,6-(Pr^i)$_2$C$_6$H$_3$

$$\text{(structure)} + \text{B(C}_6\text{F}_5)_3 \xrightarrow{\text{toluene-}d_8} \text{(structure)} \quad \text{MeB(C}_6\text{F}_5)_4 \tag{88}$$

$$\text{(structure)} + 1/2 \text{ B(C}_6\text{F}_5)_3 \xrightarrow[\substack{23\,°\text{C} \\ 83\%}]{\text{CD}_2\text{Cl}_2} \text{(structure)} \quad \text{MeB(C}_6\text{F}_5)_3 \tag{89}$$

$$\text{(structure)} + [\text{Ph}_3\text{C}]^+[\text{B(C}_6\text{F}_5)_4]^- \xrightarrow{\text{toluene-}d_8} \text{(structure)} \quad \text{B(C}_6\text{F}_5)_4 \tag{90}$$
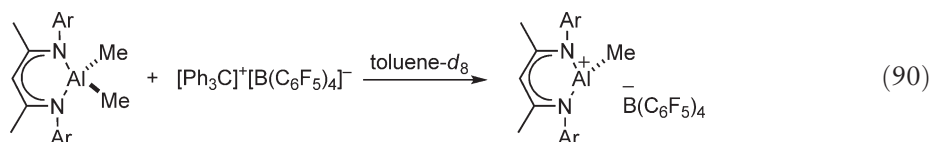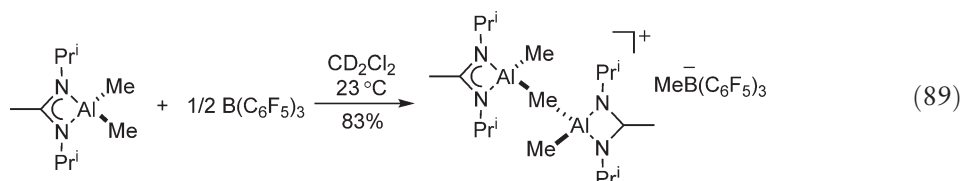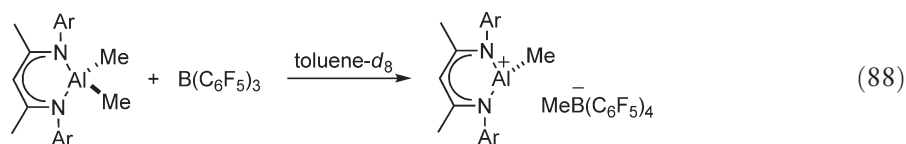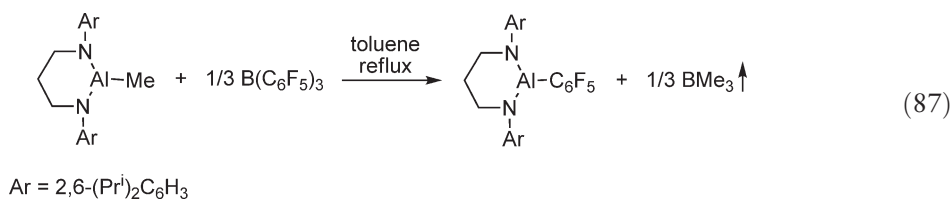
These electronic and geometrical characteristics can lead to the cationic center persisting for a reasonable lifetime. Representative examples of the general formula denoting the distinct coordination modes of aluminum cations are summarized in Figure 51. Each structure (51(a)–51(j)) was optimized through changes in ligand constituents and/or in the geometry around the aluminum atom. Cationic aluminums incorporating amidinate (Equation (89)),[304] β-diketiminate (Equation (90)),[305–307] and aminotroponiminate (Figure 52),[308–310] have been introduced by Jordan, and their catalytic applications in olefin polymerization have been thoroughly investigated.

Abstraction of one ligating group from an aluminum center is carried out to generate aluminum cations. This has been done in several ingenious ways. For example, protonated amines (Equation (91)) and B(C$_6$F$_5$)$_3$ (Equation (92)),[311] as well as carbocations such as trityl cation (Equation (90)), facilitate removal of an alkyl group from the aluminum atom. These processes end up with the favorable liberation of the corresponding hydrocarbons or formation of a strong B–C or C–C bond. In order to detach Al–halogen bonds, an ion pair such as NaBPh$_4$ was used to precipitate the sodium halides out of the solution (Equation (93)).[312] An attempt to prepare low-coordinate aluminum cations, by reaction of the aluminum iodide adducts with NaBPh$_4$, was unsuccessful, and resulted merely
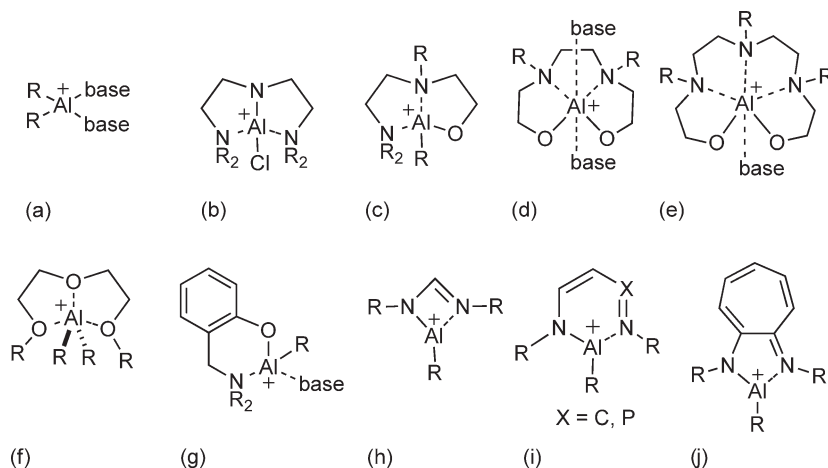
Figure 51 Distinct coordination modes of aluminum cations.
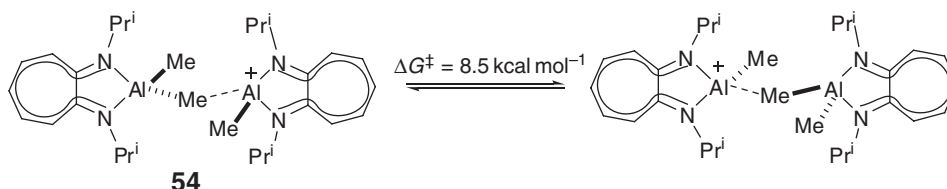
Figure 52 Energy barrier upon conformational change or cation exchange in the complex of neutral and cationic aluminum aminotroponiminate.

in phenylation products (Equation (94)).[313] In another example, MX_3 (M = Al, Ga; X = alkyl, Cl) was utilized to promote the formation of ate complexes such as $AlCl_4^-$[312] (Equation (93)) and $GaCl_4^-$.[314] In special cases, upon treatment with H_2O, such cations are generated automatically. These cationic species apparently show a Lewis acidity much greater than the parent neutral Al(III) species in many cases.

(91)

(92)

(93)

X = $AlCl_4$ or BPh_4

$(TMP)_2AlI(pyridine) + NaBPh_4 \longrightarrow (TMP)_2AlPh + Ph_3B(pyridine)$

(94)

TMP =
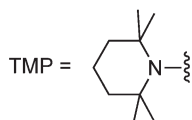
In 1988, Evans featured the high reactivity and importance of cationic aluminum species in organic synthesis.[315] Excess R_2AlCl (R = Me, Et) was found to behave differently from less than 1 equiv. of R_2AlCl in the Diels–Alder reaction of the oxazolidinone derived from an α,β-unsaturated carboxylic acid (Equation (95)). The reactivity and diastereoselectivity of the reaction strongly depends on the stoichiometry of the organoaluminum Lewis acid used to catalyze the reaction. The equilibrium $2[Et_2AlCl] \rightarrow [Et_2Al]^+ + [Et_2AlCl_2]^-$ is reinforced by unknown factors, and is invoked to account for this unusual observation. Thereafter, Castellino focused on the solution structure of the Et_2AlCl–**51** complex and supported Evans' hypothesis (Equation (96)).[316] The main species formed initially with 1 equiv. of Et_2AlCl was assumed be **52**. The species when 2 equiv. of Et_2AlCl is present was assumed to be **53**. Al-complex **53** was proved to be responsible for the high level of diastereocontrol. This conclusion was reconfirmed by an additional experiment, in which a similar cationic intermediate was generated through a separate pathway (Equation (97)). The formation of cationic aluminum species was facilitated by mixing **52** with sodium tetrakis{[3,5-bis(trifluoromethyl)phenyl]} borate.[316] This protocol to generate cationic aluminum species was subsequently utilized in the chelation-controlled Mukaiyama-aldol reaction, giving high *anti*-selectivity.[317] In all these cases, stabilization of the aluminum center with a multidentate chelation structure, facilitated by no more than two oxygen atoms of reactants and/or products, might help to accommodate the $[Et_2Al]^+$ species. Very recently, icosahedral carboranes of the type $CB_{11}H_6X_6^-$ (X = halide) have proved to stabilize $[Et_2Al]^+$, allowing its isolation and structural characterization.[318]
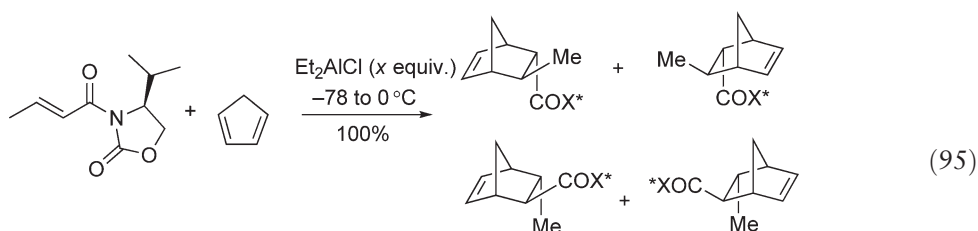
$$\text{Et}_2\text{AlCl (0.8 equiv.)}: endo:exo = 15:1, 70\%\ de$$
$$\text{Et}_2\text{AlCl (1.4 equiv.)}: endo:exo = 50:1, 90\%\ de$$

(96)

(97)
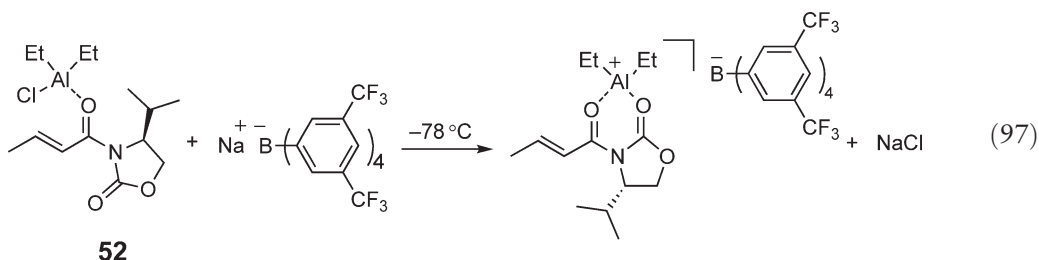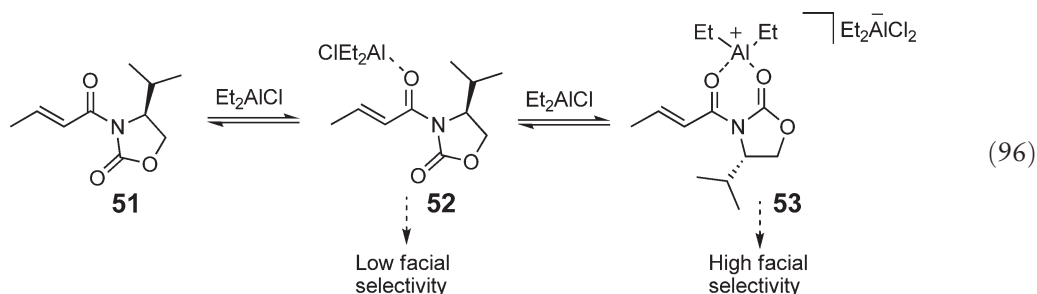
9.06.5.2.1 Low-coordinate cationic organoaluminum(III) compounds (two to four coordinate)

Group 4 elements (e.g., Ti, Zr) are used as typical catalyst precursors for olefin polymerization and serve as potent cationic components for polymer chain growth with the aid of aluminum (e.g., MAO) or boron co-catalysts. It would be more efficient and convenient if organoaluminum cations were used to polymerize olefins. From this viewpoint, following an earlier precedent with two-coordinate cations (Equation (98)),[319,320] some three-coordinate organoaluminum cations hold promise, and their ability to promote polymerization of ethylene or terminal olefins is now

emerging in the literature.[305–310] Very unstable quasi-two-coordinate, cationic aluminum species were also recently characterized.[321] In addition to the three-coordinated species, four-coordinate alkylaluminum cations have begun attracting considerable attention (Equations (99) and (100)).[322,323] A multidentate nitrogen-based structure has now become a platform for these classes of catalyst precursor. Of the two alkyl groups on the cation precursors, one is for abstraction by the co-catalyst (carbocations or $B(C_6F_5)_3$) to form the aluminum cations noted previously. The other can be adjusted in anticipation of insertion of the olefin double bond upon its coordination, that is, for initiation of polymerization. This mechanism is ideal if living polymerization is considered in view of low MWD.

$$(98)$$

$$(99)$$

Ar = $2,4,6\text{-Me}_3(C_6H_2)$

$$(100)$$
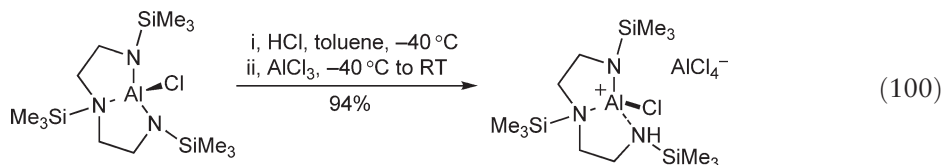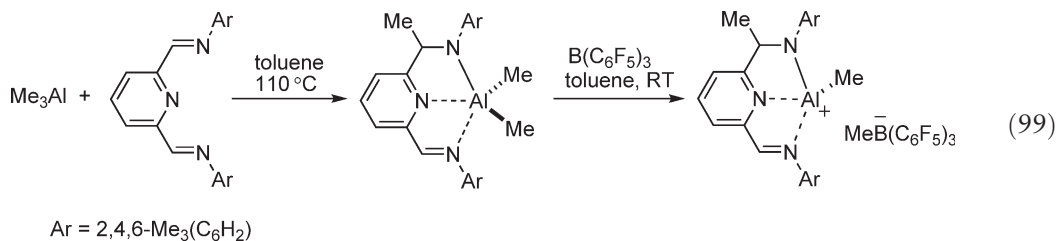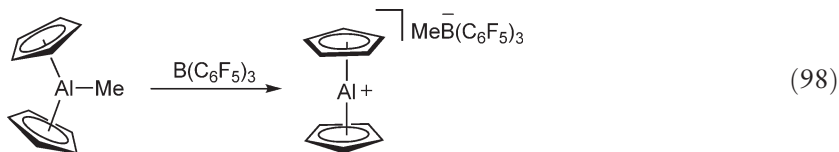
However, there is no clear evidence that supports the living (polymerization) nature. In addition, a theoretical study predicted that none of the proposed active cationic species should give a high molecular mass polymer.[324] The author also concluded that olefin polymerization at a single aluminum center is rather unlikely. Further DFT and *ab initio* calculations agree that the main chain-transfer process is the β-hydrogen transfer to the monomer, and that this is substantially easier than propagation.[325] A renewed interpretation of the NMR studies revealed the predominance of dinuclear aluminum amidinate complexes, for example, **54–57**, formed from the co-addition of the cationic species and the parent neutral species (Figures 52 and 53).[326] From additional theoretical investigations of the simplified model structure (Figure 54), a binuclear complex such as **56** was assumed to be more responsible for the polymerization catalysis,[327] although several issues are thrown into reasonable doubt. A more reliable mechanism awaits for future research.
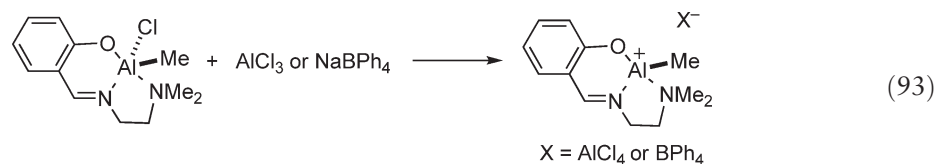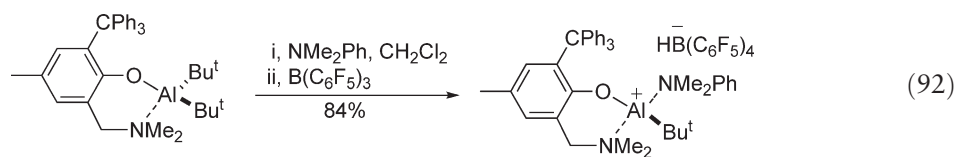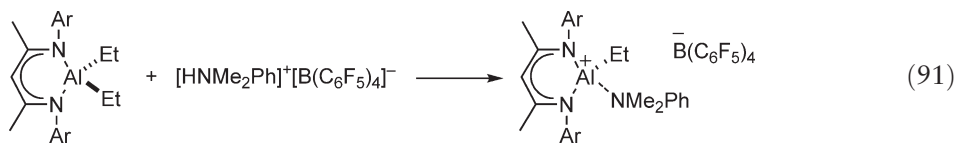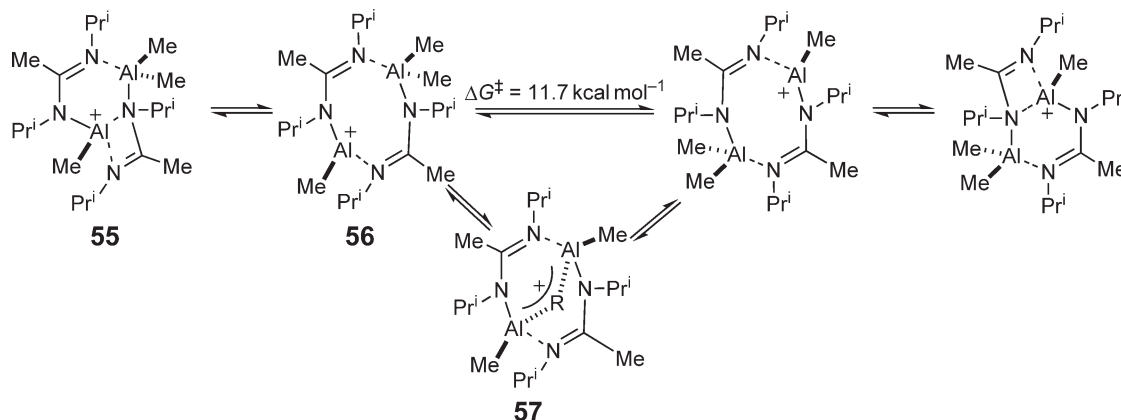

**Figure 53** Energy barrier upon conformational change or cation exchange in the complex of neutral and cationic aluminum amidinates.

Least reactive   Most reactive
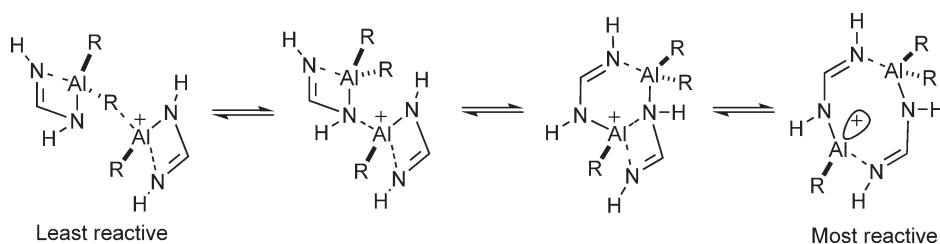
Figure 54 Theoretical results obtained from the calculation of model structure of aluminum amidinates.

9.06.5.2.2 High-coordinate cationic organoaluminum(III) compounds (five or six coordinate)

To date, a range of six-coordinate aluminum cations and their neutral precursors (latent cations) have been synthesized and isolated, and their XRD structures are identified.[328–333] In particular, salen-based aluminum cations and their latent cations are the most widely investigated in terms of substantiating their structures, coordination aptitude, and reactivity in organic synthesis as well as in polymerization processes. Subtle changes in the structure of the salen-based ligand had a significant effect on the coordination sphere in the octahedral geometry of the aluminum atom (Figures 55 and 56).

Although (salen)Al cations **58–61** are bound to two identical molecules that occupy two vacant orbitals to complete the octahedral geometry, a distinct mode of occupation is perceptible. Two H_2O molecules are in a *cis*-relationship for **61**,[328] while two THF,[329] MeOH,[330,331] or H_2O[330,332] molecules are in two apical positions corresponding to a *trans*-relationship in **58–60**. Of particular note is that structure **61** has one of the phenoxy oxygen atoms in the apical direction, whereas neutral species **62** accommodates the two phenoxy oxygen atoms in equatorial positions, or a distored trigonal-bipyramidal geometry. The fact that none of the cations degrades in water or in alcoholic solvents hints at potential aqueous, and thereby environmentally benign, processes. Due to the high oxophilicity of the salen-based aluminum cations, in certain cases, the homodimer formation prevails against solvation that would insufficiently stabilize the monomer, even though steric constraint is more substantial in the dimer (Figure 57).[333] Compound **64** was used as a catalyst precursor for living polymerization of lactide with a very narrow MWD. Production of the oxo-bridged dimer **65** is also possible (Figure 58),[334] and this type of compound has been used as an asymmetric catalyst by Jacobsen (Equation 104).[335] There exist many other organoaluminum variants adopting a five-coordinate geometry,[336,337] in which oxygen and/or nitrogen atoms are incorporated into a bidentate or tridentate ligand. These are strong candidates for the generation of cationic aluminum species, but have not yet been used as such.
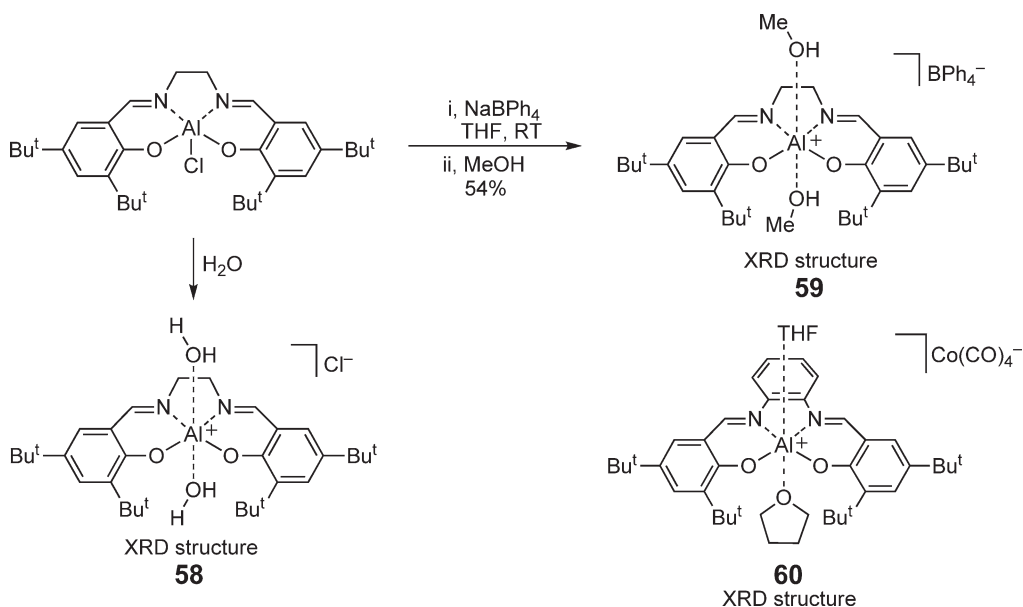
Figure 55 Salen–Al(III) complexes formed upon coordination at the two apical sites.
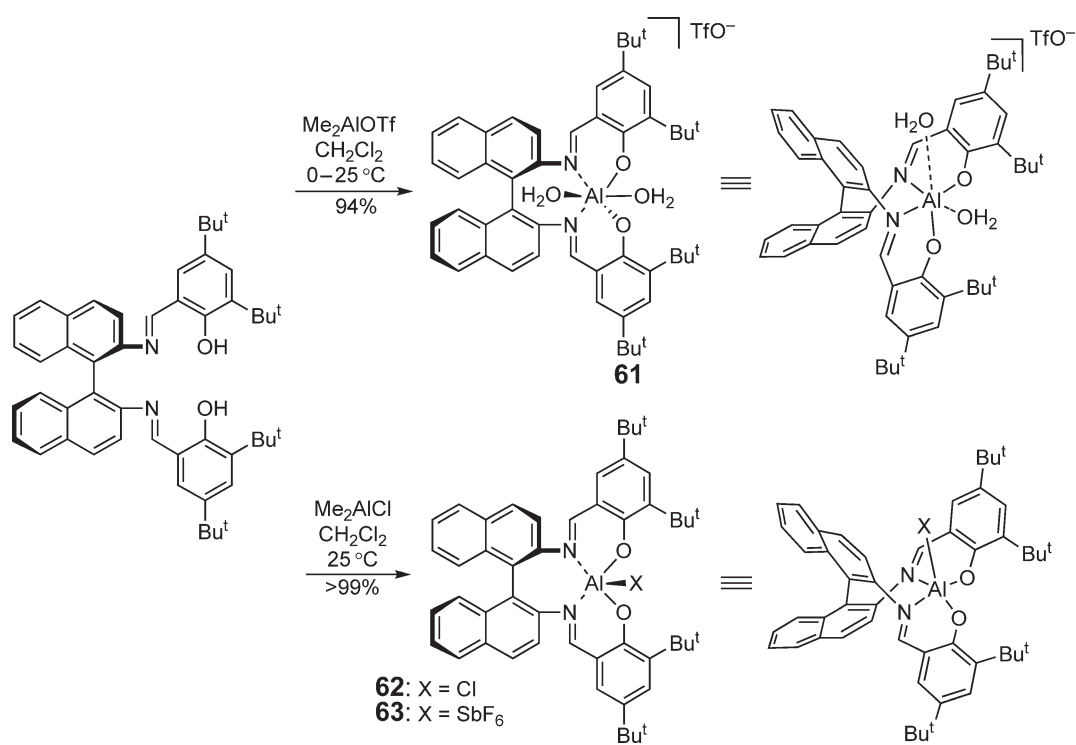
Figure 56 Difference in coordination site for phenoxy ligand.
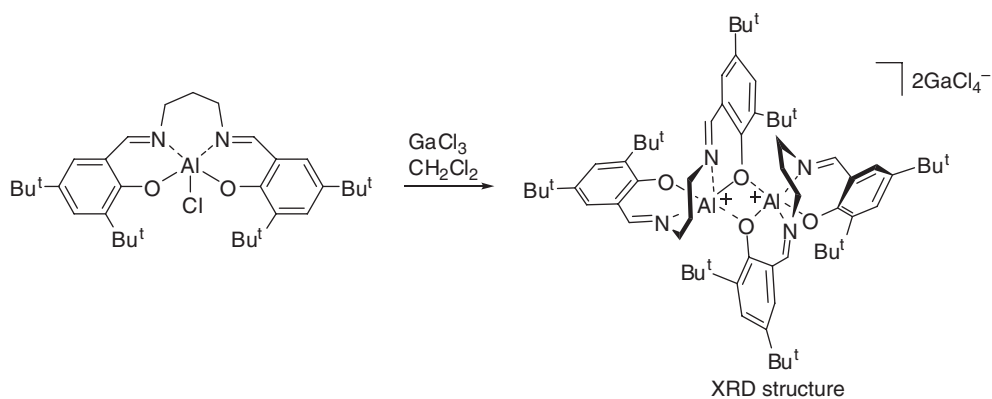
Figure 57 Dimerization of Salen–Al(ɪɪɪ) cation.
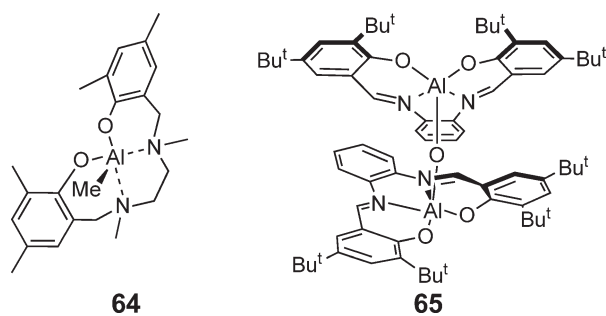
Figure 58 Oxo Salen–Al(ɪɪɪ) dimer.

These salen-based, highly coordinated aluminum cations were found to be very versatile catalysts in the asymmetric aldol reaction[328,338] (Equation (101)) and β-lactone formation upon reaction of oxiranes with carbon monoxide (Equation (102)).[329] In contrast, their precursors, that is, latent cations, have been thoroughly investigated as catalysts in the anionic polymerization of lactides,[339–344] and co-polymerization between oxiranes and carbon dioxides.[345,346] A narrow MWD, characteristic of living propagation, is generally attained with (salen)aluminum alkoxides. A series of latent cations were also widely used as effective catalysts in various bimolecular transformations and asymmetric syntheses. These include cyclic carbonate formation,[345] the Strecker reaction (Equation (103)),[220] and conjugate addition (Equations (104) and (105)).[335,347,348] By taking advantage of this rather water and air inert nature, the improvement of turnover number and frequency in the performance of these catalysts remains a significant challenge for the future.

$$
\text{4-Me(C}_6\text{H}_4) \overset{\text{N}}{\underset{\text{O}}{\diagup}} \text{OMe} \;+\; \text{ArCHO} \quad \xrightarrow[\substack{>95\%}]{\substack{\textbf{63}\,(5\,\text{mol}\%) \\ \text{CH}_2\text{Cl}_2,\,25\,°\text{C}}} \quad \text{4-Me(C}_6\text{H}_4) \overset{\text{N}}{\underset{\text{O}}{\diagup}} \overset{\text{CO}_2\text{Me}}{\text{''Ar}} \quad >95\%\ \text{ee} \tag{101}
$$

$$
\text{Et} \overset{\text{O}}{\triangle} \;+\; \text{CO} \quad \xrightarrow[\substack{>99\%}]{\substack{\textbf{60}\,(1\,\text{mol}\%) \\ 50\,°\text{C},\,880\,\text{psi}}} \quad \text{Et} \overset{\text{O}}{\underset{\text{O}}{\square}} \tag{102}
$$

$$
\underset{\text{Ph}}{\overset{\text{N}}{\diagup}}\!\!\text{H} \;+\; \text{TMSCN} \quad \xrightarrow[\substack{91\%}]{\substack{\text{i, (salen)AlMe (5\,mol\%)} \\ \text{toluene, }-70\,°\text{C} \\ \text{ii, CF}_3\text{CO}_2\text{H}}} \quad \underset{\text{Ph}}{\overset{\text{HN}}{\diagup}}\!\!\text{CN} \quad 95\%\ \text{ee} \tag{103}
$$

$$
\underset{\text{Pr}^i}{\diagup}\!\!\overset{\text{O}\quad\text{O}}{\underset{\text{H}}{\diagup\text{N}\diagup}}\!\!\text{Ph} \;+\; \text{(CN)CH}_2\text{CO}_2\text{Me} \quad \xrightarrow[\substack{89\%}]{\substack{(S,S)\text{-[(salen)Al]}_2\text{O (5\,mol\%)} \\ \text{Bu}^t\text{OH, cyclohexane} \\ 23\,°\text{C}}} \quad \underset{\text{NC}}{\overset{\text{O}\quad\text{O}}{\underset{\substack{\text{H} \\ \text{CO}_2\text{Me}}}{\diagup\text{N}\diagup\text{Ph}}}}\!\!\text{Pr}^i \quad 95\%\ \text{ee} \tag{104}
$$

$$
\overset{\text{O}}{\underset{\text{O}}{\square}}\!\!\text{NEt} \;+\; \text{HN}_3 \quad \xrightarrow[\substack{93\%}]{\substack{\text{(salen)AlN}_3\,(10\,\text{mol}\%) \\ \text{toluene, }-30\,°\text{C}}} \quad \underset{\text{N}_3}{\overset{\text{O}}{\square}}\!\!\text{NEt} \quad 94\%\ \text{ee} \tag{105}
$$
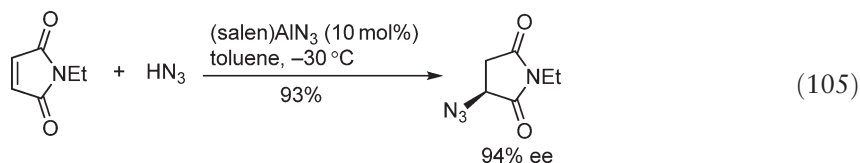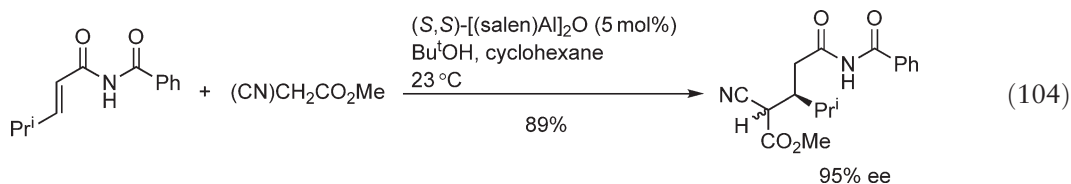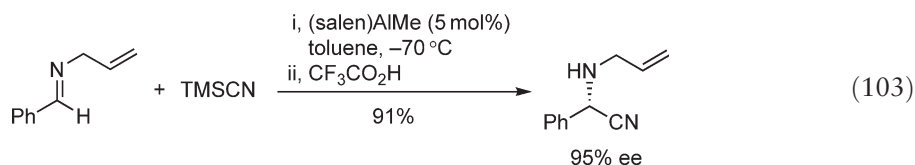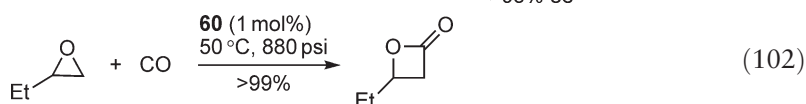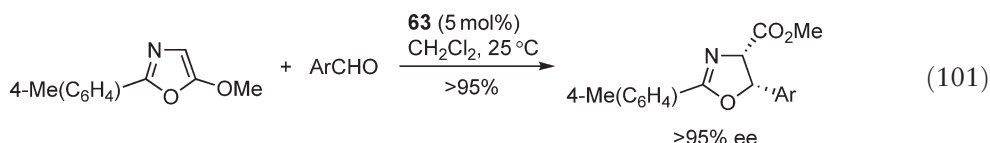
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