

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 AlCl_3 with elemental potassium. In 1859 W. Hallwachs and S. Schafarik synthesized the first organoaluminum compound $\text{Et}_3\text{Al}_2\text{I}_3$ from elemental Al and EtI ¹, but it took almost 100 years before K. Ziegler² 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 reports³⁻⁹. 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

with HX in the gas phase at 1000°C or by compression of Al with AlCl_3 at 850°C (ref. 12), with ligand organyls 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. $(\text{BrAl} \cdot \text{NEt}_3)_4$ (ref. 18), $(\text{IAl} \cdot \text{NEt}_3)_4$ (ref. 13) and $(\text{IAl} \cdot \text{PET}_3)_4$ (ref. 19).

They are stable as solids at r.t. but disproportionate even at low temperatures in solution into Al(0) and Al(III) , some with ligand exchange. Thus, dimeric complexes $(\text{X}_2\text{Al} \cdot \text{L})_2$ have been synthesized and in some of them structurally characterized with the donor ligands in *trans*-positions: X = Cl, Br, L = $\text{Me}_2\text{NSiMe}_3$ (ref. 20), X = I, L = OEt_2 , PET_3 (ref. 20) and X = Br, L = OMePh (ref. 21). The latter has been obtained by disproportionation 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 reaction at 120°C described by G. A. Olah *et al.* as well as the claim of a monomeric species $\text{Cl}_2\text{Al} \cdot 3\text{Py}$ (Py = pyridine) seem rather doubtful¹².

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

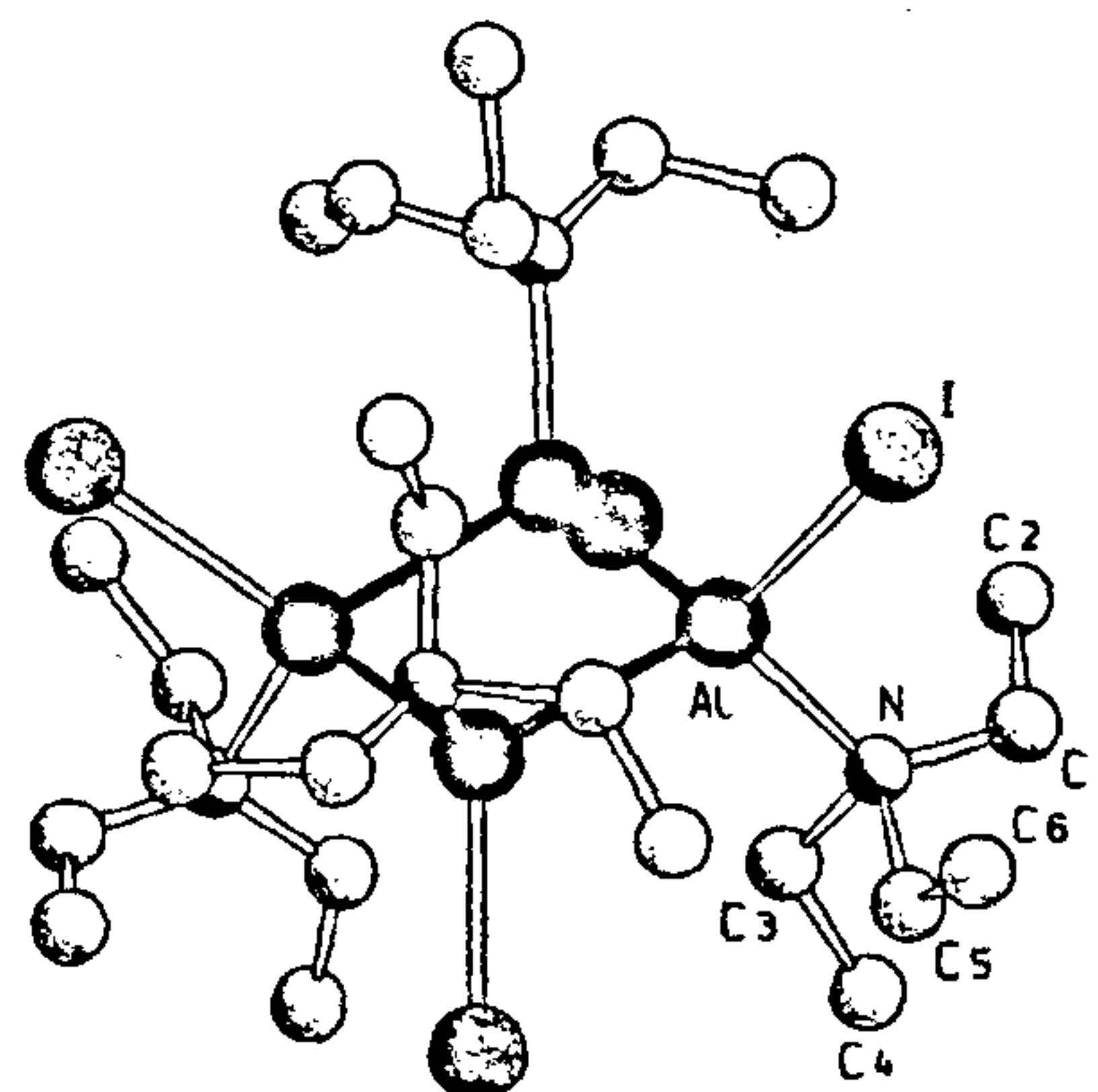


Figure 1. Structure of $(\text{IAl} \cdot \text{NEt}_3)_4$ (from ref. 13).

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

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late sixties, who investigated the reaction of $[(\text{Me}_2\text{N})_2\text{B}]_2$ with AlMe_3 . They claimed the synthesis of yellow materials of the composition $\text{Me}_6\text{Al}_4(\text{Me}_2\text{N})_3\text{B}$ (ref. 22) with an $\text{Al}(\text{Al})_3$ core and $\text{Me}_3\text{Al}_3(\text{NMe}_2)_3$ (ref. 23), respectively, with an Al_3 chain based on elemental analysis, IR and NMR spectra and oxidative hydrolysis. Another doubtful compound of composition $[(\text{H}_2\text{B})_2\text{Al}]_2$ 'proved' by deuterolysis was added later²⁴. Hoberg and Krause reported the reduction of $i\text{Bu}_2\text{AlCl}$ with K to yield $(i\text{Bu}_2\text{Al})_2$ which they claimed through solvolysis with MeOD (ref. 25). Further reduction performed by Schram was believed to result in a compound $\text{K}_3\text{Al}_5i\text{Bu}_{10}$ with an Al_5 chain via intermediate KAl_2iBu_3 (ref. 26). By repeating the reaction of $i\text{Bu}_2\text{AlCl}$ with K, Uhl and co-workers¹⁴ unambiguously proved the 'compound' to be a mixture of $\text{K}(i\text{Bu}_3\text{AlCl})$, $\text{K}(i\text{Bu}_2\text{AlCl}_2)$ and another species (*vide infra*). Similar reductions reported by Hoberg *et al.* of $i\text{Bu}_3\text{Al}$ to yield $\text{K}_2(\text{Al}i\text{Bu}_3)_2$ (ref. 27) and Et_3Al via radicalic $\text{K}(\text{AlEt}_3)$ to finally yield $\text{K}(\text{AlEt}_4)$ (ref. 28), had to be revised, the former was also found to be a tetraorganoaluminate²⁹. Similarly, the compound $\text{K}_2(i\text{Bu}_2\text{AlH})_2$ reported by Gavrilenko *et al.*³⁰ was found to be $\text{K}(i\text{Bu}_3\text{AlH})$ ³¹.

The first authentic and structurally characterized compound with an Al–Al bond was reported by Uhl in 1988, who reduced Bis_2AlCl ($\text{Bis} = (\text{Me}_3\text{Si})_2\text{CH}$) with elemental K and obtained $(\text{Bis}_2\text{Al})_2$ as colourless crystals³². The X-ray structure reveals an almost planar $\text{C}_2\text{Al}–\text{AlC}_2$ core. A second dialuminum compound, $(\text{Trip}_2\text{Al})_2$ ($\text{Trip} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$) was synthesized in 1993 by Power *et al.*³³ and fully characterized.

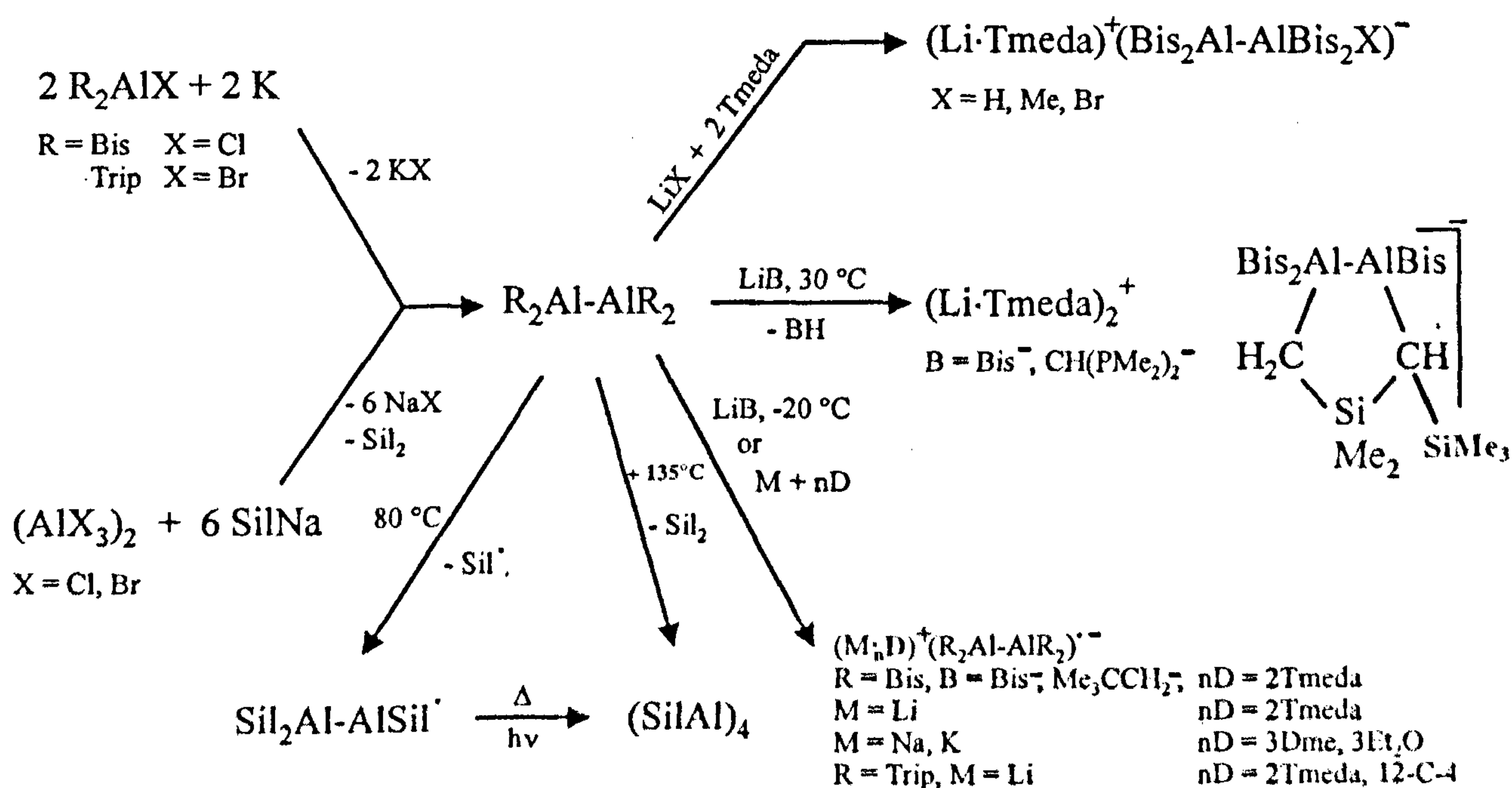
The attempted synthesis of a sterically crowded alane Si_3Al ($\text{Si} = i\text{Bu}_3\text{Si}$) afforded under elimination of Si_2

another dialane $(\text{Si}_2\text{Al})_2$ instead³⁴. Treatment of $(\text{Si}_2\text{Al})_2$ with bases like LiMe or $\text{Li}t\text{Bu}$ results in the formation of anionic species $(\text{Si}_2\text{Al}–\text{AlSi}_2\text{X})^-$, $\text{X} = \text{Me}, \text{H}$, the latter by elimination of isobutene. Both compounds have been structurally characterized³⁵ with $(\text{Li} \cdot 2\text{Tmeda})^+$ ($\text{Tmeda} = (\text{Me}_2\text{NCH}_2)_2$) 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 $\text{X} = \text{Br}$ (ref. 36). Reaction of the dialane with stronger bases like LiBis or $\text{LiCH}(\text{PMe}_2)_2$ results under C–H bond activation by the base in the formation of an anion with a five-membered $\text{Al}_2\text{C}_2\text{Si}$ 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, $(\text{Bis}_2\text{Al})_2^{\cdot-}$ 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 ($\text{Dme} = \text{dimethoxyethane}$)³⁸ or Li in Et_2O . The X-ray structure of $(\text{Li} \cdot 2\text{Tmeda})^+(\text{Bis}_2\text{Al})_2^{\cdot-}$ has been reported³⁹. The analogous anion $(\text{Trip}_2\text{Al})_2^{\cdot-}$ 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 characterized³³.

Heating the dialane $(\text{Si}_2\text{Al})_2$ to 80°C affords a black-green solution assigned to the neutral radical $\text{Si}_2\text{Al}–\text{AlSi}^\cdot$ by ESR spectroscopical investigations. Further heating of this radical or the dialane to 135°C results in the low yield formation of $(\text{SiAl})_4$ (*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, $(\text{Cp}^*\text{Al})_4$ from



'AlCl' and MgCp^*_2 , and Wiberg and co-workers, $(\text{SiAl})_4$ from 'AlCl' and NaSiI (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 $(\text{Cp}^*\text{Al})_4$ (ref. 44) and a third structurally characterized Al_4 tetrahedron $(\text{TrisAl})_4$ ($\text{Tris} = (\text{Me}_3\text{Si})_3\text{C}$) (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 $(\text{Me}_3\text{CCH}_2\text{Al})_4$ has been reported from the reduction of $(\text{Me}_3\text{CCH}_2)_2\text{AlCl}$ with K via transient $[(\text{Me}_3\text{CCH}_2)_2\text{Al}]_2$ but was not fully characterized⁴⁶.

While mass spectroscopical investigations of $(\text{TrisAl})_4$ show the molecular ion⁴⁶, and $M/2$ has been found in the MS of $(\text{SiAl})_4$ (ref. 42), the monomeric unit Cp^*Al has been detected as the peak of highest mass from $(\text{Cp}^*\text{Al})_4$ (refs 40, 44). This is consistent with gas phase electron diffraction studies of $(\text{Cp}^*\text{Al})_4$ at ca. 140°C which show monomeric Cp^*Al with the ligand bound in a η^5 fashion⁴⁷. A mixed substituted compound, $[(\text{Cp}^*\text{Al})_3\text{AlN}(\text{SiMe}_3)_2]$, available from $(\text{Cp}^*\text{Al})_4$ and $\text{LiN}(\text{SiMe}_3)_2$ under elimination of LiCp^* , has been structurally characterized⁴⁸. Several substituted cyclopentadienyl aluminum compounds have been generated *in situ* and investigated by ^{27}Al -NMR spectroscopy. While $[(\text{Cp}^*\text{Al})_3\text{AlCp}]$, $(\text{CpAl})_4$, $(t\text{BuC}_5\text{H}_4\text{Al})_4$ and $[(\text{Cp}^*\text{Al})_3\text{AlN}(\text{SiMe}_3)_2]$ do not dissociate in solution, $i\text{Pr}_4\text{C}_5\text{HAl}$, $(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2\text{Al}$ and $(\text{PhCH}_2\text{C})_5\text{Al}$ have been found monomeric and for $(\text{Cp}^*\text{Al})_n$ and $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\text{Al}]_n$ both oligomers ($n = 1, 4$) have been detected⁴⁸.

The reaction of 'AlCl' with $\text{Li}t\text{Bu}$ affords NMR spectroscopically traceable $(t\text{BuAl})_6$ which after reduction with Na/K alloy yields the radical anion $(t\text{BuAl})_6^{\cdot-}$. 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 solution⁴⁹.

As mentioned above, from the reduction of $i\text{Bu}_2\text{AlCl}$ with K a third compound is isolable in 1.5% yield. X-ray structure investigations show the compound to have the formula $\text{K}_2(i\text{BuAl})_{12}$ with an icosahedral dianion isoelectronic to the homologous boranate anion⁵⁰.

A 'carbaaluminane' of composition $[(\text{MeAl})_8(\text{CCH}_2\text{Ph})_5\text{H}]$ is available in 60% yield from the reaction of Me_2AlH with $\text{Me}_2\text{AlC}\equiv\text{CPh}$ in an approximately 2:1 molar ratio. Its structure is best described as a distorted Al_8 cube with five planes bridged by a $\mu_4\text{-C}$ atom and the remaining by $\mu\text{-H}$ (see Figure 2.) (ref. 51).

The reaction of 'AlCl' with $\text{LiN}(\text{SiMe}_3)_2$ at -78°C affords in 4% yield a compound $(\text{Li}\cdot 3\text{Et}_2\text{O})^+\{[(\text{Me}_3\text{Si})_2\text{NAl}]_3\}_2(\mu_6\text{-Al})^-$. The Al_7 unit can be regarded as a section of a cubic centered packing⁵².

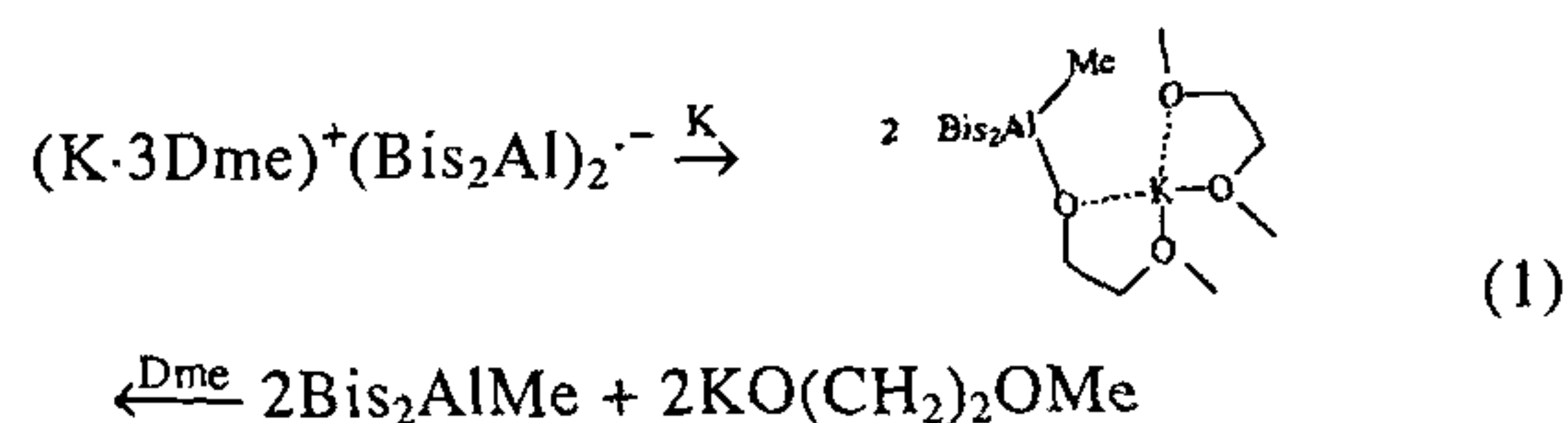
From the analogous reaction of 'AlBr' with $\text{LiN}(\text{SiMe}_3)_2$ a black compound of composition $[(\text{Me}_3\text{Si})_2\text{N}]_{20}\text{Al}_{17}$ has been isolated in very low yield. Its X-ray structure reveals a shell-like array of Al atoms not identical with the arrangement in the metal. The $(\text{Me}_3\text{Si})_2\text{N}$ ligands span Al_4 planes⁵³.

A compound of composition $(\text{Cp}^*_3\text{Al}_5\text{I}_6)$ has been obtained in low yields as colourless crystals unstable at r.t. from a suspension of $(\text{Cp}^*\text{Al})_4$ and excess $[\text{I}_2\text{Al}(\mu\text{-I})_2]$ in PhMe at -20°C . The X-ray structure shows a rather distorted geometry with a $\text{Cp}^*\text{Al}-\text{Al}(\text{I})_2-\text{AlCp}^*$ chain and a $\text{Cp}^*\text{Al}-\text{AlI}_2$ 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).

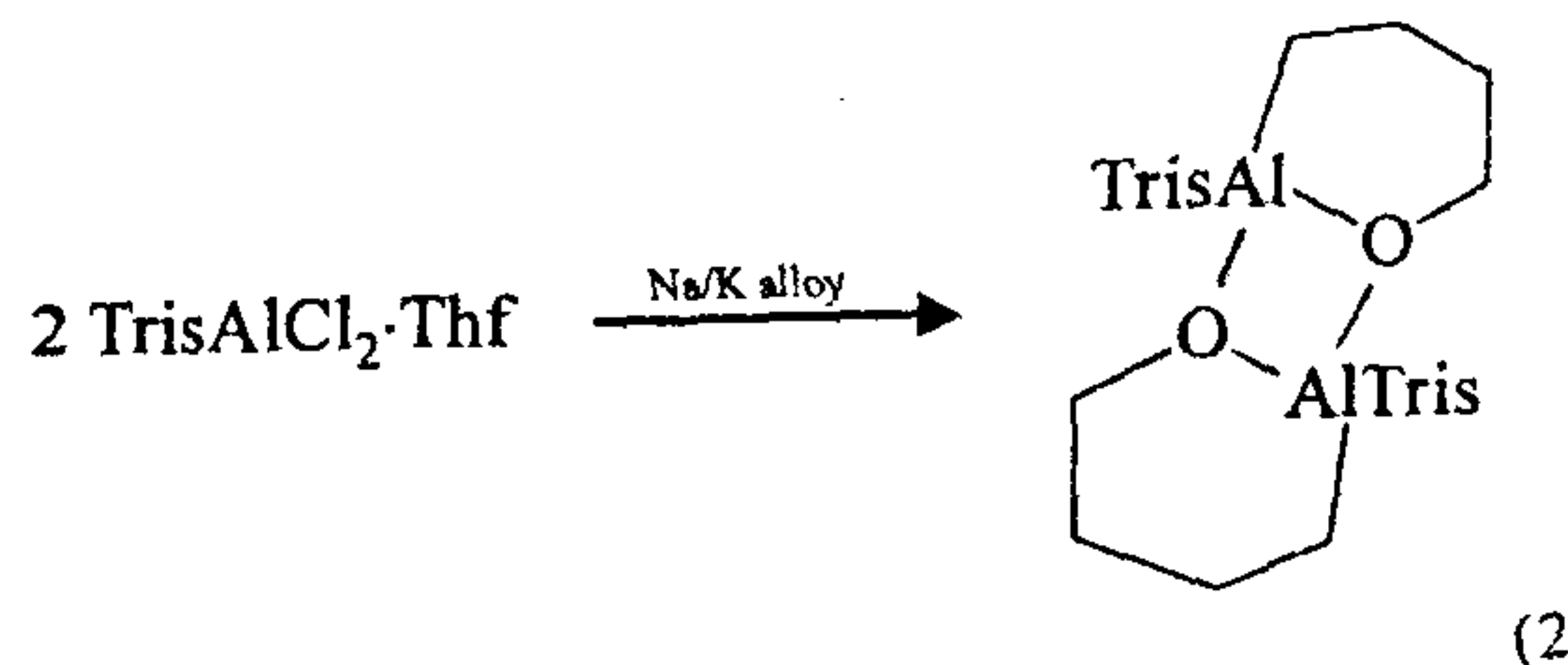
Bond activation by aluminum compounds

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 ethers⁵⁵. 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 $(\text{K}\cdot 3\text{Dme})^+(\text{Bis}_2\text{Al})_2^{\cdot-}$ 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_2AlMe 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 $(\text{Bis}_2\text{Al})_2$ in Dme⁵⁶.



While the reductive dehalogenation of TrisAlCl_2 results in the formation of a $\text{Al}(\text{I})$ compound (*vide supra*), with the adduct $\text{TrisAlCl}_2\cdot\text{Thf}$ 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 determined⁴⁵.



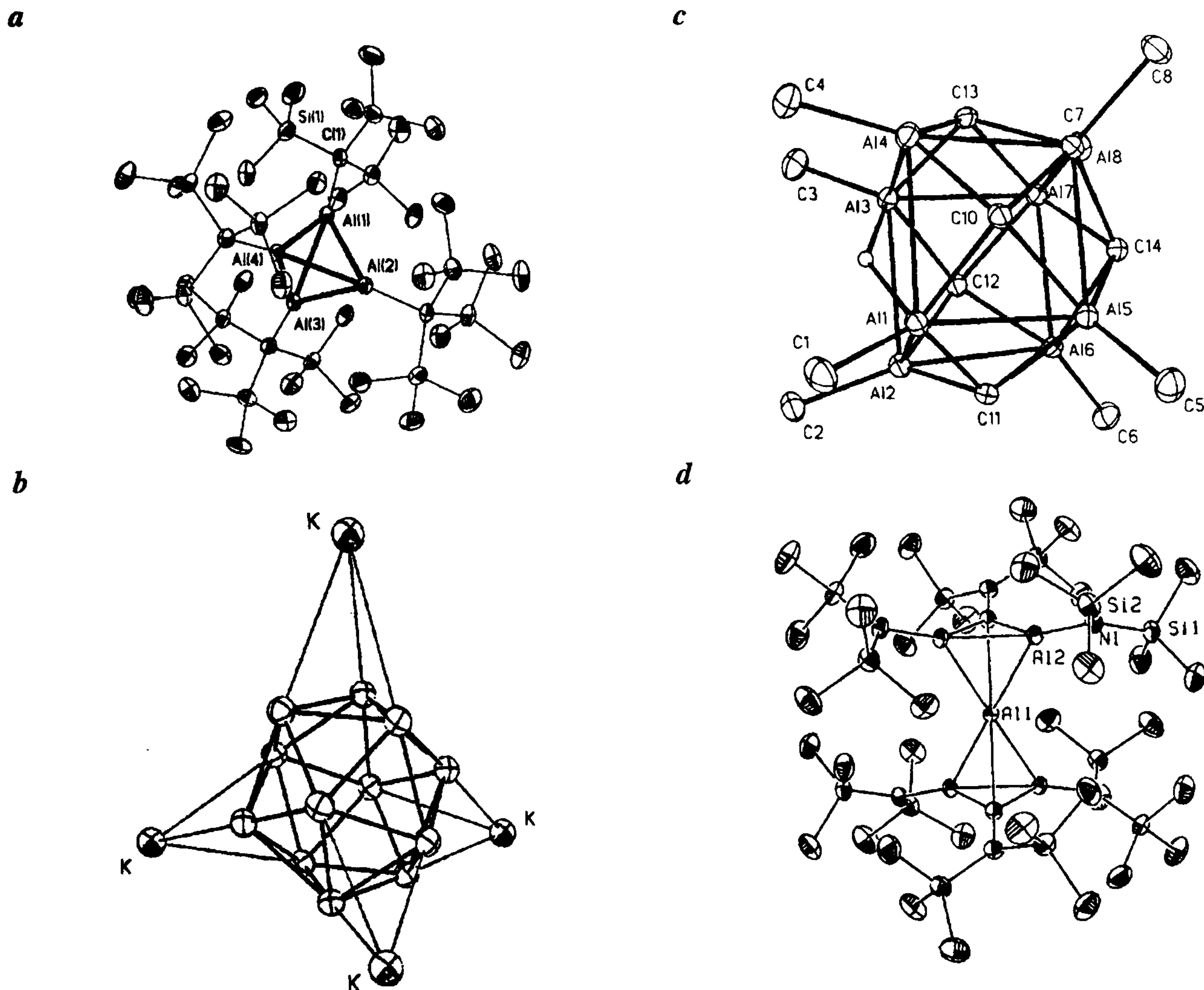
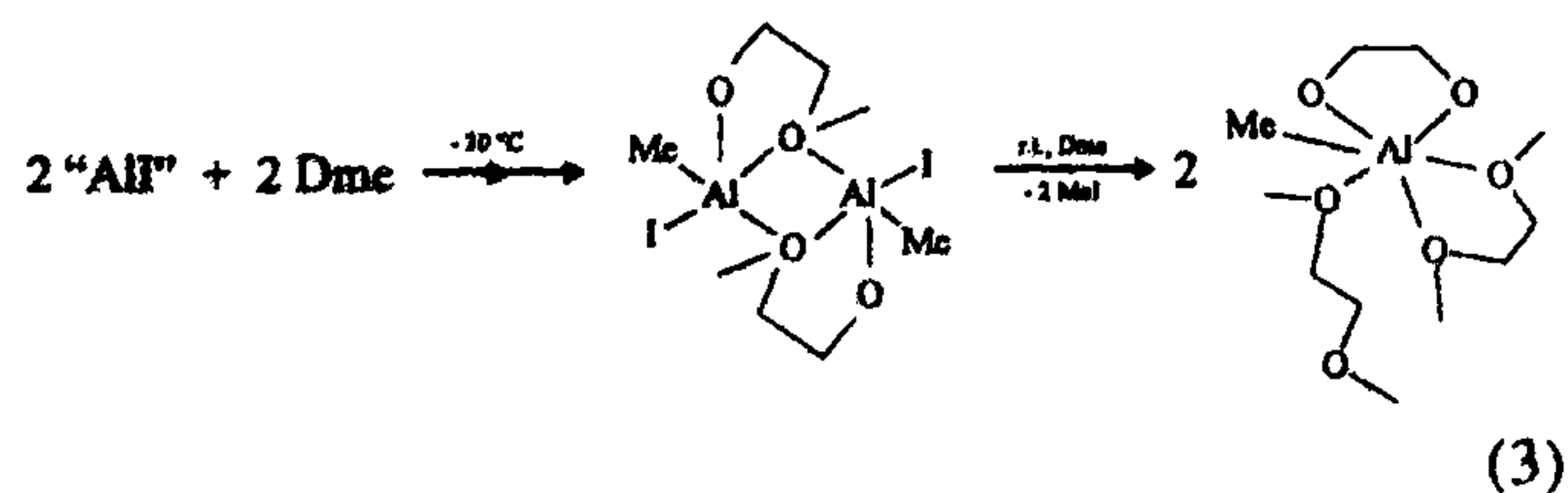


Figure 2. Structures of $(\text{TrisAl})_4$ (from ref. 45), $(i\text{BuAl})_{12}^{2-}$ (from ref. 50), $[(\text{MeAl})_8(\text{CCH}_2\text{Ph})_5\text{H}]$ (from ref. 51) and $[(\text{Me}_3\text{Si})_2\text{NAl}]_3(\mu_6\text{-Al})^-$ (from ref. 52) (outer substituents partially omitted for clarity).

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 spectroscopy⁵⁷.



A double C–O bond fission of Thf has been found in attempts to recrystallize compounds of the type $\text{Ar}(\text{R})\text{NAlF}_2\cdot\text{Thf}$, where either Ar or R have less steric requirements ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $\text{R} = \text{Me}_2t\text{BuSi}$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$, $\text{R} = \text{Me}_3\text{Si}$) than in the compounds

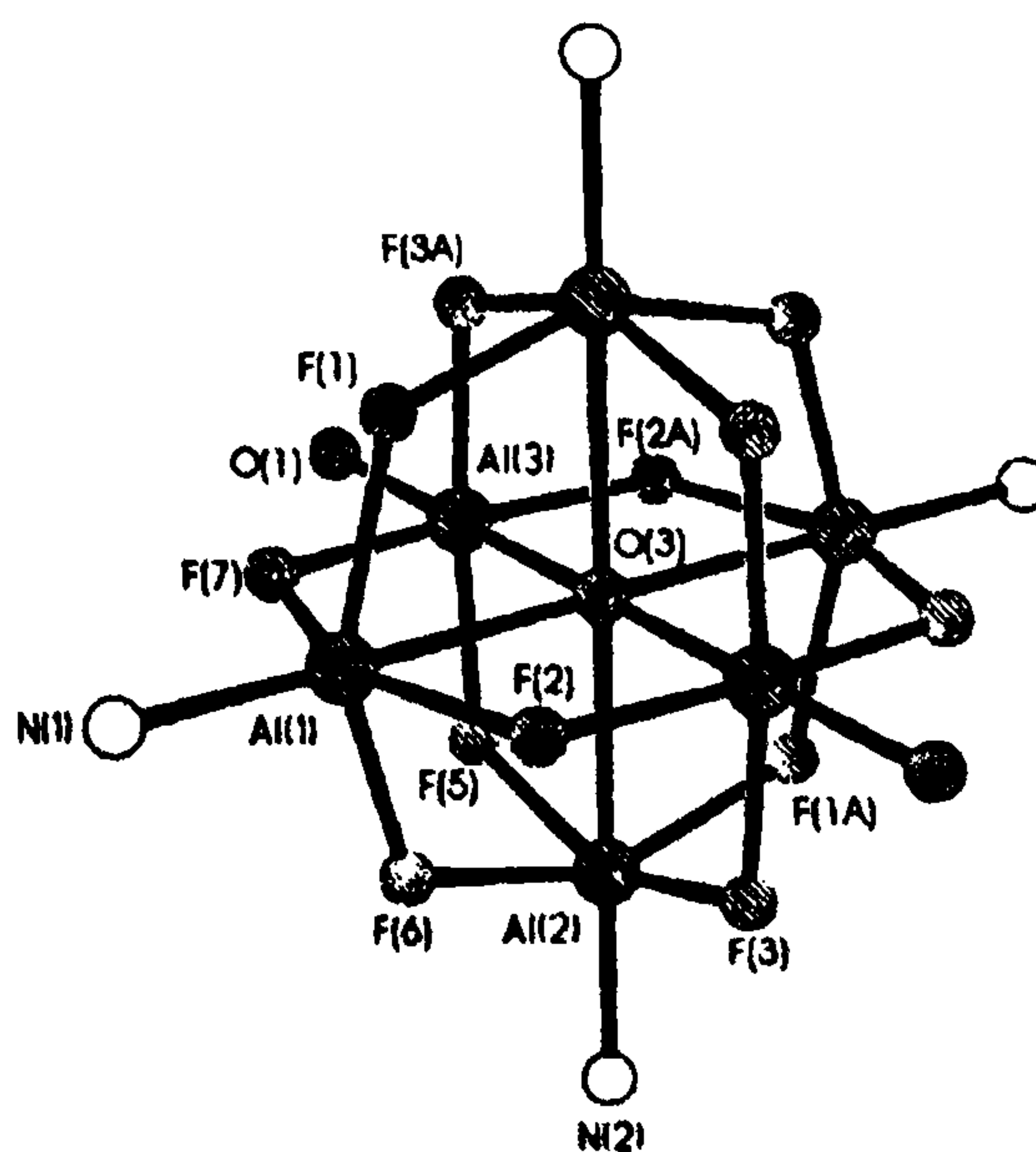


Figure 3. Core of the hexakistetrahedron of $[\text{Ar}(\text{R})\text{NAlF}_2]_4$ ($(\text{AlF}_2\cdot\text{Thf})_2(\mu_6\text{-O})$) (N bound ligands and Thf-C's omitted for clarity) (from ref. 58).

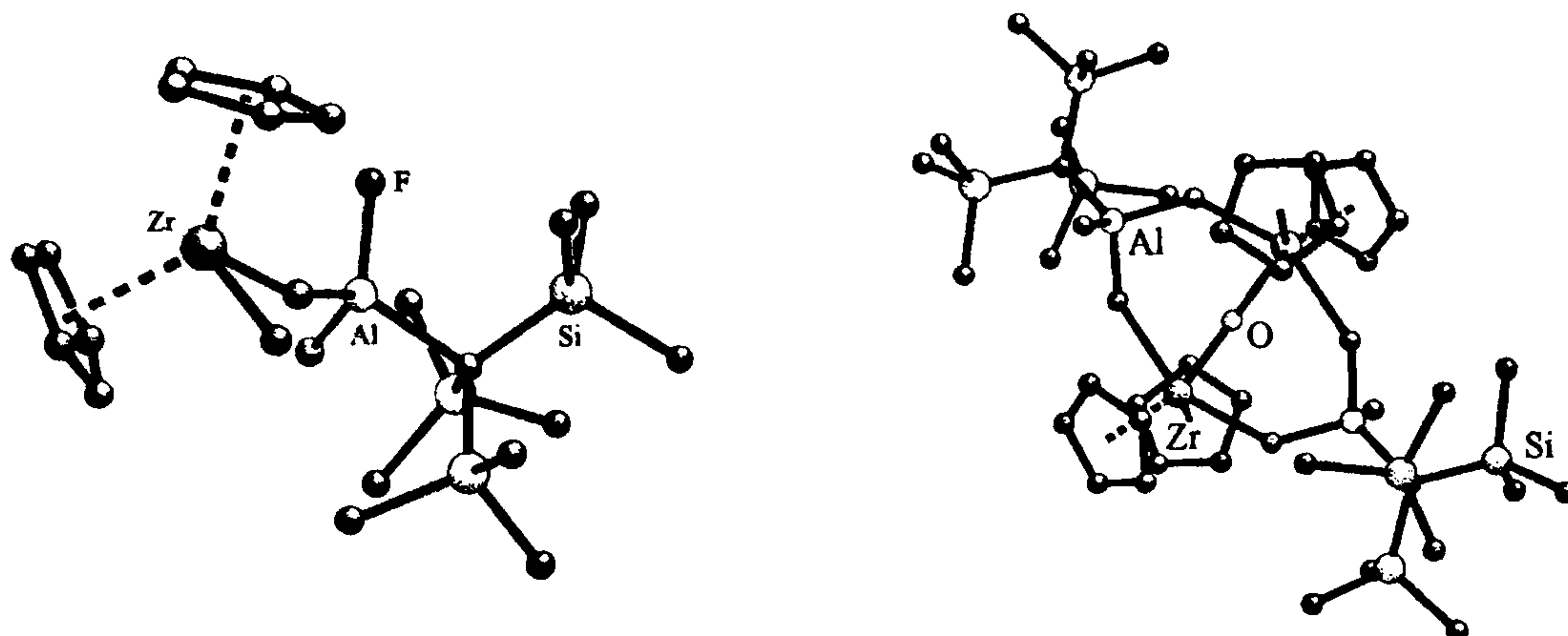


Figure 4. X-ray structures of $[\text{Cp}_2\text{ZrMe}(\mu\text{-F})\text{AlF}_2\text{Tris}]$ and $\{[\text{Cp}_2\text{Zr}(\mu\text{-F})_2\text{AlFTris}]_2(\mu\text{-O})\}$ (from ref. 59).

with $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$, $\text{R} = \text{Me}_2\text{iPrSi}$ or Me_2tBuSi , 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_6F_{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 species⁵⁸.

Attempts to recrystallize the addition product of $(\text{TrisAlF}_2)_3$ (*vide infra*) with Cp_2ZrMeF from Thf always resulted in mixtures of the expected complex $\text{Cp}_2\text{ZrMe}(\mu\text{-F})\text{AlF}_2\text{Tris}$ with $[\text{Cp}_2\text{Zr}(\mu\text{-F})_2\text{AlFTris}]_2(\mu\text{-O})$, the O atom spanning the two Al atoms arising from cleavage of Thf (Figure 4). The whereabouts of the Me groups remain unclear⁵⁹.

The first examples of C–H bond activation have been found in cyclopentadienyl complexes. The reaction of Cp_2TiCl with Et_3Al 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 bond⁶¹. Later, Tebbe and Guggenberger revised the reaction and redetermined the structure (Figure 5). The Et_2Al 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 η^5 to one Cp ring, η^5 to the Al substituted cyclopentadienyl ring and η^1 to the C atom bearing the Et_2Al unit⁶².

While in the reactions of Cp_2TiCl , Cp_2TiCl_2 and Cp_2TiPh refluxing PhMe is required⁶², the reactions of Cp_2TiF_2 with equimolar Et_3Al or $[\text{Cp}_2\text{Ti}(\mu\text{-F})_2\text{AlEt}_2]_2$ with additional Et_3Al afford this compound already at r.t.⁶³.

The reaction of Cp^*TiCl with LiAlH_4 with inadvertently present H_2O results in low yields in the compound depicted in Figure 6 with abstraction of one H atom from a methyl group of one Cp^* ring⁶⁴.

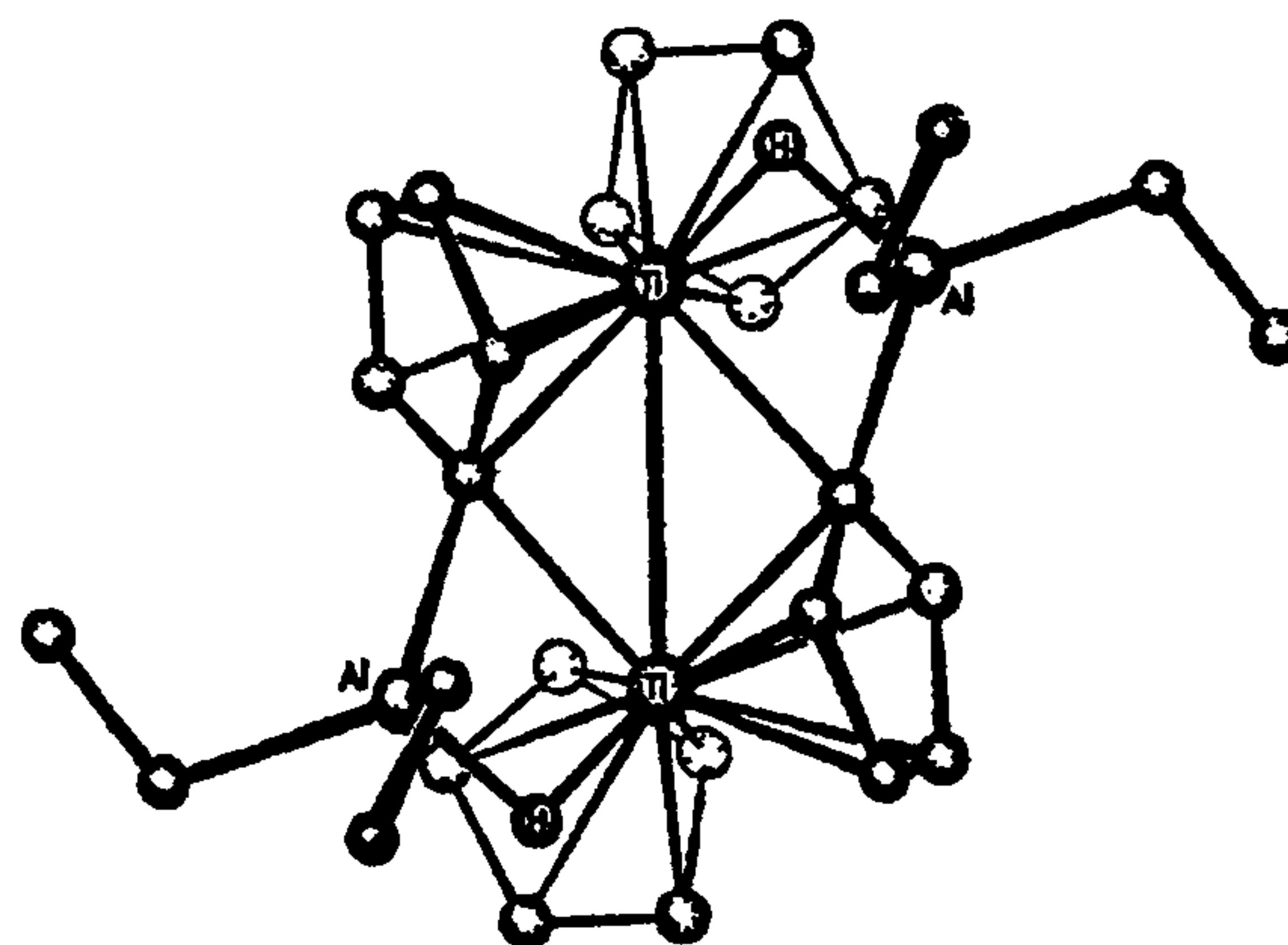


Figure 5. Structure of $[\text{CpTiC}_5\text{H}_4\text{AlEt}_2(\mu\text{-H})]_2$ (from ref. 62).

Two groups have independently investigated the reaction of Cp_2MoH_2 with Me_3Al . They isolated and structurally characterized two compounds with a Mo_2Al_3 - and a Mo_2Al_4 core (Figure 7) both arising from C–H bond fission of Cp rings^{65–69}. The $\text{Mo}-\text{Al}(\text{Me}_2)$ bonds in the Mo_2Al_3 compound are much longer than the $\text{Mo}-\text{Al}(\text{Me})$ bonds suggesting possible $\text{Mo}(\mu\text{-H})\text{Al}$ bridges^{66,68}. A totally insoluble compound with W_2Al_3 core analogous to the Mo_2Al_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_3Al affords in low yield a compound with an Al_4Fe_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 $\text{CH}_2(\text{PPh}_2\text{X})_2$ ($\text{X} = \text{O}, \text{S}$) with trialkylalanes

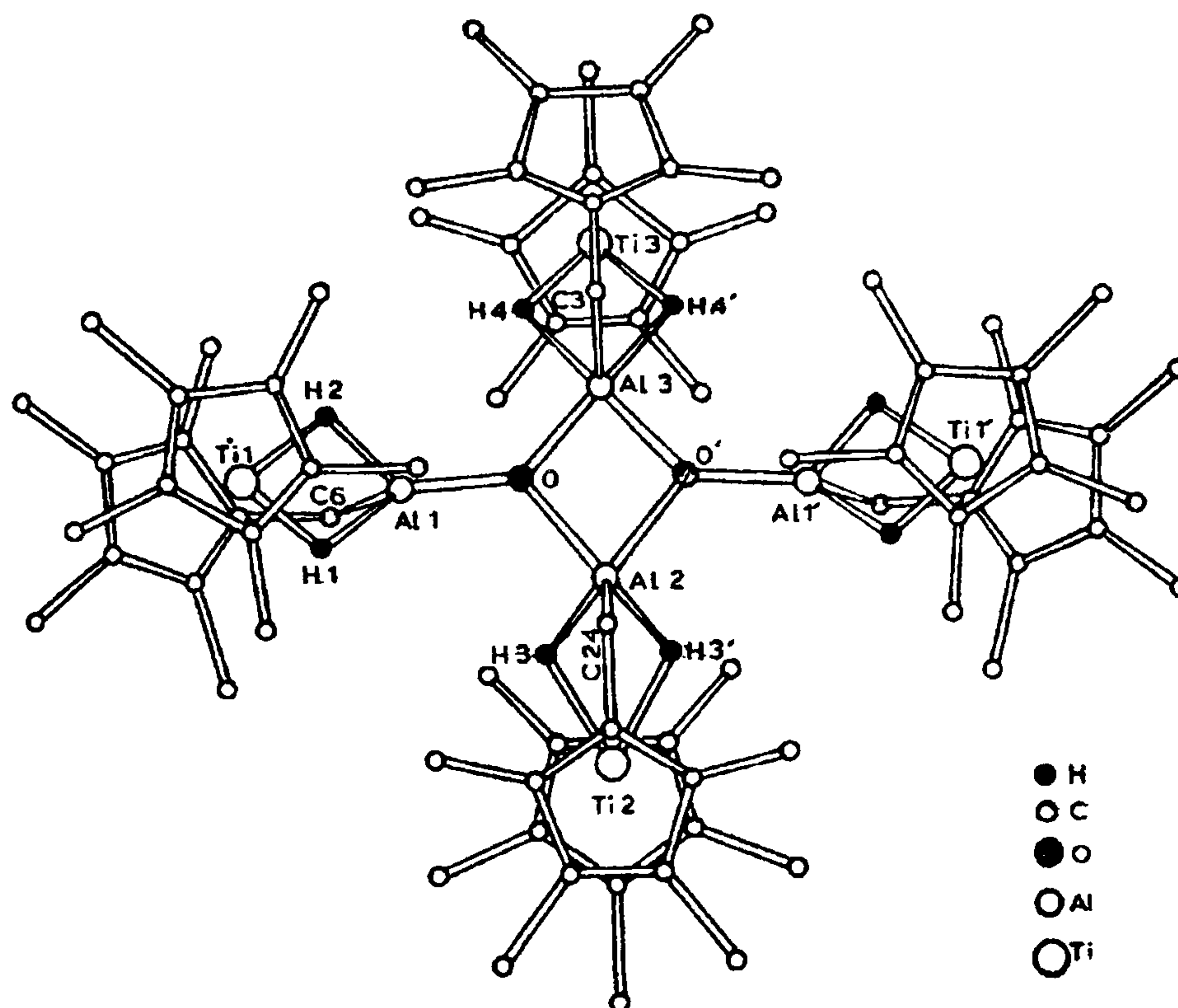
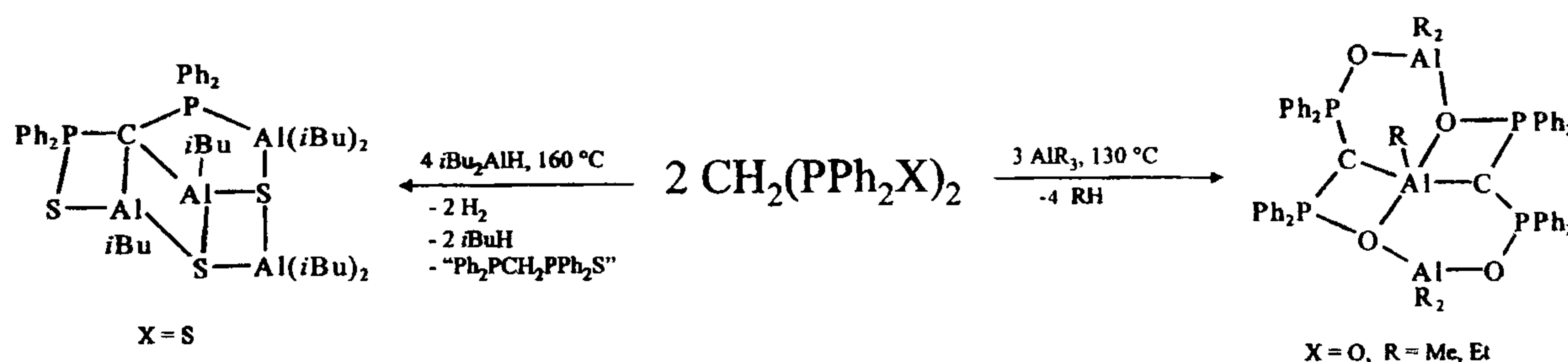


Figure 6. Structure of $\{[\eta^5\text{-Cp}^*\text{Ti}(m, \eta^5\text{-C}_5\text{Me}_4\text{CH}_2)(\mu\text{-H})_2\text{Al}_2](\mu_3\text{-O})\}_2$ (from ref. 64).



Scheme 2. Reactions of organoaluminum compounds with $\text{H}_2\text{C}(\text{PPh}_2\text{X})_2$.

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 $(\text{Me}_2\text{AlNHC}_6\text{H}_2\text{-2,4,6-}i\text{Bu}_3)_2$ 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 ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) 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 formed⁷⁶.

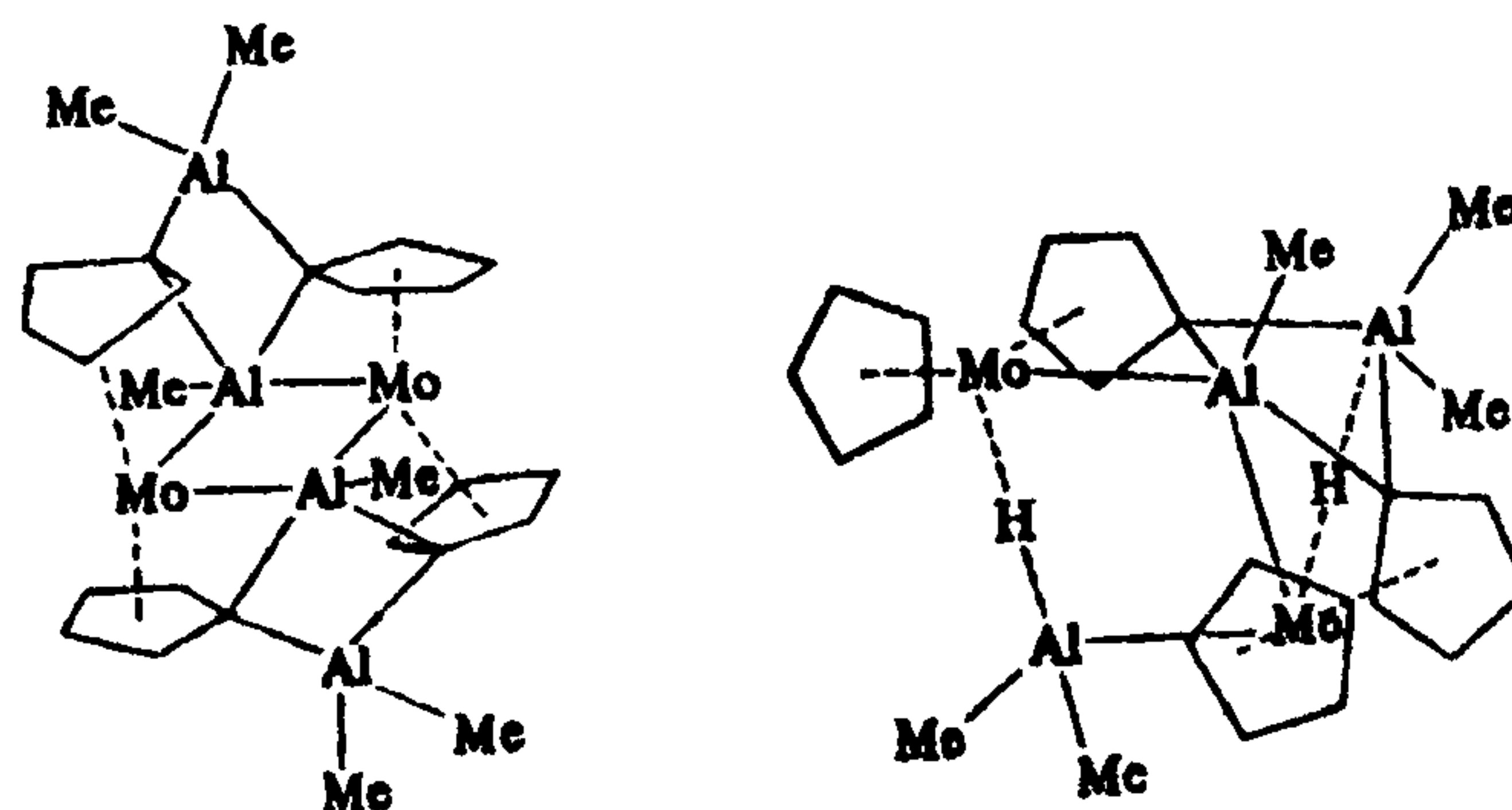


Figure 7. Structures of the two complexes from the reaction of Cp_2MoH_2 and Me_3Al .

Thermolysis of the adduct $\text{Cl}_3\text{Al}\cdot\text{NH}_2\text{C}_6\text{H}_2\text{-2,4,6-}i\text{Bu}_3$ at 150°C proceeded in a *retro*-Friedel–Crafts reaction under elimination of isobutene to the complex $\text{Cl}_3\text{Al}\cdot\text{NH}_2\text{C}_6\text{H}_3\text{-2,4-}i\text{Bu}_2$ (ref. 75).

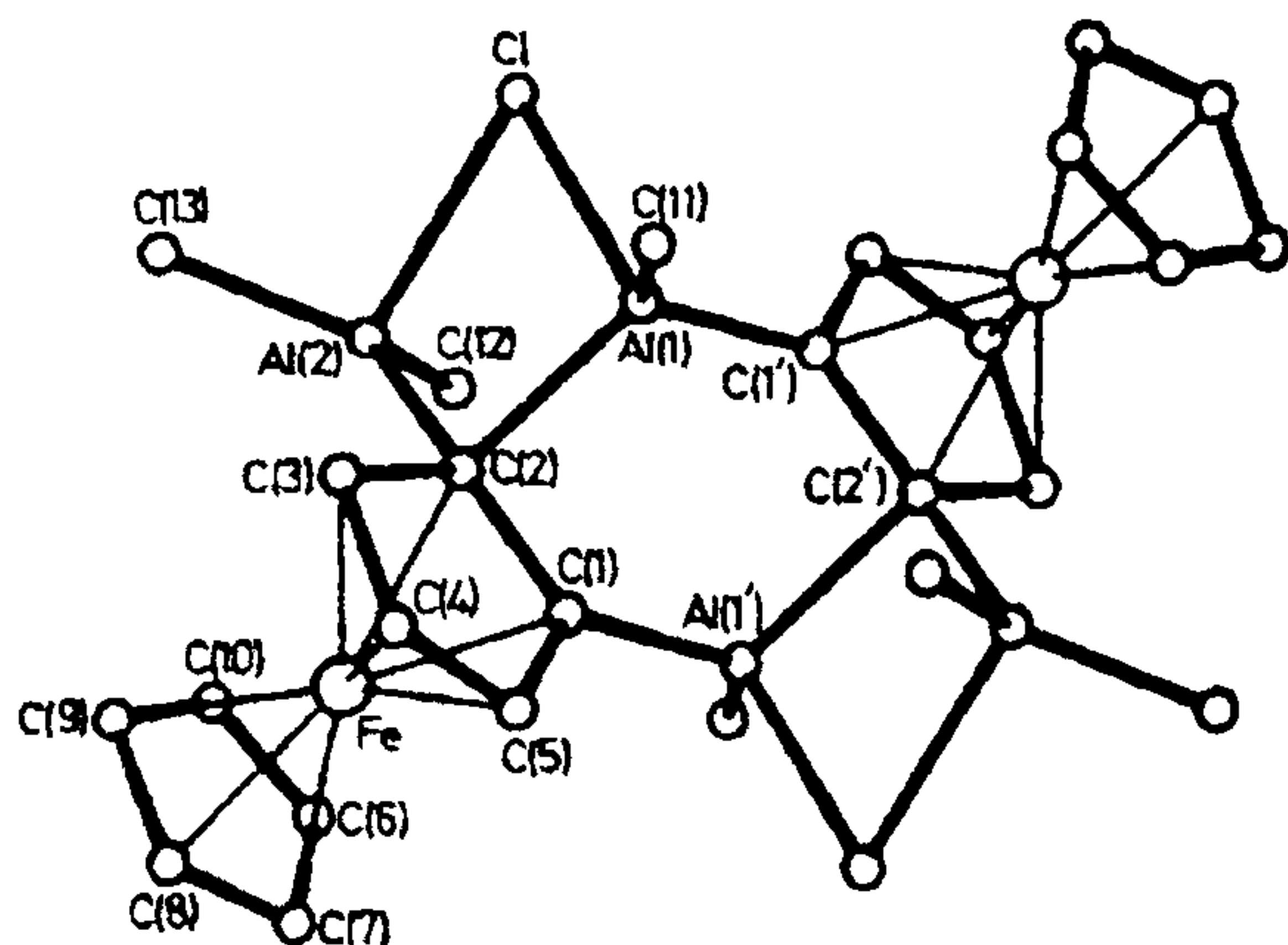


Figure 8. Structure of $[\text{CpFe}(\text{C}_5\text{H}_5)\text{Al}_2\text{Me}_3\text{Cl}]_2$ (from ref. 71).

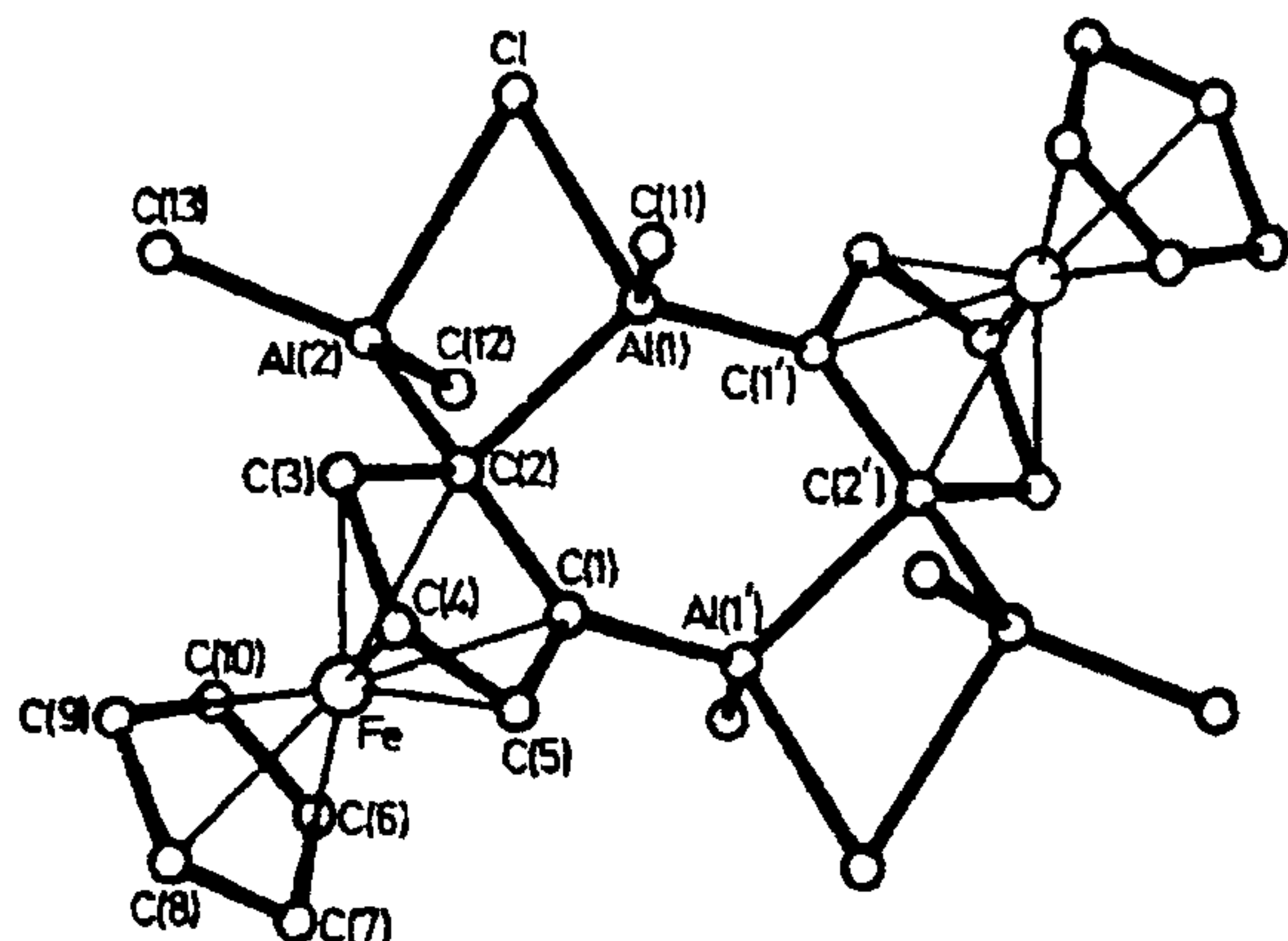


Figure 9. Structure of the dimeric aminoalane by activation of C-H bonds (from ref. 75).

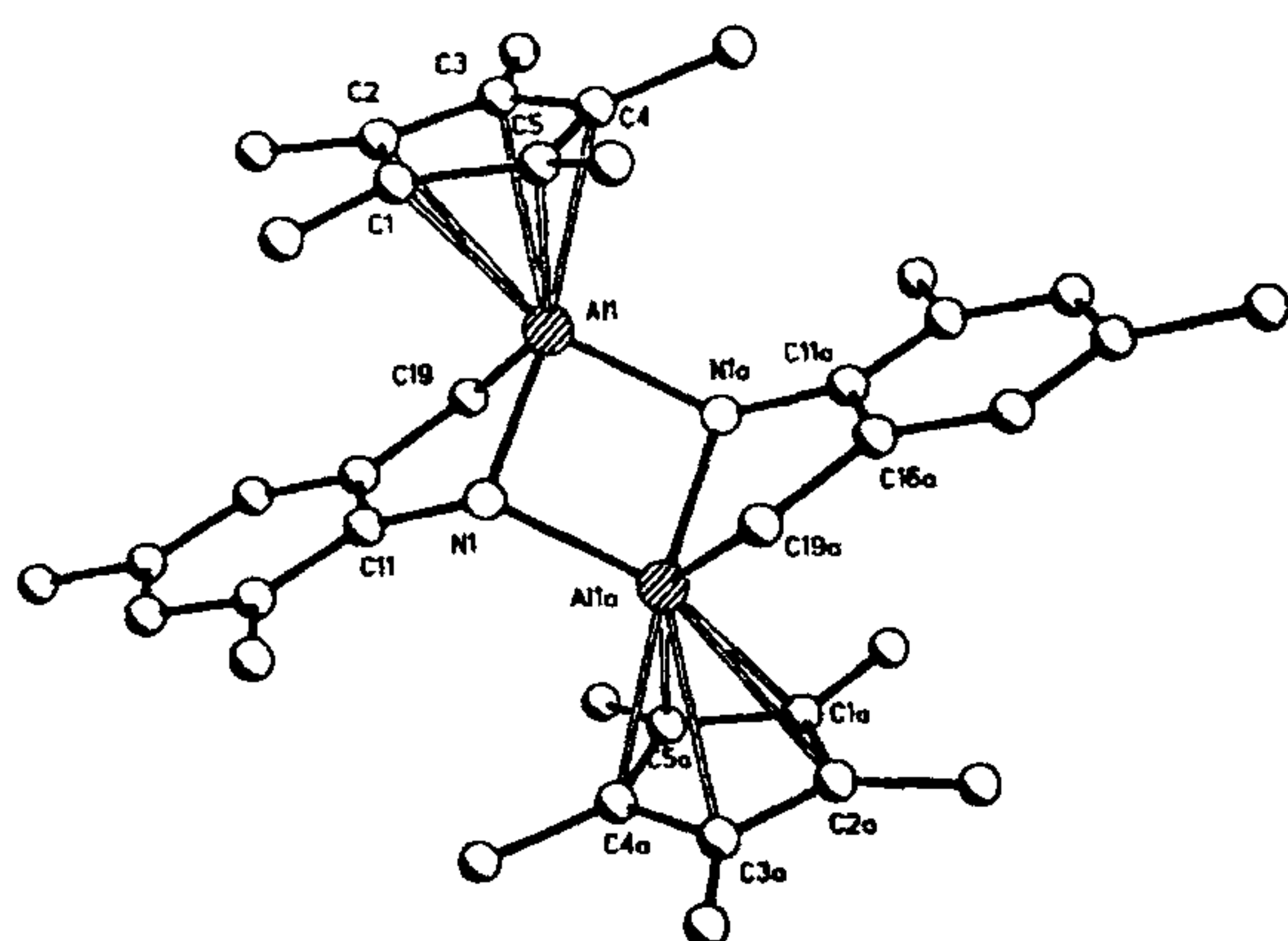


Figure 10. Structure of the dimeric aminoalane by activation of *o*-C-H bonds (from ref. 76).

Ortho-metalation with elimination of *i*BuH has also been found in the thermolysis of the monolithiated dimeric aminoalane $[(i\text{Bu}_2\text{Al})_2(\mu\text{-NHMe})(\mu\text{-NLiMe})]$.

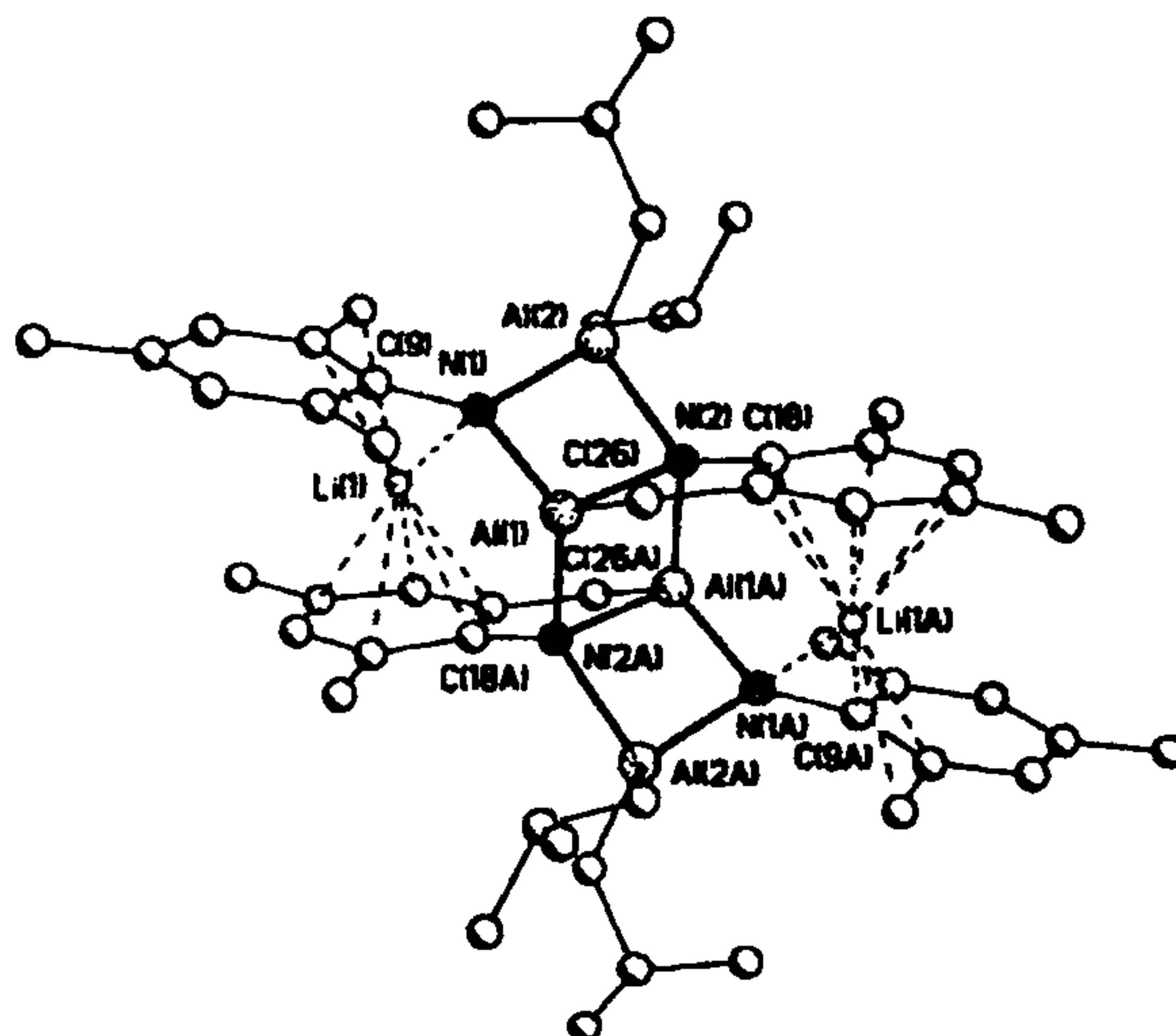


Figure 11. Structure of the ladder-shaped dimer from thermolysis of $[(i\text{Bu}_2\text{Al})_2(\mu\text{-NHMe})(\mu\text{-NLiMe})]$ (from ref. 77).

The ladder-shaped complex with an Al_4N_4 core as revealed from its X-ray structure (Figure 11) has been obtained in low yields after recrystallization from hexane⁷⁷.

The reaction of Me_3Al with excess Ph_2NH in boiling PhMe proceeds in high yield under MeH evolution and *o*-metalation of one Ph group. The X-ray structure of $[(\mu\text{-Ph}_2\text{N})_2(\text{AlMe})_2(\mu\text{-PhNC}_6\text{H}_4)]$ shows an Al_2N_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 $(\text{Et}_2\text{AlNPh}_2)_2$ and $\text{Cl}_3\text{Al}\cdot\text{HNPh}_2$. The compounds were characterized by mass spectrometry and deuterolysis experiments, but no structural data are available^{77b,c}.

The reaction of tetrameric $(\text{Cp}^*\text{ZrF}_3)_4$ with 20 equivalents of Me_3Al at r.t. affords in high yield a cluster of composition $[(\text{Cp}^*\text{Zr})_3\text{Al}_6\text{Me}_8(\mu_3\text{-CH}_2)_2(\mu_3\text{-CH})(\mu_4\text{-CH})_4]$ with elimination of methane and $(\text{Me}_2\text{AlF})_4$, whose structure is depicted in Figure 12. Its most prominent features are the hypervalent carbon atoms bridging the metal centers⁷⁸. Similarly, an $(\text{EtC}_5\text{Me}_4)\text{Zr}$ 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 methylenide transfer reagents with aromatic ketones, halides and acid halides⁷⁹.

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_3Al and

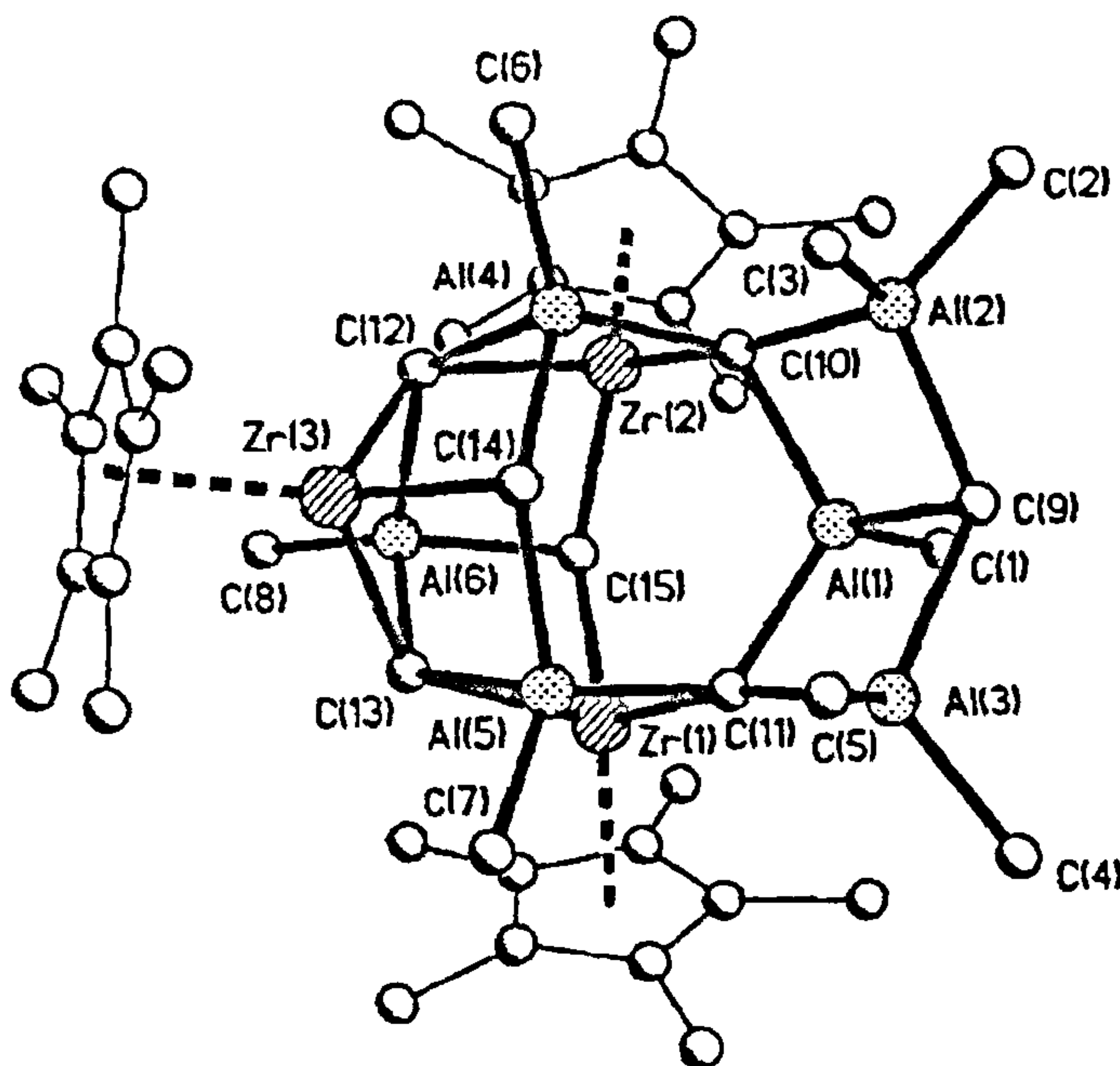


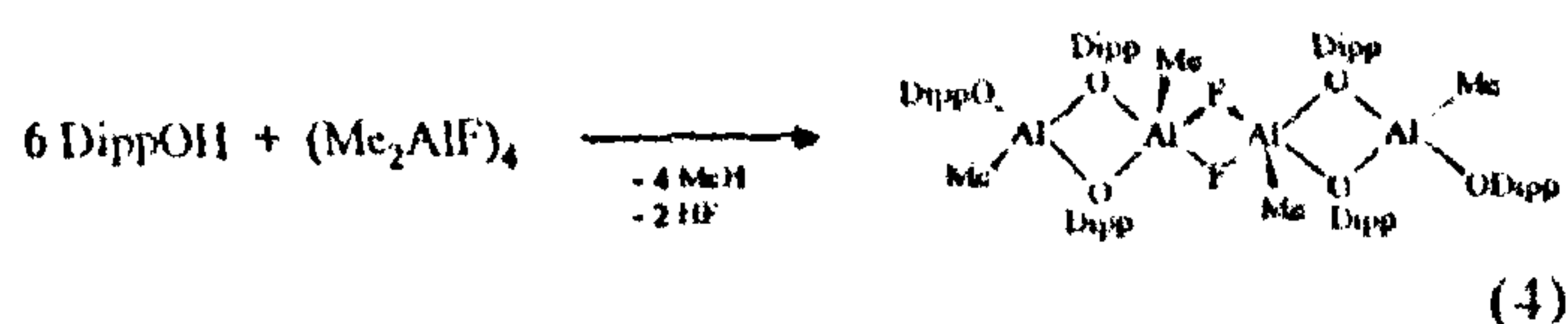
Figure 12. Structure of $[(\text{Cp}^*\text{Zr})_3\text{Al}_6\text{Me}_8(\mu_3\text{-CH}_2)_2(\mu_3\text{-CH})(\mu_4\text{-CH})_4]$ (from ref. 78).

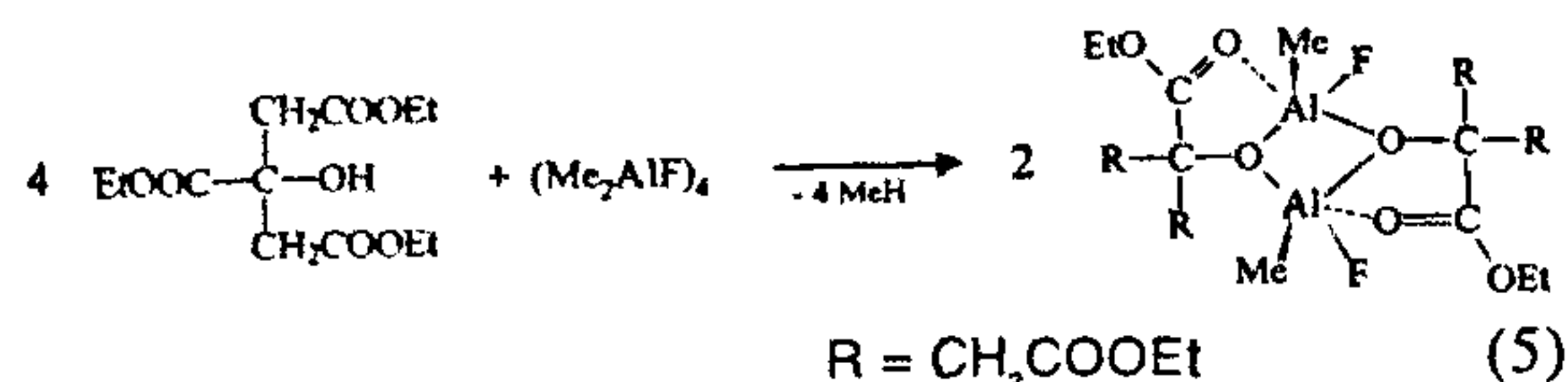
Me_2AlCl to yield Na^+ salts of anionic fluoride species $(\text{Et}_3\text{AlF})^-$, $[(\text{Et}_3\text{Al})_2(\mu\text{-F})]^-$ and $(\text{Me}_2\text{AlF}_2)^-$, respectively⁸⁰. Reviews on organoaluminum fluorides besides those mentioned in the introduction have been published by Weidlein in 1973 (ref. 81) and recently by Roesky *et al.*⁸². Neutral diorganoaluminum monofluorides with various organic substituents $(\text{R}_2\text{AlF})_n$ are available by metathesis of the appropriate aluminum chlorides with NaF (refs 80, 83–86), higher alkali fluorides⁸³, BaF_2 (ref. 87), by fluorine/alkyl exchange in triorganoalanes with $\text{BF}_3\cdot\text{OEt}_2$ (ref. 88), SiF_4 , R_2SiF_2 , ZnF_2 , CdF_2 , SbF_3 , PbF_2 (ref. 89), by thermal decomposition of the dinuclear species $\text{Me}_3\text{Si}(\mu\text{-F})\text{AlEt}_3$ (ref. 90) and by commutation of AlF_3 with Et_3Al (ref. 83). Gas phase electron diffraction shows $(\text{Me}_2\text{AlF})_4$ to exist as a puckered eight-membered ring with $\text{Al}(\mu\text{-F})\text{Al}$ bridges^{91,92}. Tetrameric aggregates are also existent in solution as seen from cryoscopic molecular weight determinations in benzene of $(\text{Me}_2\text{AlF})_4$, $(\text{Et}_2\text{AlF})_4$ (ref. 85) and $(i\text{Bu}_2\text{AlF})_4$ (ref. 88). While the tetrameric unit remains unchanged upon substitution of one Me group on each Al atom by DippNH ($\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) as seen from its EI-MS spectrum⁹³ with the ligands mutually *trans*, the reaction of $(\text{Et}_2\text{AlF})_4$ with MeNH_2 at r.t. affords a glassy oligomer $(\text{MeNHAIEtF})_x$ of unknown structure⁹⁴. In contrast, trimeric species have been postulated from cryoscopic measurements and IR investigations of $(\text{Pr}_2\text{AlF})_3$ and $(i\text{Bu}_2\text{AlF})_3$ (ref. 86). A dimeric complex $(\text{Tmp}_2\text{AlF})_2$ ($\text{Tmp} = 2,2,6,6\text{-Me}_4\text{-piperidyl}$) has been structurally characterized from the reaction of Tmp_2AlBr with AgBF_4 via intermediate formation of $\text{Tmp}_2\text{Al}(\mu\text{-F})\text{BF}_3$ (ref. 95). At low temperatures mono-

meric amine adducts $\text{Et}_2\text{AlF}\cdot\text{NMe}_3$ and $\text{Et}_2\text{AlF}\cdot\text{NH}_2\text{Me}$ are formed from Et_2AlF 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 $i\text{Bu}_2\text{AlF}$ -dioxane complex loses the donor upon distillation⁸⁸.

Mononuclear ionic complexes $\text{M}^+(\text{R}_3\text{AlF})^-$ are available from stoichiometric reactions of alkali fluorides with trialkylalanes without solvent at $>100^\circ\text{C}$ (refs 80, 96) or in solvents at r.t.^{97–99}. The X-ray structure of $\text{Cs}^+(\text{Me}_3\text{AlF})^-$ shows isolated Me_3AlF 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 network⁹⁸. $\text{Cs}^+(i\text{Bu}_3\text{AlF})^-$ has also been reported by Neumüller *et al.* but no structural details are given⁹⁹. Anhydrous $\text{Me}_4\text{N}^+\text{F}^-$ forms a similar complex as do the adducts $\text{Et}_3\text{Al}\cdot\text{NMe}_3$ and $\text{Et}_3\text{Al}\cdot\text{PMe}_3$ upon reaction with PhCH_2F (ref. 97). Addition of a second equivalent R_3Al to those complexes results in the formation of dinuclear anions $[\text{R}_3\text{Al}(\mu\text{-F})\text{AlR}_3]^-$ (refs 80, 96, 97) with a linear $\text{Al}(\mu\text{-F})\text{Al}$ bridge as seen from the X-ray structures of $\text{K}^+[(\text{Et}_3\text{Al})_2(\mu\text{-F})]^-$ with weak K–C contacts^{100,101} and $(\text{K}\cdot\eta^6\text{-C}_6\text{H}_6)^+[(\text{Me}_3\text{Al})_2(\mu\text{-F})]^-$ (ref. 102). Mixed anions $[\text{R}_3\text{Al}(\mu\text{-F})\text{AlR}'_3]^-$ with R, R' = Me, Et; Me, *i*Bu; Et, *i*Bu are available from reactions of the mononuclear ionic species with the appropriate alanes⁹⁶. K^+ salts of $[\text{C}_5\text{H}_{11}\text{CH}(\text{AlR}_2)_2(\mu\text{-F})]^-$ with R = Et, *i*Bu have been described from the reaction of KF with the gem-dialanes $\text{C}_5\text{H}_{11}\text{CN}(\text{AlR}_2)_2$ as viscous oils. They are believed to contain a bent $\text{Al}(\mu\text{-F})\text{Al}$ bridge, but a dimeric structure with linear units would also be consistent with the analytical data given¹⁰³.

A neutral compound with bent $\text{Al}(\mu\text{-F})\text{Al}$ bridges has been obtained from the reaction of DippNH_2 ($\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) with $(\text{Me}_2\text{AlF})_4$ at 0°C . Two of the original $\text{Al}(\mu\text{-F})\text{Al}$ bridges have been substituted by DippNH fragments yielding an eight-membered ring compound with an $\text{Al}_4\text{N}_2\text{F}_2$ core. The Al–F bond lengths are similar to those in $(\text{Me}_2\text{AlF})_4$. An amine adduct $\text{Me}_2\text{AlF}\cdot\text{DippNH}_2$ has been considered as intermediate prior to HF elimination. Such an adduct, $\text{Me}_2\text{AlF}\cdot t\text{BuNH}_2$, has been found in the reaction with the more basic amine $t\text{BuNH}_2$ as an infinite one-dimensional chain connected via $\text{H}\cdots\text{F}$ hydrogen bonding as the final product¹⁰⁴. Similar Al–F bond cleavage reactions have been observed in reactions of $(\text{Me}_2\text{AlF})_4$ with DippOH and triethylcitrate, respectively (eqs 4, 5) and structurally characterized¹⁰⁵.





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 $(\text{Ar}_3\text{AlF})^-$ ($\text{Ar} = 2$ -nonafluorobiphenyl) (Scheme 3).

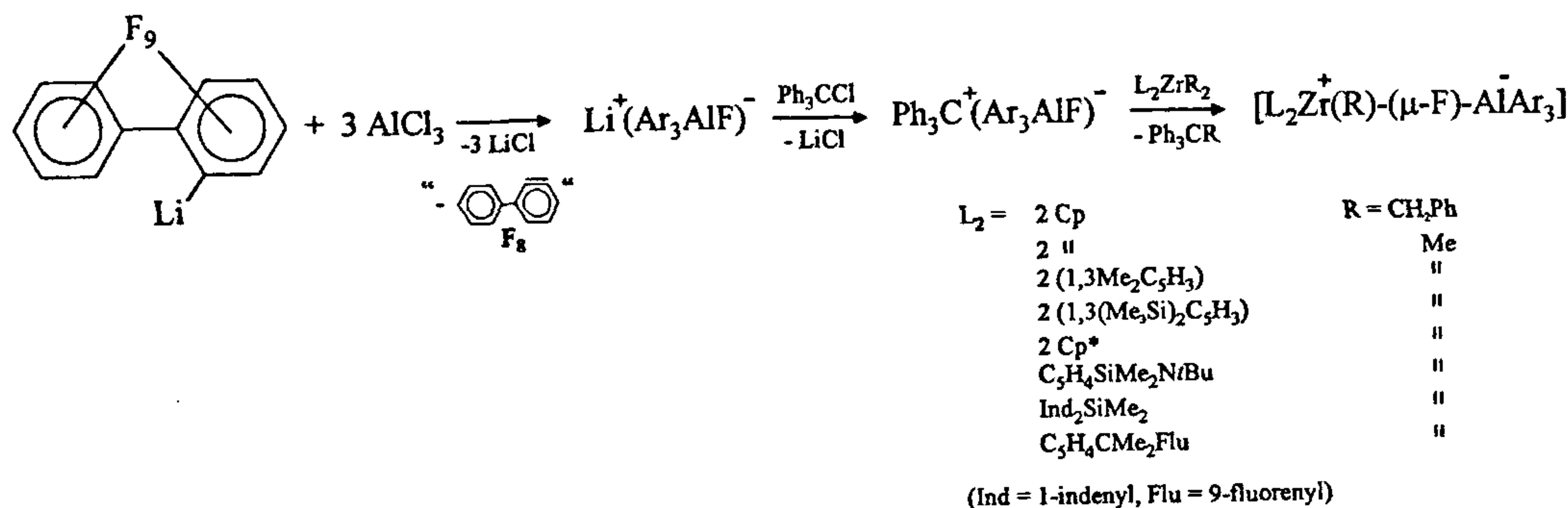
The X-ray structures of the Ph_3C^+ - and $(\text{Cp}^*_2\text{ZrMe})^+$ salts have been determined, the latter shows a linear $\text{Al}(\mu\text{-F})\text{Zr}$ bridge. Several of the Zr complexes have been found active catalysts for the isotactic polymerization of propene¹⁰⁶.

Reactions of trialkylalanes with $[\text{Cp}'\text{TiF}(\mu\text{-O})]_4$ ($\text{Cp}' = \text{Cp}^*, \text{EtC}_5\text{Me}_4$) yield adducts $\{[\text{Cp}'\text{Ti}(\mu\text{-O})]_4\text{F}_n[(\mu\text{-F})\text{AlR}]_{4-n}\}$ with almost linear $\text{Al}(\mu\text{-F})\text{Ti}$ bridges. While the tetrakis- and trisadducts are stable only at lower temperatures, with Me_3Al at r.t. only the *trans*-bisadduct is formed

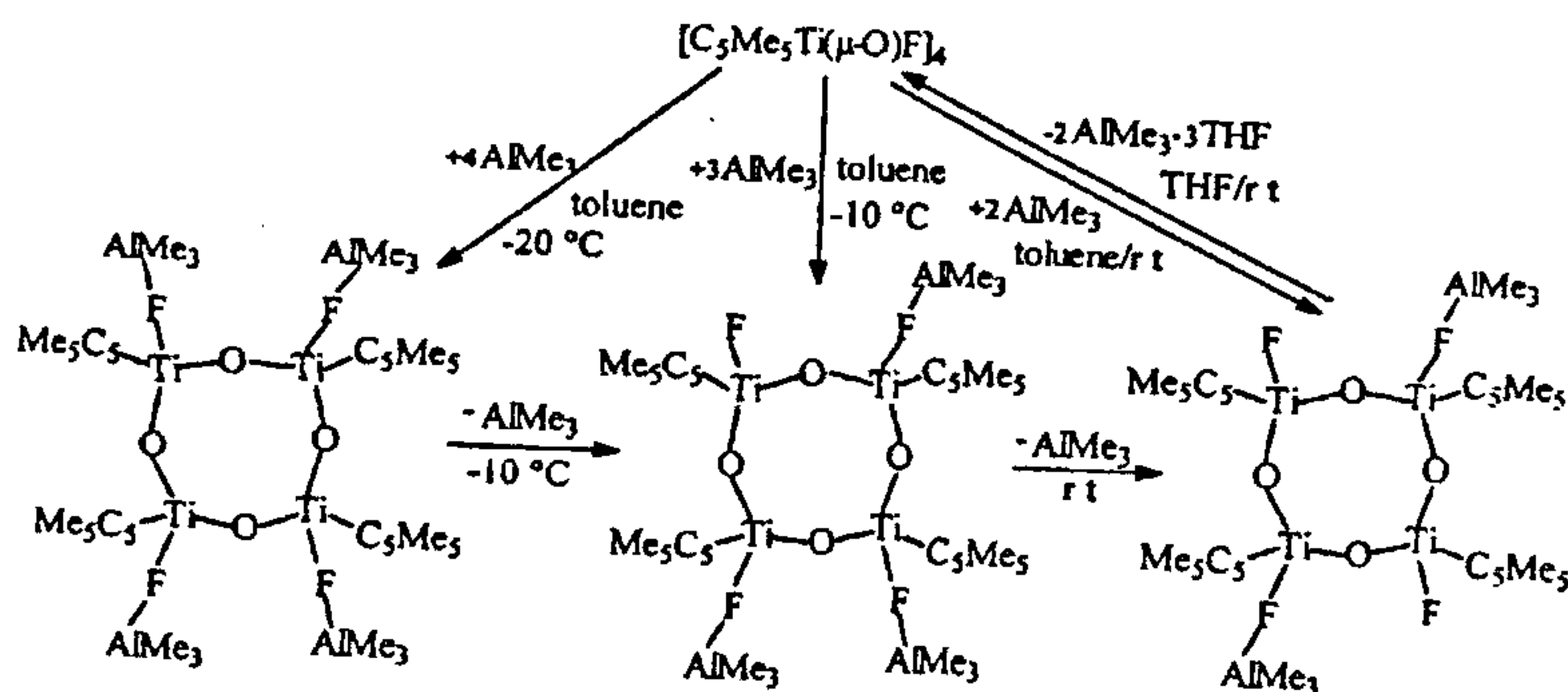
(Scheme 4). Monoadducts are exclusively formed with the bulkier alanes Et_3Al and $(\text{PhCH}_2)_3\text{Al}$. Several of the compounds have been structurally characterized^{107,108}.

Pyrolysis of the above-mentioned compound $[\text{DippNHA}(\mu\text{-F})]_4$ ($\text{Dipp} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) 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 atoms⁹³.

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 temperatures⁸³ or from EtAlCl_2 and NaF (ref. 84) and of $\text{Na}^+(\text{R}_2\text{AlF}_2)^-$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{iBu}$)^{80,83,84}, a Japanese patent describes the use of RAlF_2 compounds ($\text{R} = \text{Et}, \text{alkyl}, \text{cycloalkyl}, \text{aryl}, \text{arylalkyl}$) as co-catalysts in the polymerization of butadiene with π -complexes of Ni and Co (ref. 109) and a French patent describes the use of $(\text{Me}_3\text{NCH}_2\text{Ph})^+$ salts of $(\text{Et}_2\text{AlF}_2)^-$, $[\text{Et}_3\text{Al}(\mu\text{-F})\text{AlEt}_2\text{F}]^-$ and $(\text{EtAlF}_3)^-$ as electrolytes for the electrodeposition of Al (ref. 110).



Scheme 3. Reactions involving the $(\text{Ar}_3\text{AlF})^-$ anion.



Scheme 4. Complexes of Me_3Al with $[\text{Cp}^*\text{TiF}(\mu\text{-O})]_4$ (from ref. 108).

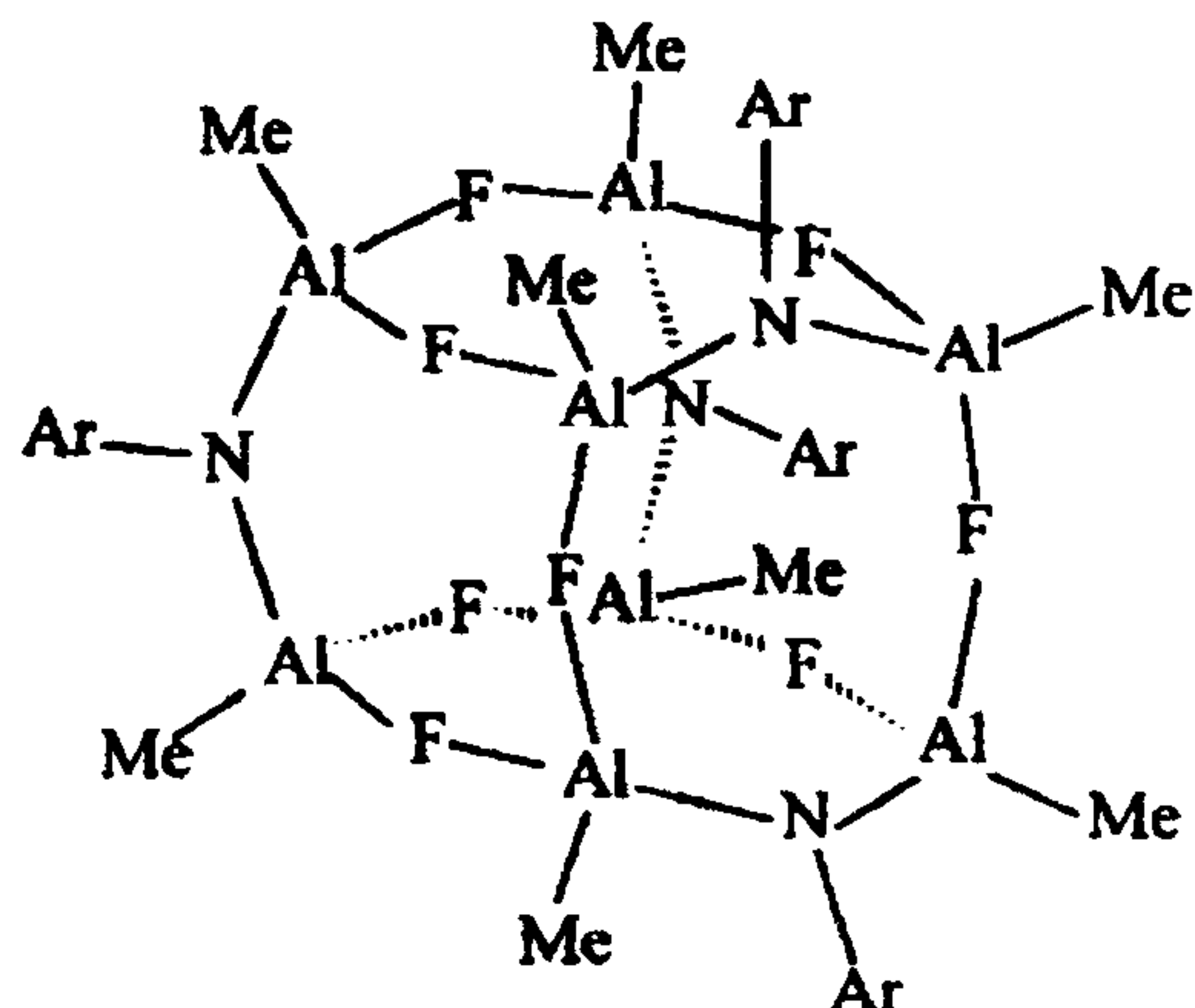


Figure 13. Structure of $[(\text{MeAl})_8(\mu\text{-F})_8(\mu\text{-NDipp})_4]$ (from ref. 93).

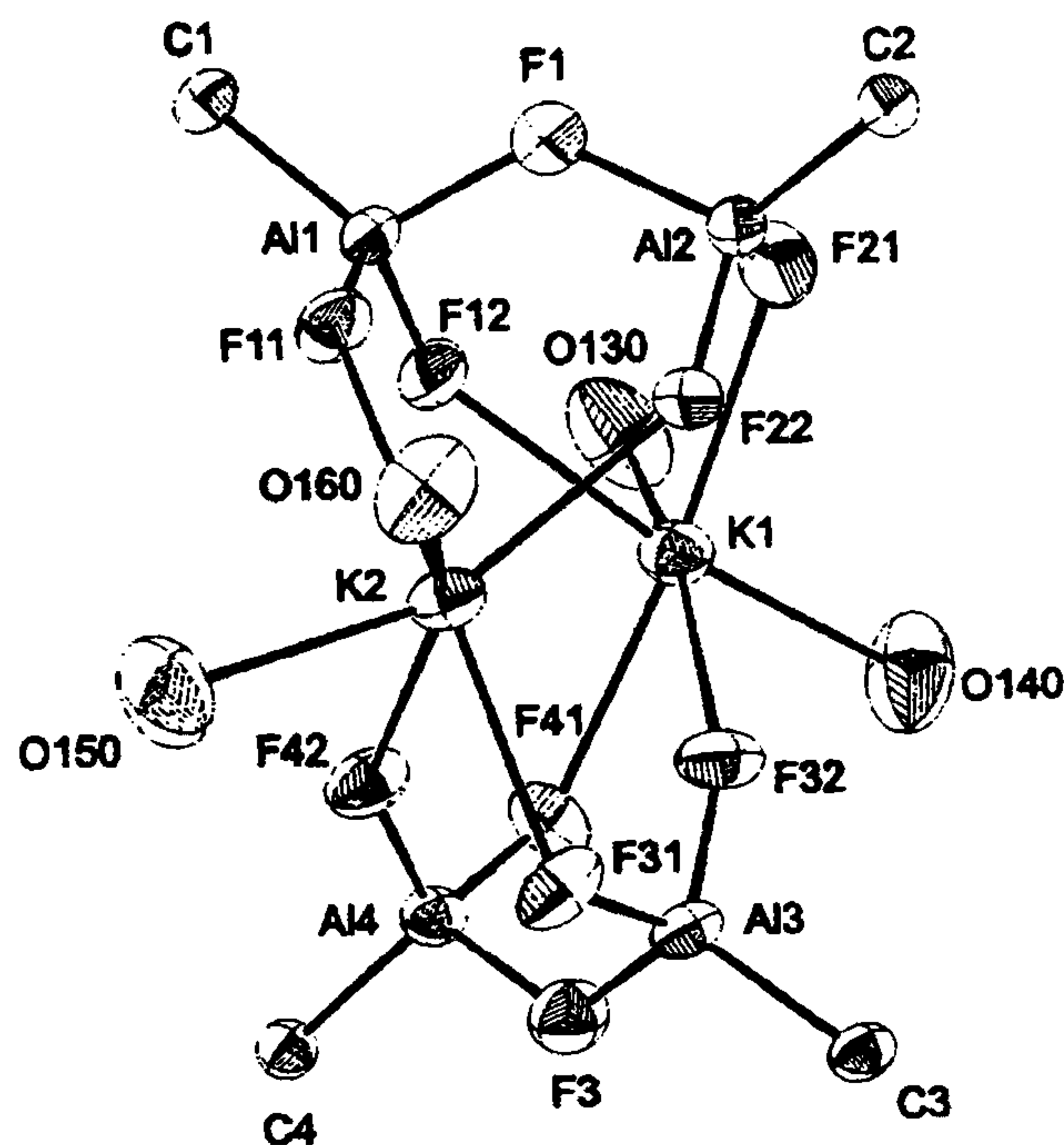
Reactions of the alanes Me_3Al and $(\text{Me}_3\text{Si})_3\text{CAI}\text{Me}_2\cdot\text{Thf}$ with $\text{Bu}_4\text{N}^+\text{HF}_2^-$ at r.t. proceed via elimination of MeH under formation of the respective $\text{Bu}_4\text{N}^+(\text{MeRAIF}_2)^-$ salts in almost quantitative yields. Both compounds have been structurally investigated¹¹¹.

$(\text{Me}_3\text{SnF})_\infty$ has been proven the fluorinating agent of choice in metathetic fluorinations of RAIMe_2 compounds to yield RAIF_2 complexes with Me_4Sn elimination. Reactions of $\text{RN}(\text{SiMe}_2\text{R}')\text{AlMe}_2\cdot\text{Thf}$ with $\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ ($=\text{Dipp}$), $\text{R}' = \text{Me}$, $i\text{Pr}$, $t\text{Bu}$ and $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $\text{R}' = t\text{Bu}$, Me in Thf at r.t. with two equivalents of Me_3SnF affords monomeric compounds $\text{RN}(\text{SiMe}_2\text{R}')\text{AlF}_2\cdot\text{Thf}$ (refs 58, 112), while the reaction of the solvent-free dimeric $[\text{DippN}(\text{SiMe}_3)\text{AlMe}_2]_2$ in toluene affords trimeric $[\text{DippN}(\text{SiMe}_3)\text{AlF}(\mu\text{-F})]_3$. While the ^{19}F -NMR spectrum at r.t. with one broad signal indicates rapid exchange of *exo*- and *endocyclic* F atoms, at -90°C four distinct triplets in a 2:2:1:1 ratio are observed assignable to an intact trimer¹¹². A compound with $\text{Me}_2\text{Si}t\text{Bu}$ as substituent on N instead of Me_3Si has also been obtained with the same fluxional behaviour¹¹³.

Analogously, $\text{TrisAlMe}_2\cdot\text{Thf}$ ($\text{Tris} = (\text{Me}_3\text{Si})_3\text{C}$) and Me_3SnF 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 *exocyclic* Al–F bonds. The adduct formation is reversible¹¹⁴. Only a dimer is found upon fluorination of the aza-allyl substituted compound $\text{Me}_3\text{SiNC}(\text{Ph})\text{C}(\text{SiMe}_3)_2\text{AlMe}_2$. The complex shows five-coordinated Al atoms in the solid state and fluxional behaviour in solution¹¹⁵.

A diorganodialuminumpentafluoride anion is formed in the reaction of $\text{TrisAlF}_2\cdot\text{Thf}$ ($\text{Tris} = (\text{Me}_3\text{Si})_3\text{C}$) with KF in Thf . Two $\text{F}_2\text{Al}(\mu\text{-F})\text{AlF}_2$ units with a bent middle $\text{Al}(\mu\text{-F})\text{Al}$ bridge are clenched by two $(\text{K}\cdot 2\text{Thf})^+$ cations resulting in a distorted geometry¹¹⁴ (Figure 14). A $[(\text{TrisAlF}_2)(\mu\text{-F})]^-$ anion with a linear $\text{Al}(\mu\text{-F})\text{Al}$ bridge

a



b

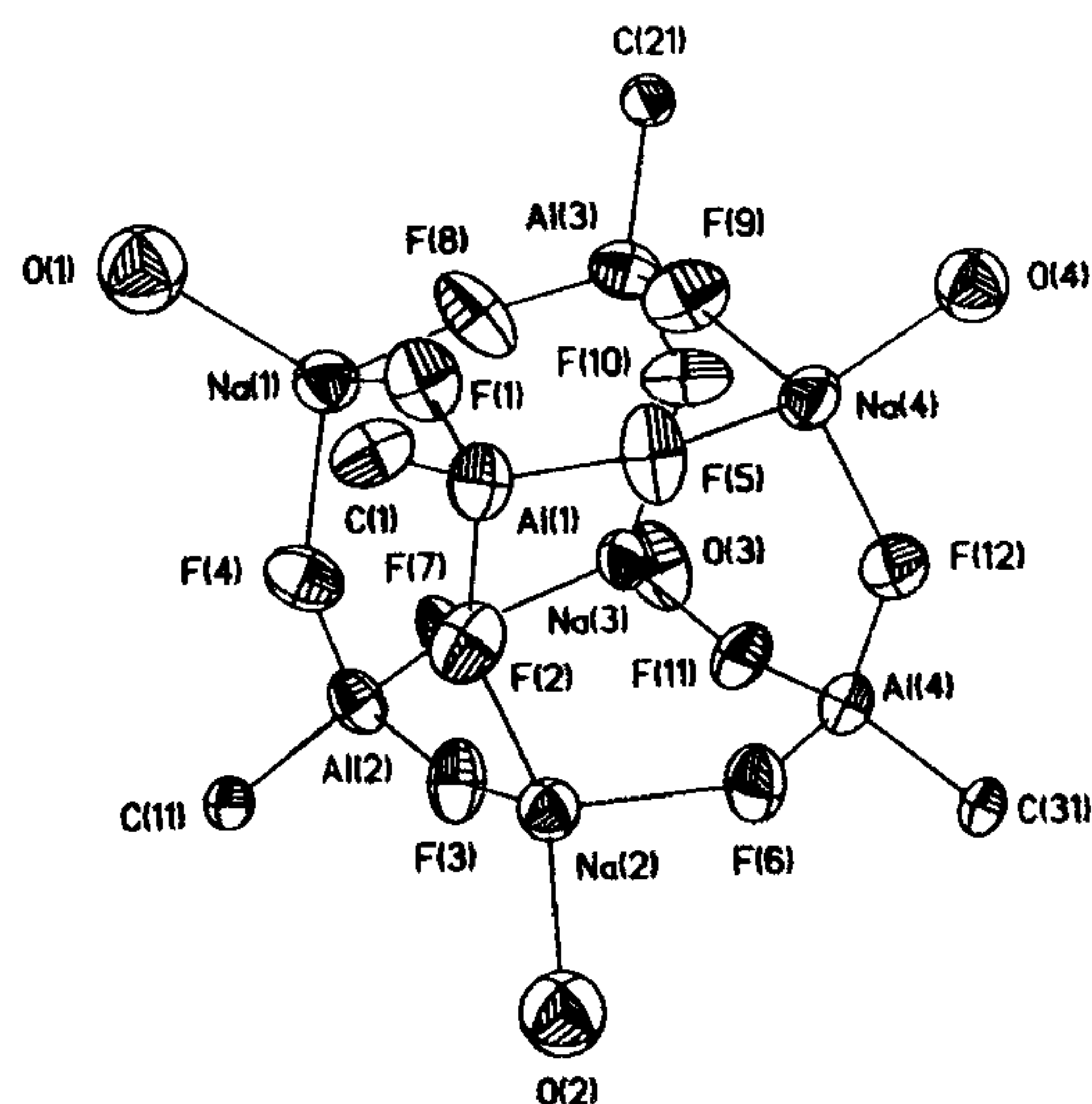


Figure 14. Structures of $[\text{K}\cdot 2\text{Thf}]^+(\text{TrisAlF}_2)_2(\mu\text{-F})^-$ (from ref. 114) and $[(\text{Na}\cdot\text{Thf})^+(\text{TrisAlF}_3)^-]_4$ (from ref. 59) (outer substituents omitted for clarity).

is present in the compound $(\text{AlF}_2\cdot 4\text{Thf})^+[(\text{TrisAlF}_2)_2(\mu\text{-F})]^-$ generated from the reaction of $(\text{TrisAlF}_2)_3$ with AgF_2 , which is also likely in $\text{NH}_4^+(\text{Tris}_2\text{Al}_2\text{F}_5)^-$, obtained in high yield from addition of NH_4^+F^- to the trimeric difluoroalane. $(\text{Ag}\cdot 3\text{PhMe})^+[\text{Li}(\text{Tris}_2\text{Al}_2\text{F}_5)_2]^-$ is the product of the concerted action of AgF and LiCl on $(\text{TrisAlF}_2)_3$. The Li atom is tetrahedrally surrounded by the outer F atoms of two $\text{FAl}(\mu\text{-F})\text{AlF}$ moieties¹¹⁶. This is in contrast to the structures of $(\text{Li}\cdot\text{Thf})^+(\text{TrisAlF}_3)^-$, obtained from fluorination of $(\text{Li}\cdot 2\text{Thf})^+(\text{TrisAlH}_3)^-$ with 70% HF in pyridine¹¹⁷ and the corresponding $(\text{Na}\cdot\text{Thf})^+$

salt generated by the reaction of $\text{TrisAlMe}_2 \cdot \text{Thf}$ with excess Me_3SnF 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 $(2,4,6\text{-Me}_3\text{C}_5\text{H}_2\text{NH})^+$ $(\text{TrisAlF}_3)^-$ with discrete isolated ions¹¹⁸.

Several complexes of Al with group 4 metals connected via $\mu\text{-F}$ bridges have been synthesized and structurally characterized. As previously mentioned, addition of Cp_2ZrMeF to $(\text{TrisAlF}_2)_3$ results in the formation of the complexes $[\text{Cp}_2\text{ZrMe}(\mu\text{-F})\text{AlF}_2\text{Tris}]$ and $[(\text{Cp}_2\text{Zr}(\mu\text{-F})_2\text{AlFTris})_2(\mu\text{-O})]$ (ref. 59). The reactions of $(\text{Cp}^*\text{MF}_3)_4$ ($\text{M} = \text{Zr}, \text{Hf}$) with Me_3Al 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, $\text{Ti}(+\text{IV})$ is reduced to $\text{Ti}(+\text{III})$ by either Al or R_3Al ($\text{R} = \text{Me}, \text{Et}$) in the following examples. Paddle-wheel shaped complexes $[\text{Cp}'_2\text{Ti}(\mu\text{-F})_2]_3\text{Al}$ ($\text{Cp}' = \text{Cp}, \text{MeC}_5\text{H}_4$) are formed from Al and three equivalents of $\text{Cp}'_2\text{TiF}_2$ (ref. 119).

Reactions of equimolar amounts of $\text{Cp}'_2\text{TiF}_2$ and Et_3Al afford non-planar eight-membered rings $[(\text{Cp}'_2\text{Ti})_2(\mu\text{-F})_4(\text{AlEt}_2)_2]$ with $\text{Cp}' = \text{Cp}$ (ref. 63), MeC_5H_4 (ref. 120) and Cp^* (ref. 120).

A compound with an $[\text{Al}_4\text{Ti}_2(\mu\text{-F})_8]$ core is formed in the reaction of Cp^*TiF_3 with Me_3Al (Figure 16) via intermediate formation of an adduct $[(\text{Cp}^*\text{TiF}_2\text{Me}) \cdot (\text{Me}_2\text{AlF})]$ in refluxing toluene. The structure consists of

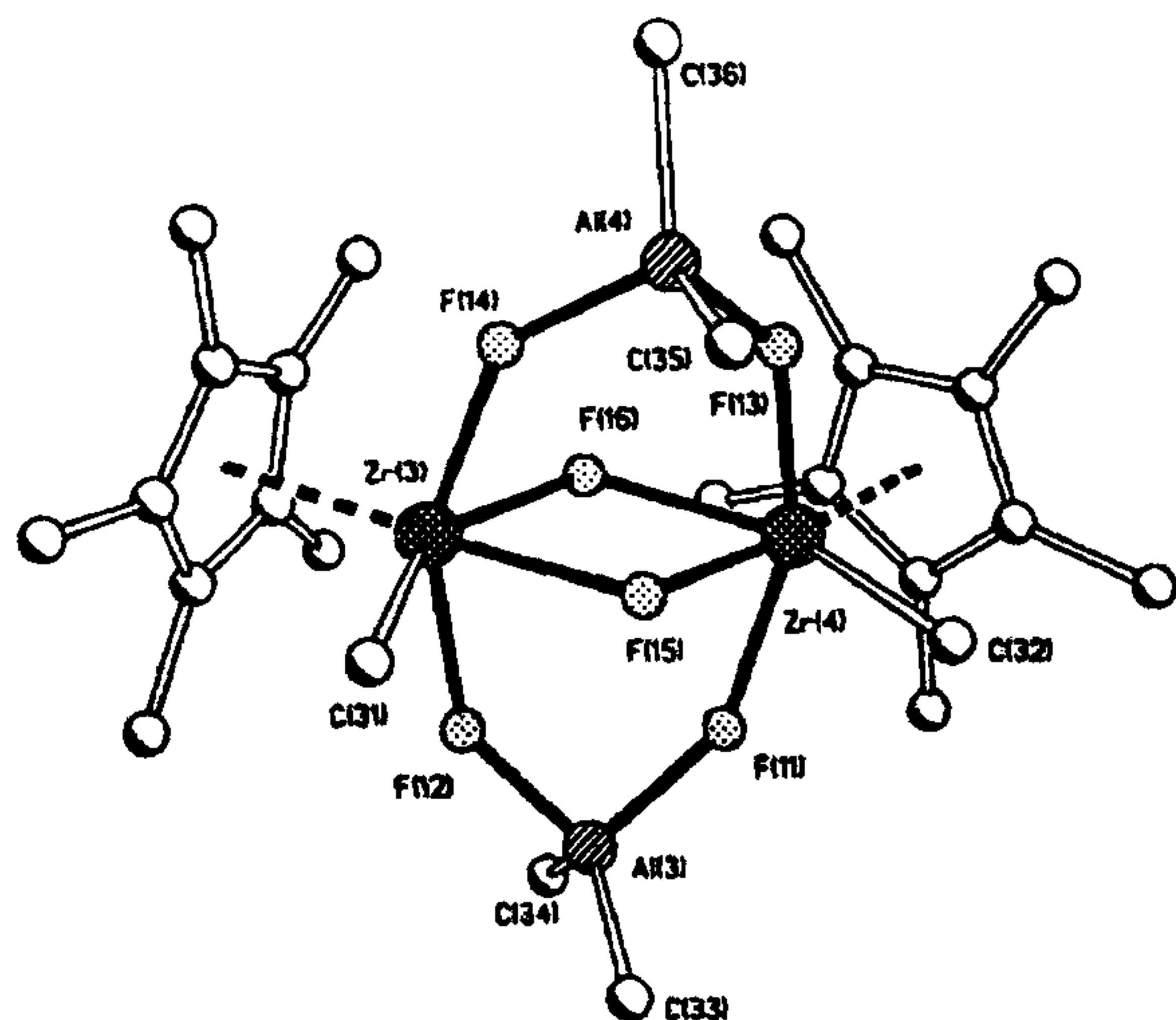


Figure 15. Structure of $[\text{Cp}^*\text{ZrMe}(\mu\text{-F})(\mu\text{-FAI Me}_2\text{F})]_2$ (from ref. 78).

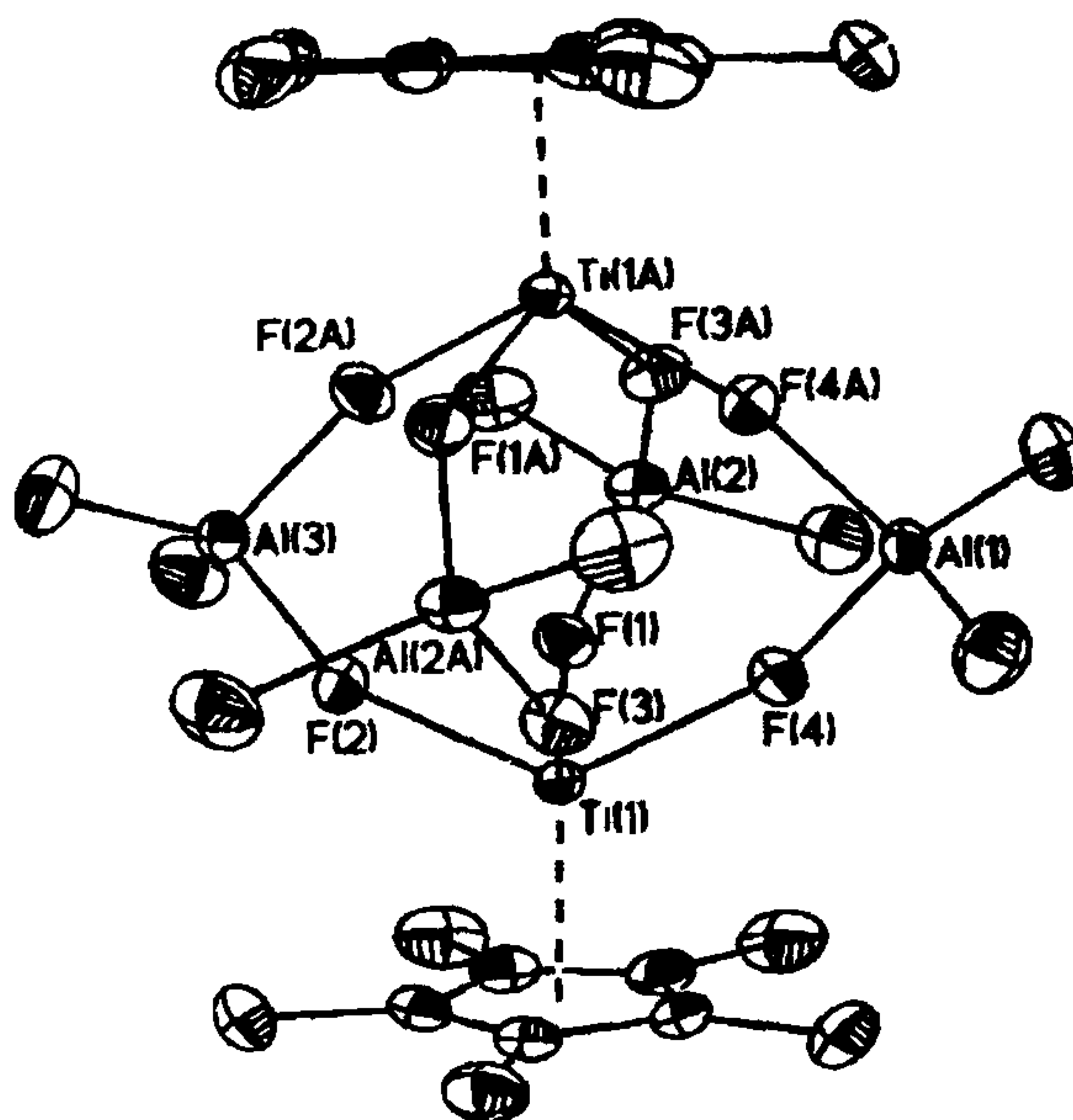


Figure 16. Structure of $[(\text{Cp}^*\text{Ti})_2(\mu\text{-F})_8(\text{AlMe}_2)_4]$ (from ref. 120).

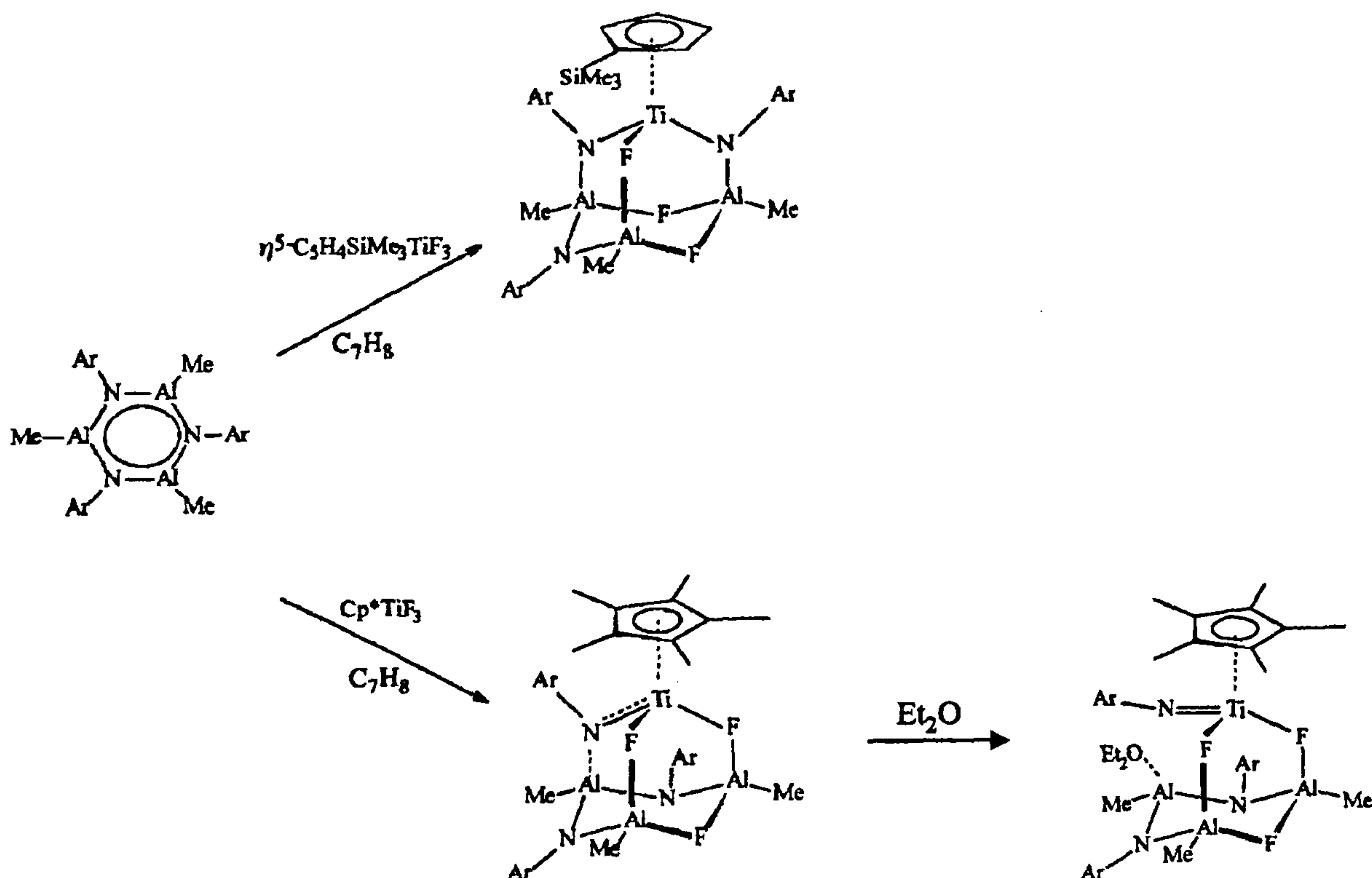
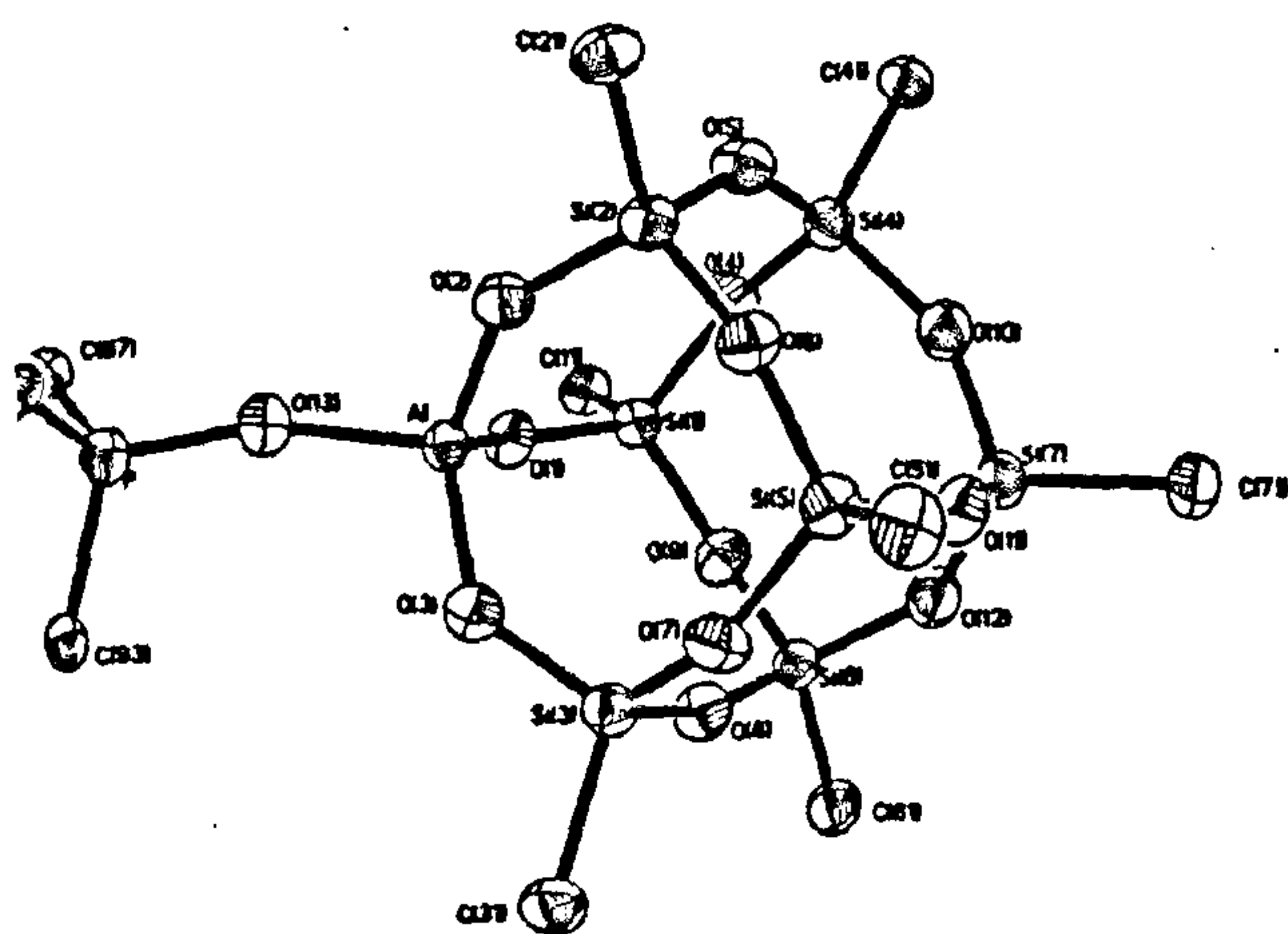
an octahedron of metal atoms bridged by fluorine atoms. The Ti atoms are in *trans* positions with a pseudo square pyramidal environment completed by the Cp^* ring¹²⁰. In contrast, the corresponding Et_2Al complex is already formed at r.t.⁶³

Positional exchange of F atoms against DippN units ($\text{Dipp} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) occurs in reactions of the trimeric iminoalane $(\text{MeAlNDipp})_3$ with $\text{Cp}'\text{MF}_3$ compounds ($\text{M} = \text{Zr}, \text{Cp}' = (\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$ (ref. 121), $\text{M} = \text{Ti}, \text{Cp}' = \text{Cp}$ (ref. 121), $\text{M} = \text{Ti}, \text{Cp}' = \text{Me}_3\text{SiC}_5\text{H}_4$ (ref. 122) and $\text{M} = \text{Ti}, \text{Cp}' = \text{Cp}^*$ (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_2O the cage opens leaving a species with a $\text{Ti} = \text{N}$ double bond, the Et_2O co-ordinates the vacant site of Al (ref. 122). All compounds have been structurally characterized.

A compound with an $\text{Al}_4(\mu\text{-F})_4(\mu\text{-Si})_2$ core will be discussed later¹²³.

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}.

Scheme 5. Reactions of $(\text{MeAlNDipp})_3$ with $\text{Cp}'\text{TiF}_3$ complexes (from ref. 122).Figure 17. Structure of $[(\text{CySi})_7(\mu\text{-O})_{12}\text{Al-OPPh}_3]$ (from ref. 126) or substituents omitted for clarity).

her and co-workers have investigated the reaction of the cyclohexyl (Cy) substituted polysiloxanetriol $(\text{CySi})_7(\mu\text{-O})_9(\text{OH})_3$ with Me_3Al (refs 126–129). Under complete elimination of methane a cluster with a cubic $[(\text{CySi})_7(\mu\text{-O})_{12}\text{Al}]_2$ is formed which is a dimer with a central four-membered Al_2O_2 ring. The dimeric structure can be broken by addition of Lewis bases as Et_3O (Figure 17) (ref. 126), Me_3NO (ref. 126) or SbOH (ref. 127). Addition occurs at the Al atom.

Anionic cages connected by linear $\text{Al}(\mu\text{-O})\text{Al}$ (ref. 127) and $\text{Al}(\mu\text{-O})\text{Si}$ (ref. 128) bridges have also been realized. Tossell has performed calculations on the 6-31G* level on the compounds $\text{Si}_2\text{Al}_4\text{O}_6\text{H}_8$ and $\text{Si}_4\text{Al}_4\text{O}_8\text{H}_{12}$. He confirmed the 'drum' structures (Figure 18) experimentally found by our group as local minima¹³⁰.

Reactions of the stable silanetriol $\text{DippN}(\text{SiMe}_3)\text{Si}(\text{OH})_3$ with $i\text{Bu}_2\text{AlH}$ in an 1:1 ratio at -78°C in dioxane or Thf afford eight-membered heterocycles $[\text{DippN}(\text{SiMe}_3)\text{Si}(\text{OH})(\mu\text{-O})_2\text{Al}i\text{Bu}\cdot\text{L}]_2$, while in a 1:2 molar ratio a cage with two six-membered rings consisting of $i\text{BuAl}$ -, $i\text{Bu}_2\text{Al}$ - and $\text{DippN}(\text{SiMe}_3)\text{Si}$ moieties each connected by $\mu_3\text{-O}$ atoms is formed^{131,132}. Performing the equimolar reaction at 65°C results in complete elimination of $i\text{BuH}$ and H_2 leaving a compound $\{[\text{DippN}(\text{SiMe}_3)\text{Si}(\mu_3\text{-O})_3\text{Al}\cdot\text{Thf}]_2\}_2$ consisting of fused eight-membered rings. The same types of aluminosiloxanes are also available with $\text{XylN}(\text{SiMe}_3)$ ($\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) (ref. 132) and $(\text{CO})_9\text{Co}_3\text{C}$ attached to Si in the reactions of the silanetriols with Me_3Al or Et_3Al (refs 133, 134). Ionic aluminosiloxanes of the type $(\text{M}\cdot\text{Thf})^+[\text{RAl}(\mu_3\text{-O})_3\text{SiN}(\text{SiMe}_3)\text{Dipp}]_4^{4-}$ with $\text{M} = \text{Li}$, $\text{R} = \text{H}$ and $\text{M} = \text{Na}$, $\text{R} = \text{Et}$ have been synthesized from the silanetriol with LiAlH_4 and $\text{Na}^+(\text{Et}_3\text{AlH}_2)^-$, respectively. The alkali metals are five-coordinated through the Thf-O and four adjacent O atoms of the aluminosiloxane (Figure 19) (ref. 134).

a

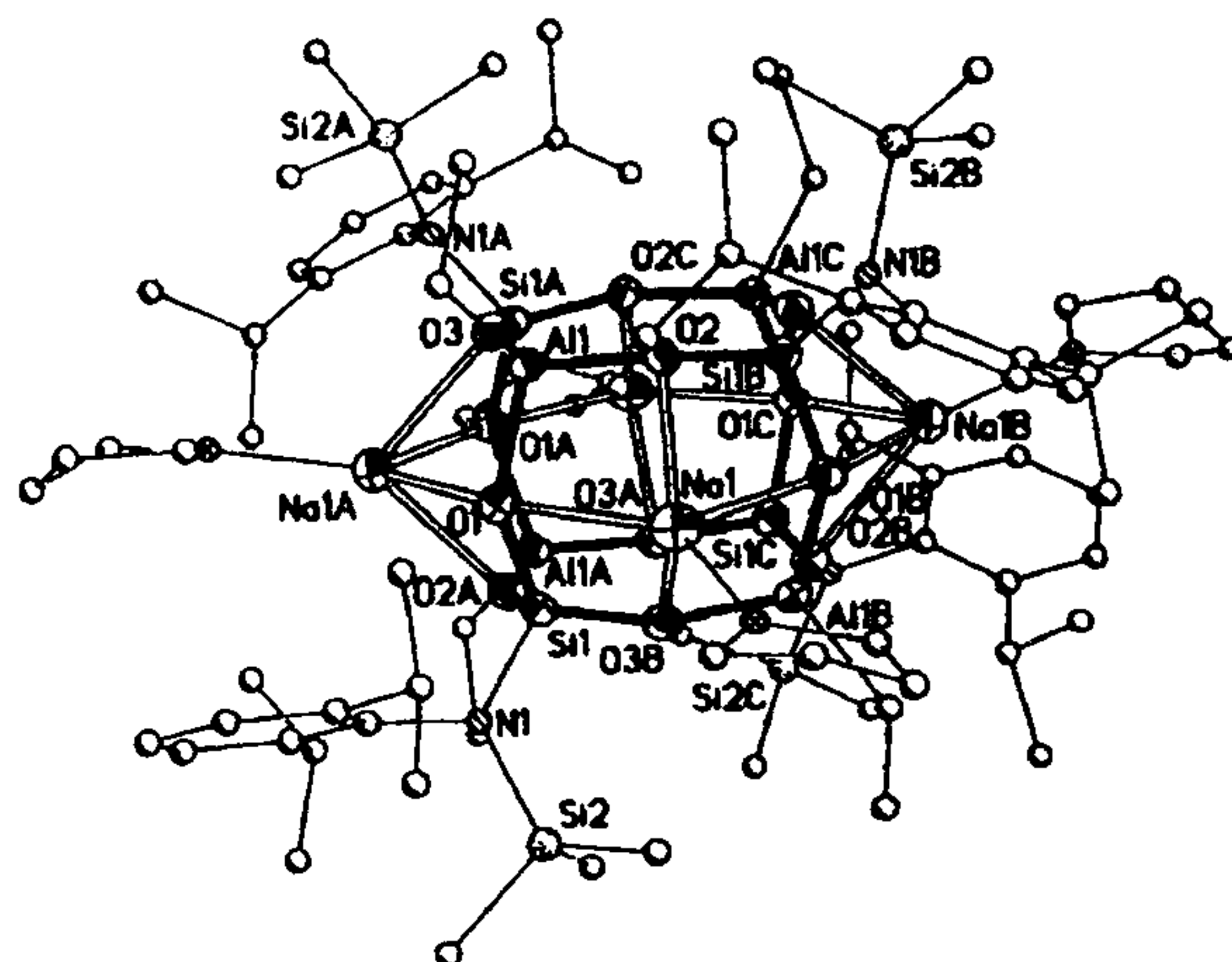
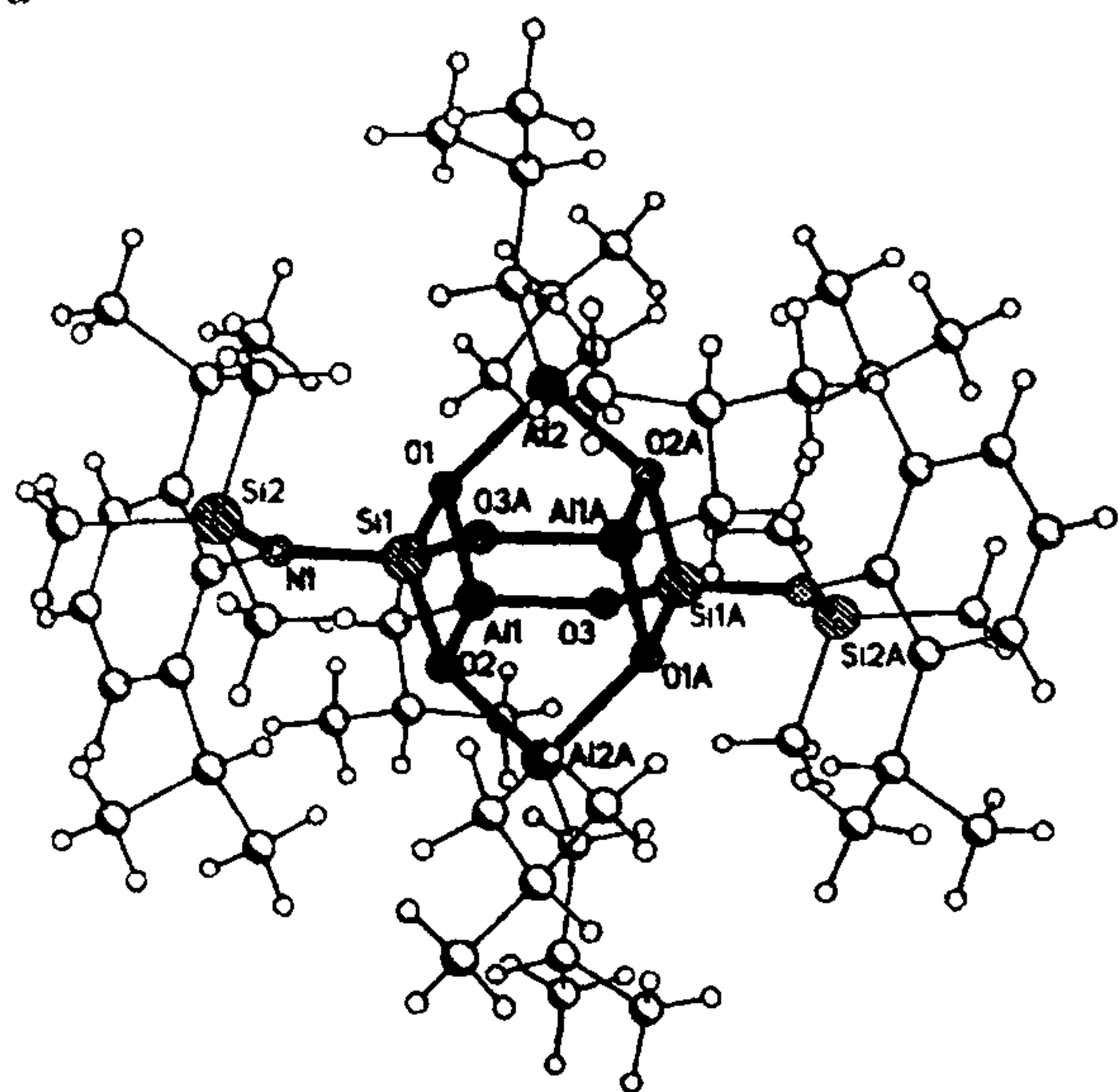


Figure 19. Structure of $(\text{Na} \cdot \text{Thf})_4[\text{EtAl}(\mu_3\text{-O})_3\text{SiN}(\text{SiMe}_3)\text{Dipp}]_4^-$ (from ref. 134).

b

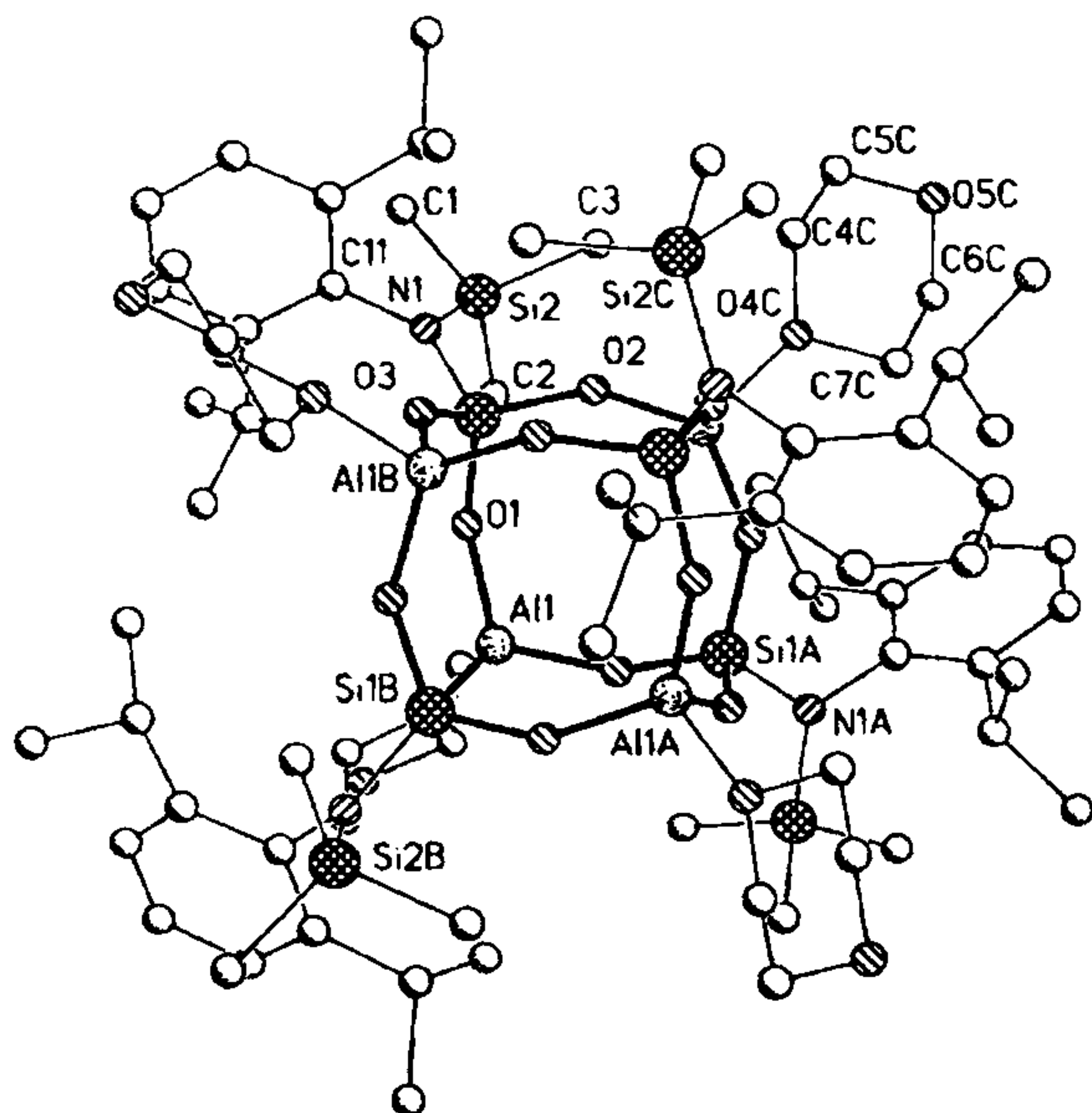


Figure 18. Structures of the D3R and D4R aluminosiloxanes (from refs 131, 132).

Aluminophosphinates were known since 1964, when Coates and Mukherjee obtained compounds of formulae $[\text{Me}_2\text{Al}(\mu\text{-O})_2\text{PR}_2]_n$ with $\text{R} = \text{Me}, \text{Ph}$ from reactions of Me_3Al with the appropriate phosphinic acids¹³⁵, 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 measurements¹³⁶ and comparison with similar heterocycles⁸¹. The same group estimated the aggregation grade n of compounds with $\text{R} = \text{F}, \text{Cl}$ and H to be three due to cryoscopic, IR- and Raman studies^{137,138}. No ring size was given by Japanese researchers, who synthesized $[\text{Et}_2\text{Al}(\mu\text{-O})_2\text{P}(\text{OR})_2]_n$ with $\text{R} = \text{Me}, \text{Et}$ via two different routes¹³⁹. In 1996 two groups independently described the structures of two complexes exhibiting the expected eight-membered rings $[\text{Me}_2\text{Al}(\mu\text{-O})_2\text{PPh}_2]_2$ (ref. 140) and $[\text{tBu}_2\text{Al}(\mu\text{-O})_2\text{P}(\text{OSiMe}_3)_2]_2$ (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 $[\text{tBu}_2\text{Al}(\mu\text{-O})_2\text{PPh}_2]_2$ and $[\text{tBu}_2\text{Al}(\mu\text{-O})_2\text{P}(\text{OSiMe}_3)\text{Ph}]_2$ (ref. 142), $[\text{R}_2\text{Al}(\mu\text{-O})_2\text{P}(\text{OSiMe}_3)_2]_2$ via intermediate Lewis acid base adducts $\text{R}_2\text{AlR}'\cdot\text{OP}(\text{OSiMe}_3)_3$ ($\text{R} = \text{Me}, \text{Et}$, $\text{R}' = \text{Me}, \text{Et}, \text{Cl}$) (ref. 143), $[\text{tBu}_2\text{Al}(\mu\text{-O})_2\text{P}(\text{tBu})\text{OSiMe}_3]_2$ and $[\text{Me}(\text{Cl})\text{Al}(\mu\text{-O})_2\text{PPh}_2]_2$ (ref. 144) from the appropriate precursors.

Probably template directed is the synthesis of the compound shown in Figure 20 from $\text{tBuP}(\text{O})(\text{OH})_2$ and $\text{Na}^+(\text{Et}_2\text{AlH}_2)^-$.

The molecule is constructed of twelve-membered $\text{Al}_3\text{P}_3\text{O}_6$ 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 $\mu_3\text{-O}$ atoms connecting the two halves of the molecule¹⁴⁵.

A tetrameric aluminophosphate $[\text{tBuAl}(\mu\text{-O})_3\text{P}(\text{OSiMe}_3)]_4$ has been formulated from the reaction of tBuAlCl_2 with $\text{OP}(\text{OSiMe}_3)_3$ from analytical and spectroscopical data¹⁴¹. Reactions of several alanes R_3Al with phosphonic acids $\text{RP}(\text{O})(\text{OH})_2$ afford smoothly with alkane elimination tetrameric aluminophosphonates

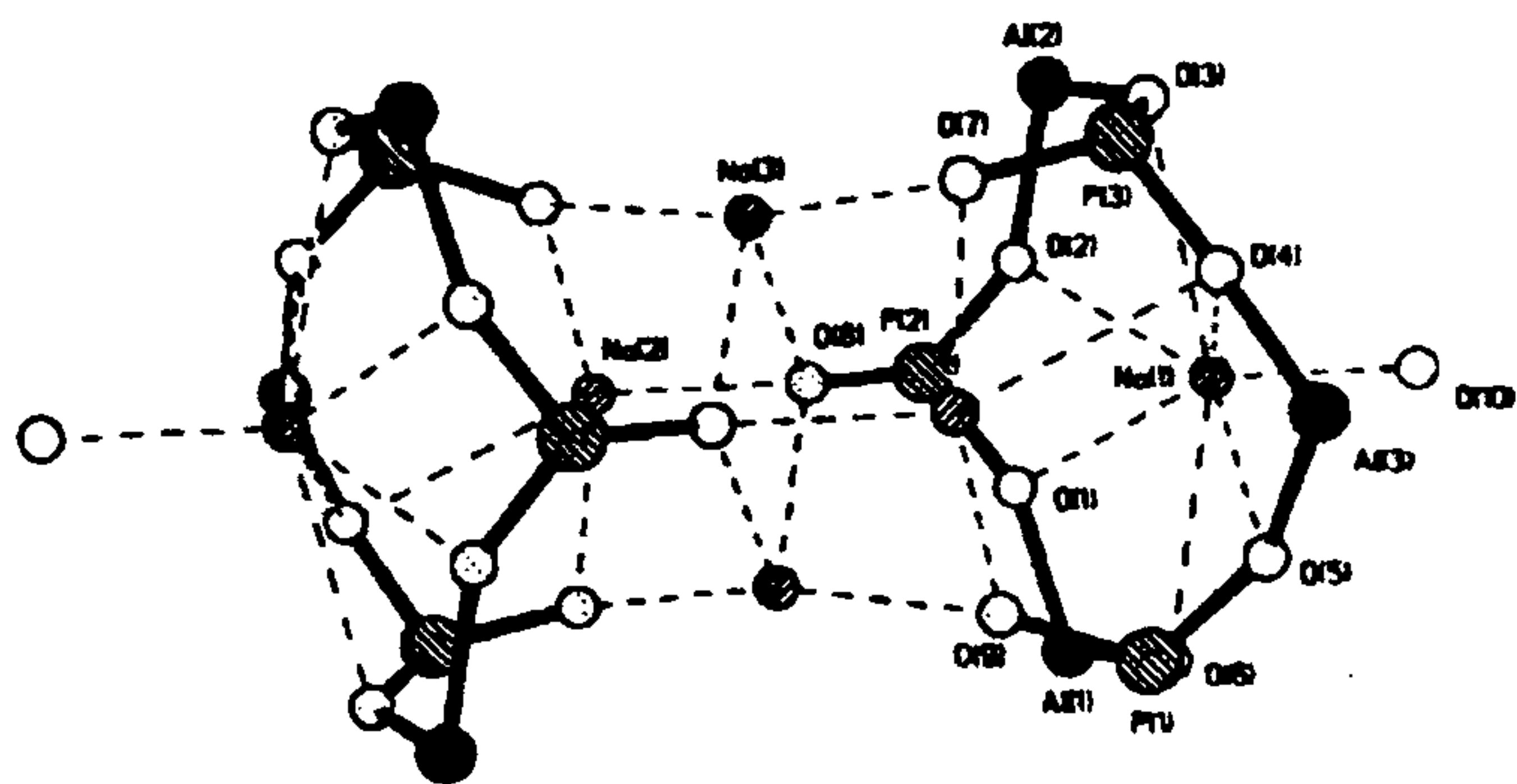
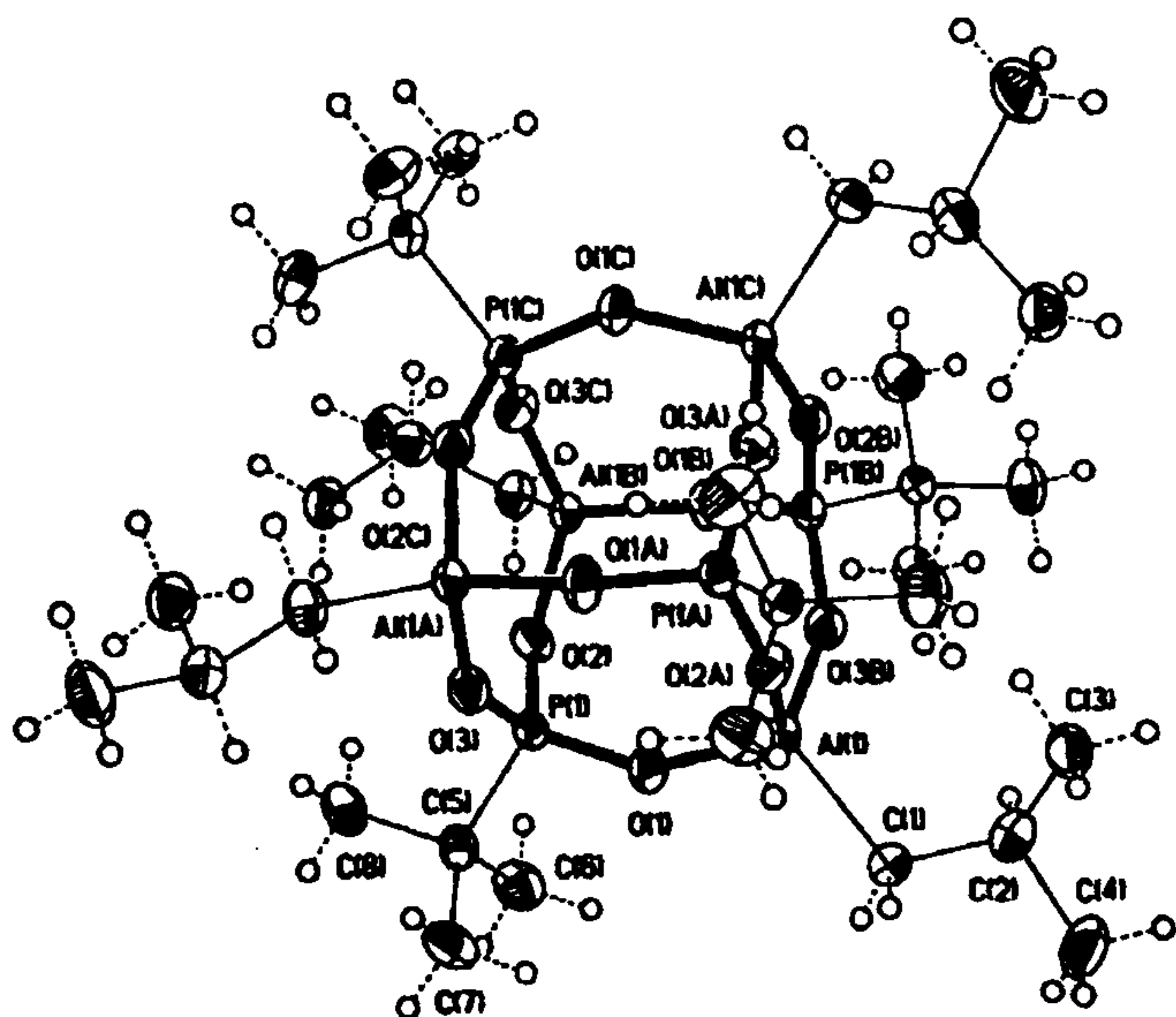
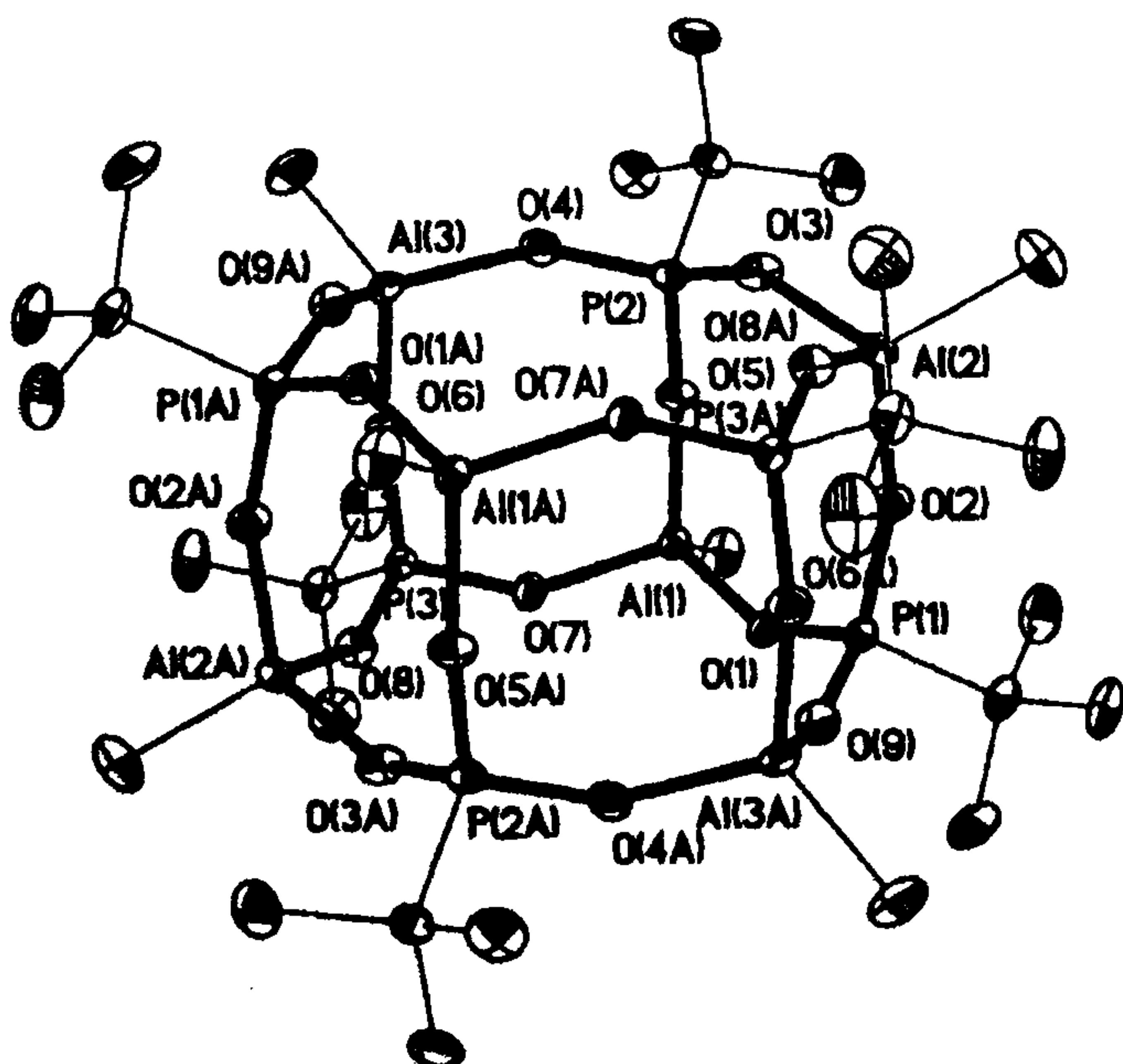


Figure 20. Structure of $\{(\text{Na}\cdot\text{Thf})\text{Na}_2[(\text{tBuP}(\mu_3\text{-O})_3\text{AlEt}_2)_3]_2\}$ (from ref. 145) (*t*Bu and Et groups and Thf-C's omitted for clarity).

a



b



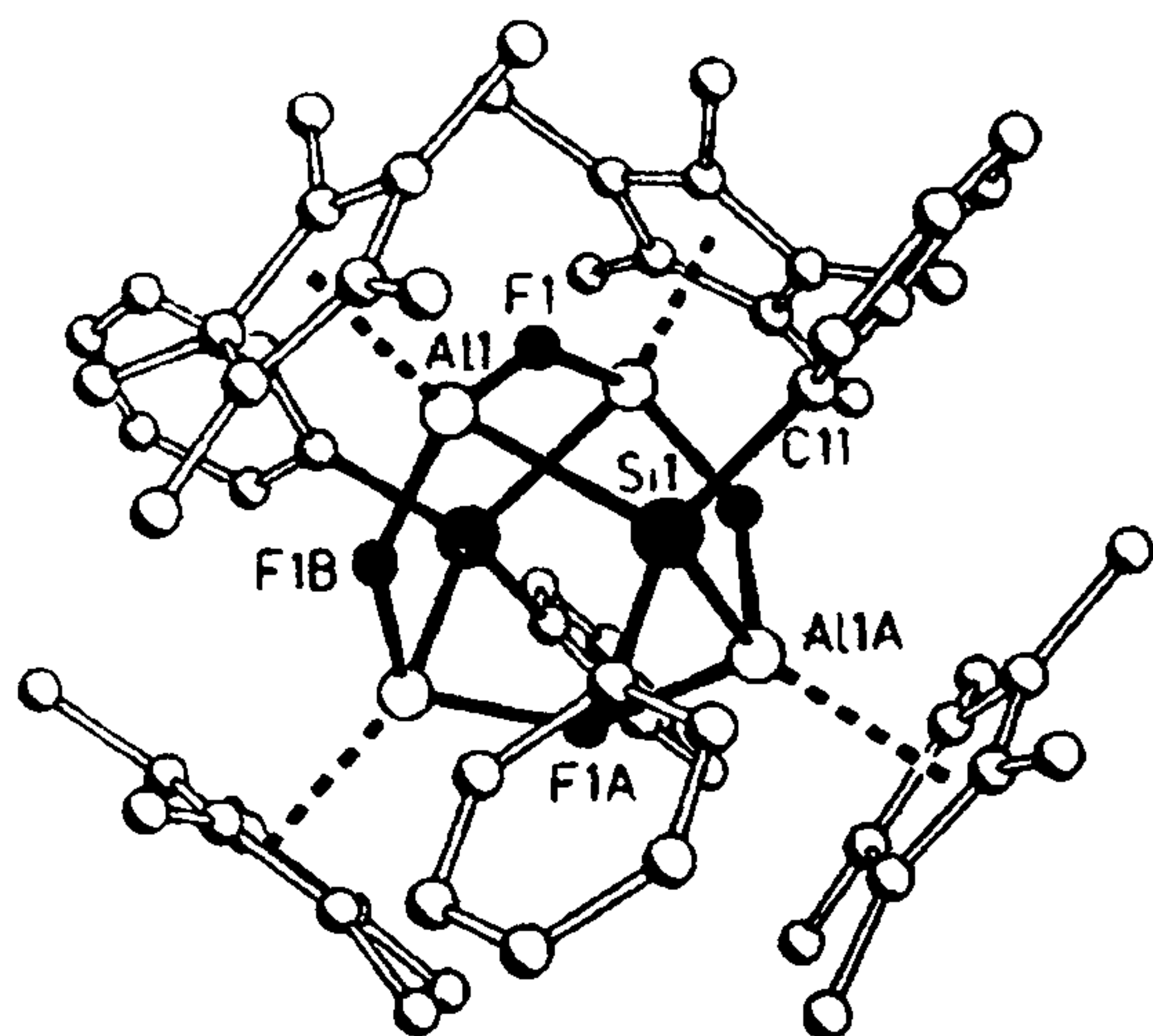


Figure 23. Structure of $[(\text{Cp}^*\text{Al})_4(\mu\text{-F})_4(\mu\text{-SiPh}_2)_2]$ (from ref. 123).

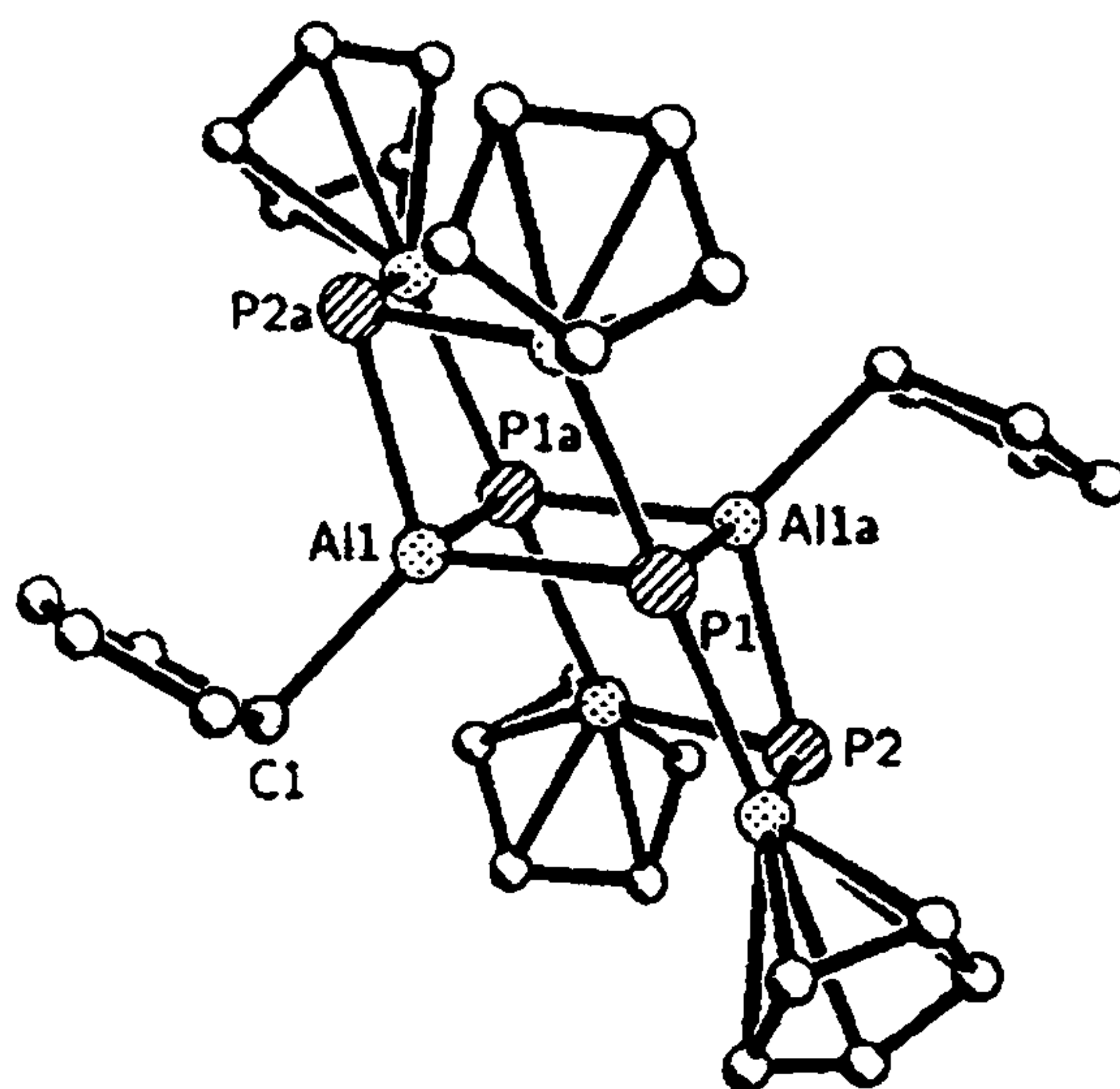


Figure 25. Structure of $[(\text{Cp}^*\text{Al})_6\text{P}_4]$ (from ref. 156).

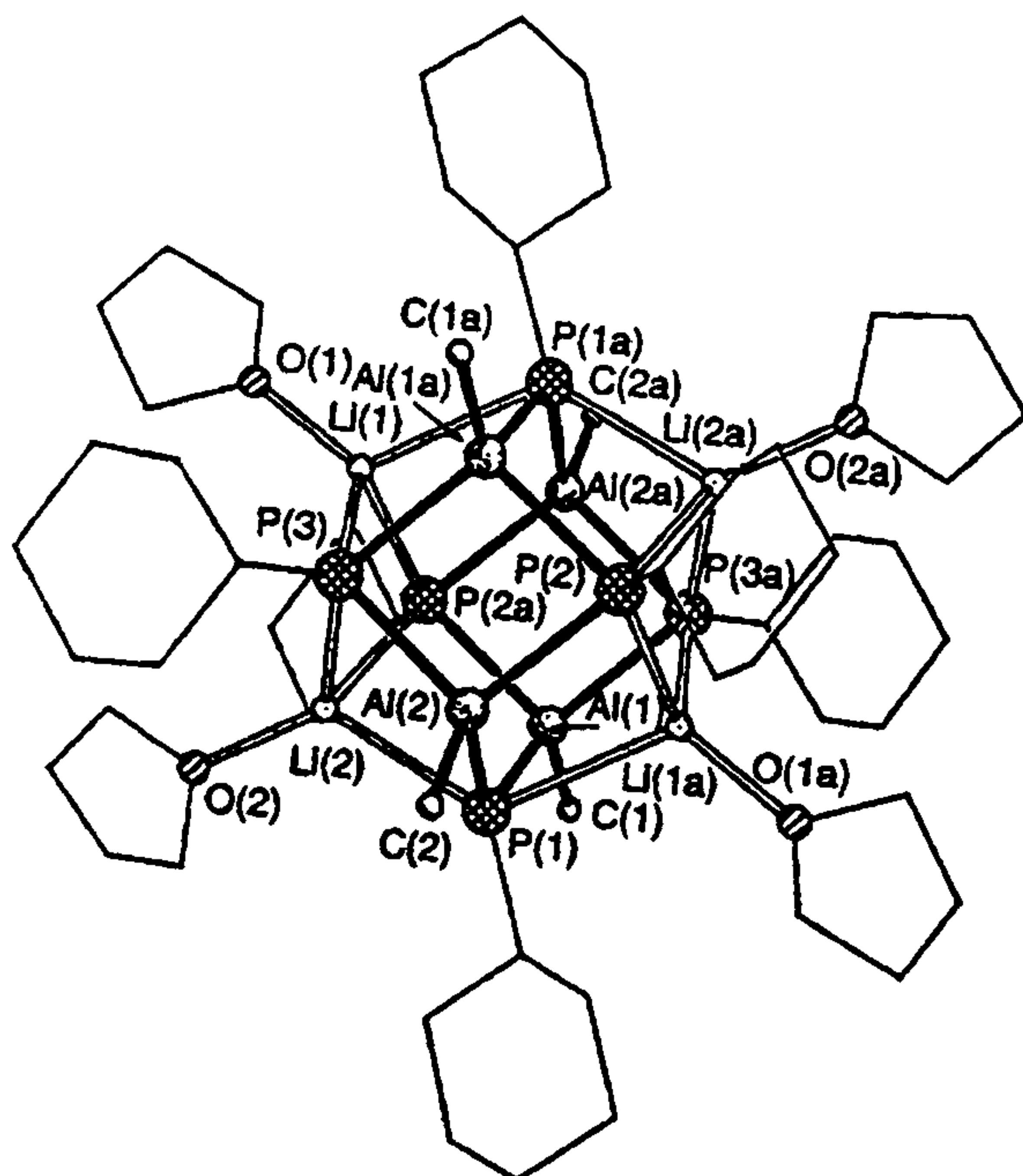


Figure 24. Structure of $(\text{Li}\cdot\text{Thf})_4[(\text{MeAl})_4(\mu\text{-PCy})_6]^{4-}$ (from ref. 155).

While Al–N cage compounds with a wide variety of structures are available from thermolysis of (predominantly) dimeric aminoalanes with $[\text{RAl}(\mu_3\text{-NR}')_2]_4$ cubanes as the best examined class^{151–153}, Al–P chemistry is mainly restricted to four- and six-membered $(\text{AlP})_n$ rings¹⁵⁴. The only structurally characterized $(\text{AlP})_4$ cubane, $[\text{iBuAl}(\mu_3\text{-PSiPh}_3)]_4$, has been obtained by A. H. Cowley *et al.* from the reaction of iBu_2AlH

with Ph_3SiPH_2 via intermediate formation of *cis/trans* isomers of $[\text{iBu}_2\text{Al}(\mu\text{-PHSiPh}_3)]_2$ and subsequent heating. Pyrolysis of the tetramer at 500°C leads to deposition of AlP (ref. 155).

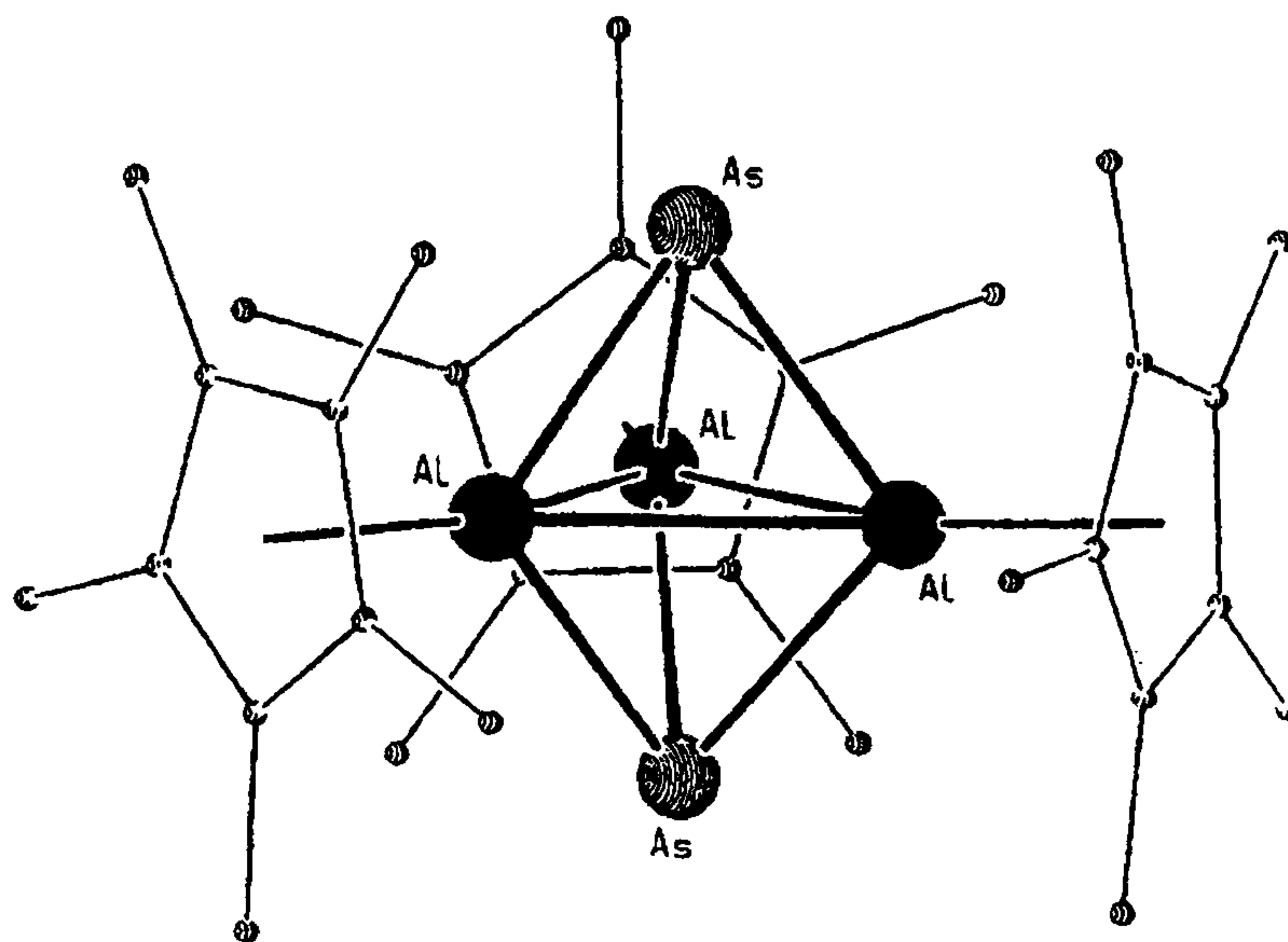
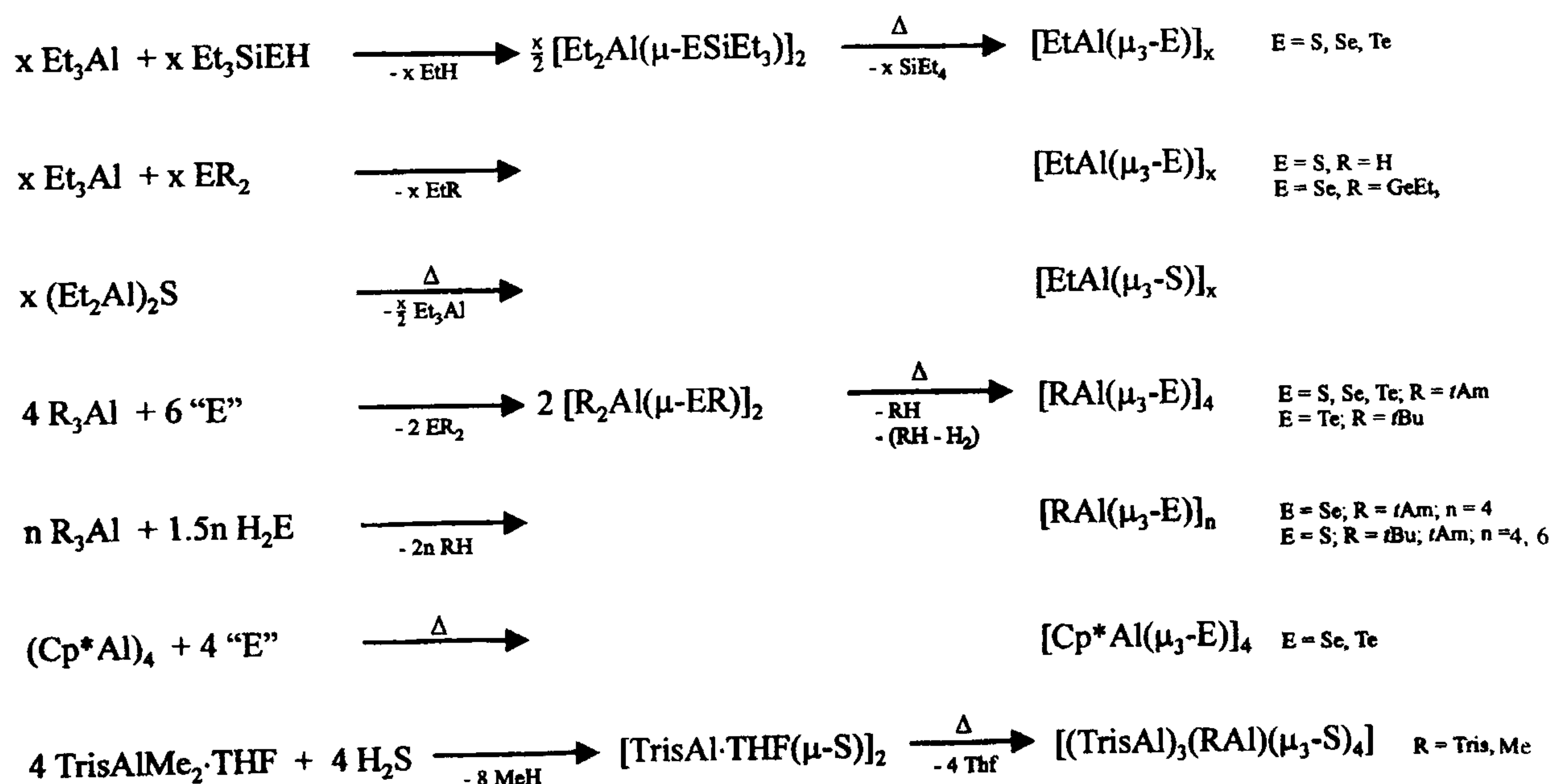
A polycyclic tetraanionic Al–P species has been found in the reaction of iminoalane $[\text{MeAl}(\mu_3\text{-NMe})]_4$ with excess LiPHCy (Mes = mesityl, Cy = cyclohexyl) under elimination of MesNH_2 and LiNHMe . Its structure is shown in Figure 24. Two $[\text{MeAl}(\mu\text{-PCy})]_2$ four-membered 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 $(\text{Cp}^*\text{Al})_4$ with white phosphorus affords a compound of composition $[(\text{Cp}^*\text{Al})_6\text{P}_4]$. 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 η^1 bound, while the two other remain η^5 co-ordinated¹⁵⁶.

Reaction of $(\text{Cp}^*\text{Al})_4$ with $(\text{tBuAs})_4$ proceeds via elimination of iBuH and Me_2CCH_2 to yield a compound $[(\text{Cp}^*\text{Al})_3(\mu_3\text{-As})_2]$ with the Cp^* ligands bound η^1 whose structure is according to Wade's rule *closo* (Figure 26) (ref. 157).

The same type of complex, $[(\text{Cp}^*\text{Al})_3(\mu_3\text{-Sb})_2]$ has been postulated earlier from elemental analysis and spectroscopic investigations from the analogous reaction with $(\text{tBuSb})_4$ (ref. 123).

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

Figure 26. Structure of $[(\text{Cp}^*\text{Al})_3(\mu_3\text{-As})_2]$ (from ref. 157).Scheme 6. Syntheses of $[\text{RAl}(\mu_3\text{-E})]_n$ 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 $[\text{RAl}(\mu_3\text{-E})]_n$, E = S, Se, Te (Scheme 6).

The syntheses of high-melting, totally insoluble compounds $[\text{EtAl}(\mu_3\text{-E})]_x$ with E = S, Se and Te from Et_3Al and 'hydrogen equivalent' sulphides, $(\text{Et}_3\text{M})_{2-n}\text{EH}_n$ (M = Si, $n = 1$, M = Ge, $n = 0$) by Vyazankin *et al.*¹⁶⁸ and of

$[\text{Et}_2\text{Al}(\mu_3\text{-S})]_y$ 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 $[t\text{BuAl}(\mu_3\text{-E})]_4$ (E = S, Se, Te) have been obtained by Cowley *et al.* from $t\text{Bu}_3\text{Al}$ and the respective chalcogenes via isolable intermediates $[t\text{Bu}_2\text{Al}(\mu\text{-E}t\text{Bu})]_2$ and characterized by mass spectroscopy¹⁷¹. Shortly afterwards our group succeeded in the synthesis and first structural characterization of

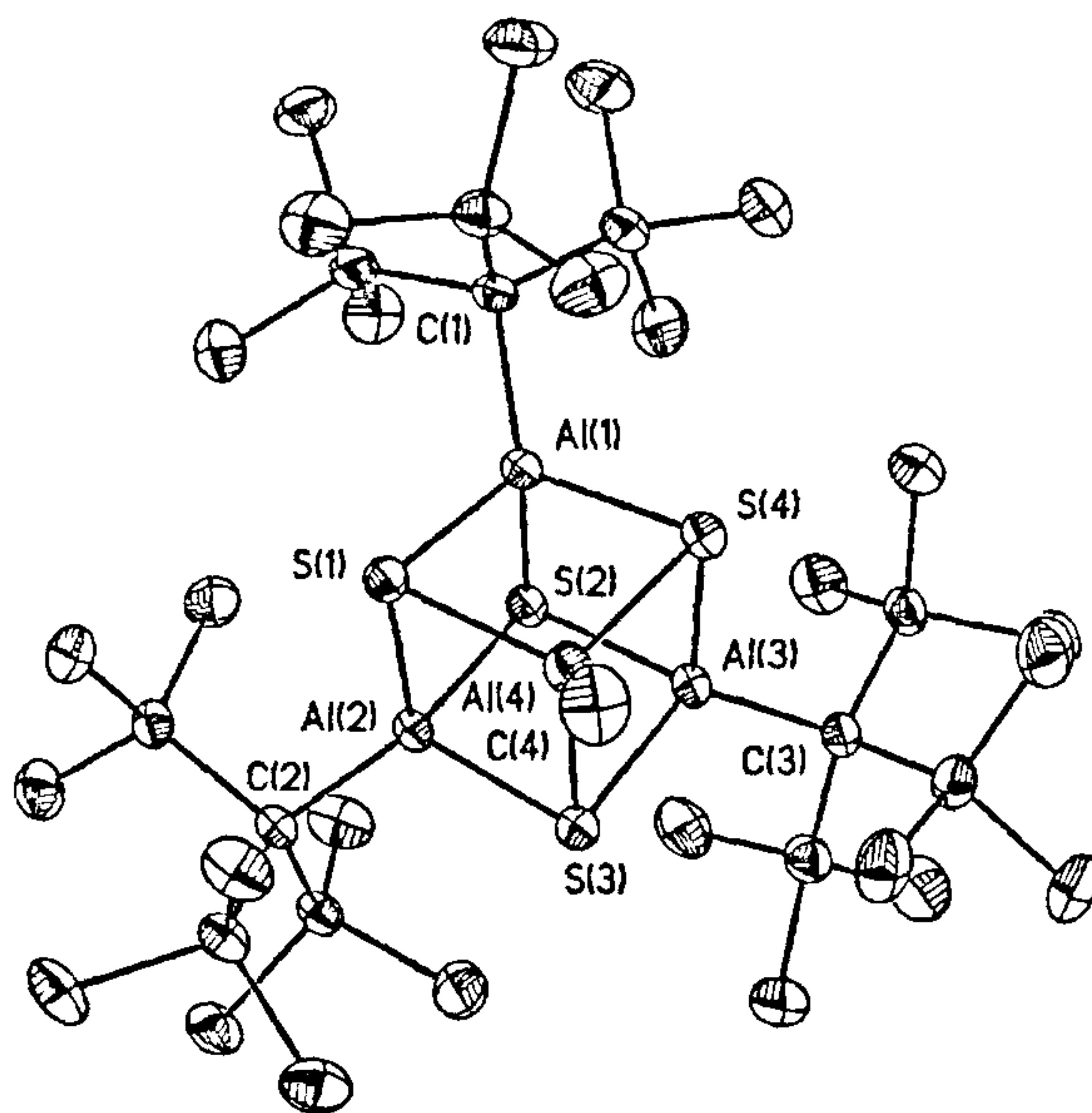


Figure 27. Structure of $[(\text{TrisAl})_3(\text{MeAl})(\mu_3\text{-S})_4]$ (from ref. 173).

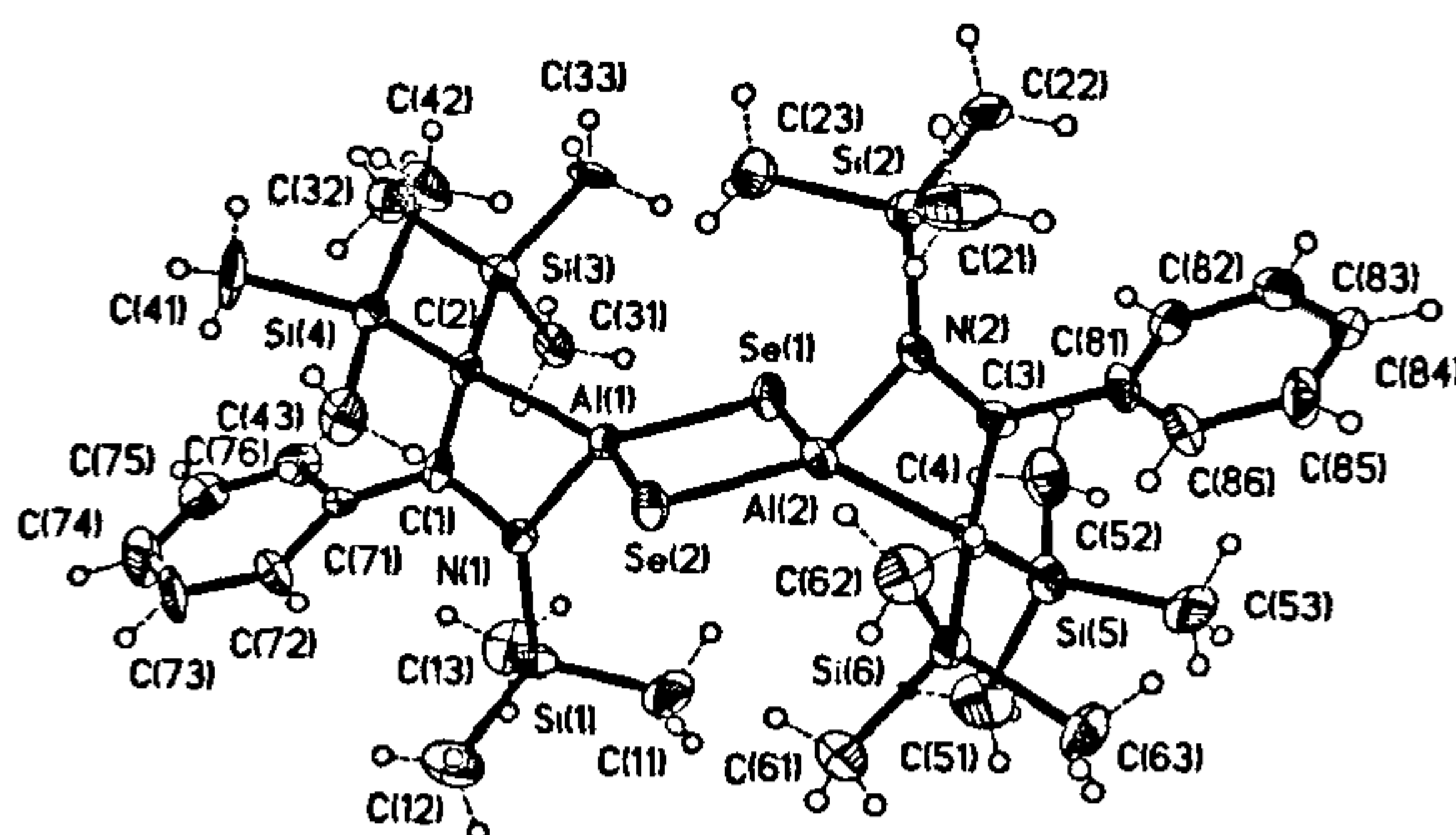


Figure 28. Structure of the dimeric aza-allylaluminum selenide (from ref. 175).

tetrameric $[\text{Cp}^*\text{Al}(\mu_3\text{-Se})]_4$ and $[\text{Cp}^*\text{Al}(\mu_3\text{-Te})]_4$ cages with slightly distorted cubic cores⁴⁴. By reactions of R_3Al compounds containing the bulky substituents *t*Bu and *t*Am ($= \text{Me}_2\text{EtC}$) with H_2S , Se_x and Te_x Barron *et al.* also obtained heterocubanes of S, Se and Te. The structures of $[\text{tAmAl}(\mu\text{-E})]_4$ with $\text{E} = \text{S}, \text{Se}$ have been determined. Additionally, the H_2S reactions yielded hexamers which have been separated from the tetramers by fractional crystallization (*t*Am) or sublimation of the tetramer (*t*Bu) and characterized spectroscopically¹⁷². Surprisingly the analogous reaction of $\text{TrisAlMe}_2 \cdot \text{Thf}$ ($\text{Tris} = (\text{Me}_3\text{Si})_3\text{C}$) with H_2S takes a different course; pyrolysis of the intermediate $[\text{TrisAl} \cdot \text{Thf}(\mu\text{-S})]_2$, which has been isolated in high yield and structurally characterized, led to two different cubanes. Aside from the

expected $[\text{TrisAl}(\mu_3\text{-S})]_4$ a second compound had formed, $[(\text{TrisAl})_3(\text{MeAl})(\mu_3\text{-S})_4]$, 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 tellurium¹⁷⁴ and aza-allyl compound $[\text{Me}_3\text{SiNCPhC}(\text{SiMe}_3)_2\text{AlH}(\mu\text{-H})]_2$ 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 $^1\text{H-NMR}$

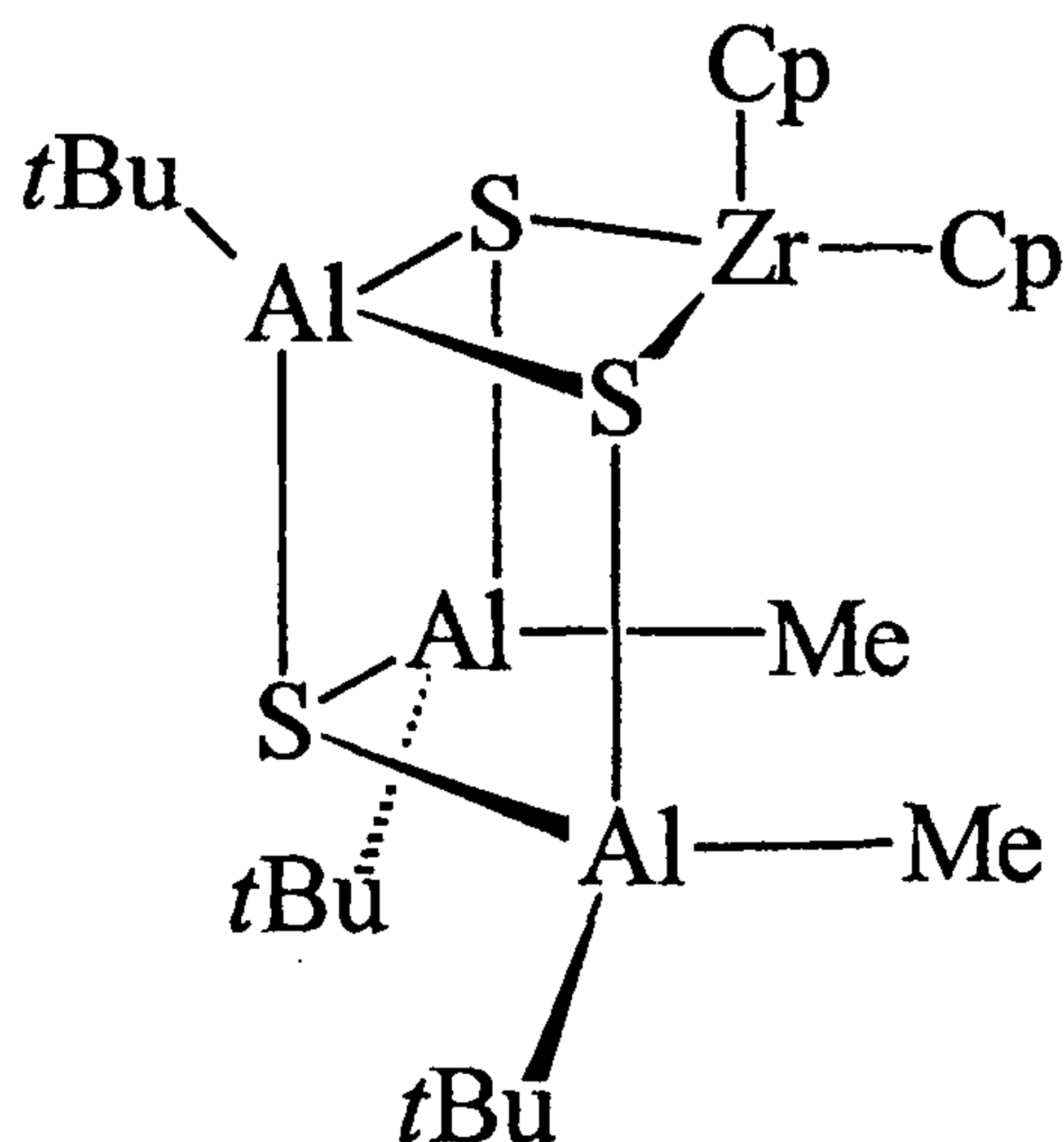


Figure 29. Proposed structure of $[(t\text{BuAl})(t\text{BuAlMe})_2(\mu_3\text{-S})_3\text{ZrCp}_2]$.

spectra, while the X-ray structure (Figure 28) only reveals the *trans* isomer in the crystal¹⁷⁵.

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 $\text{Al}_3(\mu_3\text{-S})_3\text{Zr}$ 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 determined¹⁷⁶.

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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