Organoaluminum chemistry at the forefront of research and development

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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 AlCl₃ with elemental potassium. In 1859 W. Hallwachs and S. Schafarik synthesized the first organoaluminum compound Et₃Al₂I₃ from elemental Al and EtI, but it took almost 100 years before K. Ziegler 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.

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 with HX in the gas phase at 1000°C or by comproportionation of Al with AlCl₃ at 850°C (ref. 12), with alkaliorganyls at low temperatures. The halides are monomeric in the gas phase and oligomeric in solution below –100°C. Higher temperatures lead to disproportionation into metallic Al and AlX₃. However, they can be stabilized by donor molecules. Several of them have been characterized by X-ray diffraction, they contain planar four-membered Al₄ rings with the halogens and the donors mutually trans, e.g. (BrAl·NEt₃)₄ (ref. 18), (IAl·NEt₃)₄ (ref. 13) and (IAl·PET₃)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 (X₂Al·L)₂ have been synthesized and most of them structurally characterized with the donor ligands in trans-positions: X = Cl, Br, L = Me₂NSiMe₃ (ref. 20), X = I, L = OEt₂, PET₃ (ref. 20) and X = Br, L = OMePh (ref. 21). The latter has been obtained by comproportionation of ‘AlBr’ with inadvertently present AlBr₃ 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 Cl₂Al·3Py (Py = pyridine) seem rather doubtful.

The first reports on low-valent organoaluminum compounds by E. P. Schram and co-workers date back to the late sixties, who investigated the reaction of [(Me₂N)₂B]₂ with AlMe₃. They claimed the synthesis of yellow materials of the composition Me₂Al(AlMe₃)B (ref. 22) with an Al(Al)₃...
core and Me₂Al₃(NMe₂)₃ (ref. 23), respectively, with an Al₃ chain based on elemental analysis, IR and NMR spectra and oxidative hydrolysis. Another doubtful compound of composition [(H₂B)₂Al]₂ ‘proved’ by deuterolysis was added later²⁴. Hoberg and Krause reported the reduction of iBu₃AlCl with K to yield (iBu₃Al)₂ which they claimed through solvolysis with MeOD (ref. 25). Further reduction performed by Schram was believed to result in a compound K₂Al₂Bu₁₀ with an Al₁₃ chain via intermediate KAI₂Bu₁ (ref. 26). By repeating the reaction of iBu₃AlCl with K, Uhl and co-workers¹⁴ unambiguously proved the ‘compound’ to be a mixture of K(iBu₃AlCl), K(iBu₃AlCl₂) and another species (vide infra). Similar reductions reported by Hoberg et al. of iBu₃Al to yield K₂(AlBu₁₀₂)₂ (ref. 27) and Et₃Al via radicalic K(AlEt₃) to finally yield K(AlEt₃) (ref. 28), had to be revised, the former was also found to be a tetraorganoaluminate²⁹. Similarly, the compound K₂(iBu₃AlH)₂ reported by Gavrilenko et al.³⁰ was found to be K₂(iBu₃AlH)³¹.

The first authentic and structurally characterized compound with an Al–Al bond was reported by Uhl in 1988, who reduced Bis₂AlCl (Bis = (Me₂Si)₂CH) with elemental K and obtained (Bis₂Al)₂ as colourless crystals³². The X-ray structure reveals an almost planar C₃-Al–AlC₃ core. A second dialuminum compound, (Trip₂Al)₂ (Trip = 2,4,6-iPr₃C₆H₂) was synthesized in 1993 by Power et al.³³ and fully characterized.

The attempted synthesis of a sterically crowded alane Si₃Al (Si = iBu₃Si) afforded under elimination of Si₂ another dialane (Si₂Al₃) instead³⁴. Treatment of (Si₂Al₃) with bases like LiMe or LiBu results in the formation of anionic species (Si₂Al·AlSiliX₃), X = Me, H, the latter by elimination of isobutene. Both compounds have been structurally characterized³⁵ with (Li₂Tmeda)⁺ (Tmeda = (Me₂NCH₂)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(PMe₂)₂ results under C–H bond activation by the base in the formation of an anion with a five-membered AlC₅ ring as shown by X-ray structure analysis³⁷.

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, (Bis₂Al)₂⁻ 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 = dimethoxymethane)³⁸ or Li in Et₂O. The X-ray structure of (Li₂Tmeda)⁺(Bis₂Al)₂⁻ has been reported³⁹. The analogous anion (Trip₂Al)₂⁻ 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 characterized³⁵.

Heating the dialane (Si₃Al₂) to 80°C affords a black-green solution assigned to the neutral radical Si₃Al–AlSi₃ by ESR spectroscopic investigations. Further heating of this radical or the dialane to 135°C results in the low yield formation of (Si₃Al)₄ (vide infra)⁴⁰. All reactions of dialanes are summarized in Scheme 1.

The first tetrahedrane of Al were published in 1991 independently by Schnöckel et al.⁴⁰, (Cp*Al)₄ from

\[
\begin{align*}
2 \text{R}_2 \text{AlX} + 2 \text{K} & \rightarrow \text{R}_2 \text{AlR}_2 + 2 \text{KX} \\
\text{X} = \text{Cl, Br} & \quad \text{X} = \text{Cl, Br} \\
\text{R} = \text{Bis, Trip} & \quad \text{X} = \text{Cl, Br} \\
& \rightarrow 2 \text{KX} \\
\text{AIX}_3 + 6 \text{SiNa} & \rightarrow \text{Si}_2 \text{Al} \text{AlSi}_i \rightarrow (\text{SiAl})_4 \\
\text{X} = \text{Cl, Br} & \quad \text{X} = \text{Cl, Br} \\
(\text{ALX}_3)_2 + 6 \text{SiNa} & \rightarrow 80°C \rightarrow 135°C \\
\text{X} = \text{Cl, Br} & \quad \text{X} = \text{Cl, Br} \\
\text{Si}_2 \text{Al} \text{AlSi}_i & \rightarrow (\text{SiAl})_4 \\
& \rightarrow (\text{SiAl})_4 \\
\text{Li·Tmeda} & \rightarrow (\text{Bis}_2 \text{Al} \text{AlBis}_2 \text{X})^- \quad \text{X} = \text{H, Me, Br}
\end{align*}
\]

Scheme 1. Reactions of dialanes.

‘AlCl’ and MgCp*₂, and Wiberg and co-workers, (SiAl)₄ from ‘AlCl’ and NaSi₃ (ref. 41) in moderate yields. While the former has been structurally characterized, spectroscopical and structural data on the latter have become available only recently⁴²,⁴³. Slightly better yields of (Cp*Al)₄ (ref. 44) and a third structurally characterized Al₃ tetrahedron (TrisAl)₄
isolated in very low yield. Its X-ray structure reveals a shell-of a cubic centered packing in 4% yield a compound (Li\(\text{CCH}_2\))\(_4\)AlCl with K via transient \([\text{Me}_2\text{CCH}_2\text{Al}]_2\) but was not fully characterized.\(^{40}\)

While mass spectroscopical investigations of \((\text{TrisAl})_4\) show the molecular ion\(^{40}\), and \(^{13}M/2\) has been found in the MS of \((\text{SiAl})_4\) (ref. 42), the monomeric unit \(\text{Cp*Al}\) has been detected as the peak of highest mass from \((\text{Cp*Al})_4\) (refs 40, 44). This is consistent with gas phase electron diffraction studies of \((\text{Cp*Al})_4\) at ca. 140°C which show monomeric \(\text{Cp*Al}\) with the ligand bound in a \(\%_5\) fashion.\(^{37}\) A mixed substituted compound, \([(\text{Cp*Al})_4\text{AlN(SiMe}_3)_2]\), available from \((\text{Cp*Al})_4\) and \(\text{LiN(SiMe}_3)_2\) under elimination of \(\text{LiCp*}\), has been structurally characterized.\(^{46}\) Several substituted cyclopentadienyl aluminium compounds have been generated \(\text{in situ}\) and investigated by \(^{27}\text{Al}\)-NMR spectroscopy. While \([(\text{Cp*Al})_4\text{AlCp}]\), \((\text{Cp*Al})_4\), \((\text{BuC}_2\text{H}_2\text{Al})_4\) and \([(\text{Cp*Al})_4\text{AlN(SiMe}_3)_2]\) do not dissociate in solution, \(\text{PrC}_3\text{HAl}\), \((\text{Me}_2\text{Si})_2\text{C}_2\text{H}_4\text{Al}\) and \((\text{PhCH}_2\text{C}_2\text{H}_4\text{Al}\) have been found monomeric and for \((\text{Cp*Al})_4\) and \([(\text{Me}_2\text{Si})_2\text{C}_2\text{H}_4\text{Al}]_2\), both oligomers \((n = 1, 4)\) have been detected.\(^{48}\)

The reaction of ‘\(\text{AlCl}\)’ with \(\text{LiBu}\) affords NMR spectroscopically traceable \((\text{BuAl})_6\) which after reduction with \(\text{Na/K}\) alloy yields the radical anion \((\text{BuAl})_6^{–}\). 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 3Bu\(_2\)AlCl with K a third compound is isola\(\text{ble in 1.5}\%\) yield. X-ray structure investigations show the compound to have the formula \(\text{K}_2(\text{BuAl})_3_{12}\) with an icosahedral dianion isoelectronic to the homologous boranate anion.\(^{50}\)

A ‘carbaaluminane’ of composition \([(\text{MeAl})_8((\text{CCH}_2\text{Ph})_2)]^+\) is available in 60% yield from the reaction of \(\text{Me}_2\text{AlH}\) with \(\text{Me}_2\text{AlC}═\text{CPh}\) in an approximately 2:1 molar ratio. Its structure is best described as a distorted \(\text{Al}_8\) cube with five planes bridged by a \(\%_C\)-C atom and the remaining by \(\%_H\) (see Figure 2) (ref. 51).

The reaction of ‘\(\text{AlCl}\)’ with \(\text{LiN(SiMe}_3)_2\) at \(-78°C\) affords in 4% yield a compound \((\text{Li·3Et}_2\text{O})\)\([[(\text{Me}_2\text{Si})_2\text{N}]_{\text{AlL}}]_{\text{2}}(\text{C}_6\%_H\%)\). The \(\text{AlL}\) unit can be regarded as a section of a cubic centered packing.\(^{52}\)

From the analogous reaction of ‘\(\text{AlBr}\)’ with \(\text{LiN(SiMe}_3)_2\), a black compound of composition \([(\text{Me}_2\text{Si})_2\text{N}]_{\text{2}}\text{AlL}\) has been isolated in very low yield. Its X-ray structure reveals a shell-like array of Al atoms not identical with the arrangement in the metal. The \((\text{Me}_2\text{Si})_2\text{N}\) ligands span \(\text{Al}_8\) planes.\(^{53}\)

A compound of composition \((\text{Cp*Al})_4\) has been obtained in low yields as colourless crystals unstable at r.t. from a suspension of \((\text{Cp*Al})_4\) and excess \([\text{I}_2\text{Al(}\%_I\])_2\) in \(\text{PhMe}\) at \(-20°C\). The X-ray structure shows a rather distorted geometry with a \(\text{Cp*Al}–\text{Al}(\%_I)–\text{AlCp*}\) chain and a \(\text{Cp*Al–AlI}_2\) moiety connected by two bridging I atoms. Its genesis can be rationalized by insertion of monomeric \(\text{Cp*Al}\) fragments into three of the four bridging \(\text{Al–I}\) bonds of dimeric \(\text{AlI}_3\) (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. 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 \((\text{K·3Dme})^+(\text{BisAl})_2\)\(^{–}\) 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 \(\text{BisAlMe}\) and \(\text{KO(\text{CH}_2)_2\text{OMe}}\) in Dme (eq. 1). The analogous Li compound is also available from the reaction of excess Li with \((\text{BisAl})_2\) in Dme.\(^{56}\)

\[
(K\cdot3\text{Dme})^+(\text{BisAl})_2\)\(^{–}\) \rightarrow K + 2\text{BisAlMe} + 2\text{KO(\text{CH}_2)_2\text{O}}
\]

While the reductive dehalogenation of TrisAlCl\(_2\) results in the formation of a \(\text{Al(III)}\) 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.\(^{57}\)
A similar, but five-coordinated Al species has been obtained 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 intermediates have been assigned by means of $^{27}$Al-NMR spectroscopy$^{57}$.

$$2 \text{‘AlI'} + 2 \text{Dme} \xrightarrow{-30^\circ \text{C}} \text{MeO} \xrightarrow{1,2\text{Dme}} \text{Me}$$

(3)

A double C–O bond fission of Thf has been found in attempts to recrystallize compounds of the type Ar(R)NAlF$_2$·Thf, where either Ar or R have less steric requirements (Ar = 2,6-Me$_2$C$_6$H$_3$, R = Me$_2$BuSi, Ar = 2,6-iPr$_2$C$_6$H$_3$, R = Me$_3$Si) than in the compounds

Figure 2. Structures of (TrisAl)$_4$ (from ref. 45), (iBuAl)$_{12}^{2-}$ (from ref. 50), [(MeAl)$_6$(CCH$_2$Ph)$_3$H] (from ref. 51) and [((Me$_3$Si)$_2$NAl)$_3$]$_2$(%$_6$-Al)$^+$ (from ref. 52) (outer substituents partially omitted for clarity).

Figure 3. Core of the hexakistetrahedron of [[Ar(R)NAlF$_2$]$_4$ (AlF$_2$·Thf)$_2$(%$_6$-O)] (N bound ligands and Thf-C=Cs omitted for clarity) (from ref. 58).
with \( R = 2,6-i\text{Pr}_2\text{C}_6\text{H}_3 \), \( R = \text{Me}_2i\text{PrSi} \) or \( \text{Me}_2t\text{BuSi} \), 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 \( \text{Al}_6\text{F}_{12} \) 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.

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

The first examples of C–H bond activation have been found in cyclopentadienyl complexes. The reaction of \( \text{Cp}_2\text{TiCl} \) with \( \text{Et}_3\text{Al} \) was first reported by Natta et al. in 1959 (ref. 60) and its structure was determined as \( \text{(Cp}_2\text{TiAlEt}_2}_2 \) with the Al atom bound to Ti and one C atom of a cyclopentadienyl ring and a Ti–Ti bond.

Later, Tebbe and Guggenberger revised the reaction and redetermined the structure (Figure 5). The \( \text{Et}_2\text{Al} \) 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 \( %^3 \) to one Cp ring, \( %^3 \) to the Al substituted cyclopentadienyl ring and \( %^1 \) to the C atom bearing the \( \text{Et}_2\text{Al} \) unit.

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

The reaction of \( \text{Cp}^*\text{TiCl} \) with \( \text{LiAlH}_2 \) with inadvertently present \( \text{H}_2\text{O} \) results in low yields in the compound depicted in Figure 6 with abstraction of one H atom from a methyl group of one \( \text{Cp}^* \) ring.

Two groups have independently investigated the reaction of \( \text{Cp}_2\text{MoH}_2 \) with \( \text{Me}_3\text{Al} \). They isolated and structurally characterized two compounds with a \( \text{Mo}_2\text{Al}_3 \) and a \( \text{Mo}_2\text{Al}_4 \) core (Figure 7) both arising from C–H bond fission of \( \text{Cp} \) rings.

The Mo–Al(\( \text{Me}_2 \)) bonds in the \( \text{Mo}_2\text{Al}_3 \) compound are much longer than the Mo–Al(\( \text{Me} \)) bonds suggesting possible Mo(\( %^5 \)-H)Al bridges.

A totally insoluble compound with \( \text{W}_2\text{Al}_3 \) core analogous to the \( \text{Mo}_2\text{Al}_3 \) compound has also been synthesized and characterized by elemental analysis and comparison of the IR spectra.

The reaction of \( \text{bis(chloromercuri)ferrocene} \) with two equivalents of \( \text{Me}_3\text{Al} \) affords in low yield a compound with an \( \text{Al}_4\text{Fe}_2 \) 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 \( \text{CH}_2\text{P(Ph}_2\text{X)}_2 \) (X = O, S) with trialkylalanes.
and diisobutyaluminumhydride. 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 H₂S (ref. 72). The attempted synthesis of a dimeric iminoalane from thermolysis of (Me₂AlNHC₆H₃-2,4,6-iBu₃)₂ resulted under loss of methane and cleavage of an o-C–H bond in a dimeric aminoa lane as seen from its X-ray structure (Figure 9) (ref. 75).

Similarly, the oxidation of Cp*Al with MesN₃ (Mes = 2,4,6-Me₃C₆H₂) did not yield the expected dimeric iminoa lane, instead the tricyclic compound shown in Figure 10 with migration of a proton of an o-CH₃ group to N had formed²⁶.

Thermolysis of the adduct Cl₃Al-NH₂C₆H₃-2,4,6-iBu₃ at 150°C proceeded in a retro-Friedel–Crafts reaction under elimination of isobutene to the complex Cl₃Al-NH₂C₆H₃-2,4,6-iBu₃ (ref. 75).
Ortho-metalation with elimination of iBuH has also been found in the thermolysis of the monolithiated dimeric aminoalane [(iBu₂Al)₂(⁻⁻NHMes)(⁻⁻NLiMes)].

The ladder-shaped complex with an Al₄N₄ core as revealed from its X-ray structure (Figure 11) has been obtained in low yields after recrystallization from hexane.

The reaction of Me₃Al with excess Ph₂NH in boiling PhMe proceeds in high yield under MeH evolution and o-metalation of one Ph group. The X-ray structure of [(⁻⁻Ph₂N)₂(AlMe)₂(⁻⁻PhNC₆H₄)] shows an Al₃N₂ four-membered ring with the Al atoms spanned by a NC₂ bridge. Similar o-metalations have been postulated earlier from thermolysis of (Et₂AlNPh₂)₂ and Cl₃Al·HNPh₂. The compounds were characterized by mass spectrometry and deuteration experiments, but no structural data are available.

The reaction of tetrameric (Cp*ZrF₃)₄ with 20 equivalents of Me₃Al at r.t. affords in high yield a cluster of composition [(Cp*Zr)₃AlMe₆(⁻⁻CH₂)(⁻⁻CH)(⁻⁻CH₂)] with elimination of methane and (Me₃AlF)₄, whose structure is depicted in Figure 12. Its most prominent features are the hypervalent carbon atoms bridging the metal centers. Similarly, an (EtC₅Me₄)Zr cluster and the isostructural Cp*Hf complex have been synthesized, albeit the latter in very low yields, the main product being Cp*HfMe₃ 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.

**Organooaluminum fluorides**

Pioneering work on organooaluminum fluorides has again been achieved by Ziegler and co-workers, who in 1955 reported the reactions of NaF with Et₃Al and...
Me₂AlCl to yield Na⁺ salts of anionic fluoride species (Et₂AlF)⁻, [(Et₂Al₂)(%-%)F]⁻ and (Me₂AlF₂)⁻, respectively. Reviews on organoaluminum fluorides besides those mentioned in the introduction have been published by Weidlein in 1973 (ref. 81) and recently by Rosicky et al. Neutral diorganoaluminum monofluorides with various organic substituents (R₂AlF), are available by metathesis of the appropriate aluminum chloride with NaF (refs 80, 83–86), higher alkali fluorides, BaF₂ (ref. 87), by fluorine/alkyl exchange in triorganoalanes with BF₃·OEt₂ (ref. 88), SiF₄, R₂SiF₂, ZnF₂, CdF₂, SbF₅, PbF₂ (ref. 89), by thermal decomposition of the dinuclear species Me₂Si(%-%)AlEt₂ (ref. 90) and by commutation of AlF₃ with Et₂Al (ref. 83). Gas phase electron diffraction shows (Me₂AlF), to exist as a puckered eight-membered ring with Al(%-%)FAl bridges.¹⁸ Tetrameric aggregates are also present in solution as seen from cryoscopic molecular weight determinations in benzene of (Me₂AlF)₄, (Et₂AlF)₄ (ref. 85) and (tBu₂AlF)₄ (ref. 88). While the tetrameric unit remains unchanged upon substitution of one Me group on each Al atom by DippNH (Dipp = 2,6-iPr₂C₆H₃) as seen from its EI–MS spectrum with the ligands mutually trans, the reaction of (Et₂AlF)₄ with MeNH₂ at r.t. affords a glassy oligomer (MeNHAlEtF), of unknown structure. In contrast, trimeric species have been postulated from cryoscopic measurements and IR investigations of (Pr₃AlF)₃ and (tBu₃AlF)₃ (ref. 86). A dimeric complex (Tmp₂AlBr) (Tmp = 2,2,6,6-Me₂-piperidyl) has been structurally characterized from the reaction of Tmp₂AlBr with AgBF₄ via intermediate formation of Tmp₂Al(%-%)FBF₄ (ref. 95). At low temperatures monomeric amine adducts Et₃AlF–NMMe₃ and Et₃AlF–NH₂Me are formed from Et₃AlF and the appropriate amine, the former disintegrates into the tetramer and amine at r.t. while the latter eliminates CH₃ (vide supra). A weakly associated tBu₃AlF-dioxane complex loses the donor upon distillation.

Mononuclear ionic complexes M⁺(R₂AlF)⁻ are available from stoichiometric reactions of alkali fluorides with trialkylalanes without solvent at >100°C (refs 80, 96) or in solvents at r.t. The X-ray structure of Cs⁺(Me₂AlF) shows isolated Me₂AlF 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. Cs⁺(tBu₃AlF)⁻ has also been reported by Neumüller et al. but no structural details are given. Anhydrous Me₃N⁻F⁻ forms a similar complex as do the adducts Et₃Al-NMe₃ and Et₃Al-PMe₃ upon reaction with PhCH₂F (ref. 97). Addition of a second equivalent R₂Al to those complexes results in the formation of dinuclear anions [R₂Al(%-%)AlR₂]⁻ (refs 80, 96, 97) with a linear Al(%-%)FAl bridge as seen from the X-ray structures of K⁺[Et₂Al(%-%)F]⁺ with weak K–C contacts and (K⁺⁻, C₆H₆)[(Me₂Al₂)(%-%)F]⁻ (ref. 102). Mixed anions [R₂Al(%-%)F-Al⁺%-%F]⁻ with R, R⁺⁺ = Me, Et, iBu, Et, tBu are available from reactions of the mononuclear ionic species with the appropriate alanes. K⁺ salts of [C₆H₅CH₂Al(R₂)₂(%-%)F]⁻ with R = Et, iBu have been described from the reaction of KF with the gem-dialanes C₆H₅CH₂AlR₂ as viscous oils. They are believed to contain a bent Al(%-%)FAl bridge, but a dimeric structure with linear units would also be consistent with the analytical data given.

A neutral compound with bent Al(%-%)FAl bridges has been obtained from the reaction of DippNH₂ (Dipp = 2,6-iPr₂C₆H₃) with (Me₂AlF)₃ at 0°C. Two of the original Al(%-%)FAl bridges have been substituted by DippNH fragments yielding an eight-membered ring compound with an Al₁₁N₆F₂ core. The Al–F bond lengths are similar to those in (Me₂AlF)₄. An amine adduct Me₂AlF-DippNH₂ has been considered as intermediate prior to HF elimination. Such an adduct, Me₂AlF-tBuNH₂ has been found in the reaction with the more basic amine tBuNH₂ as an infinite one-dimensional chain connected via H–F hydrogen bonding as the final product. Similar Al–F bond cleavage reactions have been observed in reactions of (Me₂AlF)₄ with DippOH and triethylcitrate, respectively (eqs 4, 5) and structurally characterized.

![Figure 12. Structure of [(Cp*Zr)₃Al₄Me₄(=C₆H₅)₂(=C₆H₅)(=C₆H₅)⁺](from ref. 78).](image-url)
The first compound comprises one of the rare examples containing a four-membered $\text{Al}_2\text{F}_2$ ring.

Marks and co-workers have synthesized several cationic $\text{Zr}$ complexes of $(\text{Ar}_3\text{AlF})^-$ (Scheme 3).

The X-ray structures of the $\text{Ph}_3\text{C}^+$- and $(\text{Cp}^\ast\text{ZrMe})^+$ salts have been determined, the latter shows a linear $\text{Al}(\%\text{-F})\text{Zr}$ bridge. Several of the Zr complexes have been found active catalysts for the isotactic polymerization of propene$^{106}$.

Reactions of trialkylalanes with $[\text{Cp}^\land\text{TiF}(\mu-O)]_4$ (Cp$^\land = \text{Cp}^\ast$, EtC(Me)$_3$) yield adducts $[\{\text{Cp}^\land\text{Ti}(\mu-O)\}_4\text{F}_2(\%\text{-F})\text{AlR}_3]_{4-n}$ with almost linear $\text{Al}(\%\text{-F})\text{Ti}$ bridges. While the tetrakis- and trisadducts are stable only at lower temperatures, with Me$_3\text{Al}$ at r.t. only the trans-bisadduct is formed (Scheme 4). Monoadducts are exclusively formed with the bulkier alanes Et$_3\text{Al}$ and (PhCH)$_3\text{Al}$. Several of the compounds have been structurally characterized$^{107,108}$.

Pyrolysis of the above-mentioned compound [DippNH$\text{AlMe}(\%\text{-F})]_4$ (Dipp = 2,6-iPr$_2$C$_6$H$_3$) at 165°C yields under elimination of DippNH$_2$ a cubane depicted in Figure 13. Two eight-membered $\text{Al}_4\text{F}_2\text{N}_2$ 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$_3\text{Al}$ and AlF$_3$ at higher temperatures$^{83}$ or from EtAlCl$_2$ and NaF (ref. 84) and of Na$^+$($\text{R}_2\text{AlF}_2$)$^-$ (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 $\odot$-complexes of Ni and Co (ref. 109) and a French patent describes the use of (Me$_3\text{NCH}_2\text{Ph})^+$ salts of (Et$_2\text{AlF})^+$, [Et$_2\text{Al}(\%\text{-F})\text{AlEt}_2\text{F}]^-$ and (EtAlF)$_3^-$ as electrolytes for the electrodeposition of Al (ref. 110).
Reactions of the alanes Me₃Al and (Me₃Si)₂CaMe₂·Thf with Bu₃NF·HF₂⁺ at r.t. proceed via elimination of MeH under formation of the respective Bu₃NF·(MeRAfF₂)⁺ salts in almost quantitative yields. Both compounds have been structurally investigated.

(Me₃SnF)₂ has been proven the fluorinating agent of choice in metathetic fluorinations of RAfMe₂ compounds to yield RAfF₃ complexes with Me₃Sn elimination. Reactions of RN(SiMe₃)₂R⁺·AlMe₂·Thf with R = 2,6-iPr₂C₆H₄ = (Dipp), R⁺ = Me, iPr, tBu and R = 2,6-Me₂C₆H₄, R⁺ = tBu, Mes in Thf at r.t. with two equivalents of Me₃SnF affords monomeric compounds RN(SiMe₃)₂R⁺·AlF₃·Thf (refs 58, 112), while the reaction of the solvent-free dimeric RN(SiMe₃)₂R⁺·AlMe₂·Thf with R = Me, iPr, tBu, and (Me₃Si)₂ instead of R⁺ 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.

A compound with Me₃SiBu as substituent on N instead of Me₃Si has also been obtained with the same fluxional behaviour.

Analogously, TrisAlMe₂·Thf (Tris = (Me₃Si)₂C) and Me₃SnF yield a monomeric Thf adduct which loses the donor upon heating to 200°C to afford another structurally characterized trimeric organoaluminum difluoride. This compound is the first structurally characterized neutral organoaluminum fluoride with exocyclic Al–F bonds. The adduct formation is reversible. Only a dimer is found upon fluorination of the aza-allyl substituted compound Me₃SiNC(Ph)C(SiMe₃)₂AlMe₂. The complex shows five-coordinated Al atoms in the solid state and fluxional behaviour in solution.

A diorganodialuminumpentafiuoride anion is formed in the reaction of TrisAlF₂·Thf (Tris = (Me₃Si)₂C) with KF in Thf. Two F₂Al(−F)AlF₂ units with a bent middle Al(−F)Al bridge are clenched by two (K·2Thf)⁺ cations resulting in a distorted geometry (Figure 14). A [(TrisAlF₂)(−F)]⁻ anion with a linear Al(−F)Al bridge is present in the compound (AlF₂·4Thf)`[(TrisAlF₂)₂(−F)]⁻ generated from the reaction of (TrisAlF₂)₂ with AgF₂, which is also likely in NH₄⁺(Tris₂AlF₃)⁻, obtained in high yield from addition of NH₄⁺F⁻ to the trimeric difluoroalane. (Ag·3PhMe)⁺[Li(TrisAlF₃)]⁻ is the product of the concerted action of AgF and LiCl on (TrisAlF₂)₂. The Li atom is tetrahedrally surrounded by the outer F atoms of two FAl(−F)Al moieties. This is in contrast to the structures of (Li·Thf)⁺(TrisAlF₃)⁻, obtained from fluorination of (Li·2Thf)⁺(TrisAlH₃)⁻ with 70% HF in pyridine 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 $\mu$-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($\mu$-F)AlF$_2$Tris] and [Cp$_2$Zr($\mu$-F)$_2$AlFTris](%-%O)] (ref. 59). The reactions of (Cp*MF)$_3$ (M = Zr, Hf) with Me$_3$Al afford 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$^\equiv$Ti($\mu$-F)$_2$AlF$_2$] are formed from Al and three equivalents of Cp$^\equiv$TiF$_2$ (ref. 119).

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

A compound with an [Al$_4$Ti$_2$($\mu$-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)$_2$MeMe$_3$AlF] in refluxing toluene. The structure consists of 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-iPr$_2$C$_6$H$_3$) occurs in reactions of the trimeric iminoalane (MeAlNDipp)$_3$ with Cp$^\equiv$MF$_3$ compounds (M = Zr, Cp$^\equiv$ = (Me$_3$Si)$_2$C$_5$H$_3$ (ref. 121), M = Ti, Cp$^\equiv$ = Cp (ref. 121), M = Ti, Cp$^\equiv$ = Me$_3$SiC$_5$H$_4$ (ref. 122) and M = Ti, Cp$^\equiv$ = Cp* (ref. 122) to yield heteroadamantane cages (Scheme 5). While with the lesser bulky Cp$^\equiv$ 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$_4$($\mu$-F)$_4$($\mu$-Si)$_2$ core will be discussed later.$^{123}$

**Organoauminum 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.$^{124,125}$
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$_9$]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(%-%-%)-OAl (ref. 127) and Al(%-%-%)-OSi (ref. 128) bridges have also been realized. Tossell has performed calculations on the 6-31G* level on the compounds Si$_2$Al$_2$O$_2$H$_8$ and Si$_2$Al$_2$O$_2$H$_2$. He confirmed the ‘drum’ structures (Figure 18) experimentally found by our group as local minima.

Reactions of the stable silanetriol DippN(SiMe$_3$)$\cdot$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$_2$AlBu$_2$Li$_2$, 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 %-%-%-O atoms is formed. Performing the equimolar reaction at 65°C results in complete elimination of iBuH and H$_2$ leaving a compound [[DippN(SiMe$_3$)Si(%-%-%-O)$_2$AlThf$_2$]]$_2$ 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$^+$)[RAI(%-%-%-O)$_2$SiN(SiMe$_3$)Dipp]$_2$– 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).
Aluminophosphinates were known since 1964, when Coates and Mukherjee obtained compounds of formulae $\left[\text{Me}_2\text{Al}(\mu-O)\text{PR}_2\right]_n$ with R = Me, Ph from reactions of $\text{Me}_3\text{Al}$ with the appropriate phosphinic acids\textsuperscript{135}, but complete structural information was not available until recently. Weidlein et al. suggested the compounds to possess eight-membered rings on the basis of IR measurements\textsuperscript{136} and comparison with similar heterocycles\textsuperscript{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\textsuperscript{137,138}. No ring size was given by Japanese researchers, who synthesized $\left[\text{Et}_2\text{Al}(\mu-O)_2\text{P(OR)}_2\right]_n$ with R = Me, Et via two different routes\textsuperscript{139}. In 1996 two groups independently described the structures of two complexes exhibiting the expected eight-membered rings $\left[\text{Me}_2\text{Al}(\mu-O)_2\text{PPh}_2\right]$ (ref. 140) and $\left[\text{tBu}_2\text{Al}(\mu-O)_2\text{P(OSiMe}_3)\right]_2$ (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 $\left[\text{tBu}_2\text{Al}(\mu-O)_2\text{PPh}_2\right]$ and $\left[\text{tBu}_2\text{Al}(\mu-O)_2\text{P(OSiMe}_3)\right]_2$ (ref. 142), $\left[\text{R}_2\text{Al}(\mu-O)_2\text{P(OSiMe}_3)\right]_2$ via intermediate Lewis acid base adducts $\text{R}_2\text{AlR}^+\cdot\text{OP(OSiMe}_3)$, (R = Me, Et, R$^+$ = Me, Et, Cl) (ref. 143), $\left[\text{tBu}_2\text{Al}(\mu-O)_2\text{P((Bu)OSiMe}_3)\right]_2$ and $\left[\text{Me(Cl)Al}(\mu-O)_2\text{PPh}_2\right]$ (ref. 144) from the appropriate precursors.

Probably template directed is the synthesis of the compound shown in Figure 20 from $\text{tBuP(O)(OH)}_2$ and $\text{Na}^+\text{(EtAlH)}^-$. The molecule is constructed of twelve-membered Al$_3$P$_3$O$_6$ 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 $\mu_5$-O atoms connecting the two halves of the molecule\textsuperscript{145}.

A tetrameric aluminophosphate $\left[\text{BuAl}(\mu-O)_2\text{P(OSiMe}_3)\right]_4$ has been formulated from the reaction of $\text{BuAlCl}_2$ with OP(OSiMe$_3$)$_3$ from analytical and spectroscopical data\textsuperscript{131}. Reactions of several alanes R$_3$Al with phosphonic acids RP(O)(OH)$_2$ afford smoothly with alkane elimination tetrameric aluminophosphonates.
Figure 20. Structure of [{Na(Thf)}Na_2(AlBuP(\text{tBu})_3)_2]_2 (from ref. 145) (\text{tBu} and Et groups and Thf-C’s omitted for clarity).

Figure 21. Structures of [{BuAl(\%\text{O})_2PrBu}_4] (from ref. 146) and [{MeAl(\%\text{O})_2PrBu}_4] (from ref. 149).
[RAI(\%\text{O})_2Pr(\text{R} = \text{tBu}, \text{Me}, \text{tBu} (refs 146–148); Me, \text{tBu} (ref. 148); Me, Me; \text{tBu}, \text{Me} and \text{tBu}, \text{Ph} (ref. 141))]. The X-ray structures of several of these molecules show the expected cubic array\textsuperscript{141,146} (Figure 21).

Aside from the tetramer, a hexamer [{MeAl(\%\text{O})_2PrBu}_6] has been isolated in low yields from the reaction of Me_3Al with \text{tBuP(O)(OH)}_2. Its X-ray structure exhibits two crown-shaped twelve-membered rings connected by six eight-membered rings (Figure 21)\textsuperscript{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})_2PMe}_10] has been postulated from molecular weight determination. Prolonged standing reforms the tetramer and minor amounts of a hexamer, suggesting equilibria in solution\textsuperscript{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\textsuperscript{142,146}. Fluorine is the structure directing element in the reaction of Cs\textsuperscript{3}(tBuAlF)\textsuperscript{3} with \text{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\textsuperscript{150}.

**Cage compounds of aluminum 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\textsuperscript{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})_2(\%\text{SiPh}_2)_2] with a distorted adamantane-like structure (Figure 23) (ref. 123).

Figure 22. Core of the structure of [{[(Cs\text{Thf})_3(\mu_4-\text{F})(\text{BuAl})_2(\text{BuPO}_3)_3][[(\text{BuAl})_2Al(\%\text{F})_2(\text{BuPO}_3)_4]]} (from ref. 150) (All outer substituents omitted for clarity).
While Al–N cage compounds with a wide variety of structures are available from thermolysis of (predominantly) dimeric aminoalanes with \([\text{RAL}(%_3\text{NR})^\bigodot]\)_4 cubanes as the best examined class\(^{151-155}\), Al-P chemistry is mainly restricted to four- and six-membered (AlP)\(_n\) rings\(^{154}\). The only structurally characterized (AlP)\(_4\) cubane, \([i\text{BuAl}(%_3\text{P})_{2}\text{PSiPh}_3]_4\), has been obtained by A. H. Cowley \textit{et al.} from the reaction of \(i\text{Bu}_2\text{AlH}\) with \(\text{Ph}_3\text{SiPH}_2\) via intermediate formation of \textit{cis}trans isomers of \([i\text{Bu}_2\text{Al}(%_3\text{PSiPh}_3)]_2\) 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 \([\text{MeAl}(%_3\text{NMes})]_4\) with excess \(\text{LiPHCy}\) (Mes = mesityl, Cy = cyclohexyl) under elimination of MesNH\(_2\) and LiNHMes. Its structure is shown in Figure 24. Two [MeAl(%_3PCy)]\(_2\) 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 \([\text{Cp}^*\text{Al}]_4\text{P}_4\). 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 \(^\text{1}\) bound, while the two other remain \(^\text{5}\) co-ordinated\(^{156}\).

Reaction of (Cp*Al)\(_4\) with \((t\text{BuAs})_4\) proceeds via elimination of \(i\text{BuH}\) and \(\text{Me}_2\text{CCH}_2\) to yield a compound \([\text{Cp}^*\text{Al}]_4\text{P}_3\text{As}_2\) with the Cp* ligands bound \(^\text{1}\) whose structure is according to Wade’s rule \textit{closo} (Figure 26) (ref. 157).

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

Additionally, several monocyclic \([R_2\text{AlSb(SiMe}_3)_2]_n\) compounds \((R_2 = 2\text{Et}, 2\text{iBu}, n = 2\) (ref. 158); \(R_2 = 2\text{Me}; \text{Me, Cl, n} = 3\) (ref. 159)) and the first complex containing Al–Bi...
bonds, [Me₂AlBi(SiMe₃)₂]₃ (ref. 160) have been synthesized and structurally characterized.

Organoaaluminum oxides and hydroxides exhibit a great structural diversity, some of them have shown catalytic activities for a variety of reactions161–163. On the other hand, non-condensed Al–S-, Al–Se- and Al–Te compounds with covalent bonds form predominantly dimeric or trimeric associates164–167. In several cases condensation, elimination or insertion reactions have been observed to yield chalcogel nolates [RAI(μ₃-E)]ₖ, E = S, Se, Te (Scheme 6).

The syntheses of high-melting, totally insoluble compounds [EtAl(μ₃-E)], with E = S, Se and Te from Et₃Al and ‘hydrogen equivalent’ sulphides, (Et₃M)₂xEH₃ (M = Si, n = 1, M = Ge, n = 0) by Vyazankin et al.168 and of [Et₂Al(μ₃-S)]ₙ from Et₃Al and H₂S with identical properties by Hirabayashi and co-workers169,170 have been reported. The latter assigned ₙ = 4 by comparison with other known structures with tetrameric cages. In the light of formation of higher aggregated cages by diminishing the steric requirements142,149, higher oligomers are more likely.

The first authentic cubanes [tBuAl(μ₃-E)]₄, (E = S, Se, Te) have been obtained by Cowley et al. from tBu₃Al and the respective chalcogens via isolable intermediates [tBu₃Al(μ₃-E/tBu)]₆ and characterized by mass spectroscopy171. Shortly after-

**Scheme 6.** Syntheses of [RAI(μ₃-E)]ₖ compounds.
wards our group succeeded in the synthesis and first structural characterization of tetrameric \([\text{Cp}^*\text{Al}(\%_3\text{-Se})_4]\) and \([\text{Cp}^*\text{Al}(\%_3\text{-Te})_4]\) cages with slightly distorted cubic cores\(^{44}\). By reactions of \(\text{R}_2\text{Al}\) compounds containing the bulky substituents \(t\text{Bu}\) and \(t\text{Am}(=\text{Me}_2\text{EtC})\) with \(\text{H}_2\text{S}\), \(\text{Se}\), and \(\text{Te}\), Barron \textit{et al.} also obtained heterocubanes of \(\text{S}\), \(\text{Se}\) and \(\text{Te}\). The structures of \([\text{tA}-\text{mAl}(\%_E)_4]\) with \(E = \text{S}, \text{Se}\) have been determined. Additionally, the \(\text{H}_2\text{S}\) reactions yielded hexamers which have been separated from the tetramers by fractional crystallization (\(t\text{Am}\)) or sublimation of the tetramer (\(t\text{Bu}\)) and characterized spectroscopically\(^{172}\). Surprisingly the analogous reaction of \(\text{TrisAlMe}_2\text{Thf}\) (\(\text{Tris} = (\text{Me}_3\text{Si})_3\text{C}\)) with \(\text{H}_2\text{S}\) takes a different course; pyrolysis of the intermediate \([\text{TrisAl-Thf(µ-S)}]_2\), which has been isolated in high yield and structurally characterized, led to two different cubanes. Aside from the expected \([\text{TrisAl}(\%_3\text{-S})_4]\), a second compound had formed, \([\text{(TrisAl)}_2(\text{MeAl})(\%_3\text{-S})_4]\), 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-(\(\text{Et}_2\text{N})_2\text{C}_6\text{H}_3\text{AlH}_2\) with elemental tellurium\(^{174}\) and aza-allyl compound \([\text{Me}_3\text{SiNCPhC(SiMe}_3)_2\text{AlH(µ-H)}]_2\) with \(\text{Se}\) and \(\text{Te}\) (ref. 175) opens up a new access to dimeric organoaluminum chalcogenides. The \(\text{Al}\) atoms of all three compounds are tetrahedrally surrounded by \(\text{C}\), \(\text{N}\) and two chalcogen atoms. The aza-allyl compounds are present in solution as an equilibrium of \(\text{cis}\) and \(\text{trans}\) isomers as seen from \(^1\text{H}-\text{NMR}\)
sponds, while the X-ray structure (Figure 28) only reveals the trans isomer in the crystal.\(^\text{175}\)

Reaction of the tBu substituted sulphur cubane with two equivalents of Cp\(_2\)ZrMe\(_2\) results in partial breakdown of the cage. One tBuAlS moiety inserts into one Zr–Me bond of one molecule Cp\(_2\)ZrMe\(_2\) while the second adds to the remainder to yield a compound with an Al\(_2\)(C\(_5\)-S\(_3\))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.\(^\text{176}\)

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.

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