Organoaluminum chemistry at the forefront of research and development

M. Witt and H. W. Roesky*

Institut für Anorganische Chemie der Universität Göttingen, D-37077 Göttingen, Germany

Aluminum, the third most abundant element on the earth's crust, occurs predominantly in oxidic and silicatic minerals. It was first obtained in a pure elemental form by F. Wöhler in 1827 by the reduction of $AlCl_3$ with elemental potassium. In 1859 W. Hallwachs and S. Schafarik synthesized the first organoaluminum compound $Et_3Al_2I_3$ from elemental Al and EtI[1], but it took almost 100 years before K. Ziegler[2] discovered the synthetic and catalytic potential of organoaluminum compounds. He was awarded the Nobel prize in 1963 together with G. Natta for the discovery of low pressure polymerization of olefins with organoaluminum/transition metal catalysts. His pioneering work opened up a whole new field of organometallic chemistry not only in synthetic organic chemistry and catalysis but also in the development of precursors of inorganic high-tech materials such as ceramics, semiconductors, zeolites and others. The increasing activity in aluminum chemistry is well documented by the growing number of original papers, patents, books and periodical reports[3-9]. Organoaluminum chemistry is sometimes hampered by the pyrophoric nature, kinetic instability and volatility of the compounds, together with a sometimes low tendency to crystallize which makes it rather difficult to characterize the compounds completely. Recent developments in organoaluminum chemistry have overcome these difficulties by the use of bulky substituents and stabilizing coordinative ligands. Due to the electron-deficient character of aluminum it has a unique co-ordination chemistry, second in main group chemistry only to its lighter homologue boron.

Low valent aluminum compounds

ORGANOALUMINUM compounds with Al–Al bonds are accessible via two different routes: i) the reduction of organoaluminum halides with the oxidation state (+III) or ii) reaction of metastable solutions of the high-temperature molecules 'AlX' (X = Cl (refs 10–12), Br (ref. 10), I (ref. 13)), available by reaction of Al atoms

This paper is dedicated to Prof. S. S. Krishnamurthy on the occasion of his 60th birthday.

*For correspondence. (e-mail: hroesky@gwdg.de)

with HX in the gas phase at 1000°C or by comproportionation of Al with $AlCl_3$ at 850°C (ref. 12), with alkalior-

ganyls at low temperatures[14-17]. The halides are monomeric in the gas phase and oligomeric in solution below –100°C. Higher temperatures lead to disproportionation into metallic Al and AlX_3. However, they can be stabilized by donor molecules. Several of them have been characterized by X-ray diffraction, they contain planar four-membered Al_4 rings with the halogens and the donors mutually *trans*, e.g. $(BrAl·NEt_3)_4$ (ref. 18), $(IAl·NEt_3)_4$ (ref. 13) and $(IAl·PEt_3)_4$ (ref. 19).

They are stable as solids at r.t. but disproportionate even at low temperatures in solution into Al(0) and Al(+II), some with ligand exchange. Thus, dimeric complexes $(X_2Al·L)_2$ have been synthesized and most of them structurally characterized with the donor ligands in *trans*-positions: X = Cl, Br, L = Me_2NSiMe_3 (ref. 20), X = I, L = OEt_2, PEt_3 (ref. 20) and X = Br, L = OMePh (ref. 21). The latter has been obtained by comproportionation of 'AlBr' with inadvertently present $AlBr_3$ due to the method of synthesis in the presence of anisole. In the light of these results the high-pressure dehalogenation or comproportionation reactions at 120°C described by G. A. Olah *et al.* as well as the claim of a monomeric species $Cl_2Al·3Py$ (Py = pyridine) seem rather doubtful[12].

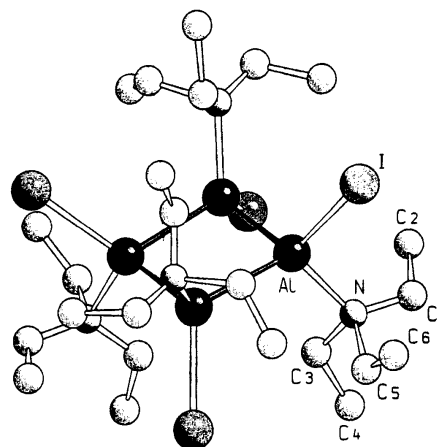The first reports on low-valent organoaluminum compounds by E. P. Schram and co-workers date back to the

Figure 1. Structure of $(IAl·NEt_3)_4$ (from ref. 13).

late sixties, who investigated the reaction of $[(Me_2N)_2B]_2$ with $AlMe_3$. They claimed the synthesis of yellow materials of the composition $Me_6Al_4(Me_2N)_3B$ (ref. 22) with an $Al(Al)_3$

core and $Me_3Al_3(NMe_2)_3$ (ref. 23), respectively, with an Al_3 chain based on elemental analysis, IR and NMR spectra and oxidative hydrolysis. Another doubtful compound of composition $[(H_2B)_2Al]_2$ 'proved' by deuterolysis was added later[24]. Hoberg and Krause reported the reduction of iBu_2AlCl with K to yield $(iBu_2Al)_2$ which they claimed through solvolysis with MeOD (ref. 25). Further reduction performed by Schram was believed to result in a compound $K_3Al_5iBu_{10}$ with an Al_5 chain via intermediate KAl_2iBu_3 (ref. 26). By repeating the reaction of iBu_2AlCl with K, Uhl and co-workers[14] unambiguously proved the 'compound' to be a mixture of $K(iBu_3AlCl)$, $K(iBu_2AlCl_2)$ and another species (vide infra). Similar reductions reported by Hoberg et al. of iBu_3Al to yield $K_2(AliBu_3)_2$ (ref. 27) and Et_3Al via radicalic $K(AlEt_3)$ to finally yield $K(AlEt_4)$ (ref. 28), had to be revised, the former was also found to be a tetraorganoaluminate[29]. Similarly, the compound $K_2(iBu_2AlH)_2$ reported by Gavrilenko et al.[30] was found to be $K(iBu_3AlH)$[31].

The first authentic and structurally characterized compound with an Al–Al bond was reported by Uhl in 1988, who reduced Bis_2AlCl ($Bis = (Me_3Si)_2CH$) with elemental K and obtained $(Bis_2Al)_2$ as colourless crystals[32]. The X-ray structure reveals an almost planar $C_2Al–AlC_2$ core. A second dialuminum compound, $(Trip_2Al)_2$ ($Trip = 2,4,6-iPr_3C_6H_2$) was synthesized in 1993 by Power et al.[33] and fully characterized.

The attempted synthesis of a sterically crowded alane Sil_3Al ($Sil = tBu_3Si$) afforded under elimination of Sil_2 another dialane $(Sil_2Al)_2$ instead[34]. Treatment of $(Sil_2Al)_2$ with bases like LiMe or LitBu results in the formation of anionic

species $(Sil_2Al–AlSil_2X)^-$, $X = Me$, H, the latter by elimination of isobutene. Both compounds have been structurally characterized[35] with $(Li\cdot2Tmeda)^+$ ($Tmeda = (Me_2NCH_2)_2$) as the counterion. Simple addition of LiBr to a solution of the dialane in the presence of Tmeda yields the same type of anion with $X = Br$ (ref. 36). Reaction of the dialane with stronger bases like LiBis or $LiCH(PMe_2)_2$ results under C–H bond activation by the base in the formation of an anion with a five-membered Al_2C_2Si ring as shown by X-ray structure analysis[37].

Conducting the same reaction at lower temperatures results in a blue solution giving an ESR-signal with 11 lines indicating the formation of a radical anion, $(Bis_2Al)_2^{\cdot-}$ with the position of an additional electron between the two Al atoms. The same anion has been obtained from the reaction of the neutral dialane with Na or K in Dme (Dme = dimethoxiethane)[38] or Li in Et_2O. The X-ray structure of $(Li\cdot2Tmeda)^+(Bis_2Al)_2^{\cdot-}$ has been reported[39]. The analogous anion $(Trip_2Al)_2^{\cdot-}$ has been synthesized from the neutral alane and Li in the presence of donors like Tmeda or 12-crown-4, the former has been structurally characterized[33].

Heating the dialane $(Sil_2Al)_2$ to 80°C affords a black-green solution assigned to the neutral radical $Sil_2Al–AlSil^\cdot$ by ESR spectroscopical investigations. Further heating of this radical or the dialane to 135°C results in the low yield formation of $(SilAl)_4$ (vide infra)[34]. All reactions of dialanes are summarized in Scheme 1.

The first tetrahedranes of Al were published in 1991 independently by Schnöckel et al.[40], $(Cp*Al)_4$ from
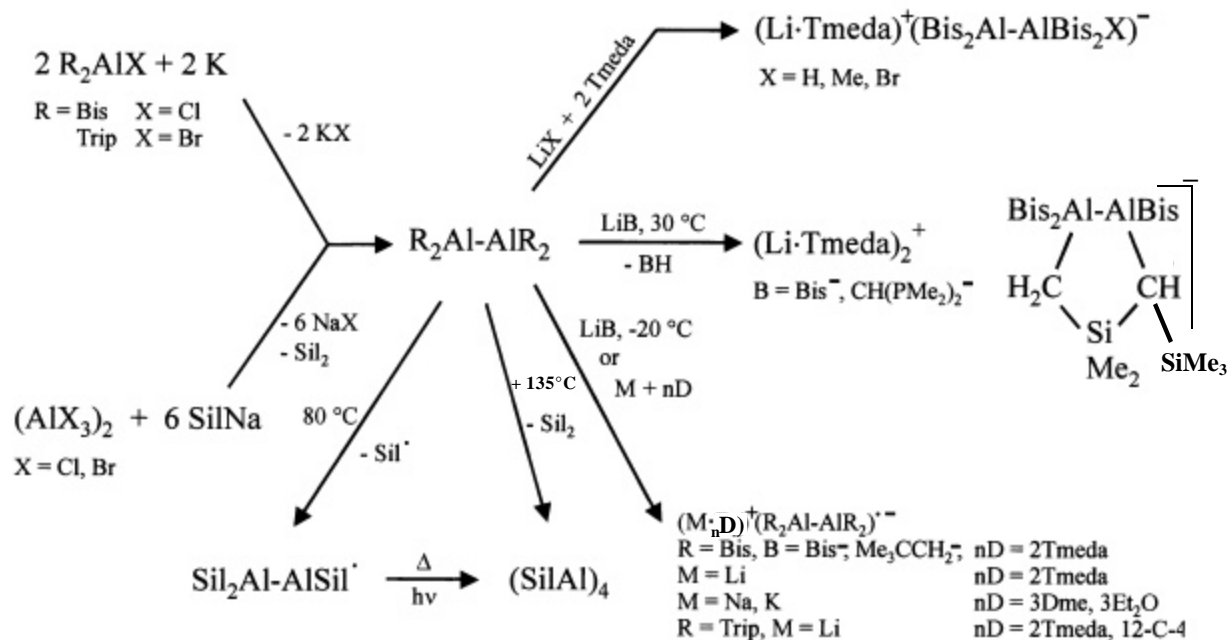
Scheme 1. Reactions of dialanes.

'AlCl' and $MgCp*_2$, and Wiberg and co-workers, $(SilAl)_4$ from 'AlCl' and NaSil (ref. 41) in moderate yields. While the former has been structurally characterized, spectroscopical

and structural data on the latter have become available only recently[42,43]. Slightly better yields of $(Cp*Al)_4$ (ref. 44) and a third structurally characterized Al_4 tetrahedron $(TrisAl)_4$

(Tris = (Me$_3$Si)$_3$C) (ref. 45) have been obtained by reductive dechlorination of the appropriate dichlorides with K or Na/K, respectively. All these compounds are red in colour, their X-ray structures reveal tetrahedral Al$_4$ cores in the solid state. A brown compound with the formula (Me$_3$CCH$_2$Al)$_4$ has been reported from the reduction of (Me$_3$CCH$_2$)$_2$AlCl with K via transient [(Me$_3$CCH$_2$)$_2$Al]$_2$ but was not fully characterized[46].

While mass spectroscopical investigations of (TrisAl)$_4$ show the molecular ion[46], and M/2 has been found in the MS of (SilAl)$_4$ (ref. 42), the monomeric unit Cp*Al has been detected as the peak of highest mass from (Cp*Al)$_4$ (refs 40, 44). This is consistent with gas phase electron diffraction studies of (Cp*Al)$_4$ at ca. 140°C which show monomeric Cp*Al with the ligand bound in a $\%^5$ fashion[47]. A mixed substituted compound, [(Cp*Al)$_3$-AlN(SiMe$_3$)$_2$], available from (Cp*Al)$_4$ and LiN(SiMe$_3$)$_2$ under elimination of LiCp*, has been structurally characterized[48]. Several substituted cyclopentadienyl aluminum compounds have been generated *in situ* and investigated by ^{27}Al-NMR spectroscopy. While [(Cp*Al)$_3$AlCp], (CpAl)$_4$, (tBuC$_5$H$_4$Al)$_4$ and [(Cp*Al)$_3$AlN(SiMe$_3$)$_2$] do not dissociate in solution, iPr$_4$C$_5$HAl, (Me$_3$Si)$_3$C$_5$H$_2$Al and (PhCH$_2$C)$_5$Al have been found monomeric and for (Cp*Al)$_n$ and [(Me$_3$Si)$_2$C$_5$H$_3$Al]$_n$ both oligomers (n = 1, 4) have been detected[48].

The reaction of 'AlCl' with LitBu affords NMR spectroscopically traceable (tBuAl)$_6$ which after reduction with Na/K alloy yields the radical anion (tBuAl)$_6^{\bullet-}$. Its equidistant 31 lines ESR spectrum is consistent with an octahedral structure. Theoretical calculations confirm this structure, though a dianion was predicted to be more stable. No attempts have been made to isolate the substances from solution[49].

As mentioned above, from the reduction of iBu$_2$AlCl with K a third compound is isolable in 1.5% yield. X-ray structure investigations show the compound to have the formula K$_2$(iBuAl)$_{12}$ with an icosahedral dianion isoelectronic to the homologous boranate anion[50].

A 'carbaaluminane' of composition [(MeAl)$_8$-(CCH$_2$Ph)$_5$H] is available in 60% yield from the reaction of Me$_2$AlH with Me$_2$AlC≡CPh in an approximately 2:1 molar ratio. Its structure is best described as a distorted Al$_8$ cube with five planes bridged by a $\%_4$-C atom and the remaining by $\%$-H (see Figure 2.) (ref. 51).

The reaction of 'AlCl' with LiN(SiMe$_3$)$_2$ at –78°C affords in 4% yield a compound (Li·3Et$_2$O)$^+${[(Me$_3$Si)$_2$-NAl]$_3$}$_2$($\%_6$-Al)$^-$. The Al$_7$ unit can be regarded as a section of a cubic centered packing[52].

From the analogous reaction of 'AlBr' with LiN(SiMe$_3$)$_2$ a black compound of composition [(Me$_3$Si)$_2$N]$_{20}$Al$_{77}$ has been isolated in very low yield. Its X-ray structure reveals a shell-

a

like array of Al atoms not identical with the arrangement in the metal. The (Me$_3$Si)$_2$N ligands span Al$_4$ planes[53].

A compound of composition (Cp*$_3$Al$_5$I$_6$) has been obtained in low yields as colourless crystals unstable at r.t. from a suspension of (Cp*Al)$_4$ and excess [I$_2$Al(%-I)]$_2$ in PhMe at –20°C. The X-ray structure shows a rather distorted geometry with a Cp*Al–Al(I)$_2$–AlCp* chain and a Cp*Al–AlI$_2$ moiety connected by two bridging I atoms. Its genesis can be rationalized by insertion of monomeric Cp*Al fragments into three of the four bridging Al–I bonds of dimeric AlI$_3$ (ref. 54).

Bond activation by aluminum compounds

As soft Lewis acids organoaluminum compounds can polarize rather unpolar bonds and form adducts. This has widespread use in organoaluminum chemistry[3,8,9]. Another 'trivial' case is the C–O bond fission of ethers[55]. But sometimes direct involvement resulting in complex formation is observed, some of the cases are compiled here.

Oxidative insertion of low-valent Al compounds in the C–O bonds of certain ethers has been observed in several cases. Storing the deep blue solution of the radical species (K·3Dme)$^+$(Bis$_2$Al)$_2^{\bullet-}$ with excess K over a longer period at r.t. results in decoloration and an oxoaluminate is formed in low yields, which is also accessible directly from Bis$_2$AlMe and KO(CH$_2$)$_2$OMe in Dme (eq. 1). The analogous Li compound is also available from the reaction of excess Li with (Bis$_2$Al)$_2$ in Dme[56].

$$(K\cdot3Dme)^+(Bis_2Al)_2{}^{\bullet-} \rightarrow K$$

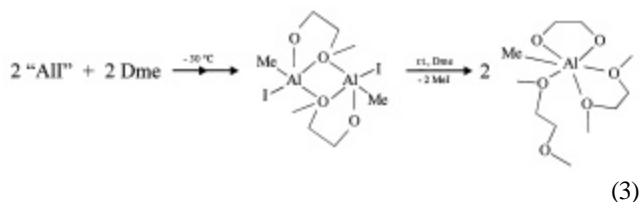$$\xleftarrow{\text{Dme}} 2Bis_2AlMe + 2KO(CH_2)_2OMe \qquad (1)$$
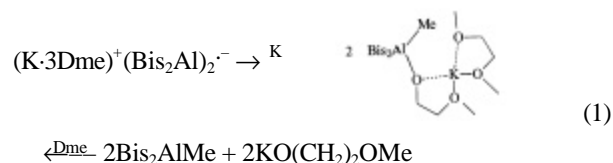
While the reductive dehalogenation of TrisAlCl$_2$ results in the formation of a Al(+I) compound (*vide supra*), with the adduct TrisAlCl$_2$·Thf the oxidation state (+III) at Al is preserved by ring opening of the Thf (eq. 2). The X-ray structure of this complex has been determined[45].

$$2 \text{ TrisAlCl}_2\cdot\text{Thf} \xrightarrow{\text{Na/K alloy}}$$

$$(2)$$

c

b

d
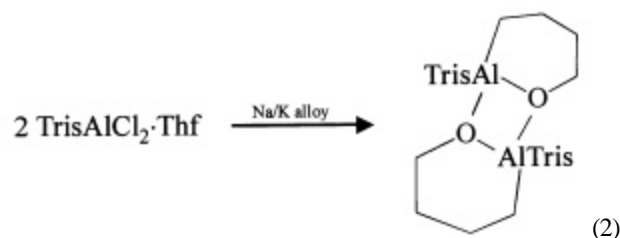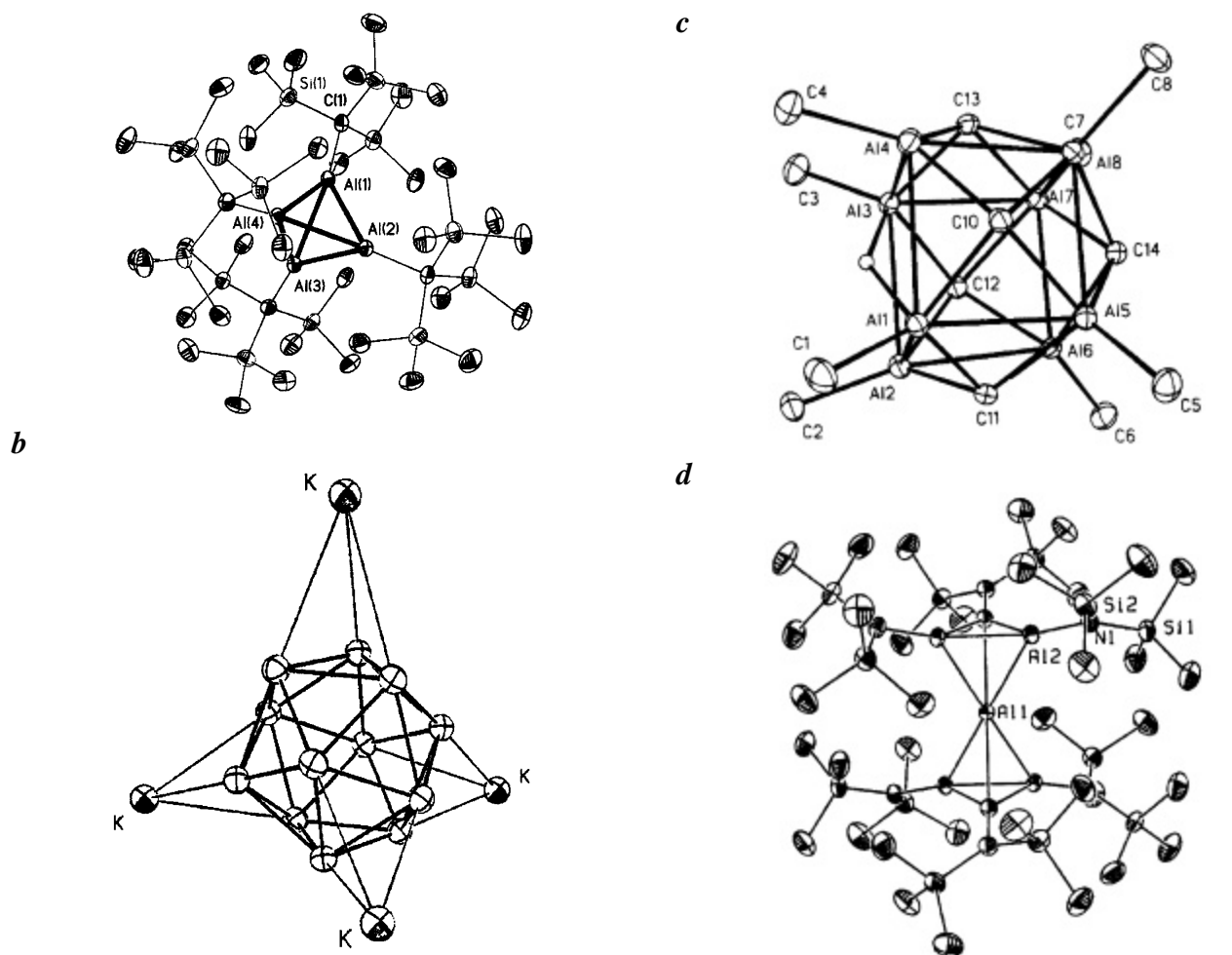
Figure 2. Structures of $(TrisAl)_4$ (from ref. 45), $(iBuAl)_{12}^{2-}$ (from ref. 50), $[(MeAl)_8(CCH_2Ph)_5H]$ (from ref. 51) and $\{[(Me_3Si)_2NAl]_3\}_2(\%_6\text{-}Al)^-$ (from ref. 52) (outer substituents partially omitted for clarity).

A similar, but five-coordinated Al species has been ob-tained and crystallographically characterized from a solution of metastable 'AlI' in Dme at –30°C which on prolonged standing results under elimination of MeI in a six-coordinated Al complex (eq. 3). All products and intermedi-ates have been assigned by means of ^{27}Al-NMR spectros-copy[57].

$$2 \text{ "AlI"} + 2 \text{ Dme} \xrightarrow{-30\,°C} \text{Me}\begin{array}{c}O\\|\\Al\\|\\I\end{array}\begin{array}{c}O\\|\\Al\\|\\O\end{array}\text{Me} \xrightarrow[-2\,MeI]{rt,\,Dme} 2 \text{ Me}\begin{array}{c}O\\|\\Al\\|\\O\end{array}O$$

(3)

A double C–O bond fission of Thf has been found in at-tempts to recrystallize compounds of the type Ar(R)NAlF$_2$·Thf, where either Ar or R have less steric re-quirements (Ar = 2,6-Me$_2$C$_6$H$_3$, R = Me$_2$*t*BuSi, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, R = Me$_3$Si) than in the compounds
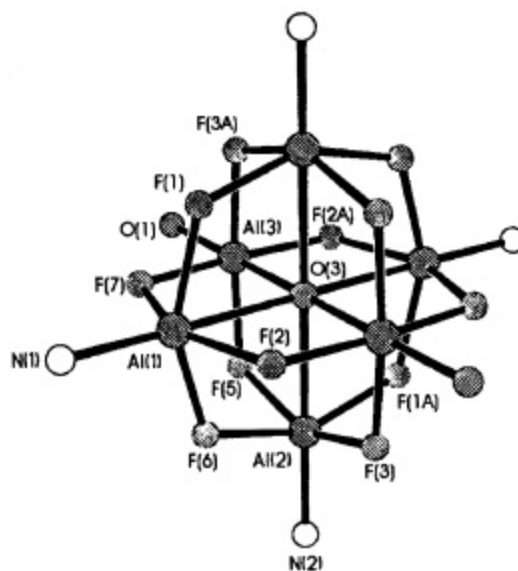
Figure 3. Core of the hexakistetrahedron of $\{[Ar(R)NAlF_2]_4$ $(AlF_2\cdot Thf)_2(\%_6\text{-}O)\}$ (N bound ligands and Thf-C$\heartsuit$s omitted for clarity) (from ref. 58).
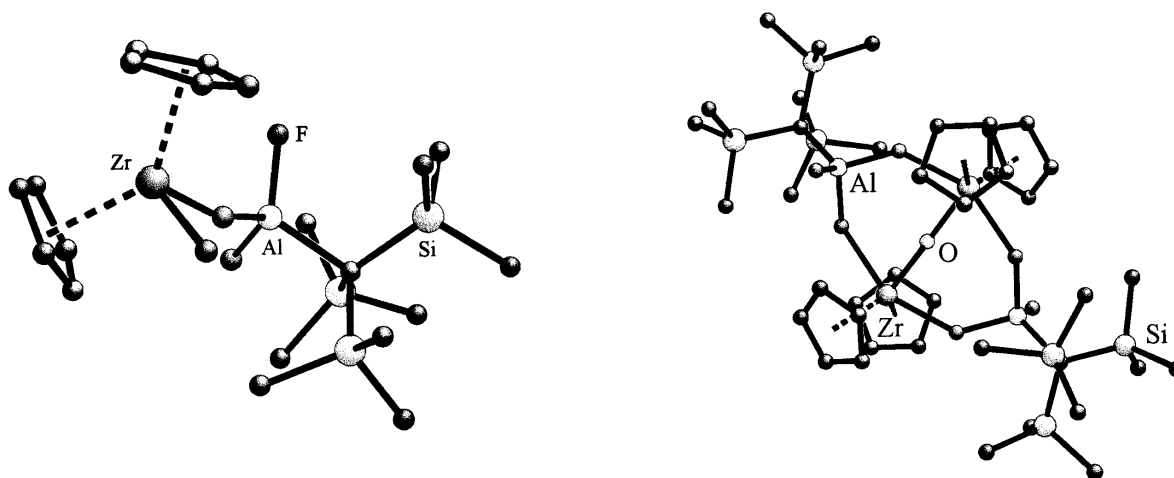
Figure 4. X-ray structures of [Cp$_2$ZrMe($\%$-F)AlF$_2$Tris] and {[Cp$_2$Zr(μ-F)$_2$AlFTris]$_2$($\%$-O)} (from ref. 59).

with Ar = 2,6-iPr$_2$C$_6$H$_3$, R = Me$_2$$i$PrSi or Me$_2$$t$BuSi, where 'normal' Thf adducts have been obtained. Under elimination of two amine molecules clusters are formed with an interstitial six-co-ordinated oxygen atom (Figure 3) surrounded by an Al$_6$F$_{12}$ cage. The oxygen unambiguously arose from cleavage of Thf, since careful hydrolysis experiments resulted in the formation of the corresponding fluorosilanes and unidentified Al species[58].

Attempts to recrystallize the addition product of (TrisAlF$_2$)$_3$ (*vide infra*) with Cp$_2$ZrMeF from Thf always resulted in mixtures of the expected complex Cp$_2$ZrMe($\%$-F)AlF$_2$Tris with [Cp$_2$Zr($\%$-F)$_2$AlFTris]$_2$-($\%$-O), the O atom spanning the two Al atoms arising from cleavage of Thf (Figure 4). The whereabouts of the Me groups remain unclear[59].

The first examples of C–H bond activation have been found in cyclopentadienyl complexes. The reaction of Cp$_2$TiCl with Et$_3$Al was first reported by Natta *et al.* in 1959 (ref. 60) and its structure was determined as (Cp$_2$TiAlEt$_2$)$_2$ with the Al atom bound to Ti and one C atom of a cyclopentadienyl ring and a Ti–Ti bond[61]. Later, Tebbe and Guggenberger revised the reaction and redetermined the structure (Figure 5). The Et$_2$Al fragment had inserted into a C–H bond of one cyclopentadienyl ring, the H atom bridging Ti and Al, while the Ti atoms are bonded $\%^5$ to one Cp ring, $\%^5$ to the Al substituted cyclopentadienyl ring and $\%^1$ to the C atom bearing the Et$_2$Al unit[62].

While in the reactions of Cp$_2$TiCl, Cp$_2$TiCl$_2$ and Cp$_2$TiPh refluxing PhMe is required[62], the reactions of Cp$_2$TiF$_2$ with equimolar Et$_3$Al or [Cp$_2$Ti($\%$-F)$_2$AlEt$_2$]$_2$ with additional Et$_3$Al afford this compound already at r.t.[63].

The reaction of Cp*$_2$TiCl with LiAlH$_4$ with inadvertently present H$_2$O results in low yields in the compound depicted in Figure 6 with abstraction of one H atom from a methyl group of one Cp* ring[64].
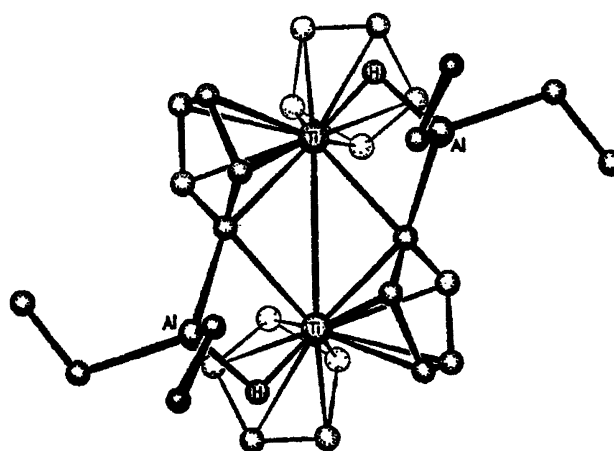
Figure 5. Structure of [CpTiC$_5$H$_4$AlEt$_2$($\%$-H)]$_2$ (from ref. 62).

Two groups have independently investigated the reaction of Cp$_2$MoH$_2$ with Me$_3$Al. They isolated and structurally characterized two compounds with a Mo$_2$Al$_3$– and a Mo$_2$Al$_4$ core (Figure 7) both arising from C–H bond fission of Cp rings[65–69]. The Mo–Al(Me$_2$) bonds in the Mo$_2$Al$_3$ compound are much longer than the Mo–Al(Me) bonds suggesting possible Mo($\%$-H)Al bridges[66,68]. A totally insoluble compound with W$_2$Al$_3$ core analogous to the Mo$_2$Al$_3$ compound has also been synthesized and characterized by elemental analysis and comparison of the IR spectra[69,70].

The reaction of *bis*(chloromercuri)ferrocene with two equivalents of Me$_3$Al affords in low yield a compound with an Al$_4$Fe$_2$ core. Substitution of Al vs Hg has been assumed as the first step with ensuing Al/H exchange resulting in the dimeric species depicted in Figure 8 (ref. 71).

Robinson and co-workers have studied the reactions of CH$_2$(PPh$_2$X)$_2$ (X = O, S) with trialkylalanes
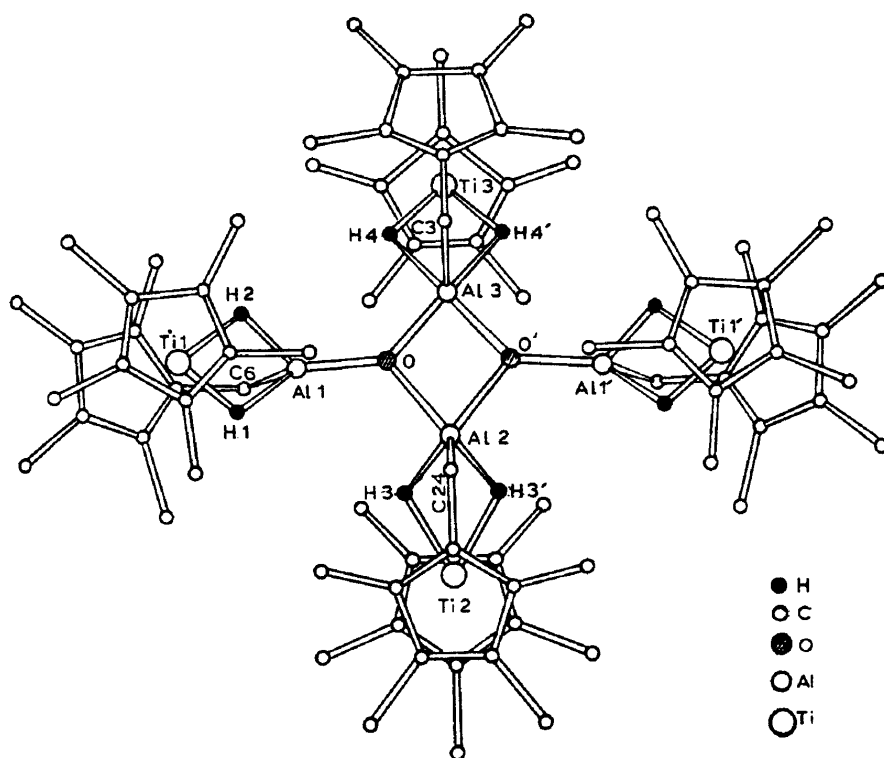
Figure 6. Structure of $\{[\eta^5\text{-}Cp^*Ti(m, \eta^5\text{-}C_5Me_4CH_2)(\mu\text{-}H)_2Al_2](\mu_3\text{-}O)\}_2$ (from ref. 64).

X = S

X = O, R = Me, Et
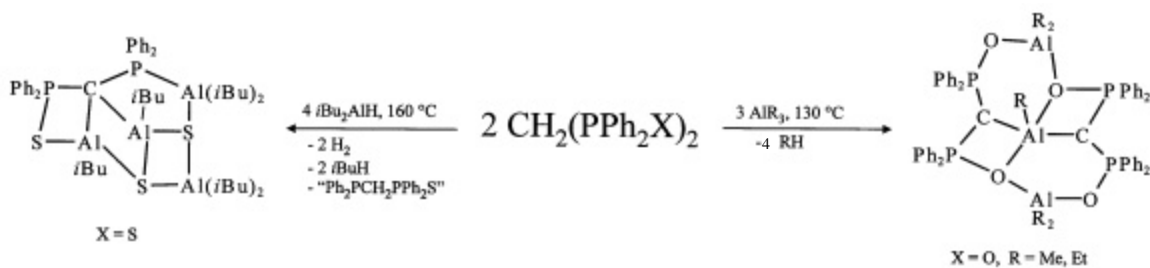
Scheme 2. Reactions of organoaluminum compounds with $H_2C(PPh_2X)_2$.

and diisobutylaluminumhydride. In each case both of the slightly acidic methylene protons are substituted by Al atoms leaving polycyclic compounds shown in Scheme 2 (refs 72–74).

All three compounds have been structurally characterized, the P–S–Al complex arises from simultaneous cleavage of Al–H, Al–C, C–H and P=S bonds, a possible reaction mechanism involves the intermediacy of H_2S (ref. 72). The attempted synthesis of a dimeric iminoalane from thermolysis of $(Me_2AlNHC_6H_2\text{-}2,4,6\text{-}tBu_3)_2$ resulted under loss of methane and cleavage of an o-C–H bond in a dimeric aminoalane as seen from its X-ray structure (Figure 9) (ref. 75).

Similarly, the oxidation of Cp*Al with $MesN_3$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) did not yield the expected dimeric iminoalane, instead the tricyclic compound shown in Figure 10 with migration of a proton of an o-CH$_3$ group to N had formed[76].

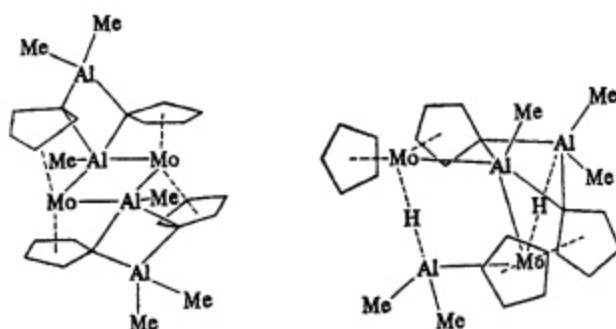**Figure 7.** Structures of the two complexes from the reaction of Cp_2MoH_2 and Me_3Al.

Thermolysis of the adduct $Cl_3Al\cdot NH_2C_6H_2\text{-}2,4,6\text{-}tBu_3$ at 150°C proceeded in a *retro*-Friedel–Crafts reaction under elimination of isobutene to the complex $Cl_3Al\cdot NH_2C_6H_3\text{-}2,4\text{-}tBu_2$ (ref. 75).
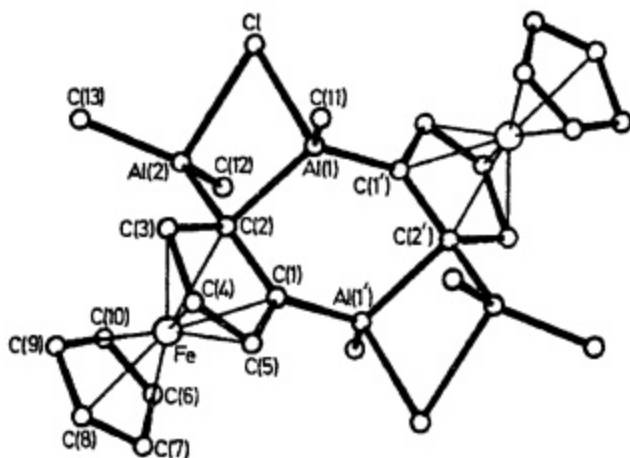
Figure 8. Structure of [CpFe(C$_5$H$_3$)Al$_2$Me$_3$Cl]$_2$ (from ref. 71).
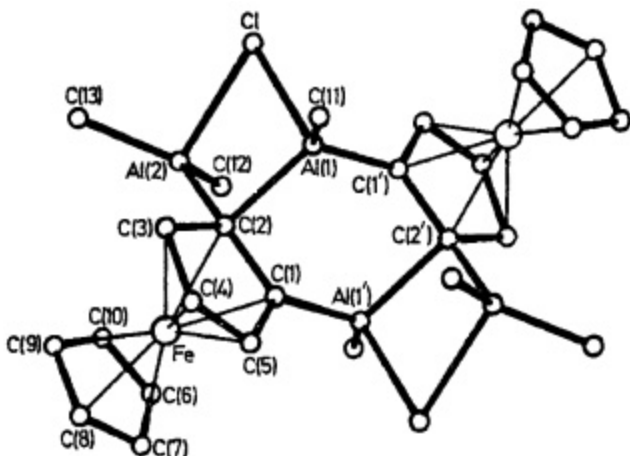

Figure 9. Structure of the dimeric aminoalane by activation of C–H bonds (from ref. 75).
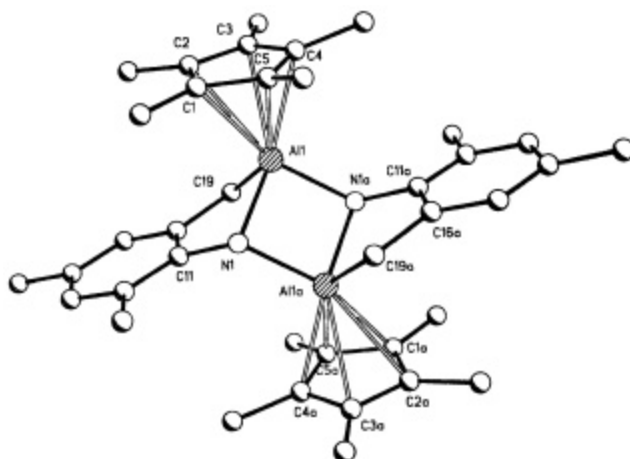

Figure 10. Structure of the dimeric aminoalane by activation of *o*-C–H bonds (from ref. 76).

Ortho-metalation with elimination of *i*BuH has also been found in the thermolysis of the monolithiated dimeric aminoalane [(*i*Bu$_2$Al)$_2$(‰-NHMes)(‰-NLiMes)].
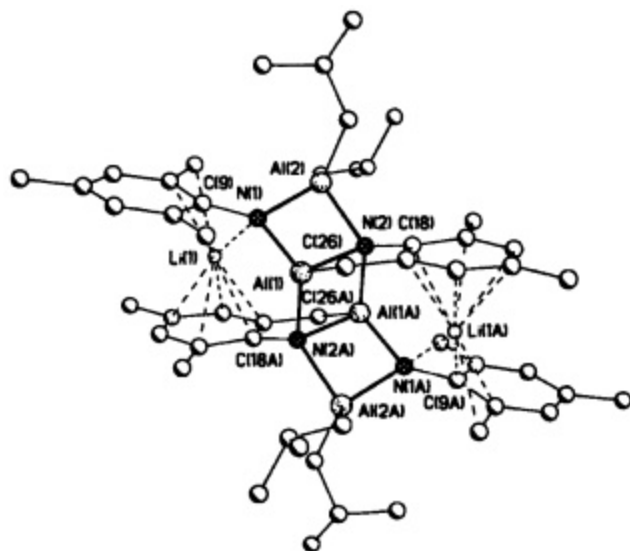
**Figure 11.** Structure of the ladder-shaped dimer from thermolysis of [(*i*Bu$_2$Al)$_2$(‰-NHMes)(‰-NLiMes)] (from ref. 77).

The ladder-shaped complex with an Al$_4$N$_4$ core as revealed from its X-ray structure (Figure 11) has been obtained in low yields after recrystallization from hexane[77].

The reaction of Me$_3$Al with excess Ph$_2$NH in boiling PhMe proceeds in high yield under MeH evolution and *o*-metalation of one Ph group. The X-ray structure of [(‰-Ph$_2$N)$_2$(AlMe)$_2$(‰-PhNC$_6$H$_4$)] shows an Al$_2$N$_2$ four-membered ring with the Al atoms spanned by a NC$_2$ bridge[77a]. Similar *o*-metalations have been postulated earlier from thermolysis of (Et$_2$AlNPh$_2$)$_2$ and Cl$_3$Al·HNPh$_2$. The compounds were characterized by mass spectrometry and deuterolysis experiments, but no structural data are available[77b,c].

The reaction of tetrameric (Cp*ZrF$_3$)$_4$ with 20 equivalents of Me$_3$Al at r.t. affords in high yield a cluster of composition [(Cp*Zr)$_3$Al$_6$Me$_8$(‰$_3$-CH$_2$)$_2$(‰$_3$-CH)(‰$_4$-CH)$_4$] with elimination of methane and (Me$_2$AlF)$_4$, whose structure is depicted in Figure 12. Its most prominent features are the hypervalent carbon atoms bridging the metal centers[78]. Similarly, an (EtC$_5$Me$_4$)Zr cluster and the isostructural Cp*Hf complex have been synthesized, albeit the latter in very low yields, the main product being Cp*HfMe$_3$ via methyl transfer to the transition metal. These compounds have been found to act as methyl and methylidene transfer reagents with aromatic ketones, halides and acid halides[79].

Organoaluminum fluorides

Pioneering work on organoaluminum fluorides has again been achieved by Ziegler and co-workers, who in 1955 reported the reactions of NaF with Et$_3$Al and
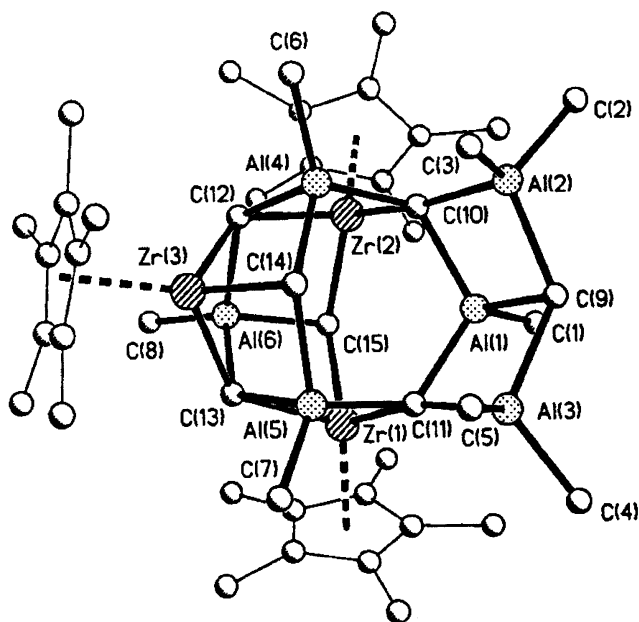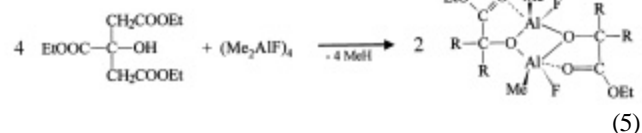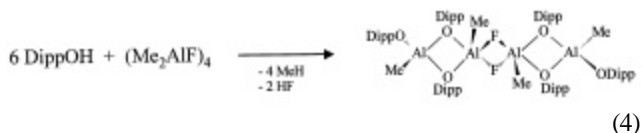
Figure 12. Structure of $[(Cp*Zr)_3Al_6Me_8(\%_3\text{-}CH_2)_2(\%_3\text{-}CH)(\%_4\text{-}CH)_4]$ (from ref. 78).

Me$_2$AlCl to yield Na$^+$ salts of anionic fluoride species (Et$_3$AlF)$^-$, [(Et$_3$Al)$_2$(%-F)]$^-$ and (Me$_2$AlF$_2$)$^-$, respectively[80]. Reviews on organoaluminum fluorides besides those mentioned in the introduction have been published by Weidlein in 1973 (ref. 81) and recently by Roesky *et al.*[82]. Neutral diorganoaluminum monofluorides with various organic substituents (R$_2$AlF)$_n$ are available by metathesis of the appropriate aluminum chlorides with NaF (refs 80, 83–86), higher alkali fluorides[83], BaF$_2$ (ref. 87), by fluorine/alkyl exchange in triorganoalanes with BF$_3$·OEt$_2$ (ref. 88), SiF$_4$, R$_2$SiF$_2$, ZnF$_2$, CdF$_2$, SbF$_3$, PbF$_2$ (ref. 89), by thermal decomposition of the dinuclear species Me$_3$Si(%-F)AlEt$_3$ (ref. 90) and by commutation of AlF$_3$ with Et$_3$Al (ref. 83). Gas phase electron diffraction shows (Me$_2$AlF)$_4$ to exist as a puckered eight-membered ring with Al(%-F)Al bridges[91,92]. Tetrameric aggregates are also existent in solution as seen from cryoscopic molecular weight determinations in benzene of (Me$_2$AlF)$_4$, (Et$_2$AlF)$_4$ (ref. 85) and (tBu$_2$AlF)$_4$ (ref. 88). While the tetrameric unit remains unchanged upon substitution of one Me group on each Al atom by DippNH (Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$) as seen from its EI–MS spectrum[93] with the ligands mutually *trans*, the reaction of (Et$_2$AlF)$_4$ with MeNH$_2$ at r.t. affords a glassy oligomer (MeNHAlEtF)$_x$ of unknown structure[94]. In contrast, trimeric species have been postulated from cryoscopic measurements and IR investigations of (Pr$_2$AlF)$_3$ and (*i*Bu$_2$AlF)$_3$ (ref. 86). A dimeric complex (Tmp$_2$AlF)$_2$ (Tmp = 2,2,6,6-Me$_4$-piperidyl) has been structurally characterized from the reaction of Tmp$_2$AlBr with AgBF$_4$ via intermediate formation of Tmp$_2$Al(%-F)BF$_3$ (ref. 95). At low temperatures monomeric amine adducts Et$_2$AlF·NMe$_3$ and Et$_2$AlF·NH$_2$Me are formed from Et$_2$AlF and the appropriate amine, the former disintegrates into the tetramer and

amine at r.t. while the latter eliminates CH$_4$ (*vide supra*)[94]. A weakly associated tBu$_2$AlF·dioxane complex loses the donor upon distillation[88].

Mononuclear ionic complexes M$^+$(R$_3$AlF)$^-$ are available from stoichiometric reactions of alkali fluorides with trialkylalanes without solvent at >100°C (refs 80, 96) or in solvents at r.t.[97–99]. The X-ray structure of Cs$^+$(Me$_3$AlF)$^-$ shows isolated Me$_3$AlF tetrahedra, the F atoms forming four-membered rings with the Cs atoms which themselves are connected to F atoms of neighbouring units thus forming a two-dimensional network[98]. Cs$^+$(*i*Bu$_3$AlF)$^-$ has also been reported by Neumüller *et al.* but no structural details are given[99]. Anhydrous Me$_4$N$^+$F$^-$ forms a similar complex as do the adducts Et$_3$Al·NMe$_3$ and Et$_3$Al·PMe$_3$ upon reaction with PhCH$_2$F (ref. 97). Addition of a second equivalent R$_3$Al to those complexes results in the formation of dinuclear anions [R$_3$Al(%-F)AlR$_3$]$^-$ (refs 80, 96, 97) with a linear Al(%-F)Al bridge as seen from the X-ray structures of K$^+$[(Et$_3$Al)$_2$(%-F)]$^-$ with weak K–C contacts[100,101] and (K·%^{6}-C$_6$H$_6$)$^+$[(Me$_3$Al)$_2$(%-F)]$^-$ (ref. 102). Mixed anions [R$_3$Al(%-F)AlR$\heartsuit_3$]$^-$ with R, R$\heartsuit$ = Me, Et; Me, *i*Bu; Et, *i*Bu are available from reactions of the mononuclear ionic species with the appropriate alanes[96]. K$^+$ salts of [C$_5$H$_{11}$CH(AlR$_2$)$_2$(%-F)]$^-$ with R = Et, *i*Bu have been described from the reaction of KF with the gem-dialanes C$_5$H$_{11}$CN(AlR$_2$)$_2$ as viscous oils. They are believed to contain a bent Al(%-F)Al bridge, but a dimeric structure with linear units would also be consistent with the analytical data given[103].

A neutral compound with bent Al(%-F)Al bridges has been obtained from the reaction of DippNH$_2$ (Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$) with (Me$_2$AlF)$_4$ at 0°C. Two of the original Al(%-F)Al bridges have been substituted by DippNH fragments yielding an eight-membered ring compound with an Al$_4$N$_2$F$_2$ core. The Al–F bond lengths are similar to those in (Me$_2$AlF)$_4$. An amine adduct Me$_2$AlF·DippNH$_2$ has been considered as intermediate prior to HF elimination. Such an adduct, Me$_2$AlF·tBuNH$_2$, has been found in the reaction with the more basic amine tBuNH$_2$ as an infinite one-dimensional chain connected via H··F hydrogen bonding as the final product[104]. Similar Al–F bond cleavage reactions have been observed in reactions of (Me$_2$AlF)$_4$ with DippOH and triethylcitrate, respectively (eqs 4, 5) and structurally characterized[105].

$$6 \text{ DippOH} + (Me_2AlF)_4 \xrightarrow[-2\text{HF}]{-4\text{ MeH}}$$

$$(4)$$

$$4 \text{ EtOOC}-\underset{\mathrm{CH_2COOEt}}{\overset{\mathrm{CH_2COOEt}}{\underset{|}{\overset{|}{C}}}}-\text{OH} + (Me_2AlF)_4 \xrightarrow{-4\text{ MeH}} 2$$

$$R = CH_2COOEt$$

$$(5)$$

The first compound comprises one of the rare examples containing a four-membered Al_2F_2 ring.

Marks and co-workers have synthesized several cationic Zr complexes of $(Ar_3AlF)^-$ (Ar = 2-nonafluorobiphenyl) (Scheme 3).

The X-ray structures of the Ph_3C^+- and $(Cp^*_2ZrMe)^+$ salts have been determined, the latter shows a linear $Al(\%\text{-}F)Zr$ bridge. Several of the Zr complexes have been found active catalysts for the isotactic polymerization of propene[106].

Reactions of trialkylalanes with $[Cp^\heartsuit TiF(\mu\text{-}O)]_4$ ($Cp^\heartsuit = Cp^*$, EtC_5Me_4) yield adducts $\{[Cp^\heartsuit Ti(\mu\text{-}O)]_4F_n[(\%\text{-}F)AlR]_{4-n}\}$ with almost linear $Al(\%\text{-}F)Ti$ bridges. While the tetrakis- and trisadducts are stable only at lower temperatures, with Me_3Al at r.t. only the *trans*-bisadduct is formed

(Scheme 4). Monoadducts are exclusively formed with the bulkier alanes Et_3Al and $(PhCH_2)_3Al$. Several of the compounds have been structurally characterized[107,108].

Pyrolysis of the above-mentioned compound $[DippNHAlMe(\%\text{-}F)]_4$ (Dipp = $2,6\text{-}iPr_2C_6H_3$) at 165°C yields under elimination of $DippNH_2$ a cubane depicted in Figure 13. Two eight-membered $Al_4F_2N_2$ rings twisted by 90° are connected by F atoms[93].

Information on fluorine-rich organoaluminum compounds was scarce until recently. Ziegler and Köster reported the formation of $EtAlF_2$ from Et_3Al and AlF_3 at higher temperatures[83] or from $EtAlCl_2$ and NaF (ref. 84) and of $Na^+(R_2AlF_2)^-$ (R = Me, Et, Pr, iBu)[80,83,84], a Japanese patent describes the use of $RAlF_2$ compounds (R = Et, alkyl, cycloalkyl, aryl, arylalkyl) as co-catalysts in the polymerization of butadiene with ©-complexes of Ni and Co (ref. 109) and a French patent describes the use of $(Me_3NCH_2Ph)^+$ salts of $(Et_2AlF_2)^-$, $[Et_3Al(\%\text{-}F)AlEt_2F]^-$ and $(EtAlF_3)^-$ as electrolytes for the electrodeposition of Al (ref. 110).
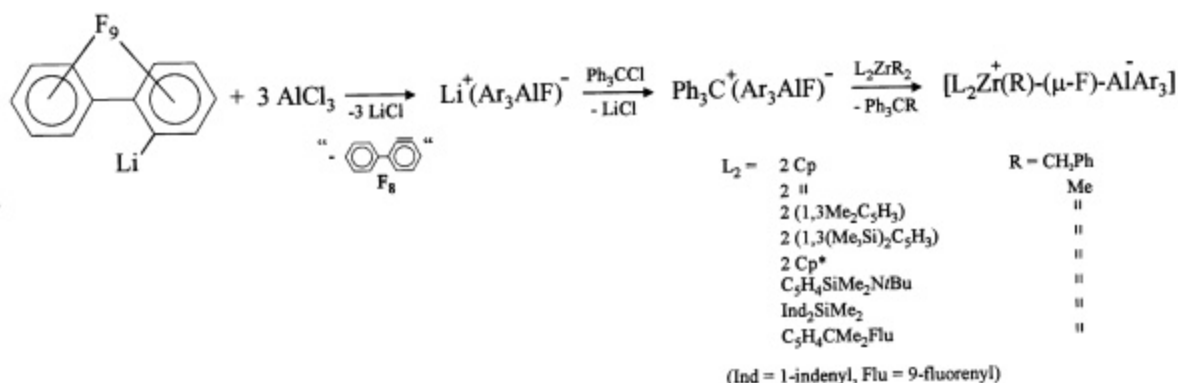
Scheme 3. Reactions involving the $(Ar_3AlF)^-$ anion.
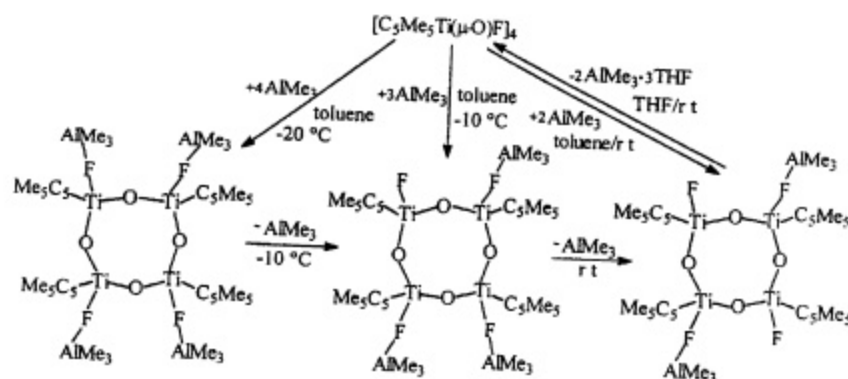
Scheme 4. Complexes of Me_3Al with $[Cp^*TiF(\%\text{-}O)]_4$ (from ref. 108).
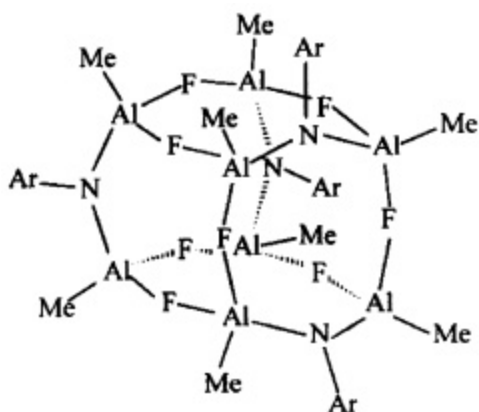
Figure 13. Structure of [(MeAl)$_8$(%-F)$_8$(%-NDipp)$_4$] (from ref. 93).

Figure 14. Structures of [K·2Thf]$^+$(TrisAlF$_2$)$_2$(%-F)$^-$]$_2$ (from ref. 114) and [(Na·Thf)$^+$(TrisAlF$_3$)$^-$]$_4$ (from ref. 59) (outer substituents omitted for clarity).

Reactions of the alanes Me$_3$Al and (Me$_3$Si)$_3$CAlMe$_2$·Thf with Bu$_4$N$^+$HF$_2^-$ at r.t. proceed via elimination of MeH under formation of the respective Bu$_4$N$^+$(MeRAlF$_2$)$^-$ salts in almost quantitative yields. Both compounds have been structurally investigated[111].

(Me$_3$SnF)$_\infty$ has been proven the fluorinating agent of choice in metathetic fluorinations of RAlMe$_2$ compounds to yield RAlF$_2$ complexes with Me$_4$Sn elimination. Reactions of RN(SiMe$_2$R$\heartsuit$)AlMe$_2$·Thf with R = 2,6-iPr$_2$C$_6$H$_3$ (=Dipp), R$\heartsuit$ = Me, iPr, tBu and R = 2,6-Me$_2$C$_6$H$_3$, R$\heartsuit$ = tBu, Mes in Thf at r.t. with two equivalents of Me$_3$SnF affords monomeric compounds RN(SiMe$_2$R$\heartsuit$)AlF$_2$·Thf (refs 58, 112), while the reaction of the solvent-free dimeric [DippN(SiMe$_3$)AlMe$_2$]$_2$ in toluene affords trimeric [DippN(SiMe$_3$)AlF(%-F)]$_3$. While the ^{19}F-NMR spectrum at r.t. with one broad signal indicates rapid exchange of *exo*- and *endo*cyclic F atoms, at –90°C four distinct triplets in a 2:2:1:1 ratio are observed assignable to an intact trimer[112]. A compound with Me$_2$SitBu as substituent on N instead of Me$_3$Si has also been obtained with the same fluxional behaviour[113].

Analogously, TrisAlMe$_2$·Thf (Tris = (Me$_3$Si)$_3$C) and Me$_3$SnF yield a monomeric Thf adduct which loses the donor upon heating to 200°C to afford another structurally characterized trimeric organoaluminum difluoride. This compound was the first structurally characterized neutral organoaluminum fluoride with *exo*cyclic Al–F bonds. The adduct formation is reversible[114]. Only a dimer is found upon fluorination of the aza-allyl substituted compound Me$_3$SiNC(Ph)C(SiMe$_3$)$_2$ AlMe$_2$. The complex shows five-coordinated Al atoms in the solid state and fluxional behaviour in solution[115].

A diorganodialuminumpentafluoride anion is formed in the reaction of TrisAlF$_2$·Thf (Tris = (Me$_3$Si)$_3$C) with KF in Thf. Two F$_2$Al(%-F)AlF$_2$ units with a bent middle Al(%-F)Al bridge are clenched by two (K·2Thf)$^+$ cations resulting in a distorted geometry[114] (Figure 14). A [(TrisAlF$_2$)(%-F)]$^-$ anion with a linear Al(%-F)Al bridge
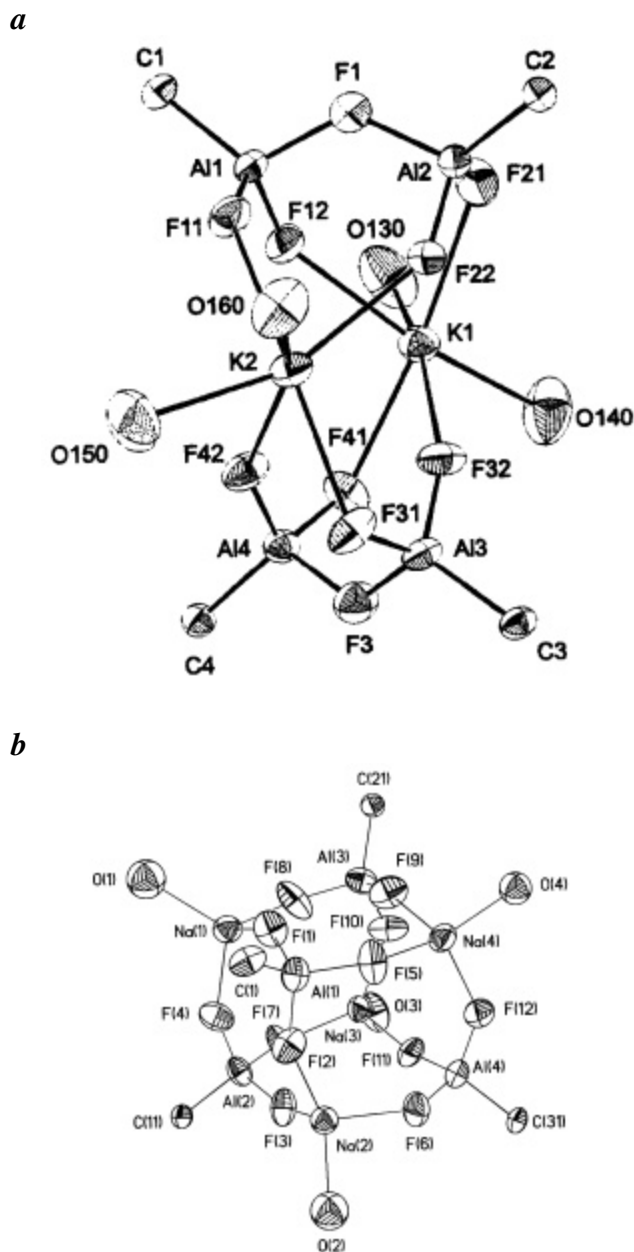
is present in the compound (AlF$_2$·4Thf)$^+$[(TrisAlF$_2$)$_2$(%-F)]$^-$ generated from the reaction of (TrisAlF$_2$)$_3$ with AgF$_2$, which is also likely in NH$_4^+$(Tris$_2$Al$_2$F$_5$)$^-$, obtained in high yield from addition of NH$_4^+$F$^-$ to the trimeric difluoroalane. (Ag·3PhMe)$^+$[Li(Tris$_2$Al$_2$F$_5$)$_2$]$^-$ is the product of the concerted action of AgF and LiCl on (TrisAlF$_2$)$_3$. The Li atom is tetrahedrally surrounded by the outer F atoms of two FAl(%-F)AlF moieties[116]. This is in contrast to the structures of (Li·Thf)$^+$(TrisAlF$_3$)$^-$, obtained from fluorination of (Li·2Thf)$^+$(TrisAlH$_3$)$^-$ with 70% HF in pyridine[117] and the corresponding (Na·Thf)$^+$ salt generated by the reaction of

TrisAlMe$_2$·Thf with excess Me$_3$SnF and NaCl, where cubic arrays have been found (Figure 14). The structures are best described as organotrifluoroaluminate anions held together by solvated alkali cations.

No close cation–anion contacts are present in the corresponding collidinium salt (2,4,6-Me$_3$C$_5$H$_2$NH)$^+$ (TrisAlF$_3$)$^-$ with discrete isolated ions[118].

Several complexes of Al with group 4 metals connected via %-F bridges have been synthesized and structurally characterized. As previously mentioned, addition of Cp$_2$ZrMeF to (TrisAlF$_2$)$_3$ results in the formation of the complexes [Cp$_2$ZrMe(%-F)AlF$_2$Tris] and {[Cp$_2$Zr(%-F)$_2$AlFTris]$_2$(%-O)} (ref. 59). The reactions of (Cp*MF$_3$)$_4$ (M = Zr, Hf) with Me$_3$Al affords isostructural complexes (shown with Zr in Figure 15) with migration of a Me group from Al to the transition metal. The Cp* and Me groups have been found exclusively in a *cis*-arrangement[78,79].

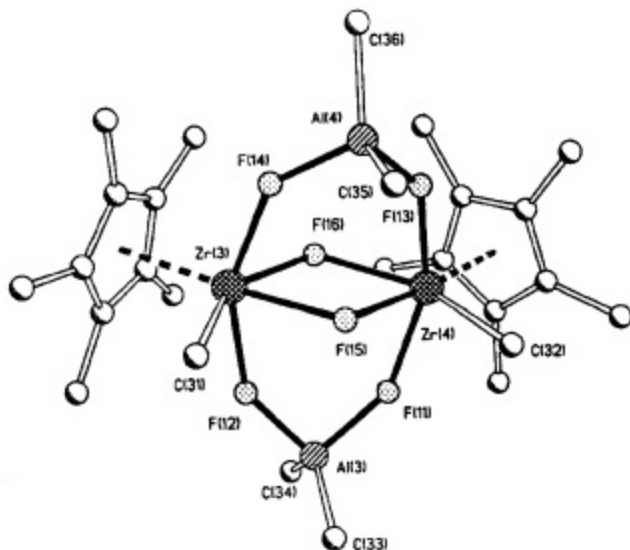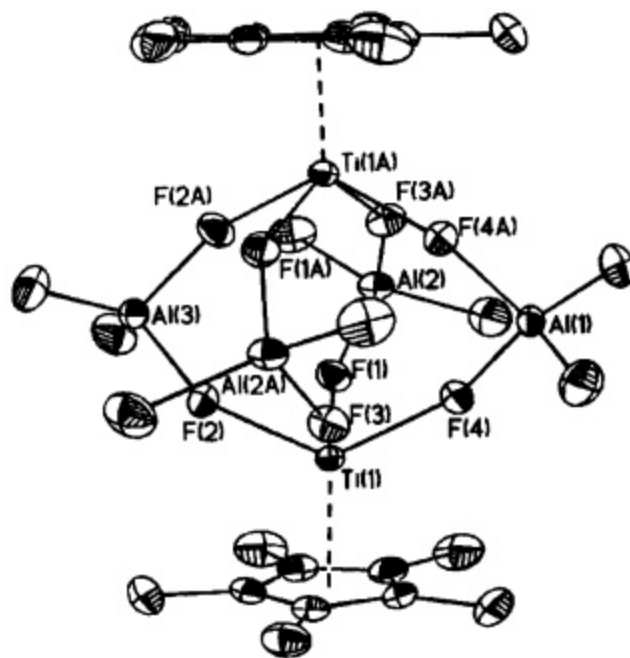While these reactions proceed with retention of the oxidation state, Ti(+IV) is reduced to Ti(+III) by either Al or R$_3$Al (R = Me, Et) in the following examples. Paddle-wheel shaped complexes [Cp♡$_2$Ti(%-F)$_2$]$_3$Al (Cp♡ = Cp, MeC$_5$H$_4$) are formed from Al and three equivalents of Cp♡$_2$TiF$_2$ (ref. 119).

Reactions of equimolar amounts of Cp♡$_2$TiF$_2$ and Et$_3$Al afford non-planar eight-membered rings [(Cp♡$_2$Ti)$_2$(%-F)$_4$(AlEt$_2$)$_2$] with Cp♡ = Cp (ref. 63), MeC$_5$H$_4$ (ref. 120) and Cp* (ref. 120).

A compound with an [Al$_4$Ti$_2$(%-F$_8$)] core is formed in the reaction of Cp*TiF$_3$ with Me$_3$Al (Figure 16) via intermediate formation of an adduct [(Cp*TiF$_2$Me)·(Me$_2$AlF)] in refluxing toluene. The structure consists of

Figure 16. Structure of [(Cp*Ti)$_2$(%-F)$_8$(AlMe$_2$)$_4$] (from ref. 120).

an octahedron of metal atoms bridged by fluorine atoms. The Ti atoms are in *trans* positions with a pseudo square pyramidal environment completed by the Cp* ring[120]. In contrast, the corresponding Et$_2$Al complex is already formed at r.t.[63]

Positional exchange of F atoms against DippN units (Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$) occurs in reactions of the trimeric iminoalane (MeAlNDipp)$_3$ with Cp♡MF$_3$ compounds (M = Zr, Cp♡ = (Me$_3$Si)$_2$C$_5$H$_3$ (ref. 121), M = Ti, Cp♡ = Cp (ref. 121), M = Ti, Cp♡ = Me$_3$SiC$_5$H$_4$ (ref. 122) and M = Ti, Cp♡ = Cp* (ref. 122) to yield heteroadamantane cages (Scheme 5). While with the lesser bulky Cp♡ ligands the exchange happens twice, only one F adopts the position of a DippN moiety with Cp*TiF$_3$. Upon addition of Et$_2$O the cage opens leaving a species with a Ti = N double bond, the Et$_2$O co-ordinates the vacant site of Al (ref. 122). All compounds have been structurally characterized.

A compound with an Al$_4$(%-F)$_4$(%-Si)$_2$ core will be discussed later[123].

Organoaluminum siliconates and phosphates

Metal doped silicates can serve as catalysts for a variety of reactions. The polymeric nature of these materials makes insight of the processes involved difficult. Breaking down the polymeric framework by adding organic groups to the periphery of smaller units render the compounds soluble thus allowing further studies[124,125].

Figure 15. Structure of [Cp*ZrMe(%-F)(%-FAlMe$_2$F)]$_2$ (from ref. 78).
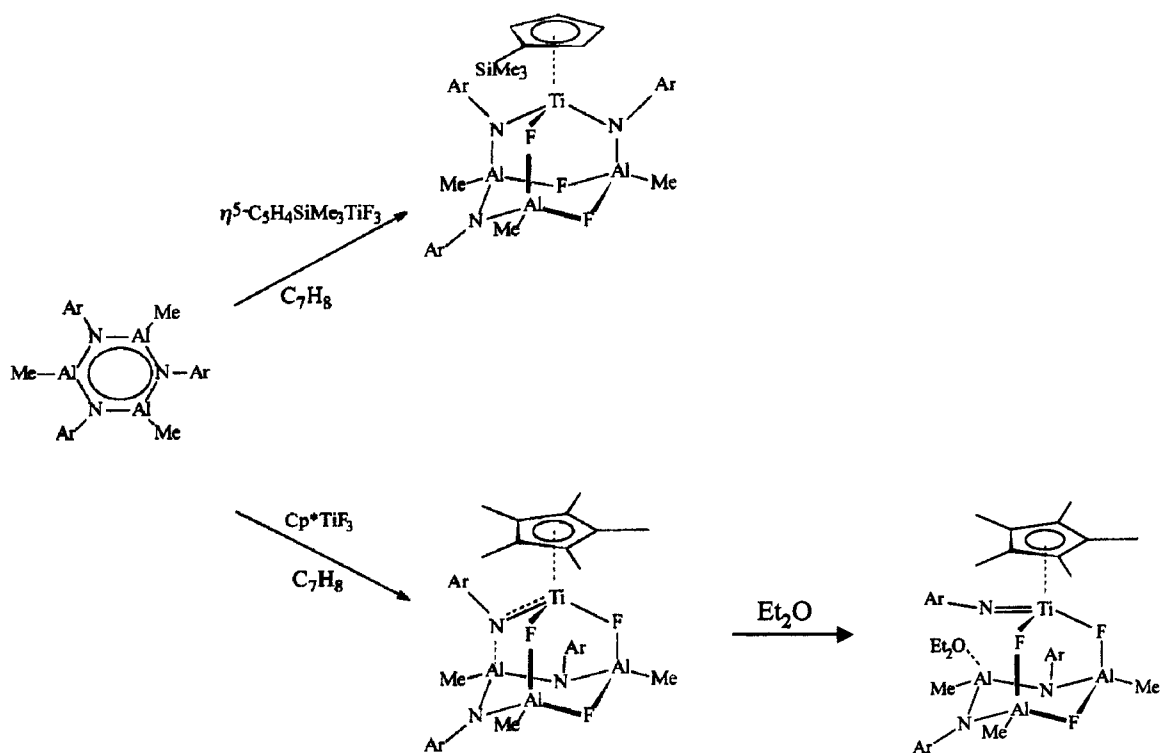
Scheme 5. Reactions of (MeAlNDipp)$_3$ with Cp$^\heartsuit$TiF$_3$ complexes (from ref. 122).
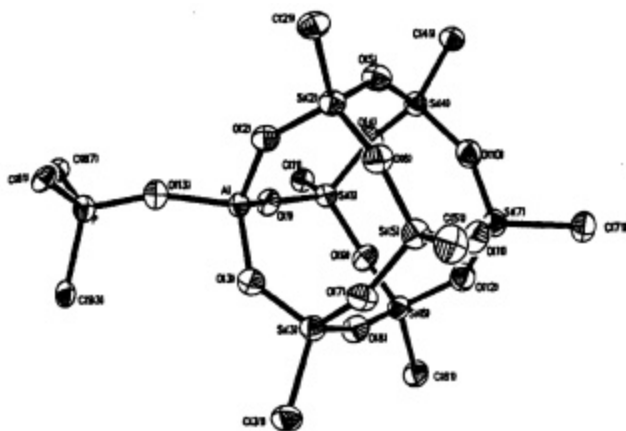
Figure 17. Structure of [(CySi)$_7$($\%$-O)$_{12}$Al·OPPh$_3$] (from ref. 126) (Outer substituents omitted for clarity).

Feher and co-workers have investigated the reaction of the cyclohexyl (Cy) substituted polysiloxanetriol (CySi)$_7$($\%$-O)$_9$(OH)$_3$ with Me$_3$Al (refs 126–129). Under complete elimination of methane a cluster with a cubic core [(CySi)$_7$($\%$-O)$_{12}$Al]$_2$ is formed which is a dimer with a central four-membered Al$_2$O$_2$ ring. The dimeric structure can be broken by addition of Lewis bases as Ph$_3$PO (Figure 17) (ref. 126), Me$_3$NO (ref. 126) or Me$_4$SbOH (ref. 127). Addition occurs at the Al atom.

Anionic cages connected by linear Al($\%$-O)Al (ref. 127) and Al($\%$-O)Si (ref. 128) bridges have also been realized. Tossell has performed calculations on the 6-31G* level on the compounds Si$_2$Al$_4$O$_6$H$_8$ and Si$_4$Al$_4$O$_8$H$_{12}$. He confirmed the 'drum' structures (Figure 18) experimentally found by our group as local minima[130].

Reactions of the stable silanetriol DippN(SiMe$_3$)Si(OH)$_3$ with iBu$_2$AlH in an 1:1 ratio at –78°C in dioxane or Thf afford eight-membered heterocycles [DippN(SiMe$_3$)Si(OH)($\%$-O)$_2$AliBu·L]$_2$, while in a 1:2 molar ratio a cage with two six-membered rings consisting of iBuAl-, iBu$_2$Al- and DippN(SiMe$_3$)Si moieties each connected by $\%_3$-O atoms is formed[131,132]. Performing the equimolar reaction at 65°C results in complete elimination of iBuH and H$_2$ leaving a compound {[DippN(SiMe$_3$)Si($\%_3$-O)$_3$Al·Thf]$_2$}$_2$ consisting of fused eight-membered rings. The same types of aluminosiloxanes are also available with XylN(SiMe$_3$) (Xyl = 2,6-Me$_2$C$_6$H$_3$) (ref. 132) and (CO)$_9$Co$_3$C attached to Si in the reactions of the silanetriols with Me$_3$Al or Et$_3$Al (refs 133, 134). Ionic aluminosiloxanes of the type (M·Thf$^+$)$_4$[RAl($\%_3$-O)$_3$SiN(SiMe$_3$)Dipp]$_4^{4-}$ with M = Li, R = H and M = Na, R = Et have been synthesized from the silanetriol with LiAlH$_4$ and Na$^+$(Et$_2$AlH$_2$)$^-$, respectively. The alkali metals are five-coordinated through the Thf–O and four adjacent O atoms of the aluminosiloxane (Figure 19) (ref. 134).

a
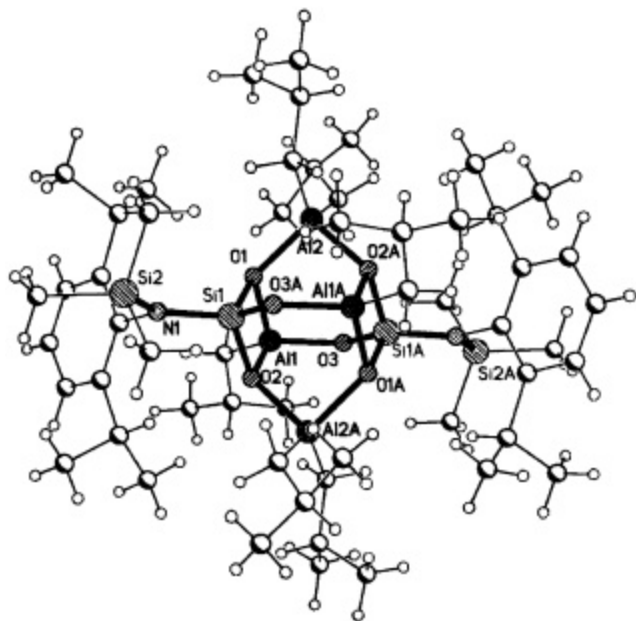
b
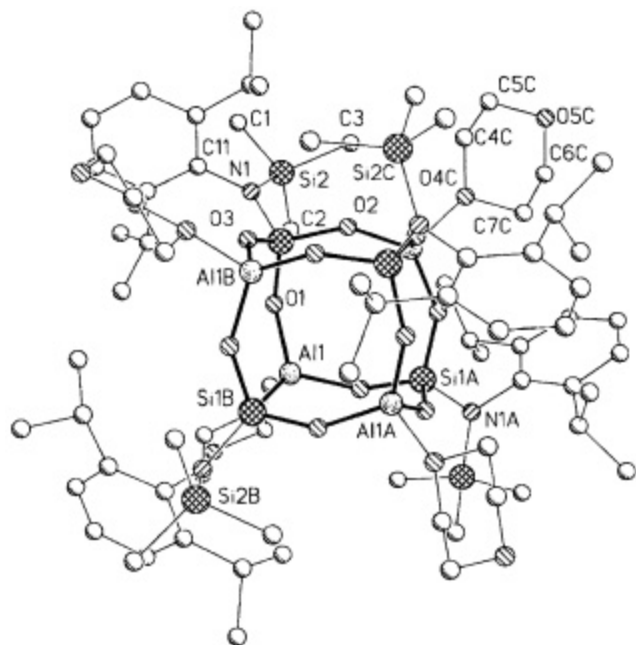
Figure 18. Structures of the D3R and D4R aluminosiloxanes (from refs 131, 132).

Aluminophosphinates were known since 1964, when Coates and Mukherjee obtained compounds of formulae $[Me_2Al(\%\text{-}O)_2PR_2]_n$ with R = Me, Ph from reactions of Me_3Al with the appropriate phosphinic acids[135], but complete structural information was not available until re-

cently. Weidlein *et al.* suggested the compounds to possess eight-membered rings on the
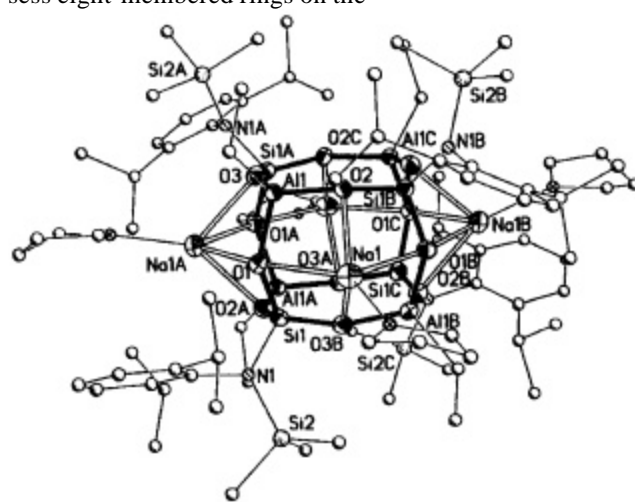
Figure 19. Structure of $(Na\cdot Thf^+)_4[EtAl(\%_3\text{-}O)_3SiN(SiMe_3)Dipp]_4{}^{4-}$ (from ref. 134).

basis of IR measurements[136] and comparison with similar heterocycles[81]. The same group estimated the aggregation grade *n* of compounds with R = F, Cl and H to be three due to cryoscopic, IR- and Raman studies[137,138]. No ring size was given by Japanese researchers, who synthesized $[Et_2Al(\%\text{-}O)_2P(OR)_2]_n$ with R = Me, Et via two different routes[139]. In 1996 two groups independently described the structures of two complexes exhibiting the expected eight-membered rings $[Me_2Al(\%\text{-}O)_2PPh_2]_2$ (ref. 140) and $[tBu_2Al(\%\text{-}O)_2P(OSiMe_3)_2]_2$ (ref. 141). More recently, Mason *et al.* and our group succeeded in the synthesis and structural characterization of additional dimeric organoaluminum phosphorus systems with various functionalities, namely $[tBu_2Al(\%\text{-}O)_2PPh_2]$ and $[tBu_2Al(\%\text{-}O)_2P(OSiMe_3)Ph]_2$ (ref. 142), $[R_2Al(\%\text{-}O)_2P(OSiMe_3)_2]_2$ via intermediate Lewis acid base adducts $R_2AlR\heartsuit\cdot OP(OSiMe_3)_3$ (R = Me, Et, R$\heartsuit$ = Me, Et, Cl) (ref. 143), $[tBu_2Al(\%\text{-}O)_2P(tBu)OSiMe_3]_2$ and $[Me(Cl)Al(\%\text{-}O)_2PPh_2]_2$ (ref. 144) from the appropriate precursors.

Probably template directed is the synthesis of the compound shown in Figure 20 from $tBuP(O)(OH)_2$ and $Na^+(Et_2AlH_2)^-$.

The molecule is constructed of twelve-membered $Al_3P_3O_6$ rings, a motif often found in zeolites. One Na atom is surrounded by six O atoms of one ring in a crown ether fashion and one Thf–O atom, while the others are four-coordinated by μ_3-O atoms connecting the two halves of the molecule[145].

A tetrameric aluminophosphate $[tBuAl(\%\text{-}O)_3P(OSiMe_3)]_4$ has been formulated from the reaction of $tBuAlCl_2$ with $OP(OSiMe_3)_3$ from analytical and spectroscopical data[141]. Reactions of several alanes R_3Al with phosphonic acids $RP(O)(OH)_2$ afford smoothly with alkane elimination tetrameric aluminophosphonates
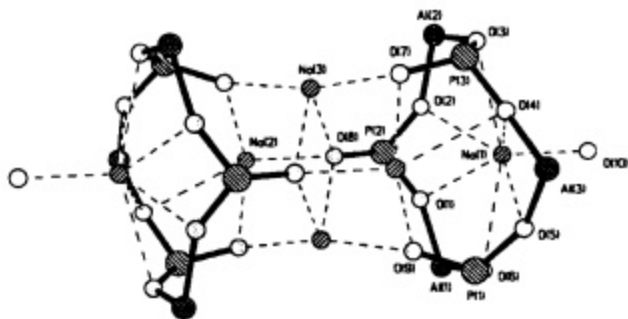
Figure 20. Structure of $\{(Na\cdot Thf)Na_2[(tBuP(\%_3\text{-}O)_3AlEt_2]_3\}_2$ (from ref. 145) (*t*Bu and Et groups and Thf-C's omitted for clarity).

a
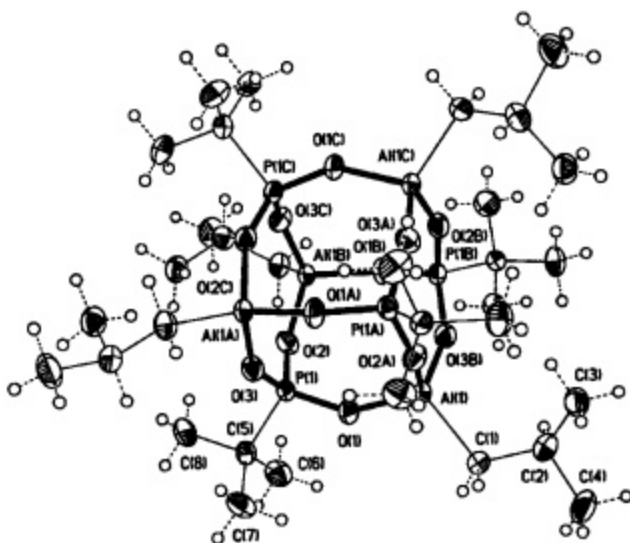
b
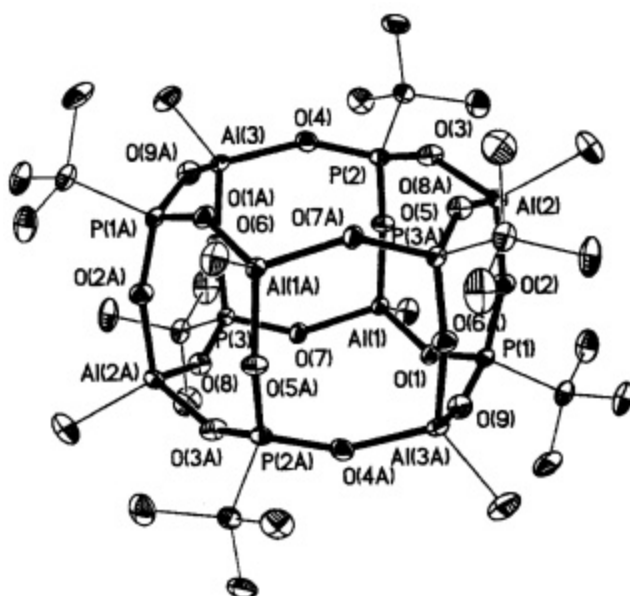
Figure 21. Structures of $[iBuAl(\%\text{-}O)_3PtBu]_4$ (from ref. 146) and $[MeAl(\%\text{-}O)_3PtBu]_6$ (from ref. 149).

$[RAl(\%\text{-}O)_3PR\heartsuit]_4$ (R, $R\heartsuit = i$Bu, *t*Bu (refs 146–148); Me, *t*Bu (ref. 148); Me, Me; *t*Bu, Me and *t*Bu, Ph (ref. 141)). The X-ray structures of several of these molecules show the expected cubic array[141,146] (Figure 21).

Aside from the tetramer, a hexamer $[MeAl(\%\text{-}O)_3PtBu]_6$ has been isolated in low yields from the reaction of Me_3Al with $tBuP(O)(OH)_2$. Its X-ray structure exhibits two crown-shaped twelve-membered rings connected by six eight-membered rings (Figure 21)[149]. While inverse substitution at Al and P resulted at r.t. in predominant formation of the tetramer, which when heated to 70°C is found to yield higher oligomers, a decamer $[tBuAl(\%\text{-}O)_3PMe]_{10}$ has been postulated from molecular weight determination. Prolonged standing reforms the tetramer and minor amounts of a hexamer, suggesting equilibria in solution[142]. These results show that the size and the geometry of the rings can be directed by the steric requirements of the substituents leading to yet unknown structures[142,149]. Fluorine is the structure directing element in the reaction of $Cs^+(iBu_3AlF)^-$ with $tBuP(O)(OH)_2$. The main product isolated is a compound with a complex structure depicted in Figure 22. Several of the structural and geometric features of this compound are also found in zeolites[150].

Cage compounds of aluminium with higher group 14–16 elements

While the chemistry of polycyclic Al compounds of the first row of the periodic table has been extensively investigated[3–9], information on such complexes with the higher homologues is scarce.

Only one example of an Al–Si cage compound is documented to date from oxidative insertion of $(Cp^*Al)_4$ into the Si–F bonds of Ph_2SiF_2 to afford $[(Cp^*Al)_4(\%\text{-}F)_4(\%\text{-}SiPh_2)_2]$ with a distorted adamantane-like structure (Figure 23) (ref. 123).
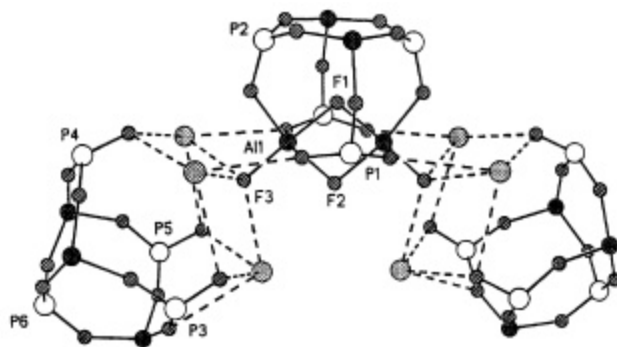
Figure 22. Core of the structure of $\{[(Cs\cdot Thf)_3(\mu_4\text{-}F)(iBuAl)_3(tBuPO_3)_4][(iBuAl)_2Al_2(\%\text{-}F)_2(tBuPO_3)_4]\}$ (from ref. 150) (All outer substituents omitted for clarity).
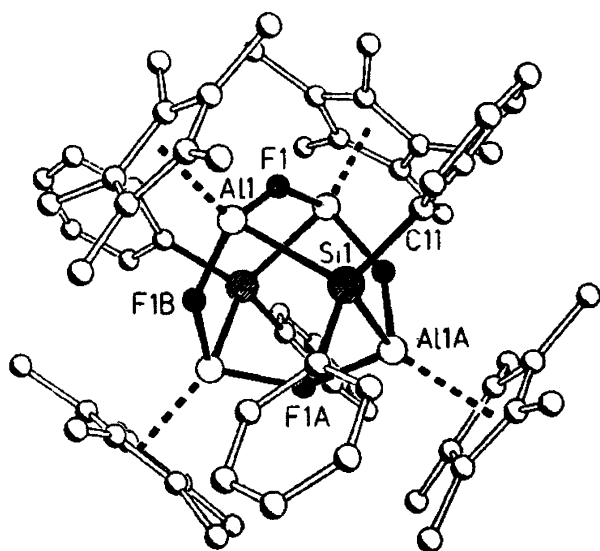
Figure 23. Structure of [(Cp*Al)$_4$(%-F)$_4$(%-SiPh$_2$)$_2$] (from ref. 123).
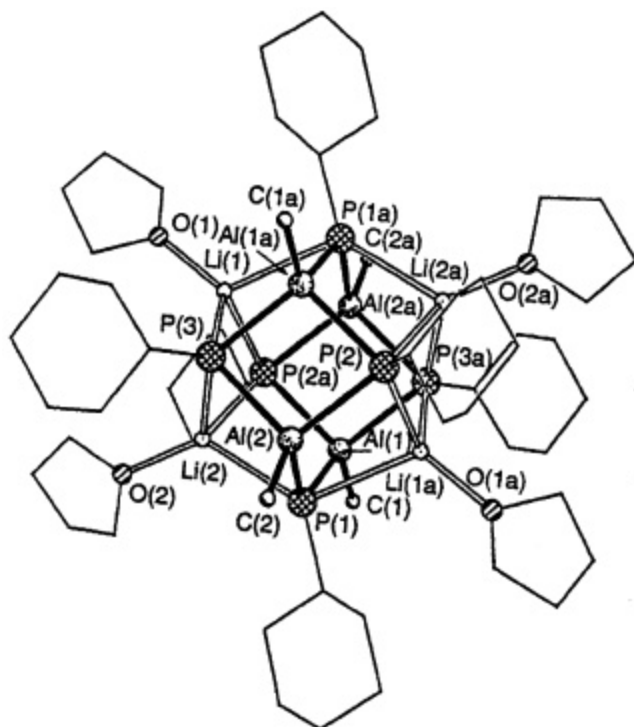
Figure 24. Structure of (Li·Thf$^+$)$_4$[(MeAl)$_4$(%-PCy)$_6$]$^{4-}$ (from ref. 155).

While Al–N cage compounds with a wide variety of structures are available from thermolysis of (predominantly) dimeric aminoalanes with [RAl(%$_3$-NR♡)]$_4$ cubanes as the best examined class[151–153], Al-P chemistry is mainly restricted to four- and six-membered (AlP)$_n$ rings[154]. The only structurally characterized (AlP)$_4$ cubane, [iBuAl(%$_3$-

PSiPh$_3$)]$_4$, has been obtained by A. H. Cowley *et al.* from the reaction of iBu$_2$AlH
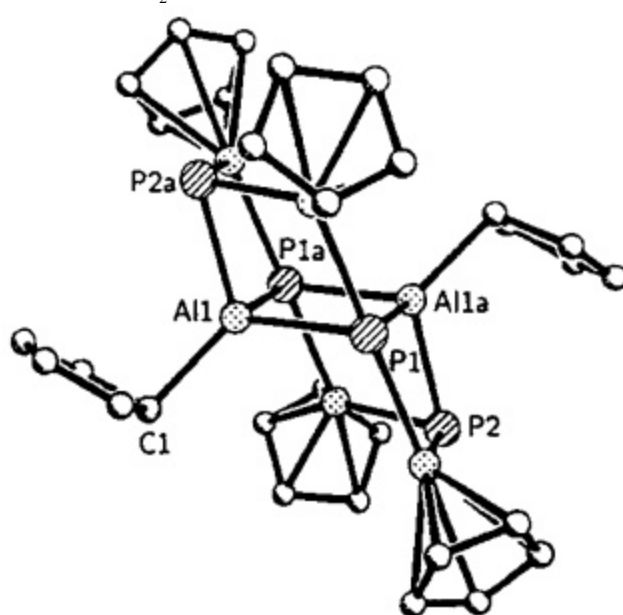
Figure 25. Structure of [(Cp*Al)$_6$P$_4$] (from ref. 156).

with Ph$_3$SiPH$_2$ via intermediate formation of *cis/trans* isomers of [iBu$_2$Al(%-PHSiPh$_3$)]$_2$ and subsequent heating. Pyrolysis of the tetramer at 500°C leads to deposition of AlP (ref. 155).

A polycyclic tetraanionic Al–P species has been found in the reaction of iminoalane [MeAl(%$_3$-NMes)]$_4$ with excess LiPHCy (Mes = mesityl, Cy = cyclohexyl) under elimination of MesNH$_2$ and LiNHMes. Its structure is shown in Figure 24. Two [MeAl(%-PCy)]$_2$ four-membered rings are fused by two PCy bridges, the Li atoms are tetrahedrally surrounded by three adjacent P atoms and the Thf–O (ref. 155).

Oxidation of (Cp*Al)$_4$ with white phosphorus affords a compound of composition [(Cp*Al)$_6$P$_4$]. Its X-ray structure (Figure 25) reveals two fused cubes with one unoccupied corner each. The Cp* ligands at the Al atoms sharing both cubes become %^{1} bound, while the two other remain %^{5} co-ordinated[156].

Reaction of (Cp*Al)$_4$ with (*t*BuAs)$_4$ proceeds via elimination of iBuH and Me$_2$CCH$_2$ to yield a compound [(Cp*Al)$_3$(%$_3$-As)$_2$] with the Cp* ligands bound %^{1} whose structure is according to Wade's rule *closo* (Figure 26) (ref. 157).

The same type of complex, [(Cp*Al)$_3$(%$_3$-Sb)$_2$] has been postulated earlier from elemental analysis and spectroscopic investigations from the analogous reaction with (*t*BuSb)$_4$ (ref. 123).

Additionally, several monocyclic [R$_2$AlSb(SiMe$_3$)$_2$]$_n$ compounds (R$_2$ = 2 Et, 2 iBu, *n* = 2 (ref. 158); R$_2$ = 2 Me; Me, Cl, *n* = 3 (ref. 159)) and the first complex containing Al–Bi

bonds, $[Me_2AlBi(SiMe_3)_2]_3$ (ref. 160) have been synthesized   and   structurally   characterized.
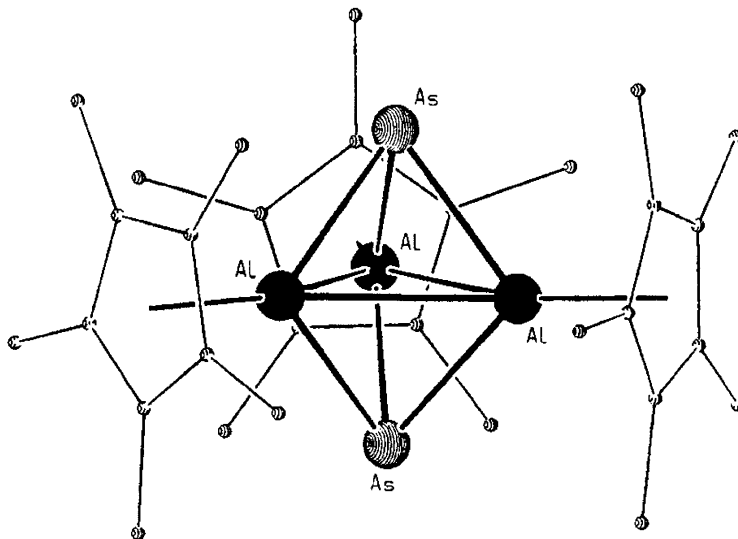
Figure 26. Structure of $[(Cp*Al)_3(\mu_3\text{-As})_2]$ (from ref. 157).
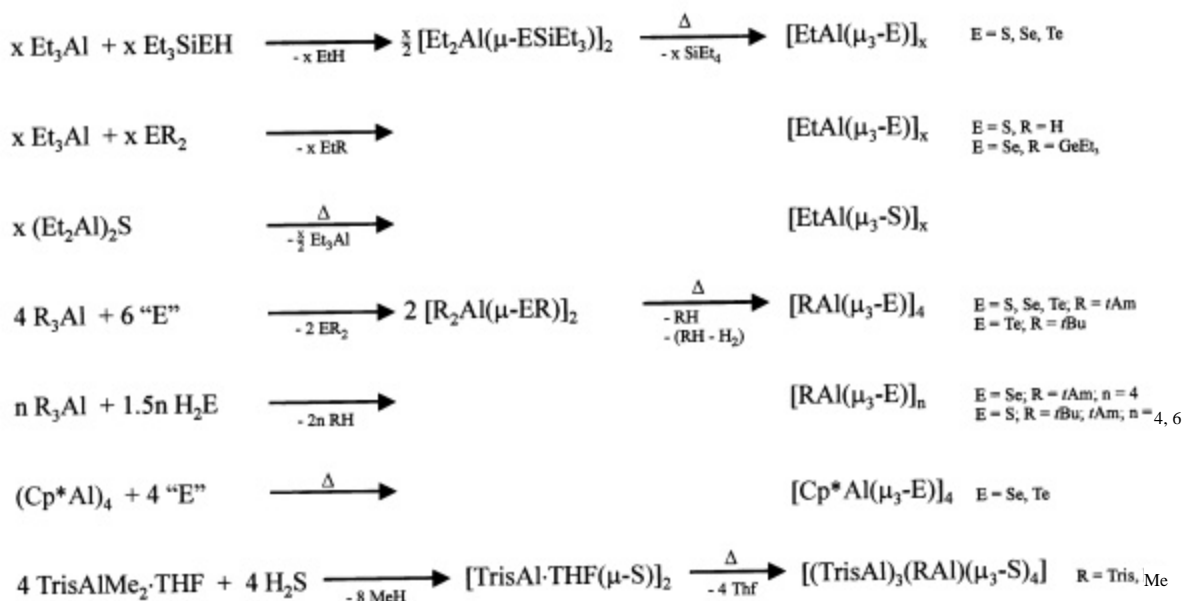
Scheme 6. Syntheses of $[RAl(\mu_3\text{-E})]_n$ compounds.

Organoaluminum oxides and hydroxides exhibit a great structural diversity, some of them have shown catalytic activities for a variety of reactions[161–163]. On the other hand, non-condensed Al–S-, Al–Se- and Al–Te compounds with covalent bonds form predominantly dimeric or trimeric associates[164–167]. In several cases condensation, elimination or insertion reactions have been observed to yield chalcogenolates $[RAl(\mu_3\text{-E})]_n$, E = S, Se, Te (Scheme 6).

The syntheses of high-melting, totally insoluble compounds $[EtAl(\mu_3\text{-E})]_x$ with E = S, Se and Te from Et_3Al and 'hydrogen equivalent' sulphides, $(Et_3M)_{2-n}EH_n$ (M = Si, $n = 1$, M = Ge, $n = 0$) by Vyazankin *et al*.[168] and of

$[Et_2Al(\mu_3\text{-S})]_y$ from Et_3Al and H_2S with identical properties by Hirabayashi and co-workers[169,170] have been reported. The latter assigned $y = 4$ by comparison with other known structures with tetrameric cages. In the light of formation of higher aggregated cages by diminishing the steric requirements of the substituents[142,149], higher oligomers are more likely.   The   first authentic cubanes $[tBuAl(\mu_3\text{-E})]_4$ (E = S, Se, Te) have been obtained by Cowley *et al*. from tBu_3Al and the respective chalcogenes via isolable intermediates $[tBu_2Al(\mu\text{-E}tBu)]_2$ and characterized by mass spectroscopy[171]. Shortly after-

wards our group succeeded in the synthesis and first struc- tural characterization of
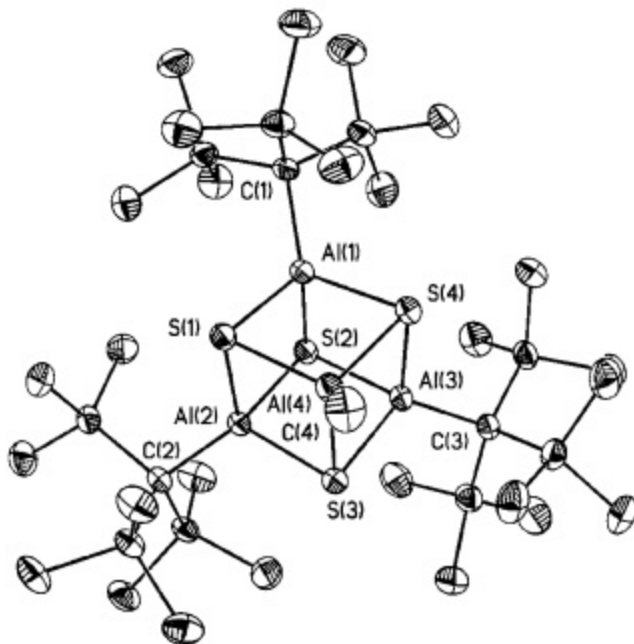
Figure 27. Structure of [(TrisAl)$_3$(MeAl)($\%_3$-S)$_4$] (from ref. 173).
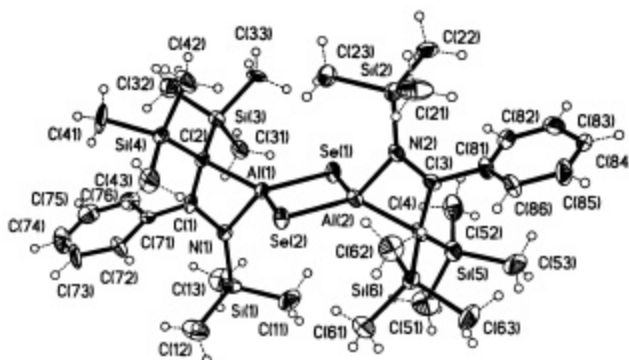
Figure 28. Structure of the dimeric aza-allylaluminum selenide (from ref. 175).

tetrameric [Cp*Al($\%_3$-Se)]$_4$ and [Cp*Al($\%_3$-Te)]$_4$ cages with slightly distorted cubic cores[44]. By reactions of R$_3$Al compounds containing the bulky substituents tBu and tAm (= Me$_2$EtC) with H$_2$S, Se$_x$ and Te$_x$ Barron et al. also obtained heterocubanes of S, Se and Te. The structures of [tA-mAl($\%$-E)]$_4$ with E = S, Se have been determined. Additionally, the H$_2$S reactions yielded hexamers which have been separated from the tetramers by fractional crystallization (tAm) or sublimation of the tetramer (tBu) and characterized spectroscopically[172]. Surprisingly the analogous reaction of TrisAlMe$_2$·Thf (Tris = (Me$_3$Si)$_3$C) with H$_2$S takes a different course; pyrolysis of the intermediate [TrisAl·Thf(μ-S)]$_2$, which has been isolated in high yield and structurally characterized, led to two different cubanes. Aside from the

expected [TrisAl($\%_3$-S)]$_4$ a second compound had formed, [(TrisAl)$_3$(MeAl)($\%_3$-S)$_4$], the crystals of which could be manually separated from the former and have been structurally characterized (Figure 27) (ref. 173).

Only four-membered aluminum selenides and tellurides are formed when one co-ordination site in aluminum hydrides is clogged by a donor ligand. The reactions of 2,6-(Et$_2$N)$_2$C$_6$H$_3$AlH$_2$ with elemental tellurium[174] and aza-allyl compound [Me$_3$SiNCPhC (SiMe$_3$)$_2$AlH($\%$-H)]$_2$ with Se and Te (ref. 175) opens up a new access to dimeric organoaluminum chalcogenides. The Al atoms of all three compounds are tetrahedrally surrounded by C, N and two chalcogen atoms. The aza-allyl compounds are present in solution as an equilibrium of cis and $trans$ isomers as seen from ^{1}H-NMR
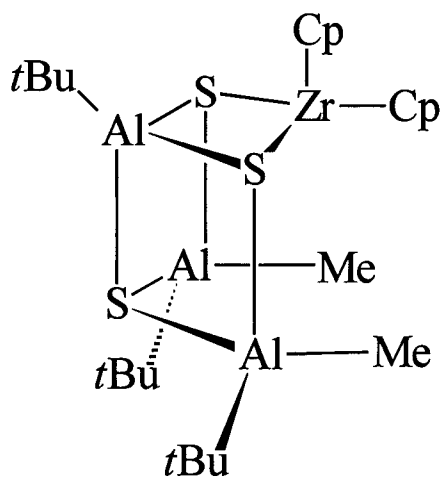
Figure 29. Proposed structure of $[(t\text{BuAl})(t\text{BuAlMe})_2(\%_3\text{-S})_3\text{ZrCp}_2]$.

spectra, while the X-ray structure (Figure 28) only reveals the *trans* isomer in the crystal[175].

Reaction of the *t*Bu substituted sulphur cubane with two equivalents of Cp_2ZrMe_2 results in partial breakdown of the cage. One *t*BuAlS moiety inserts into one Zr–Me bond of one molecule Cp_2ZrMe_2 while the second adds to the remainder to yield a compound with an $\text{Al}_3(\%_3\text{-S})_3\text{Zr}$ framework shown in Figure 29. Though rather unstable, its structure has been derived from spectroscopic analogy to its Ga congener, whose X-ray structure has been determined[176].

Conclusions and outlook

In recent years the organoaluminum chemistry has made a tremendous development, documented by the growing number of publications. Especially compounds of aluminum containing transition metal complexes have contributed to this field due to their catalytic properties in polymerization reactions and various organic transformations. Another new branch of interest are compounds containing Al–Al bonds. In this promising field many new developments could be expected. Compounds of this type are excellent precursors for the preparation of so far unknown compounds with aluminum-metal bonds. It can thus be concluded that organoaluminum chemistry will have a prosperous future.

1. Hallwachs, W. and Schafarik, A., *Liebigs Ann. Chem.*, 1859, **109**, 206–209.
2. For a complete list of K. Ziegler's publications see: Wilke, G., *Liebigs Ann. Chem.*, 1975, 805–833.
3. Mole, T. and Jeffery, E. A., *Organoaluminum Compounds*, Elsevier, Amsterdam, 1972, and refs therein.
4. McKillop, A., Smith, J. D. and Worrall, I. J. (eds), *Organometallic Compounds of Aluminum, Gallium, Indium and Thallium*, Chapman and Hall, London, 1985, and refs. therein.
5. Robinson, G. H. (ed), *Coordination Chemistry of Aluminum*, VCH, New York, 1993, and refs. therein.
6. Downs, A. J. (ed), *Chemistry of Aluminum, Gallium, Indium and Thallium*, Blackie Academic, Glasgow, 1993, and refs therein.
7. Eisch, J. J., in *Comprehensive Organometallic Chemistry* (eds Wilkinson, G., Stone, F. G. A. and Abel, E. W.), Pergamon, Oxford and elsewhere, 1981, vol. 1, pp. 555–682.
8. Abel, E. W. and Stone, F. G. A. (eds), *Organometallic Chemistry. A Specialist Report*, Chem. Soc., London, vols. 1 (1972) – 27 (1998). See the Al sections and refs therein.
9. *Annu. Rep. Prog. Chem., Sect. A, Inorg. Chem.*, R. Soc. Chem., Cambridge, vols. 76 (1979) – 94 (1998). See the Al sections and refs therein.
10. Klemm, W., Voss, E. and Geiersberger, K., *Z. Anorg. Chem.*, 1948, **256**, 15–24.
11. Tacke, M. and Schnöckel, H., *Inorg. Chem.*, 1989, **28**, 2895–2896.
12. Olah, G. A., Farooq, O., Farnia, S. M. F., Bruce, M. R., Clouet, F. L., Morton, P. R., Prakash, G. K. S., Stevens, R. C., Bau, R., Lammertsma, K., Suzer, S. and Andrews, L., *J. Am. Chem. Soc.*, 1988, **110**, 3231–3238.
13. Ecker, A. and Schnöckel, H., *Z. Anorg. Allg. Chem.*, 1996, **622**, 149–152.
14. Uhl, W., *Angew. Chem.*, 1993, **105**, 1449–1461; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1386–1397.
15. Dohmeier, C., Loos, D. and Schnöckel, H., *Angew. Chem.*, 1996, **108**, 141–161; *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 129–149.
16. Uhl, W., *Coord. Chem. Rev.*, 1997, **163**, 1–32.
17. Uhl, W., *Rev. Inorg. Chem.*, 1998, **18**, 239–282.
18. Mocker, M., Robl, C. and Schnöckel, H., *Angew. Chem.*, 1994, **106**, 1860–1861; *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 1754–1755.
19. Ecker, A. and Schnöckel, H., *Z. Anorg. Allg. Chem.*, 1998, **624**, 813–816.
20. Ecker, A., Baum, E., Friesen, M. A., Junker, M. A., Üffing, C., Köppe, R. and Schnöckel, H., *Z. Anorg. Allg. Chem.*, 1998, **624**, 513–516.
21. Mocker, M., Robl, C. and Schnöckel, H., *Angew. Chem.*, 1994, **106**, 946–948; *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 862–863.
22. Schram, E. P., *Inorg. Chem.*, 1966, **5**, 1291–1294.
23. Schram, E. P., Hall, R. E. and Glore, J. D., *J. Am. Chem. Soc.*, 1969, **91**, 6643–6648.

24. Miller, M. A. and Schram, E. P., *Organometallics*, 1985, **4**, 1362–1364.

25. Hoberg, H. and Krause, S., *Angew. Chem.*, 1976, **88**, 760–761; *Angew. Chem. Int. Ed. Engl.*, 1976, **15**, 694–695.

26. Schram, E. P., *Inorg. Chim. Acta*, 1988, **141**, 69–73.

27. Hoberg, H. and Krause, S., *Angew. Chem.*, 1978, **90**, 1013; *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 949.

28. Hoberg, H., Krause, S. and Ziegler, E., *J. Organomet. Chem.*, 1980, **184**, 1–5.

29. Uhl, W. and Wagner, J., *J. Organomet. Chem.*, 1992, **427**, 151–160.

30. Gavrilenko, V. V., Chekulaeva, L. A. and Zakharkin, L. I., *Zh. Obshch. Khim.*, 1983, **53**, 481–482; *J. Gen. Chem. USSR*, 1983, **53**, 423–424.

31. Schram, E. P., *Inorg. Chim. Acta*, 1987, **134**, 117–121.

32. Uhl, W., *Z. Naturforsch.*, 1988, **B43**, 1113–1118.

33. Wehmschulte, R. J., Ruhlandt-Senge, K., Olmstead, M. M., Hope, H., Sturgeon, B. E. and Power, P. P., *Inorg. Chem.*, 1993, **32**, 2983–2984.

34. Wiberg, N., Amelunxen, K., Blank, T., Nöth, H. and Knizek, J., *Organometallics*, 1998, **17**, 5431–5433.

35. Uhl, W. and Vester, A., *Chem. Ber.*, 1993, **126**, 941–945.

36. Uhl, W., Schütz, U., Pohl, S. and Saak, W., *Z. Naturforsch.*, 1994, **B49**, 637–641.

37. Uhl, W., Karsch, H. H., Schütz, U. and Vester, A., *Chem. Ber.*, 1993, **126**, 2637–2641.

38. Uhl, W., Vester, A., Kaim, W. and Poppe, J., *J. Organomet. Chem.*, 1993, **454**, 9–13.

39. Pluta, C., Pörschke, K.-R., Krüger, C. and Hildenbrand, K., *Angew. Chem.*, 1993, **105**, 451–453; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 388–390.

40. Dohmeier, C., Robl, C., Tacke, M. and Schnöckel, H., *Angew. Chem.*, 1991, **103**, 594–595; *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 564–565.

41. Wiberg, N., in *Frontiers of Organosilicon Chemistry* (eds Bassindale, A. R. and Gaspar, P. P.), R. Soc. Chem., Cambridge, 1991, pp. 263–270.

42. Wiberg, N., Amelunxen, K., Nöth, H., Schmidt, M. and Schwenk, H., *Angew. Chem.*, 1996, **108**, 110–112; *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 65–67.

43. Purath, A., Dohmeier, C., Ecker, A., Schnöckel. H., Amelunxen, K., Passler, T. and Wiberg, N., *Organometallics*, 1998, **17**, 1894–1896.

44. Schulz, S., Roesky, H. W., Koch, H.-J., Sheldrick, G. M., Stalke, D. and Kuhn, A., *Angew. Chem.*, 1993, **105**, 1828–1830; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1729–1731.

45. Schnitter, C., Roesky, H. W., Röpken, C., Herbst-Irmer, R., Schmidt, H.-G. and Noltemeyer, M., *Angew. Chem.*, 1998, **110**, 2059–2062; *Angew. Chem. Int. Ed.*, 1998, **37**, 1952–1954.

46. Schram, E. P. and Sudha, N., *Inorg. Chim. Acta*, 1991, **183**, 213–216.

47. Haaland, A., Martinsen, K.-G., Shlykov, S. A., Voldan, H. V., Dohmeier, C. and Schnöckel, H., *Organometallics*, 1995, **14**, 3116–3119.

48. Sitzmann, H., Lappert, M. F., Dohmeier, C., Üffing, C. and Schnöckel, H., *J. Organomet. Chem.*, 1998, **561**, 203–208.

49. Dohmeier, C., Mocker, M., Schnöckel, H., Lötz, A., Schneider, U. and Ahlrichs, R., *Angew. Chem.*, 1993, **105**, 1491–1493; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1428–1430.

50. Hiller, W., Klinkhammer, K.-W., Uhl, W. and Wagner, J., *Angew. Chem.*, 1991, **103**, 182–183; *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 179–180.

51. Uhl, W. and Breker, F., *Angew. Chem.*, 1999, **111**, 1578–1581; *Angew. Chem. Int. Ed.*, 1999, **38**, 1477–1479.

52. Purath, A., Köppe, R. and Schnöckel, H., *Angew. Chem.*, 1999, **111**, 3114–3116; *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 2926–2928.

53. Ecker, A., Weckert, E. and Schnöckel, H., *Nature*, 1997, **387**, 379–381.

54. Üffing, C., Baum, E., Köppe, R. and Schnöckel, H., *Angew. Chem.*, 1998, **110**, 2488–2491; *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 2397–2400.

55. Bhatt, M. V. and Kulkarni, S. U., *Synthesis*, 1983, 249–282.

56. Uhl, W., Vester, A., Fenske, D. and Baum, G., *J. Organomet. Chem.*, 1994, **464**, 23–34.

57. Ecker, A., Köppe, R., Üffing, C. and Schnöckel, H., *Z. Anorg. Allg. Chem.*, 1998, **624**, 817–822.

58. Waezsada, S. D., Liu, F.-Q., Barnes, C. E., Roesky, H. W., Montero, M. L. and Usón, I., *Angew. Chem.*, 1997, **109**, 2738–2739; *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 2625–2626.

59. Hatop, H., Roesky, H. W., Labahn, T., Fischer, A., Schmidt, H.-G. and Noltemeyer, M., *Organometallics*, in press.

60. Natta, G., Mazzanti, G., Corradini, P., Giannini, U. and Cesca, S., *Atti Accad. Naz. Lincei, Rend., Classe Sci., Fis., Mat., Nat.*, 1959, **26**, 150–154; *Chem. Abstr.*, 1960, **54**, 17357e.

61. Corradini, P. and Sirigu, A., *Inorg. Chem.*, 1967, **6**, 601–605.

62. Tebbe, F. N. and Guggenberger, L. J., *J. Chem. Soc., Chem. Commun.*, 1973, 227–228.

63. Yu, P., Montero, M. L., Barnes, C. E., Roesky, H. W. and Usón, I., *Inorg. Chem.*, 1998, **32**, 2595–2597.

64. Lobkovskii, E. B., Sizov, A. I., Bulychev, B. M., Sokolova, I. V. and Soloveichik, G. L., *J. Organomet. Chem.*, 1987, **319**, 69–75.

65. Storr, A. and Thomas, B. S., *Can. J. Chem.*, 1971, **49**, 2504–2507.

66. Rettig, S. J., Storr, A., Thomas, B. S. and Trotter, J., *Acta Crystallogr.*, 1974, **B30**, 666–673.

67. Forder, R. A. and Prout, K., *Acta Crystallogr.*, 1974, **B30**, 2312–2317.

68. Forder, R. A., Green, M. L. H., MacKenzie, R. E., Poland, J. S. and Prout, K., *J. Chem. Soc., Chem. Commun.*, 1973, 426–427.

69. Green, M. L. H., MacKenzie, R. E. and Poland, J. S., *J. Chem. Soc., Dalton Trans.*, 1976, 1993–1994.

70. Benfield, F. W., Francis, B. R., Green, M. L. H., Luong-Thi, N.-T., Moser, G., Poland, J. S. and Roe, D. M., *J. Less Common Metals*, 1974, **36**, 187–192.

71. Atwood, J. L. and Shoemaker, A. L., *J. Chem. Soc., Chem. Commun.*, 1976, 536–537.

72. Robinson, G. H., Self, M. F., Pennington, W. T. and Sangokoya, S. A., *Organometallics*, 1988, **7**, 2424–2426.

73. Robinson, G. H., Lee, B., Pennington, W. T. and Sangokoya, S. A., *J. Am. Chem. Soc.*, 1988, **110**, 6260–6261.

74. Lee, B., Sangokoya, S. A., Pennington, W. T. and Robinson, G. H., *J. Coord. Chem.*, 1990, **21**, 99–105.

75. Hitchcock, P. B., Jasim, H. A., Lappert, M. F. and Williams, H. D., *Polyhedron*, 1990, **9**, 245–251.

76. Schulz, S., Häming, L., Herbst-Irmer, R., Roesky, H. W. and Sheldrick, G. M., *Angew. Chem.*, 1994, **106**, 1052–1054; *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 969–970.

77. Horchler, S., Parisini, E., Roesky, H. W., Schmidt, H.-G. and Noltemeyer, M., *J. Chem. Soc., Dalton Trans.*, 1997, 2761–2763; (a) Waggoner, K. M., Olmstead, M. M. and Power, P. P., *Polyhedron*, 1990, **9**, 257–263; (b) Hoberg, H., *Liebigs Ann. Chem.*, 1972, **766**, 142–145; (c) Hoberg, H. and Barluenga-Mur, J., *Liebigs Ann. Chem.*, 1971, **748**, 163–172.

78. Herzog, A., Roesky, H. W., Zak, Z. and Noltemeyer, M., *Angew. Chem.*, 1994, **106**, 1035–1037; *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 967–968.

79. Herzog, A., Roesky, H. W., Jäger, F., Steiner, A. and Noltemeyer, M., *Organometallics*, 1996, **15**, 909–917.

80. Ziegler, K., Holzkamp, E., Köster, R. and Lehmkuhl, H., *Angew. Chem.*, 1955, **67**, 213–214.

81. Weidlein, J., *J. Organomet. Chem.*, 1972, **43**, 257–286.

82. Jagirdar, B. R., Murphy, E. F. and Roesky, H. W., *Prog. Inorg. Chem.*, 1999, **48**, 351–455.

83. Ziegler, K. and Köster, R., *Liebigs Ann. Chem.*, 1957, **608**, 1–7.

84. Ziegler, K., *Br. Pat.* 779,873, 1957; *Chem. Abstr.*, 1957, **51**, 17981b; *Ger. Pat.* 921, 450, 1954; *Chem. Abstr.*, 1958, **52**, 13791b.

85. Weidlein, J. and Krieg, V., *J. Organomet. Chem.*, 1968, **11**, 9–16.

86. Krieg, V. and Weidlein, J., *J. Organomet. Chem.*, 1970, **21**, 281–284.

87. Hamprecht, G. and Tittel, M., *Ger. Pat.* 1,116,660, 1960; *Chem. Abstr.*, 1962, **56**, 10189b.

88. Jenkner, H., *Z. Naturforsch.*, 1957, **B12**, 809.

89. Jenkner, H., *Ger. Pat.* 1,009,630, 1957; *Chem. Abstr.*, 1959, **53**, 21667b.

90. Schmidbaur, H. and Klein, H. F., *Angew. Chem.*, 1966, **78**, 750; *Angew. Chem. Int. Ed. Engl.*, 1966, **5**, 726.

91. Gundersen, G., Haugen, T. and Haaland, A., *J. Chem. Soc., Chem. Commun.*, 1972, 708.

92. Gundersen, G., Haugen, T. and Haaland, A., *J. Organomet. Chem.*, 1973, **54**, 77–86.

93. Wessel, H., Park, H.-S., Müller, P., Roesky, H. W. and Usón, I., *Angew. Chem.*, 1999, **111**, 850–852; *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 813–815.

94. Laubengayer, A. W. and Lengnick, G. F., *Inorg. Chem.*, 1966, **5**, 503–507.

95. Krossing, I., Nöth, H., Tacke, C., Schmidt, M. and Schwenk, H., *Chem. Ber.*, 1997, **130**, 1047–1052.

96. Ziegler, K., Köster, R., Lehmkuhl, H. and Reinert, K., *Liebigs Ann. Chem.*, 1960, **629**, 33–49.

97. Dötzer, R., *Chem.-Ing.-Techn.*, 1964, **36**, 616–637.

98. Werner, B. and Neumüller, B., *Chem. Ber.*, 1996, **129**, 355–359.

99. Kopp, M. R., Kräuter, T., Werner, B. and Neumüller, B., *Z. Anorg. Allg. Chem.*, 1998, **624**, 881–886.

100. Natta, G., Allegra, G., Perego, G. and Zambelli, A., *J. Am. Chem. Soc.*, 1961, **83**, 5033.

101. Allegra, G. and Perego, G., *Acta Crystallogr.*, 1963, **16**, 185–190.

102. Atwood, J. L. and Newberry, W. R. III, *J. Organomet. Chem.*, 1974, **66**, 15–21.

103. Gavrilenko, V. V., Chekulaeva, L. A., Antonovich, V. A. and Zakharkin, L. I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, **30**, 713–716; *Bull. Acad. Sci. USSR, Bull. Chem. Sci.*, 1981, **30**, 505–508.

104. Rennekamp, C., Stasch, A., Müller, P., Roesky, H. W., Noltemeyer, M., Schmidt, H.-G. and Usón, I., *J. Fluorine Chem.*, in press.

105. Rennekamp, C., Wessel, H., Roesky, H. W., Müller, P., Schmidt, H.-G., Noltemeyer, M., Usón, I. and Barron, A. R., *Inorg. Chem.*, 1999, **38**, 5235–5240.

106. Chen, Y.-X., Metz, M. V., Li, L., Stern, C. L. and Marks, T. J., *J. Am. Chem. Soc.*, 1998, **120**, 6287–6305.

107. Yu, P., Roesky, H. W., Demsar, A., Albers, T., Schmidt, H.-G. and Noltemeyer, M., *Angew. Chem.*, 1997, **109**, 1846–1847; *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1766–1767.

108. Yu, P., Pape, T., Usón, I., Said, M. A., Roesky, H. W., Montero, M. L., Schmidt, H.-G. and Demsar, A., *Inorg. Chem.*, 1998, **37**, 5117–5124.

109. Yasui, S., Shinohara, Y. and Yagi, Y., *Jpn. Kokai* 73 100,490; *Chem. Abstr.*, 1974, **81**, 26960k.

110. Siemens, A. G., *Fr. Pat.* 1,461,819 (1966); *Chem. Abstr.*, 1967, **67**, 17386m.

111. Roesky, H. W., Stasch, A., Hatop, H., Rennekamp, C., Hamilton, D., Noltemeyer, M. and Schmidt, H.-G., *Angew. Chem.*, 2000, **112**, 177–179; *Angew. Chem. Int. Ed. Engl.*, 2000, **39**, 171–173.

112. Waezsada, S. D., Liu, F.-Q., Murphy, E. F., Roesky, H. W., Teichert, M., Usón, I., Schmidt, H.-G., Albers, T., Parisini, E. and Noltemeyer, M., *Organometallics*, 1997, **16**, 1260–1264.

113. Waezsada, S. D., Dr Thesis, Göttingen (FRG), 1997.

114. Schnitter, C., Klimek, K., Roesky, H. W., Albers, T., Schmidt, H.-G., Röpken, C. and Parisini, E., *Organometallics*, 1998, **17**, 2249–2257.

115. Cui, C., Roesky, H. W., Noltemeyer, M., Lappert, M. F., Schmidt, H.-G. and Hao, H., *Organometallics*, 1999, **18**, 2256–2261.

116. Hatop, H., Roesky, H. W., Labahn, T., Röpken, C., Sheldrick, G. M. and Bhattacharjee, M., *Organometallics*, 1998, **17**, 4326–4328.

117. Avent, A. G., Chen, W.-Y., Eaborn, C., Gorell, I. B., Hitchcock, P. B. and Smith, J. D., *Organometallics*, 1996, **15**, 4343–4345.

118. Hatop, H., Gomm, S., Roesky, H. W. and Noltemeyer, M., unpublished results.

119. Liu, F.-Q., Gornitzka, H., Stalke, D. and Roesky, H. W., *Angew. Chem.*, 1993, **105**, 447–448; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 442–443.

120. Yu, P., Müller, P., Said, M. A., Roesky, H. W., Usón, I., Bai, G. and Noltemeyer, M., *Organometallics*, 1999, **18**, 1669–1674.

121. Wessel, H., Rennekamp, C., Roesky, H. W., Montero, M. L., Müller, P. and Usón, I., *Organometallics*, 1998, **17**, 1919–1921.

122. Wessel, H., Montero, M. L., Rennekamp, C., Roesky, H. W., Yu, P. and Usón, I., *Angew. Chem.*, 1998, **110**, 862–864; *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 843–845.

123. Schulz, S., Schoop, T., Roesky, H. W., Häming, L., Steiner, A. and Herbst-Irmer, R., *Angew. Chem.*, 1995, **107**, 1015–1016; *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 919–920.

124. Murugavel, R., Voigt, A., Walawalkar, M. G. and Roesky, H. W., *Chem. Rev.*, 1996, **96**, 2205–2236, and refs therein.

125. Murugavel, R., Bhattacharjee, M. and Roesky, H. W., *Appl. Organomet. Chem.*, 1999, **13**, 227–243.

126. Feher, F. J., Budzichowski, T. A. and Weller, K. J., *J. Am. Chem. Soc.*, 1989, **111**, 7288–7289.

127. Feher, F. J., Weller, K. J. and Ziller, J. W., *J. Am. Chem. Soc.*, 1992, **114**, 9686–9688.

128. Feher, F. J. and Weller, K. J., *Organometallics*, 1990, **9**, 2638–2640.

129. Feher, F. J. and Budzichowski, T. A., *Polyhedron*, 1995, **14**, 3239–3253.

130. Tossell, J. A., *Inorg. Chem.*, 1998, **37**, 2223–2226.

131. Montero, M. L., Usón, I. and Roesky, H. W., *Angew. Chem.*, 1994, **106**, 2198–2200; *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 2103–2105.

132. Chandrasekhar, V., Murugavel, R., Voigt, A., Roesky, H. W., Schmidt, H.-G. and Noltemeyer, M., *Organometallics*, 1996, **15**, 918–922.

133. Ritter, U., Winkhofer, N., Murugavel, R., Voigt, A., Stalke, D. and Roesky, H. W., *J. Am. Chem. Soc.*, 1996, **118**, 8580–8587.

134. Montero, M. L., Voigt, A., Teichert, M., Usón, I. and Roesky, H. W., *Angew. Chem.*, 1995, **107**, 2761–2763; *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2504–2506.

135. Coates, G. E. and Mukherjee, R. N., *J. Chem. Soc.*, 1964, 1295–1303.

136. Olapinski, H., Schaible, B. and Weidlein, J., *J. Organomet. Chem.*, 1972, **43**, 107–116.

137. Schaible, B., Haubold, W. and Weidlein, J., *Z. Anorg. Allg. Chem.*, 1974, **403**, 289–300.

138. Schaible, B. and Weidlein, J., *Z. Anorg. Allg. Chem.*, 1974, **403**, 301–309.

139. Urata, K., Itoh, K. and Ishii, Y., *J. Organomet. Chem.*, 1974, **76**, 203−213.
140. Corker, J. M., Browning, D. J. and Webster, M., *Acta Crystallogr.*, 1996, **C52**, 583−585.
141. Mason, M. R., Matthews, R. M., Mashuta, M. S. and Richardson, J. F., *Inorg. Chem.*, 1996, **35**, 5756−5757.
142. Mason, M. R., *J. Cluster Sci.*, 1998, **9**, 1−23, and refs therein.
143. Pinkas, J., Chakraborty, D., Yang, Y., Murugavel, R., Noltemeyer, M. and Roesky, H. W., *Organometallics*, 1999, **18**, 523−528.
144. Chakraborty, D., Roesky, H. W., Krätzner, R. *et al.*, to be published.
145. Yang, Y., Pinkas, J., Noltemeyer, M. and Roesky, H. W., *Inorg. Chem.*, 1998, **37**, 6404−6405.
146. Yang, Y., Schmidt, H.-G., Noltemeyer, M., Pinkas, J. and Roesky, H. W., *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3609−3610.
147. Walawalkar, M. G., Roesky, H. W. and Murugavel, R., *Acc. Chem. Res.*, 1999, **32**, 117−126.
148. Walawalkar, M. G., Murugavel, R., Roesky, H. W. and Schmidt, H.-G., *Inorg. Chem.*, 1997, **36**, 4202−4207.
149. Yang, Y., Walawalkar, M. G., Pinkas, J., Roesky, H. W. and Schmidt, H.-G., *Angew. Chem.*, 1998, **110**, 101−103; *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 96−98.
150. Yang, Y., Pinkas, J., Schäfer, M. and Roesky, H. W., *Angew. Chem.*, 1998, **110**, 2795−2798; *Angew. Chem. Int Ed. Engl.*, 1998, **37**, 2650−2653.
151. Sangokoya, S. A., Pennington, W. T., Robinson, G. H. and Hrncir, D. C., *J. Organomet. Chem.*, 1990, **385**, 23−31.
152. Cesari, M. and Cucinella, S., in *The Chemistry of Inorganic Homo- and Heterocycles* (eds Haiduc, I. and Sowerby, D. B.), Academic Press, London, 1987, vol. 1, pp. 167−190, and refs therein.
153. Robinson, G. H., in ref. 5, pp. 57−84, and refs therein.
154. Haaland, A., in ref. 5, pp. 1−56, and refs therein.
155. Allan, R. E., Beswick, M. A., Raithby, P. R., Steiner, A. and Wright, D. S., *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4153−4154.
156. Dohmeier, C., Schnöckel, H., Robl, C., Schneider, U. and Ahlrichs, R., *Angew. Chem.*, 1994, **106**, 225−227; *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 199−200.
157. Hänisch, C. K. F., Üffing, C., Junker, M. A., Ecker, A., Kneisel, B. O. and Schnöckel, H., *Angew. Chem.*, 1996, **108**, 3003−3005; *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 2875−2877.
158. Schulz, S. and Nieger, M., *Organometallics*, 1998, **17**, 3398−3400.
159. Schulz, S. and Nieger, M., *Organometallics*, 1999, **18**, 315−319.
160. Schulz, S. and Nieger, M., *Angew. Chem.*, 1999, **111**, 1020−1021; *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 967−968.
161. Sinn, H. and Kaminsky, W. (eds), *Macromolecular Symposia*: *Alumoxanes*, Hüthig und Wepf, Zug, 1995, **97**, 1−246, and refs therein.
162. Fink, G., Mülhaupt, R. and Brintzinger, H. H. (eds), *Ziegler Catalysts*, Springer, Berlin, 1995, and refs therein.
163. Kaminsky, W. and Sinn, H. (eds), *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer, Berlin, 1988, and refs therein.
164. Oliver, J. P., Kumar, R. and Taghiof, M., in ref. 5, pp. 167−195, and refs therein.
165. Barron, A. R., *Comments Inorg. Chem.*, 1993, **14**, 123−153, and refs therein.
166. Barron, A. R., *Chem. Soc. Rev.*, 1993, **22**, 93−99, and refs therein.
167. Oliver, J. P. and Kumar, R., *Polyhedron*, 1990, **9**, 409−427, and refs therein.
168. Vyazankin, N. S., Bochkarev, M. N. and Charov, A. I., *J. Organomet. Chem.*, 1971, **27**, 175−180.
169. Hirabayashi, T., Inoue, K. and Yokota, K., *J. Organomet. Chem.*, 1975, **92**, 139−145.
170. Imaeda, H., Hirabayashi, T., Itoh, K. and Ishii, Y., *Organomet. Chem. Synth.*, 1970/1971, **1**, 115−125.
171. Cowley, A. H., Jones, R. A., Harris, P. R., Atwood, D. A., Contreras, L. and Burek, C. J., *Angew. Chem.*, 1991, **103**, 1164−1166; *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 1146−1148.
172. Harlan, C. J., Gillan, E. G., Bott, S. G. and Barron, A. R., *Organometallics*, 1996, **15**, 5479−5488.
173. Schnitter, C., Klemp, A., Roesky, H. W., Schmidt, H.-G., Röpken, C., Herbst-Irmer, R. and Noltemeyer, M., *Eur. J. Inorg. Chem.*, 1998, 2033−3039.
174. Cui, C., Roesky, H. W. and Noltemeyer, M., to be published.
175. Cui, C., Roesky, H. W., Noltemeyer. M. and Schmidt, H.-G., *Organometallics*, 1999, **18**, 5120−5123.
176. Harlan, C. J. and Barron, A. R., *J. Cluster Sci.*, 1996, **7**, 455−467.