Synthesis, Structures and Reactions of Aluminum(I) and Aluminum(III) Compounds

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Dedicated to my parents and my husband

for their love and affection

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Abbreviations

av.	average
br.	broad
Calcd.	calculated
Cp*	pentamethylcyclopentadienyl
d	doublet
dec	decompose
EI	electron impact ionization
equiv	equivalent
g	gram
h	hour
Hz	hertz
*i*Pr	*iso*-propyl
IR	infrared
J	coupling constant
K	kelvin
L	ligand
m	multiplet
M	metal
M^+	molecular ion
Me	methyl
mL	milliliter
mmol	millimol(ar)
MS	mass spectrometry, mass spectra
M/z	mass / charge
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million

R	organic substituent
s	singlet
sept.	septet
t	triplet
Tert.	tertiary
THF	tetrahydrofuran
Z	number of molecules in the unit cell
δ	chemical shift
λ	wavelength
μ	bridging
ν	wave number

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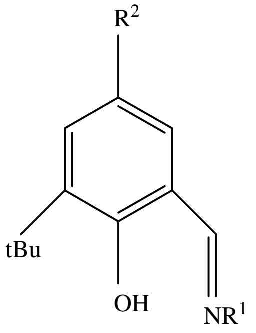
1. Introduction

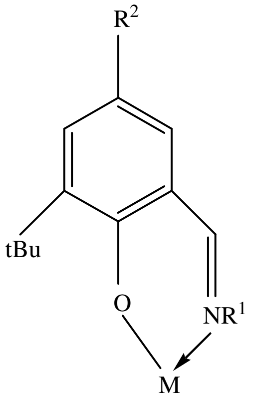
Aluminum derives its name from alum, a double sulphate, $KAl(SO_4)_2 \cdot 12H_2O$ which has been used medicinally as an astrigent since Classical Greek and Roman times. Aluminum is a grayish white metal and the most abundant metal in the lithosphere. As an extremely reactive metal aluminum rapidly obtains a stable surface oxide layer on exposure to air and moisture, thus it is found mostly in its oxidized and complexed forms. The high abundance of aluminum has resulted in a multitude of applications for the element and its compounds. It is the major constituent of many common minerals, including feldspars and micas. Moreover, aluminum plays an important role as a part of alloys.

In 1859, W. Hallwachs and A. Schafarik reported the first organoaluminum compound $Et_3Al_2I_3$ from the reaction of elemental Al and EtI.[1a] Although known as a highly reactive species for more than a century it was only since 1950 that organoaluminum compounds have gained interest. This development was triggered by the pioneering work of K. Ziegler et al. for the discovery of low pressure polymerisation of olefins with organoaluminum/transition metal catalysts.[1b,1c] Since then organoaluminum complexes generated considerable attention due to their increasing role in polymerisation chemistry, e.g. in cationic,[2a,2b] anionic[2c-2e] and ring-opening polymerisation,[2f] and as cocatalyts/activators in transition metal-catalysed olefin polymerisation.[2g] In addition, neutral aluminum alkyls have long been known to promote the oligomerisation of ethylene to yield α-olefins at elevated temperature and pressure.[2h] More recently, cationic aluminum alkyls have shown to polymerise ethylene under mild conditions.

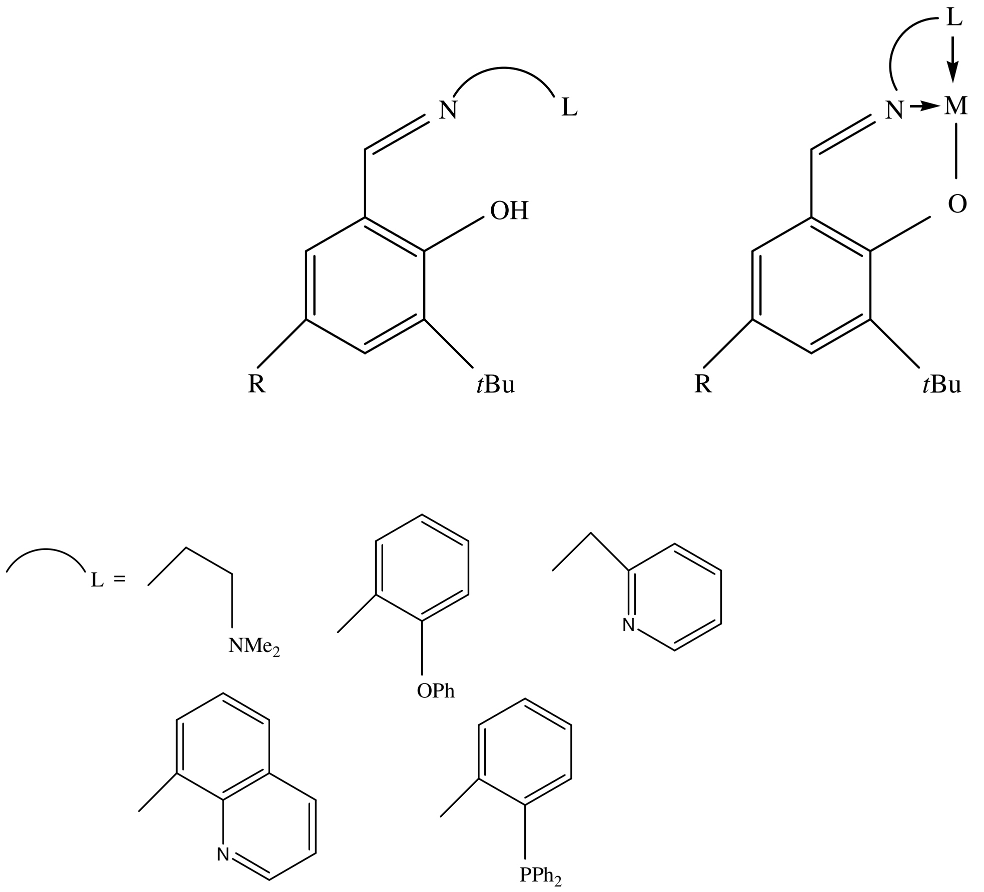
1.1. Organometallic compounds with salicylaldiminato ligand

In recent years there has been considerable and growing interest in the coordination chemistry of bulky bi- and tridentate ligands, in part because these ligands can be used to provide protective shielding for catalytically active metal centers. This protection strategy is the one which we employed in aluminum chemistry to get some unusual compounds. The salicylaldiminato ligand framework has a long history as an ancillary ligand system in coordination and organometallic chemistry. It is readily accessible and shows good solubility in common organic solvents. Moreover, salicylaldiminato ligands have played an important role in a range of olefin polymerisation catalyst systems.[3] The alkyl or aryl groups on the aldimine nitrogen and the phenoxide ring show the diversity of such ligands with flexible coordination abilities. The common coordination mode is bidentate, and tridentate with pendant arm on the aldimine nitrogen atom.





R^1 = 2,6-$Me_2C_6H_3$, 2,6-*i*$Pr_2C_6H_3$, 3,5-$(CF_3)_2C_6H_3$, 4-$(NO_2)C_6H_4$, 4-ClC_6H_4, 1-naphthyl, *t*Bu, C_6H_5, C_6F_5 ; R^2 = *t*Bu, H; M = metal

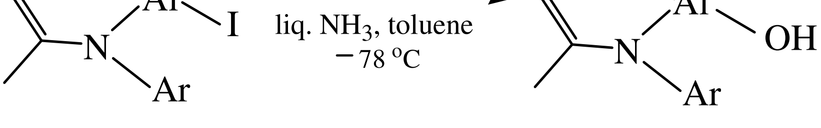


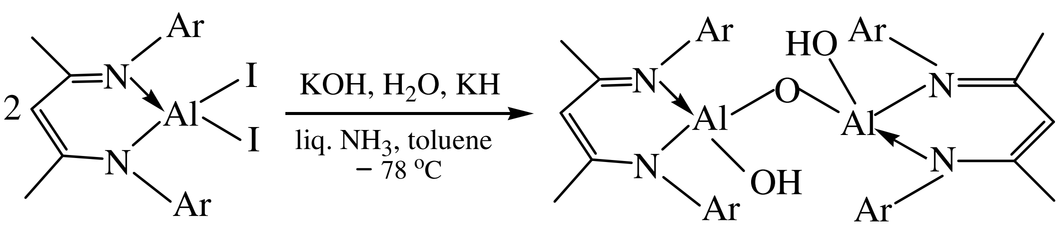
R = *t*Bu, H

It is extensively employed in both early and late transition metals.[3a,3c,4] This type of ligand was introduced to aluminum chemistry mainly to prepare alkyl aluminum complexes[5] and their cationic derivatives by reactions with AlR_2X (R = alkyl group, X = alkyl group or Cl), which can be used as ethylene polymerisation catalysts.[5d] To the best of our knowledge, there have been no reports of aluminum hydride species stabilised by Schiff base [N,O] chelate ligands.

1.2. Hydrolysis of organoaluminum compounds

In 1980 the investigation by Sinn and Kaminsky et al. that methylaluminoxane (MAO) is a highly active cocatalyst in ethylene and propylene polymerisation by group 4 metallocenes,[6] has promoted the studies on the structural determination of aluminoxane to exemplify its role in the polymerisation reactions. Although the role of MAO seems clear,[6c-6e] the molecular structure of the active aluminoxane species is an open question. Aluminoxanes, containing the Al–O–Al unit, are generally prepared by the controlled hydrolysis of aluminum alkyls or aryls with water or reactive oxygen-containing species such as CO_2, $RCONR_2$, $MeCO_2H$ and Me_2SO.[7-9,11] To obtain the related aluminoxanes, controlled amounts of water have to be introduced into a solution of R_3Al at low temperatures. Aluminoxanes easily associate to yield di-, tri-, tetra-, and oligoaluminoxanes.[9b,9c,40a] These properties of aluminoxanes make the preparation of a particular aluminoxane in a crystalline form and the determination of their crystal structures difficult. However, reactions with organoaluminum hydrides have been only investigated in a few cases.[10] Recent studies demonstrated two effective methods for the hydrolysis of aluminum compounds.[12-13] In a liquid ammonia/toluene two-phase system the first terminal aluminum dihydroxide $LAl(OH)_2$ ($L = HC(CMeNAr)_2$, $Ar = 2,6\text{-}i\text{Pr}_2C_6H_3$)[12a] was obtained by the reaction of $LAlI_2$ with KOH containing water and KH. In the same system a dinuclear aluminoxane[12b] containing a terminal hydroxide and six-membered aluminoxane was obtained.





Ar = 2,6-iPr$_2$C$_6$H$_3$

Another method is the reaction of water with organoaluminum dichlorides and an N-heterocyclic carbene is used as HCl acceptor.[13] This method is also effective in the hydrolysis of germanium chloride.[14]

$$\mathrm{LAlCl_2} \xrightarrow[-2\,\mathrm{Ct}\cdot\mathrm{HCl}]{2\,\mathrm{Ct},\,2\,\mathrm{H_2O}} \mathrm{LAl(OH)_2}$$

L = HC(CMeNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$; Ct = 1,3-tBu$_2$imidazole-2-ylidene

In numerous studies several low aggregated aluminoxanes containing bridging OH groups have been described.[9c,15] However, the synthesis and isolation of aluminum compounds with terminal hydroxides are rarely known.

1.3. Heteroatom-containing organoaluminum cage compounds

Much attention was paid recently to oligomeric and polyhedral compounds of aluminum containing Al-N and Al-C cores. Heteroatom-containing organoaluminum cage compounds are potential precursor for the chemical vapor deposition of aluminum nitride.[16] Moreover, their application in catalysis,[17] as reducing agents, and as synthetic intermediates[18] have attracted much interest. $AlH_3\cdot NMe_3$ is an effective precursor to prepare low aggregated organoaluminum hydrides.[10b,19] When it is used to react with compounds containing C-N and

C-C multiple bonds, structural interesting Al-N and Al-C clusters containing reactive Al-H bonds were obtained.[20] There have been some reports on the formation of aluminum imides from reactions 1-3.

$$AlH_3{\cdot}NMe_3 + RNH_2 \longrightarrow 1/n\ (RNAlH)_n + 2H_2 + NMe_3 \qquad (1)$$

$$LiAlH_4 + RNH_2{\cdot}HCl \longrightarrow 1/n\ (RNAlH)_n + 3H_2 + LiCl \qquad (2)$$

$$AlH_3{\cdot}NMe_3 + RCN \longrightarrow 1/n\ (RCH_2NAlH)_n \qquad (3)$$

The degree of Al-N association is predominantly dependent on three factors:

(a) Steric bulk of the alkyl group R on the amine,

(b) The organic substituents coordinating to aluminum atoms,

(c) The reaction conditions.

A few crystal structures of aluminum imides ($n = 4$, 6 or 8) containing hydridic hydrogen bound to aluminum atoms have been obtained.[21,22] However, compounds of composition $(RNAlH)_7$ with Al-H bonds are not known. The reaction of heteroalkyne with an excess of $AlH_3{\cdot}NMe_3$ results in the formation of a carbaaminoalane with an $Al_4C_4N_4$ skeleton.[20a] The hydrides on the aluminum atoms of these aluminum imides and carbaaminoalane are highly reactive and readily replaceable by nucleophilic reagents while the core of the cluster seems to be rather stable.

1.4. Chemical properties of organoaluminum(I) compounds

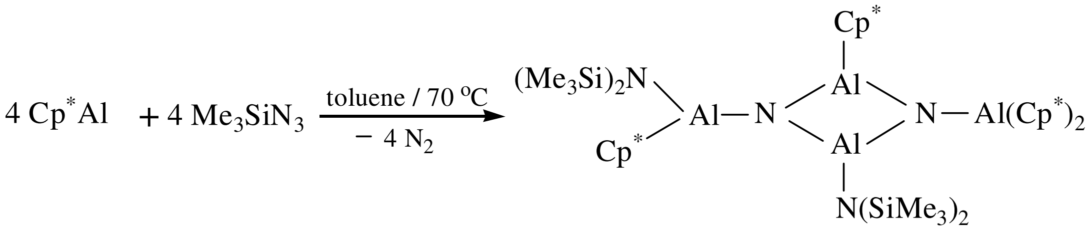
Aluminum is known to have a rich chemistry in its trivalent state.[23] Compared with the fascinating variety of the borane structures or the vast field of the subhalides of indium and thallium, the chemistry of subvalent aluminum compounds are less studied especially for the organoaluminum(I) compounds. Aluminum(I) species have been often postulated as intermediates in photochemical and free radical reactions of organoaluminum(III) reagents.[1c] In 1991 Schnöckel et al. reported the first stable organoaluminum(I) compound $(Cp^*Al)_4$,[24] which readily dissociates into the more reactive monomer (Cp^*Al)[25] in the gas phase or in solution at higher temperatures. There are some reviews[26,27] about the reactivity of the tetramer $(Cp^*Al)_4$. For example, $(Cp^*Al)_4$ can be oxidised with the elements P,[28] Se and Te[29] to afford interesting products.

$$6\ Cp^{*}Al \ + P_4 \xrightarrow[25\ ^{o}C]{toluene} (Cp^{*}Al)_6P_4$$

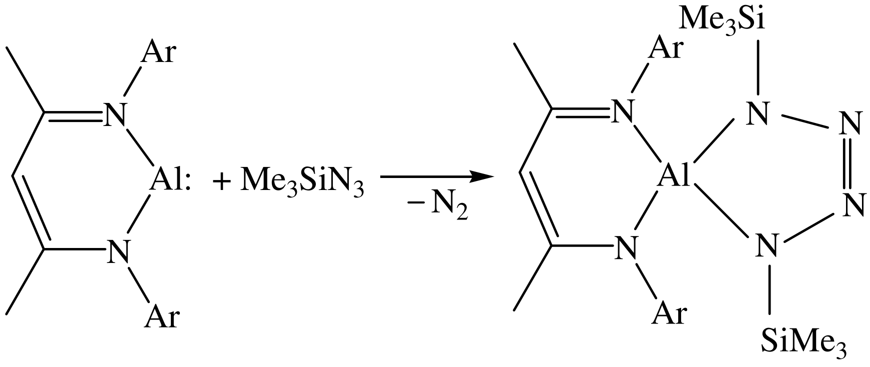
$$4\ Cp^{*}Al \ + 4\ E \xrightarrow[25\ ^{o}C]{toluene} (Cp^{*}Al)_4E_4$$

E = Se, Te

When $(Cp^*Al)_4$ is reacted with Me_3SiN_3, a dimeric iminoalane is obtained.[30]

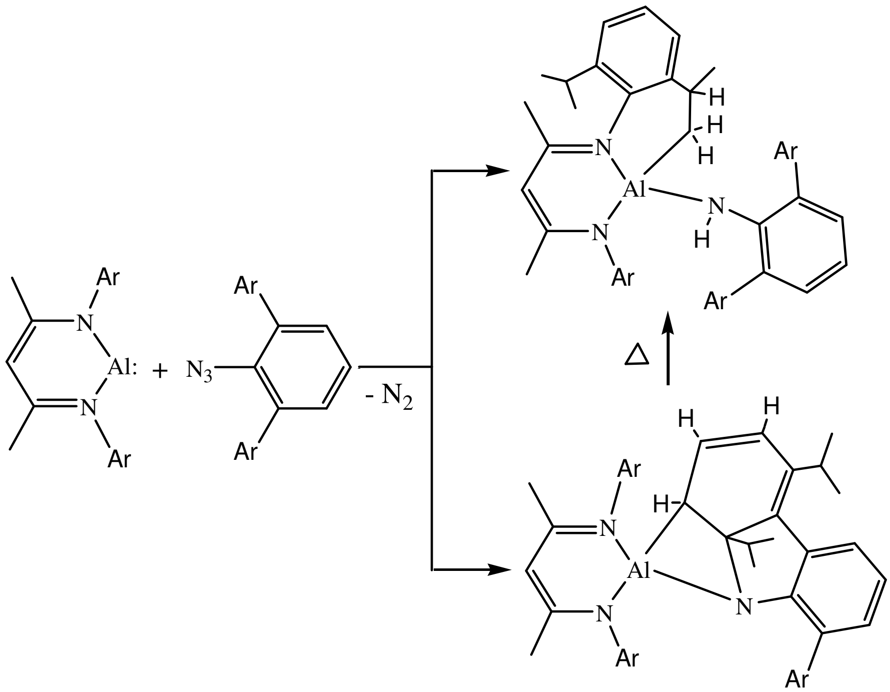


By exploring the bulky β-diketiminato ligand L, the first stable monomeric Al^I compound LAl^I ($L = HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) was reported.[31] Compared to $(Cp^*Al)_4$, LAl^I is more active and shows a completely different chemical behaviour. When treated with Me_3SiN_3, a cyclic aluminum-containing tetrazole was formed.[32]

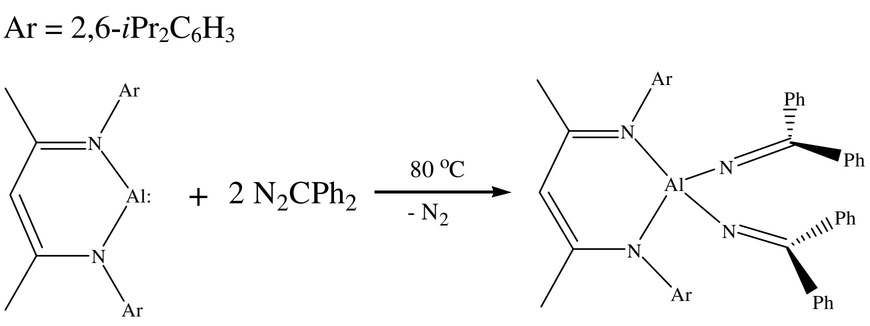


Ar = 2,6-iPr$_2$C$_6$H$_3$

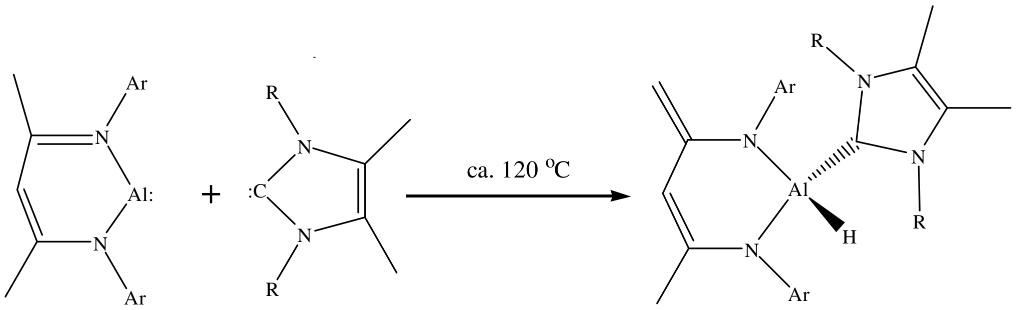
More examples of reactions with LAl^{I} are listed below:[33]



Ar = 2,6-iPr$_2$C$_6$H$_3$



Ar = 2,6-iPr$_2$C$_6$H$_3$



Ar = 2,6-*i*$Pr_2C_6H_3$; R = *i*Pr, Me

In this thesis some more reactions will be reported to enrich the LAl^I chemistry.

1.5. Scope and aims of this dissertation

As discussed above, organoaluminum compounds have been widely investigated as cocatalysts, reagents as well as precursor for inorganic materials such as ceramics, semidonductors, zeolites. The bulky ligand is very important to synthesise low-aggregated and low-valent aluminum species.

The objectives of the present work are:

(1) Studies of aluminum compounds stabilised by the bidentate salicylaldiminato ligand.

(2) Preparation of terminal hydroxide containing dinuclear aluminoxane.

(3) Synthesis of heptameric aluminum imide and surface fluorination products of the Al_7N_7 and $Al_4C_4N_4$ cores.

(4) Examination of the reactivities of monomeric organoaluminum(I) compounds.

2. Results and Discussion

2.1. Aluminum monohydride and chalcogenides bearing a bidentate [N,O] ligand

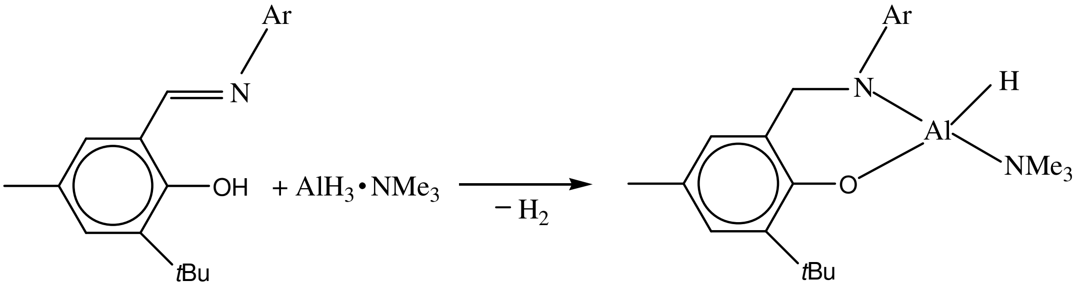
Salicylaldiminato ligands are extensively used in transition metal complexes,[3a,3c,4] and there are some reports on the aluminum chemistry by exploring this kind of ligands.[5] No example is known for an aluminum hydride bearing this type of ligand. Heavier group 13 element chalcogenides have been widely studied due to their important applications in chemical vapour deposition (CVD) and catalysis,[34] and organoaluminum hydrides of low aggregation have proved to be effective reagents for preparing chalcogenide compounds with elemental chalcogens or organochalcogenides,[35] such as $LAl(SeH)_2$, $LAl(SeH)Se(SeH)AlL$ (L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$),[19a] $LAl(SH)_2$ (L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$),[36] $Al_4Se_5(H)_2(NMe_3)_4$.[35d] As an extension of this type of reaction, we explored a bidentate salicylaldimine [3-*t*Bu-5-Me-2-OH-C_6H_2CH=N-2,6-*i*$Pr_2C_6H_3$] (**1**)[37] to react with $AlH_3 \cdot NMe_3$ to afford an aluminum monohydride (3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)$AlH \cdot NMe_3$ (**2**) under elimination of hydrogen together with hydrogen migration from the metal to the ligand backbone. We also described its chalcogenide derivatives [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(μ-E)$]_2$ [E = S (**3**), Se (**4**)] from the reaction of **2** with sulphur and selenium, and the possible reaction mechanism was discussed as well.

2.1.1. Preparation of bidentate salicylaldimine [3-*t*Bu-5-Me-2-OH-C_6H_2CH=N-2,6-*i*$Pr_2C_6H_3$] (1)

The bidentate salicylaldimine **1** was obtained as a yellow crystalline solid in good yield (90 %) by condensation of 4-methyl-6-tertbutylsalicylaldehyde with 2,6-diisopropylaniline in refluxing ethanol in the presence of catalytic amounts of formic acid. Spectroscopic data are consistent with the composition of **1** shown in Scheme 1 and satisfactory elemental analysis were obtained. The EI mass spectrum of **1** exhibits an intense peak for the molecular ion. The IR absorptions at 3400 cm^{-1} and 1620 cm^{-1} show the existence of O-H and CH=N stretches respectively, and resonances at δ 8.03 (C*H*=N) and 13.89 (-O*H*) in the ^{1}H NMR spectrum also support the presence of these groups in **1**.[5a]

2.1.2. Preparation of aluminum monohydride ($3\text{-}t\text{Bu-5-Me-2-O-}C_6H_2CH_2\text{-N-2,6-}i\text{Pr}_2C_6H_3)AlH\cdot NMe_3$ (2)

Reaction of **1** with a small excess of $AlH_3{\cdot}NMe_3$[38] in toluene at 0 °C or alternatively under refluxing conditions in toluene afforded the aluminum monohydride ($3\text{-}t\text{Bu-5-Me-2-O-}C_6H_2CH_2\text{-N-2,6-}i\text{Pr}_2C_6H_3)Al{\cdot}H(NMe_3)$ (**2**) in good yield under elimination of hydrogen. (Scheme 1). Furthermore, hydrogen migration from the aluminum atom to the



1 **2**

Ar = $2,6\text{-}i\text{Pr}_2C_6H_3$

Scheme 1

ligand backbone occurred at the CH=N double bond to give the CH_2N species. A migration reaction of a methyl group was not observed when $AlMe_3$ was used instead, and the CH=N double bond was retained in the bidentate salicylaldiminato ligand.[5a-5c] We assume that this is due to the higher reactivity of $AlH_3 \cdot NMe_3$ compared to that of $AlMe_3$. However, a methyl group migration was noted in the reaction of the tridentate salicylaldimine [3,5-$t$$Bu_2$-2-OH-$C_6H_2$CH=NR] (R = 8-$C_9H_6N$ (quinoline) with $AlMe_3$ at 110 °C.[5e] Moreover, we believe that both the 2,6-$i$$Pr_2C_6H_3$ group on the aldimine nitrogen and the bulky ortho *t*Bu group on the phenoxide ring of **1** prevent the dimerization of **2**. Compound **2** is well soluble in common organic solvents, such as toluene, benzene-d_6, hexane and pentane. The broad IR band at 1837 cm^{-1} can be assigned to the Al-H stretching frequency.[39] Absorptions for the CH=N double bond and the O-H group are absent in the IR of **2**.

2.1.3. Molecular structure of 2

Compound **2** crystallises in the monoclinic space group $P2_1/c$ with one molecule of toluene in the unit cell. The structure of **2** shows a distorted tetrahedral aluminum centre (Figure 1). Selected bond lengths and angles for **2** are listed in Table 1. The terminal Al-H bond length (1.479(2) Å) is similar to that of [ArN$(CH_2)_3$NAr]Al$HNMe_3$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (1.52 Å)[35a]. The Al-N(1) bond distance (1.799(1) Å) is much shorter than those of (3,5-$t$$Bu_2$-2-O-$C_6H_2$CH=NR)$AlMe_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-$i$$Pr_2C_6H_3$) (1.972(3), 1.972(3) Å) bearing the unchanged bidentate salicylaldiminato ligands.[5a] The Al-N(2) bond length (2.000(1) Å) in **2** is comparable to those of [ArN$(CH_2)_3$NAr]Al$RNMe_3$ (Ar = 2,6-$i$$Pr_2C_6H_3$, R = H, F) (2.024(2), 2.000(2) Å).[35a] The reason for the shorter Al-N(1) is due to the covalent bond character, while all the other Al-N bonds mentioned above are coordinating bonds. The Al-O distance (1.741(1) Å) is a little shorter than those of (3,5-*t*Bu_2-2-O-C_6H_2CH=NR)$AlMe_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-*i*$Pr_2C_6H_3$) (1.755(3), 1.773(3) Å).[5a] Compared to the corresponding retained CH=N double bond in (3,5-*t*Bu_2-2-O-C_6H_2CH=NR)$AlMe_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-*i*$Pr_2C_6H_3$) (1.285(5), 1.300(5) Å),[5a] the N(1)-C(24) bond length (1.478(2) Å) in **2** shows a typical C-N single bond character. In **1** the two phenyl rings are coplanar because they are conjugated through the CH=N double bond. However in **2**, as the result of the hydrogen migration the conjugation is broken and the two planes become nearly vertical for steric reasons. O(1)-Al(1)-N(1)-C(24) is nearly coplanar and the same is observed for C(24)-C(14)-C(13)-O(1). The angle between the two planes is about 40° and may be due to the steric effects.

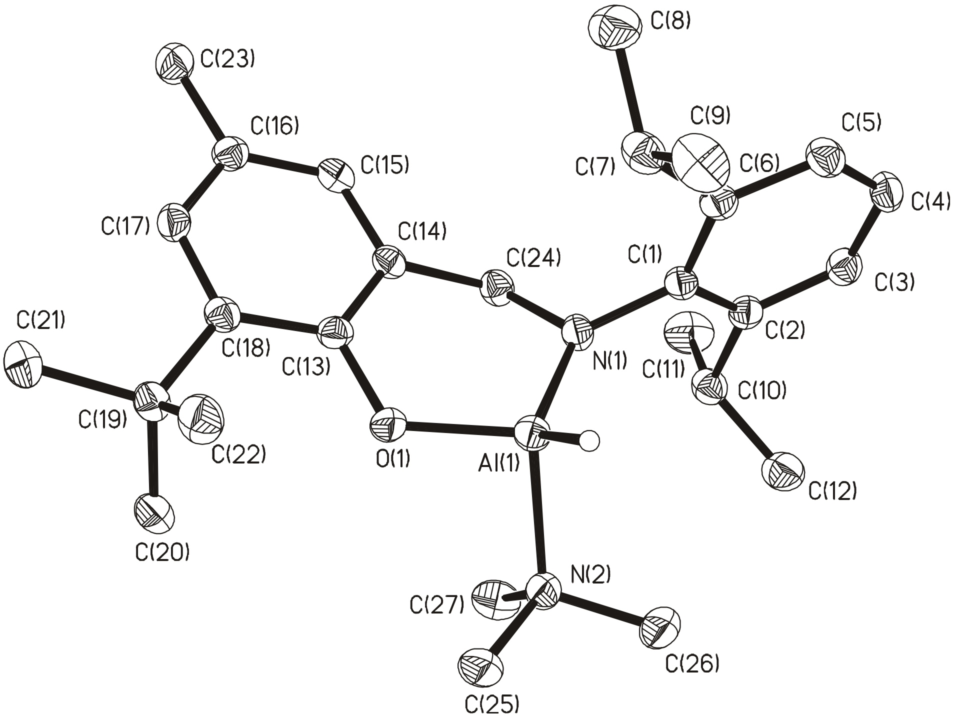
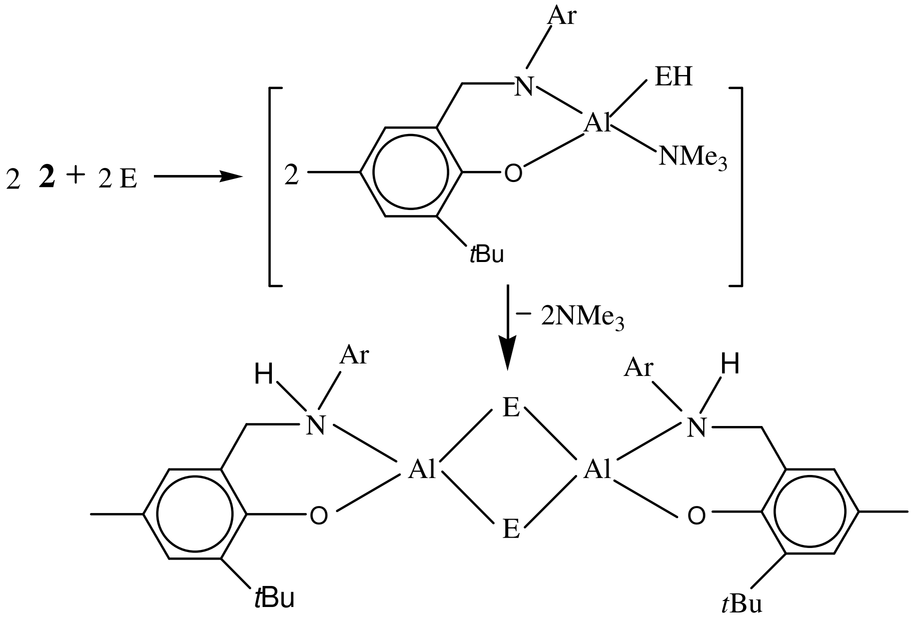


Figure 1. The molecular structure of **2**. The solvent molecule and the hydrogen atoms are omitted for clarity except for the Al-H hydrogen atom.

Table 1. Selected bond lengths (Å) and angles (°) for **2**.

Al(1)-O(1)	1.741(1)	N(1)-Al(1)-N(2)	117.07(6)
Al(1)-N(1)	1.799(1)	H(1)-Al(1)-O(1)	121.2(6)
Al(1)-N(2)	2.000(1)	H(1)-Al(1)-N(1)	118.9(6)
Al(1)-H(1)	1.479(2)	H(1)-Al(1)-N(2)	100.3(6)
N(1)-C(24)	1.478(2)	C(24)-N(1)-Al(1)	117.19(9)
C(14)-C(24)	1.521(2)	N(1)-C(24)-C(14)	115.63(1)
C(14)-C(13)	1.405(2)	C(13)-C(14)-C(24)	121.56(13)
O(1)-C(13)	1.3649(18)	O(1)-C(13)-C(14)	119.58(13)
O(1)-Al(1)-N(1)	102.32(6)	C(13)-O(1)-Al(1)	124.49(9)
O(1)-Al(1)-N(2)	95.45(5)		

2.1.4. Preparation of the chalcogenide derivatives [(3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(*μ*-E)]$_2$ [E = S (3), Se (4)]



3, 4

E = S (**3**), Se (**4**); Ar = 2,6-*i*$Pr_2C_6H_3$

Scheme 2

Treatment of **2** with elemental sulphur and selenium in toluene yielded the dimeric aluminum chalcogenides [(3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(μ-E)]$_2$ [E = S (**3**), Se (**4**)] bearing the hydrogenated bidentate salicylaldiminato ligand (Scheme 2). Compounds **3** and **4** are air and moisture sensitive, soluble in toluene, and only sparingly soluble in benzene. They were characterised by IR, NMR and EI mass spectrometry as well as elemental analysis. No bands for the CH=N stretches were found in the IR spectra. We assume that the formation of **3** and **4** might proceed through the reactive intermediate [(3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(EH)(NMe_3)] (E = S, Se) (Scheme 2). The conversion of Al-H to Al-EH was observed in compounds stabilized by the bulky β-diketiminato ligand.[19a,36] The intermediate then dimerises to [(3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(μ-EH)]$_2$ with elimination of NMe_3. Under heating the unstable [(3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(μ-EH)]$_2$ is converted to the stable products **3** and **4** with hydrogen migration from μ-EH to nitrogen. The absorption bands at 3175 and 3220 cm^{-1} assigned to the NH stretching frequencies in the IR spectrum of **3** and **4** respectively support the proposed hydrogen migration. The protons of the NH groups are also localised in the molecular structures by X-ray analysis and ^1H NMR spectroscopy (δ 1.52 ppm **3**; δ 1.88 ppm **4**). A comparable migration phenomenon was observed in previous reactions.[35a] Both compounds decompose without melting at temperatures above 110 ºC.

2.1.5. X-ray crystallographic analysis of compounds 3 and 4

The molecular structures of compounds **3** and **4** are shown in Figures 2 and 3 respectively. Selected bond distances and angles are listed in Tables 2 and 3 respectively.

Compounds **3** and **4** crystallise in the triclinic space group $P\bar{1}$ with two molecules of toluene. The molecular structures of **3** and **4** are similar, both of them are in D_{2d} symmetry, and have a dimeric structure featuring a planar four-membered ring with a central Al_2E_2 core. The Al-N bond lengths (2.005(1) Å for **3**; 2.009(2) Å for **4**) are much longer than that in **2** (1.799(1) Å), however they are comparable to those in (3,5-$t$$Bu_2$-2-O-$C_6H_2$CH=NR)$AlMe_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-$i$$Pr_2C_6H_3$) (1.972(3), 1.972(3) Å) bearing the unchanged bidentate salicylaldiminato ligand.[5a] The reason is the same as discussed above: here the Al-N bond is a coordinating one. The Al-O distances (1.750(1) Å for **3**; 1.749(2) Å for **4**) are comparable to

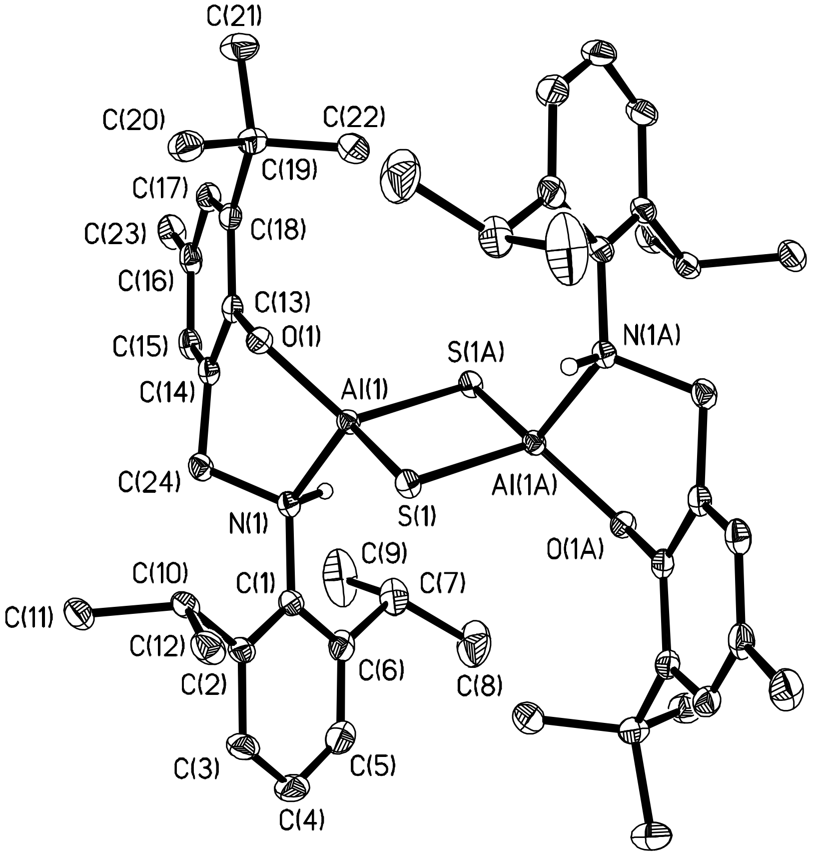


Figure 2. The molecular structure of **3**. Solvent molecules and the hydrogen atoms are omitted for clarity except for the N-H hydrogen atoms.

that in **2** (1.741(1) Å). The N-C bond lengths (1.510(2) Å for **3;** 1.511(3) Å for **4**) have single bond character like that of **2**. The Al-E distances (2.185(2), 2.232(2) Å for **3;** 2.314(1), 2.366(1) Å for **4**) are analogous to those of similar Al_2E_2 species.[35] The E(1)-Al-E(1A) angles (102.47(3)° E = S **3**; 104.50 (3)° E = Se **4**) are in the range of those reported.[35b] It is obvious that the slight difference of the Al-E distances is due to the covalent radii of the chalcogen atoms, as the covalent radii of S and Se differ by about 0.15 Å (1.02 Å for S and 1.17 Å for Se).[35c]

Table 2. Selected bond lengths (Å) and angles (°) for **3**.

S(1)-Al(1)	2.185(2)	O(1)-Al(1)-S(1)	119.92(4)
S(1)-Al(1A)	2.232(2)	N(1)-Al(1)-S(1)	118.01(5)
O(1)-Al(1)	1.750(1)	O(1)-Al(1)-S(1A)	117.74(4)
Al(1)-N(1)	2.005(1)	N(1)-Al(1)-S(1A)	100.86(5)
N(1)-C(24)	1.510(2)	S(1)-Al(1)-S(1A)	102.47(3)
C(14)-C(24)	1.500(2)	C(24)-N(1)-Al(1)	110.60(10)
C(13)-C(14)	1.403(2)	C(1)-N(1)-Al(1)	122.85(10)
O(1)-C(13)	1.3719(19)	C(14)-C(24)-N(1)	111.15(1)
N(1)-C(1)	1.470(2)	C(13)-C(14)-C(24)	118.72(14)
Al(1)-S(1)-Al(1A)	77.53(3)	O(1)-C(13)-C(14)	117.65(14)
O(1)-Al(1)-N(1)	96.99(5)	C(13)-O(1)-Al(1)	115.85(9)

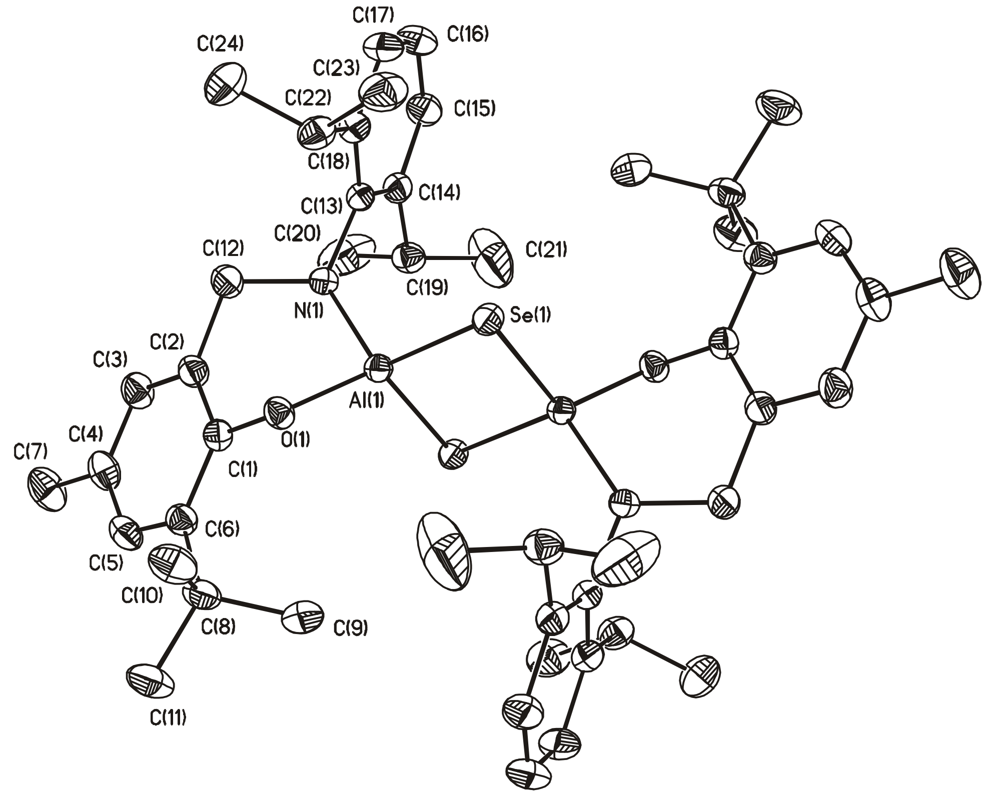


Figure 3. The molecular structure of **4**. Solvent molecules and hydrogen atoms including the N-H hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for **4**.

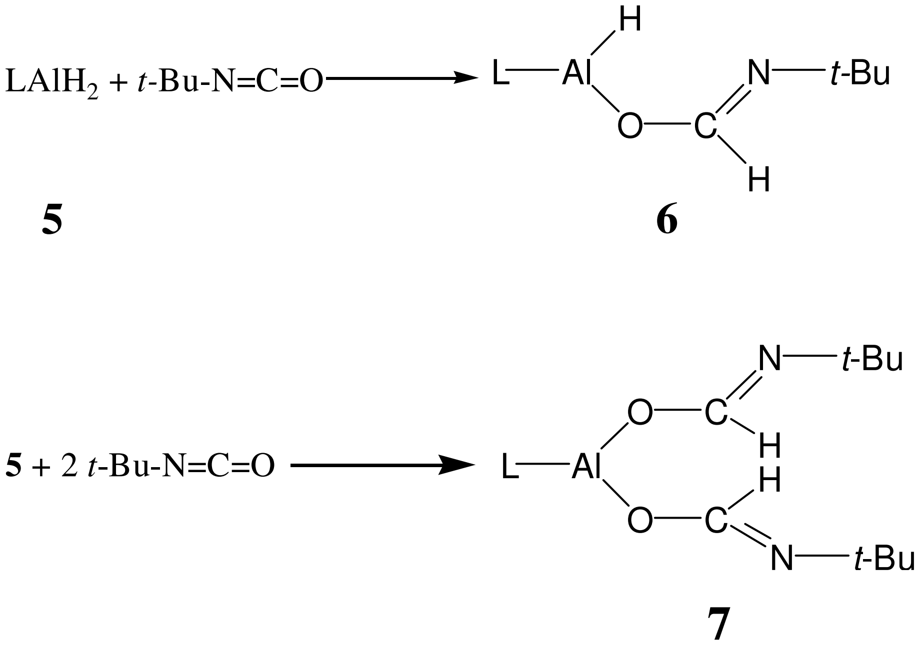
Se(1)-Al(1)	2.314(1)	N(1)-Al(1)-Se(1)	118.48(7)
Se(1)-Al(1A)	2.366(1)	O(1)-Al(1)-Se(1A)	116.08(6)
Al(1)-O(1)	1.749(2)	N(1)-Al(1)-Se(1A	102.25(7)
Al(1)-N(1)	2.009(2)	Al(1)-Se(1)-Al(1A)	75.50(3)
N(1)-C(12)	1.511(3)	Se(1)-Al(1)-Se(1A)	104.50(3)
C(2)-C(12)	150.2(3)	C(12)-N(1)-Al(1)	111.09(15)
C(1)-C(2)	140.0(3)	C(2)-C(12)-N(1)	110.7(2)
O(1)-C(1)	136.6(3)	C(1)-C(2)-C(12)	118.9(2)
N(1)-C(13)	147.1(3)	O(1)-C(1)-C(2)	117.9(2)
O(1)-Al(1)-Se(1)	118.45(6)	C(1)-O(1)-Al(1)	117.78(14)
O(1)-Al(1)-N(1)	96.43(8)	C(13)-N(1)-Al(1)	123.51(15)

2.2. Hydrolysis of aluminum hydrides

Despite of a number of publications concerning organoaluminoxanes, no synthesis of organoaluminoxane hydroxides from aluminum hydrides and water were reported. Herein we report the synthesis of the first aluminoxane hydroxide LAl(OH)OAlL(OCH=N-*t*Bu) (**8**) (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) by the reaction of the aluminum dihydride LAlH$_2$ (**5**)[19a] and *tert*-butylisocyanate in the presence of trace amounts of water and from **5** and LAlH(OCH=N-*t*Bu) (**6**) with water respectively.

2.2.1. Reactions of 5 with *tert*-butylisocyanate

The reaction of excess LAlH$_2$ (**5**) with *tert*-butylisocyanate in refluxing toluene followed by removal of the solvent resulted in a mixture of the products **5** and **6**, interaction between **5** and **6** has not been observed during the NMR investigations. When the reaction was carried out in a 1:1 ratio between **5** and *tert*-butylisocyanate, the nucleophilic addition product LAlH(OCH=N-*t*Bu) (**6**, Scheme 3) was isolated. The analytical and spectroscopic data correspond with the formula of **6**. The band at 1868 cm^{-1} in the IR spectrum indicates the presence of an Al-H bond.[10b] The most intense peak in the EI mass spectrum of **6** appears at *m/z* 544 $(M - H)^+$, and the peak at *m/z* 545 (38 %) is assigned to the molecular ion M^+. Compound **5** reacts with 2 or more equiv. of *tert*-butylisocyanate to afford the product LAl(OCH=N-*t*Bu)$_2$ (**7**, Scheme 3). Compound **7** was characterised by NMR and EI-MS, IR spectra, and elemental analysis, which are consistent with the composition depicted in Scheme 3. Al-H absorptions are absent in the IR spectrum.

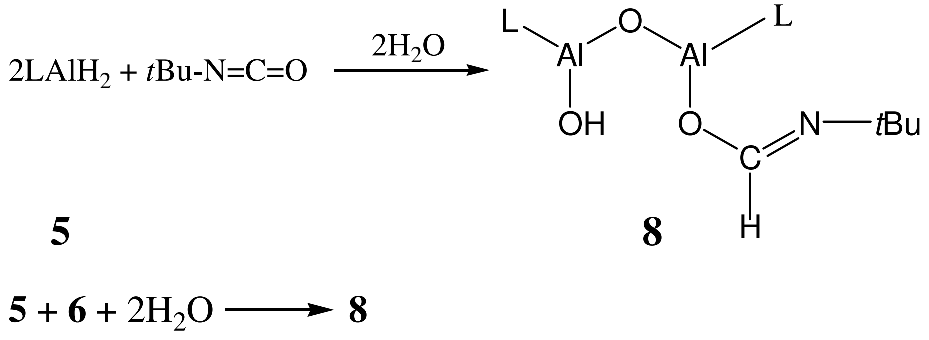


L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$

Scheme 3

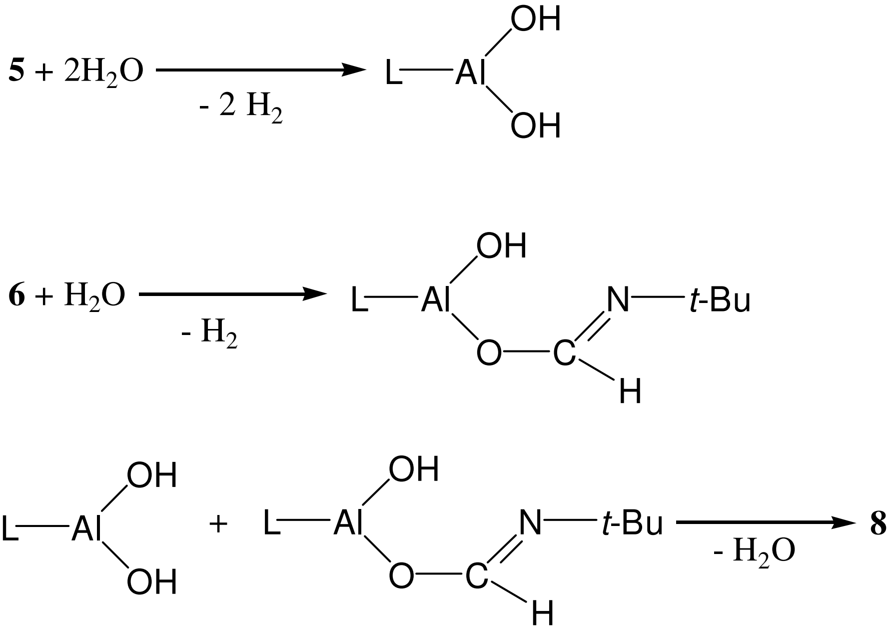
2.2.2. Preparation of aluminoxane hydroxide LAl(OH)OAlL(OCH=N-*t*Bu) (8)

The crude mixture of **5** and **6** was dissolved in pentane, and the resulting filtrate reacted with water when it was stored at 0 °C to obtain **8** as colorless crystals in low yield (Scheme 4). Compound **8** is soluble in common organic solvents such as pentane, hexane, toluene etc. The presence of the Al-OH bond was confirmed by IR (ν_{OH} 3458 cm^{-1}) and ^1H NMR (δ_H -0.30 ppm in C_6D_6). The resonance signal is in the range of that reported for the compound ($Mes_3Ga{\cdot}OHLi$)·3THF (δ_H –0.56 ppm in THF-d_8).[40a] Treatment of a mixture of **5** and **6** (1:1 molar ratio) with 2 equiv. of water in THF also led to **8** (Scheme 4a), an excess of water resulted in the decomposition of **8**. A proposed mechanism for the formation of **8** is shown in Scheme 4b. In this reaction aluminumdihydroxide[12a] was obtained as an intermediate in the first step. Compound **6** can react cleanly with 1 equiv. of water, and the two products mixed together to yield **8** by elimination of water. **8** can also be prepared from **6** without adding compound **5** from the reaction between **6** and water in a 2:3 molar ratio. We believe that the coordination of the OCH=N-*t*Bu group and the bulky L ligand to the Al centre is essential for stabilising the L–Al bond and the terminal reactive OH group of **8**.



L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 4a



L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Scheme 4b

2.2.3. Molecular structure of 8

Compound **8** crystallises in the monoclinic space group $P2_1/c$ with one molecule of pentane. As shown in Figure 4, **8** contains a bent Al–(μ-O)-Al unit with two tetrahedral distorted Al centres. Al(1) is surrounded by one terminal OH group, one bridging oxygen atom and two nitrogen atoms of the L ligand. The coordination sphere of Al(2) is completed by two nitrogen atoms of the ligand, one bridging oxygen atom, and one oxygen atom of the *tert*-butylisocyanate moiety. The selected bond lengths and angles are listed in Table 4. The

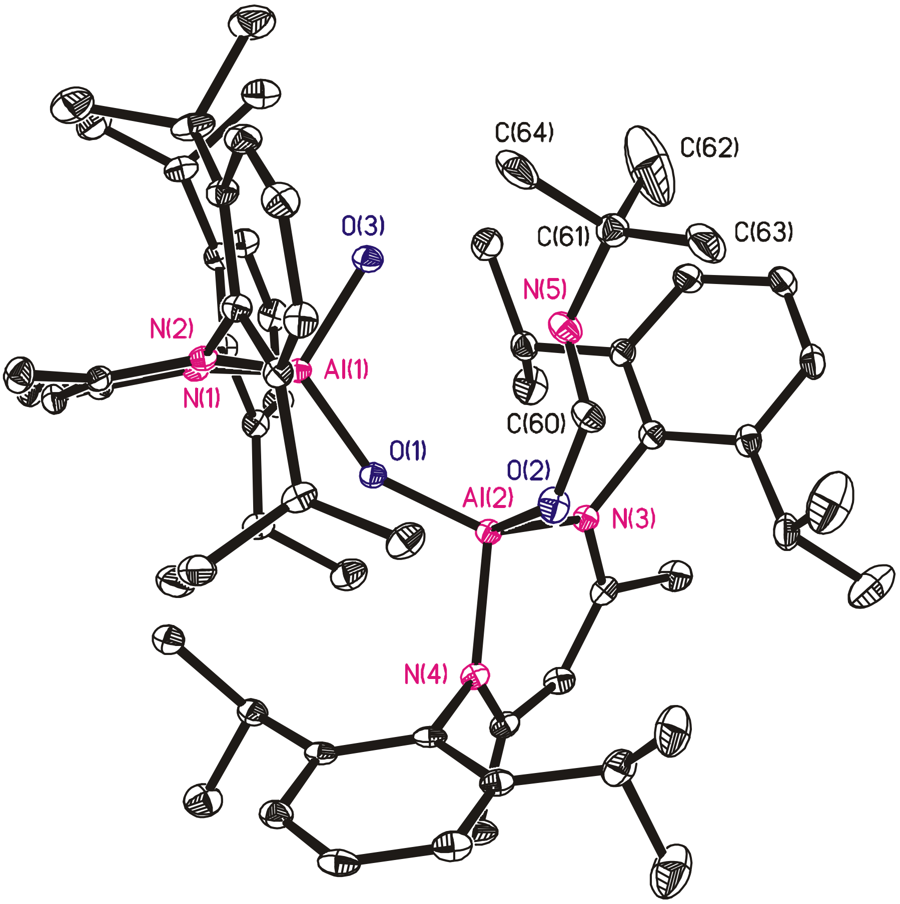


Figure 4. The crystal structure of **8**. The hydrogen atoms of the C-H bonds are omitted for clarity.

Table 4. Selected bond lengths (Å) and angles (°) for **8**.

Al(1)-O(1)	1.699(2)	O(1)-Al(1)-N(2)	119.83(9)
Al(1)-O(3)	1.727(2)	O(1)-Al(1)-N(1)	111.34(9)
Al(1)-N(2)	1.926(2)	O(3)-Al(1)-N(1)	109.57(10)
Al(1)-N(1)	1.932(2)	N(2)-Al(1)-N(1)	94.94(10)
Al(2)-O(1)	1.706(2)	O(3)-Al(1)-N(2)	107.33(9)
Al(2)-O(2)	1.739(2)	O(1)-Al(2)-O(2)	114.38(9)
Al(2)-N(3)	1.930(2)	O(2)-Al(2)-N(3)	106.18(10)
Al(2)-N(4)	1.911(2)	O(1)-Al(2)-N(4)	110.11(10)
O(2)-C(60)	1.313(5)	Al(1)-O(1)-Al(2)	147.85(10)
C(60)-N(5)	1.223(7)	C(60)-O(2)-Al(2)	134.3(3)
O(3)···N(5)	3.175(5)	N(5)-C(60)-O(2)	123.7(5)
O(1)-Al(1)-O(3)	112.35(9)	C(60)-N(5)-C(61)	118.8(5)

dihedral angles are 30.20(24)° for O(3)-Al(1)-O(1)-Al(2) and 37.90(24)° for O(2)-Al(2)-O(1)-Al(1). The distance between O(3) and N(5) is 3.175(5) Å, which is only a little longer than the sum of their van der Waals radii, 3.07 Å (N is 1.55 Å and O is 1.52 Å).[40b] The Al(1)-OH bond length (1.727(2) Å) is comparable to those in $\mathrm{LAl(OH)_2}$ (1.6947 (15) and 1.7107(16) Å),[12a] and significantly shorter than those of Al-(μ-OH) and Al-(μ_3-OH) bonds in $[(t\mathrm{Bu})_2\mathrm{Al}(\mu\text{-OH})]_3$ (1.848 Å),[9c] and $[\mathrm{Al}_5(t\mathrm{Bu})_5(\mu_3\text{-O})_2(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu\text{-O}_2\mathrm{CPh})_2]$ (Al-(μ-OH) 1.820(3) to 1.828(3) Å; Al-(μ_3-OH) 1.914(5) to 2.086(4) Å).[41] The Al-(μ-O) bond length of **8** (1.703 Å) is similar to those of the compounds $[(t\mathrm{Bu})_2\mathrm{Al(py)}_2]_2(\mu\text{-O})$ (1.710 Å)[9c] and $[\{(t\mathrm{Bu})_2\mathrm{Al(NH(Me)CH_2CH_2NMe_2)}\}_2(\mu\text{-O})]$ (1.690(7) and 1.714(7) Å).[42] The Al(2)–O(2) bond length (1.739(2) Å) in **8** is slightly longer than those of the Al-OH (1.727(2) Å) and

Al-(μ-O) (1.703 Å). The Al-N bond lengths (from 1.912(2) to 1.931(2) Å, av. 1.925 Å) are within the range of those previously observed ($LAlMe_2$ av. 1.922 Å).[43]

2.2.4. Theoretical calculation of 8

A broad band at 3458 cm^{-1} was observed in the IR spectrum of **8**, assigned to the OH stretch.[12a] Therefore, we believe that there is an intra- or intermolecular hydrogen bond in the solid state structure of **8**. However, we cannot find the proton position in the X-ray structural analysis of **8**. Theoretical calculations, based on the DFT method RI-BP86/SV(P)[44] within Turbomole,[45] were carried out to verify the existence of the H atom and investigate its character. The four $CHMe_2$ groups which are far away from O(3) were replaced by H during the calculation in order to reduce the computer time. The full geometry optimisation was carried out for both compound **8** with H and without the H atom. The calculations proved the existence of the H atom in compound **8**: with H in the optimised geometry the distance of O(3)···N(5) is 2.93 Å and close to that of the X-ray structure (3.175(5) Å), while without H the optimised O(3)···N(5) distance is 5.87 Å. Also the structure of compound **8** with the H atom is more similar to that of the X-ray structure (mean deviation for all Al bonds: 0.02 Å, bond angles: 3.3°) than without H (mean deviation for all Al bond lengths: 0.05 Å, bond angles: 5.7°).

The calculated result shows that there is a strong O–H···N hydrogen bond[46] between the OH group and the N atom of the O-CH=N-*t*Bu moiety (H-O 1.00 Å, H···N 1.93 Å, O–H···N 172.6°, H-O-Al 110.1°) in agreement with the IR spectrum of **8**. Furthermore, as shown in Figure 5, the formation of the intramolecular O–H···N hydrogen bond leads to good shielding of the OH group from the bulky *t*Bu group, and the O-CH=N-*t*Bu moiety will be far away from O(3) if the H atom is not present (as mentioned above in this case r(O(3)···N(5)) = 5.87 Å). This shielding together with the bulky L ligand on the Al atom protects the OH group from attack by another Lewis acidic Al center. Obviously that is the reason why the binuclear terminal hydroxide-containing **8** does not aggregate to larger clusters.

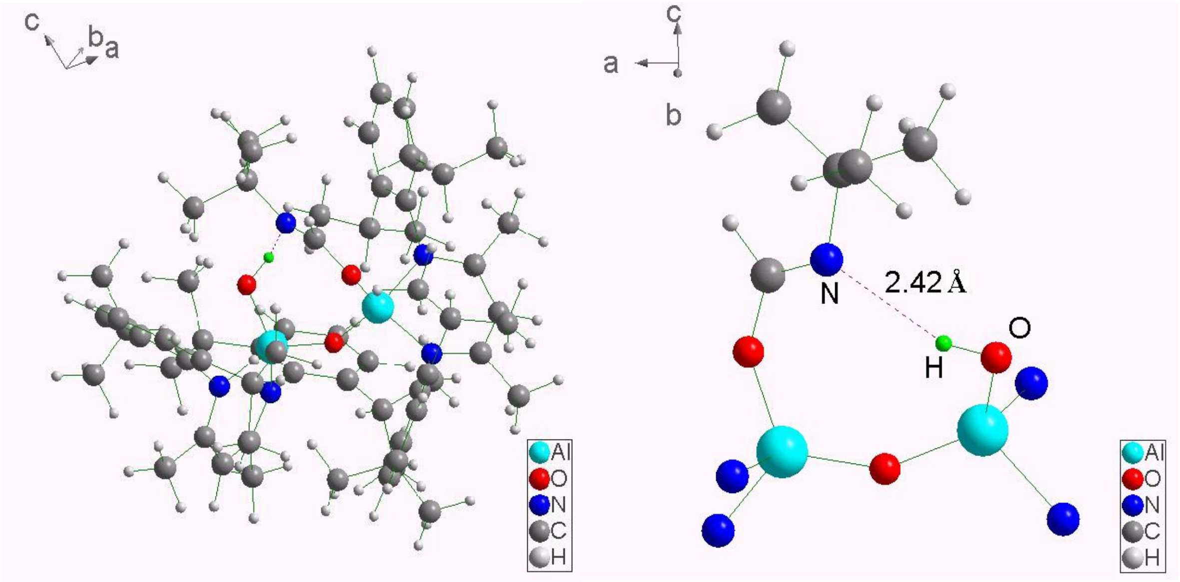


Figure 5. The intramolecular hydrogen bond in compound **8**. The position of the H atom (green) was obtained by AM1 geometry optimisation. Left: The position of H(O) in the whole molecule. Right: the local region of the intramolecular hydrogen bond.

In summary, we describe a new method for the synthesis of an aluminoxane hydroxide by the direct hydrolysis of aluminum hydrides with water. The intramolecular hydrogen bond and the bulky L ligand on the Al atom stabilise the reactive terminal OH group in **8**. **8** should react with other less bulky organometallic compounds in solution, which provides the possibility for the synthesis of aluminum containing homo- or heteroorganometallic compounds and their application for the polymerization of olefins.

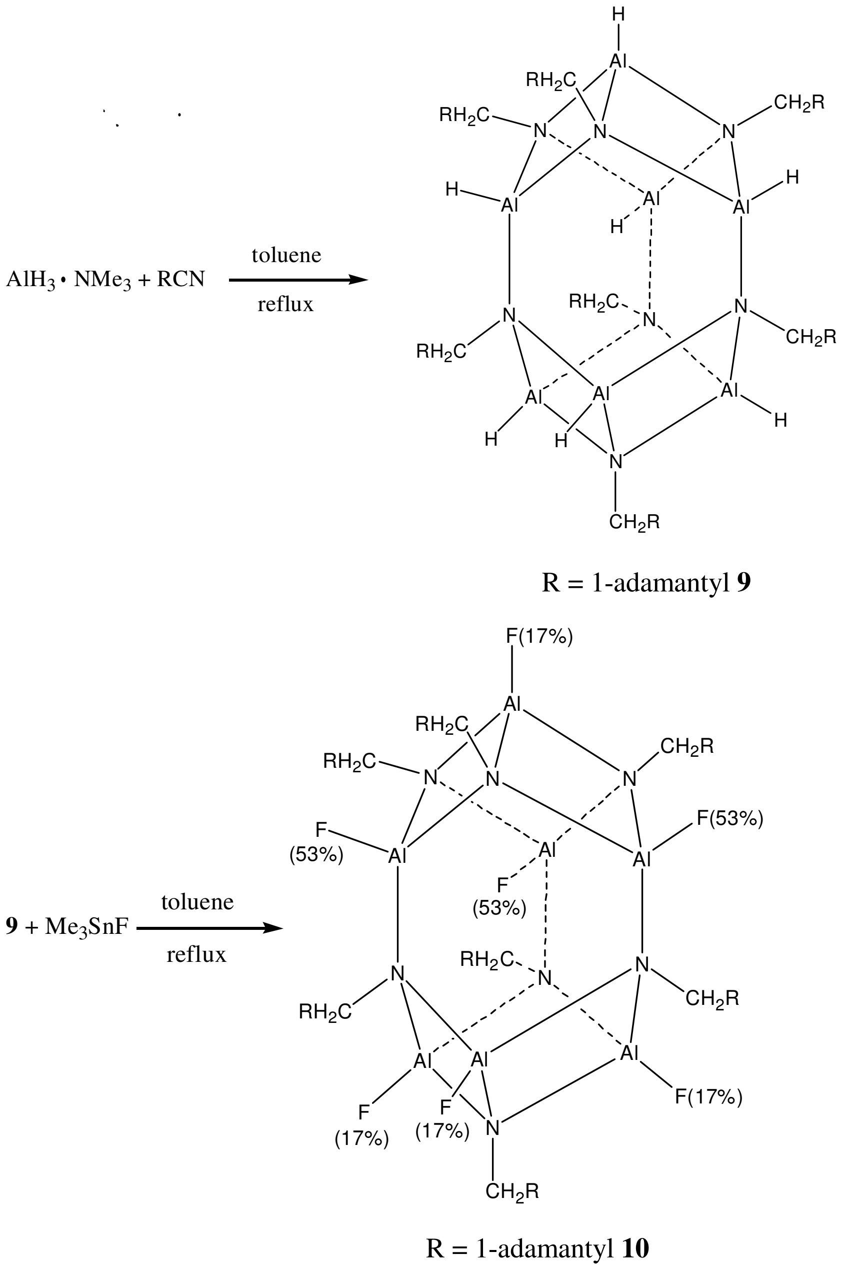
2.3. Synthesis and reactions of Al-N and Al-C-N clusters

Compounds containing Al-N bonds have attracted much attention due to their application in catalysis,[17] as synthetic intermediates,[18] and as potential precursor for the chemical vapour deposition of aluminum nitride.[16] Al-N rings and clusters have been reviewed recently.[47] In 1973, J. D. Smith et al. reported the first heptameric aluminum imide $(MeAlNMe)_7$ structurally characterised by X-ray diffraction methods which was obtained from the thermal decomposition of the adduct $Me_3Al·NH_2Me$ in toluene at 215 °C. [48-49] However, neither yields nor further reactivity have been reported. Additionally, the preparation, NMR spectra and the mass spectrum of $(EtAlNMe)_n$ were mentioned,[49-50] and based on these limited data alone it was thought to be an octamer, its unambiguous geometry has never been reported. The degree of oligomerisation of these thermal decomposition products is dependent on the temperature of thermolysis and the substituents on nitrogen.[51] To the best of our knowledge no other heptameric aluminum imide has been structurally characterized. More attention was paid to organoaluminum fluorides due to the potential importance[52a] of these compounds as models for certain catalytic reactions. Pioneering work on organoaluminum fluorides has been achieved by K. Ziegler et al. who reported the reactions of NaF with Et_3Al and Me_2AlCl to yield Na^+ salts of anionic fluoride species $(Et_3AlF)^-$, $[(Et_3Al)_2(\mu\text{-}F)]^-$ and $(Me_2AlF_2)^-$ respectively in 1955.[52b] Reviews on organoaluminum fluorides have been published by J. Weidlein[52c] and by H. W. Roesky et al.[52d] Several compounds containing both terminal and bridging Al-F bonds[53-55] or only bridging Al-F-Al bonds[56] are known, and some others with Al-F-M (M = Li, Na, K, Ti, Zr)[57] building units are also reported. The number of compounds having only terminal Al-F bonds is limited.[58-60] However, no chemistry of aggregates containing only terminal Al-F bonds is known so far. Herein we report an efficient synthetic route involving the reaction of RCN (R = 1-adamantyl) with an excess of $AlH_3{\cdot}NMe_3$ in boiling toluene to form the first $(RCH_2NAlH)_7$ **(9)** compound containing Al-H bonds, and the fluorination of the Al_7N_7 and $Al_4C_4N_4$ species to get the first two aggregates $(RCH_2NAl)_7F_{2.26}H_{4.74}$ **(10)** and $(t\text{BuNCH}_2\text{AlF})_4$ **(11)** containing only terminal Al-F bonds.

2.3.1. Preparation and reactions of the novel heptameric aluminum imides 9 and 10

The reaction between RCN and 1.5 equiv. of $AlH_3{\cdot}NMe_3$ in boiling toluene resulted in the formation of compound **9**, while **9** reacted with 7 equiv. of Me_3SnF in refluxing toluene to afford compound **10** (Scheme 5). For the synthesis of **9** we followed the procedure for the preparation of hexameric aluminum imides $(RCH_2NAlH)_6$ with various R groups (R = Ph, p-MeC_6H_4, p-$CF_3C_6H_4$).[20b]

The IR spectrum of compound **9** shows strong bands in the region from 1851 to 1916 cm^{-1} due to Al-H stretching frequencies,[61] and just a weak band at 1895 cm^{-1} attributed to the non-substituted Al-H bond in **10** is present. In the ^{27}Al NMR spectra of **9** and **10** no resonances were detected due to the quadrupole moment of aluminum. In the case of the hexameric aluminum imides $(RCH_2NAlH)_6$ (R= Ph, p-MeC_6H_4, p-$CF_3C_6H_4$),[20b] there is only one resonance in the ^{1}H NMR spectrum at about 4.2 ppm for the CH_2 group connecting the R group and nitrogen atom, whereas in compounds **9** and **10** there are 3 and 6 singlets respectively ranging from 2.76 to 3.08 ppm due to the environmentally different arranged hydrogen atoms. The increase of singlets for the CH_2 group going from **9** to **10** is due to the partially fluorinated Al-H groups resulting in a more differentiated environment.



Scheme 5

Compound **10** was prepared from **9** using Me_3SnF as a fluorinating agent (Scheme 5).

This metathesis reaction resulted in the formation of Me_3SnH. Compound **10** is a partially fluorinated derivative. In order to obtain a complete fluorination product, we used Me_3SnF in excess (molar ratio 1:8) in refluxing toluene or alternatively tried the reaction at room temperature in CH_2Cl_2. In both cases the IR spectra contained no Al-H stretching frequencies. However, a complex mixture of products (as seen from ^1H and ^{19}F NMR spectra) was formed. It is noteworthy that an excess of Me_3SnF or other attempts to achieve a higher degree of fluorination of **10** leads to the destruction of the core structure. We also examined the reactions of **9** with Me_3SiCl and Me_3SiBr in boiling toluene. In both cases partially substituted products were obtained as deduced from the IR spectra. In contrast, the metathesis reactions of hexameric aluminum imide $(PhCH_2NAlH)_6$[20b] with Me_3SiBr and $PhC{\equiv}CH$ proceeded smoothly to give the completely substituted products.

The electronegativity of the H atom is a little higher than that of the Al atom, therefore it is slightly negatively charged in Al-H bonds, and correspondingly the core is slightly positive charged (Here we omit the effect of the ligand as it plays the same role throughout the discussion). When H is substituted by an atom with a larger electronegativity such as halogens, the core becomes more positive and shows significant internal electrostatic repulsion. This type of electrostatic repulsion reduces the stability of the core, and if exceeding to some extent the core will decompose. We think this is the reason why only partially F, Cl and Br substituted products are obtained. In the case of complete substitution, the internal electrostatic repulsion grows with the increase of the size of the core, and the electronegativity of the substituting atoms. Therefore the order of completely substituted species is expected to be: larger core < smaller core, F < Cl < Br < I < R group. This assumption agrees with the experimental results found so far, as for small cores there are some completely fluorine substituted compounds reported, such as complex **11**, while for large cores (more than 5 Al atoms) none was known.

2.3.2. Molecular structures of 9 and 10

The molecular structure of compound **9** is shown in Figure 6. Compound **9** crystallises in the triclinic space group $P\bar{1}$ with one molecule of toluene. Selected bond lengths and angles for **9** are shown in Table 5. From the molecular structure it can be seen that Al(1), Al(2) and Al(3) form a regular triangle while Al(4), Al(5) and Al(6) are arranged in a larger regular triangle paralleling the first one but is rotated by 60°. The Al(1), Al(2) and Al(3) triangle is capped by N(7), and Al(7) is capping the Al(4), Al(5) and Al(6) triangle. Each plane of the Al triangle on the surface of the cluster is capped by a N atom except those formed by two Al atoms from the larger regular triangle and one Al atom from the smaller one. The Al_7N_7 core has an approximate C_{3v} symmetry, and the C_3 axis lies along Al(7) and N(7). After including the CH_2R group, the molecule has C_1 symmetry. The Al atoms have a coordination number of four surrounded by three N atoms and one H atom (the electron density of H is too weak to be detected by the X-ray analysis). Each N atom connects three Al atoms and one CH_2R group thus forming a cage structure. All the CH_2R groups are located outside of the cage. Al-N bond lengths of different Al-N cage compounds are given in Table 6. From Table 6 it can be seen that the mean Al-N bond length (1.930 Å) of **9** is comparable to those found in tetrameric, hexameric, heptameric and octameric aluminum imides due to the similar coordination environment within the cage where each Al atom is connected with three N atoms and each N atom binds to three Al atoms.

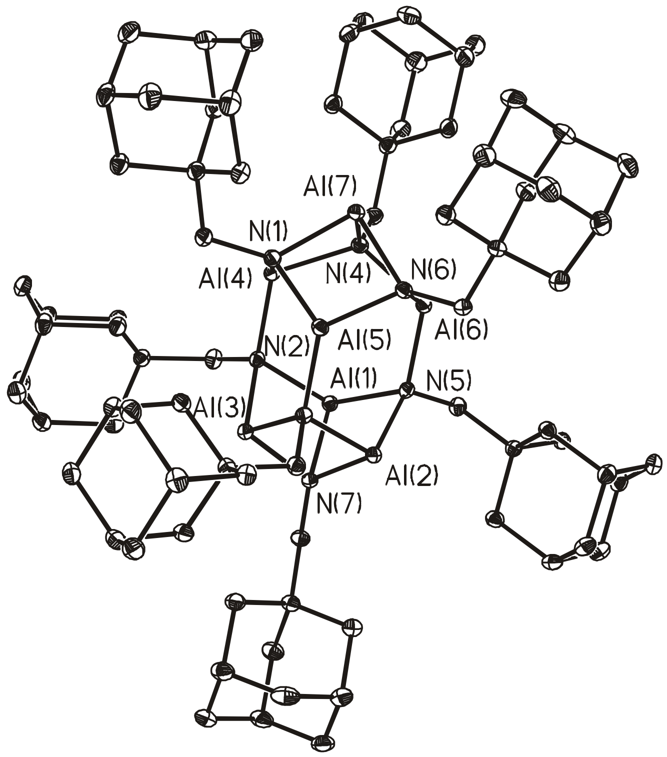
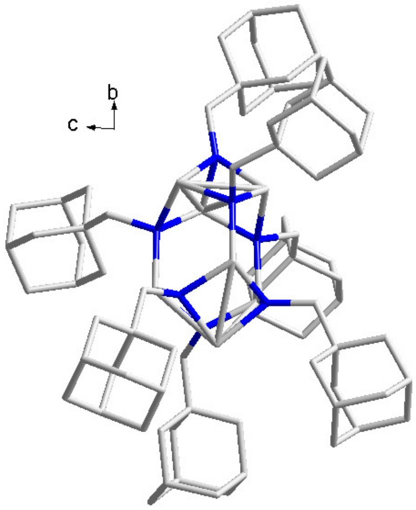
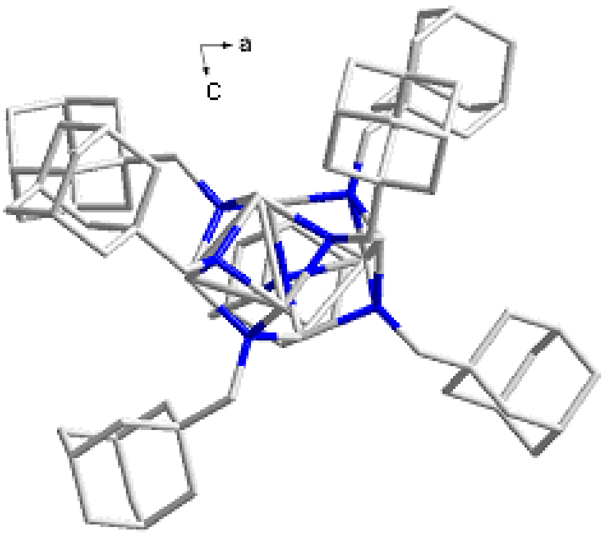


Figure 6. The crystal structure of **9** (50 % probability). Hydrogen atoms and toluene molecule have been omitted for clarity.





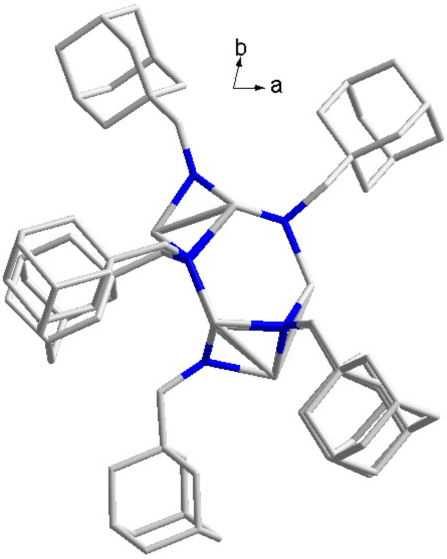


Figure 7. Core structure of **9** viewed along a, b, c directions.

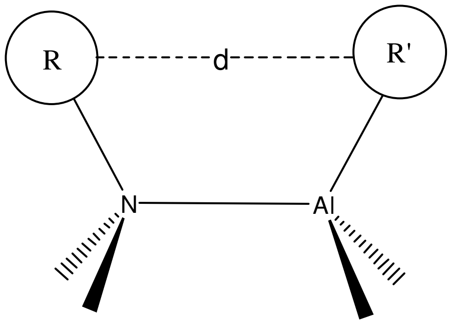
Table 5. Selected bond lengths (Å) and angles (°) for **9**.

Al(1)-N(7)	1.937(2)	N(7)-Al(1)-N(2)	91.87(9)
Al(1)-N(2)	1.943(2)	N(2)-Al(4)-N(1)	113.92(8)
Al(1)-N(5)	1.940(2)	N(1)-Al(4)-N(4)	90.63(8)
Al(4)-N(2)	1.911(2)	N(2)-Al(4)-N(4)	115.37(9)
Al(4)-N(1)	1.920(2)	N(6)-Al(7)-N(4)	89.03(9)
Al(4)-N(4)	1.928(2)	Al(1)-N(2)-Al(3)	86.84(9)
Al(7)-N(1)	1.941(2)	Al(4)-N(2)-Al(1)	115.35(9)
Al(7)-N(4)	1.930(2)	Al(4)-N(2)-Al(3)	123.57(9)
Al(7)-N(6)	1.918(2)	Al(6)-N(4)-Al(4)	115.95(10)
N(1)-C(75)	1.498(3)	Al(4)-N(4)-Al(7)	88.57(9)
N(7)-Al(1)-N(5)	91.64(8)	Al(6)-N(4)-Al(7)	88.21(9)
N(5)-Al(1)-N(2)	112.70(8)	Al(2)-N(7)-Al(1)	86.91(7)

Table 6. Al-N bond lengths (Å) of different Al-N cage compounds

Compound	range of Al-N bond lengths	av Al-N bond lengths
$(i\mathrm{PrNAlH})_4$ [22a]	1.897 - 1.923	1.914
$(i\mathrm{PrNAlMe})_4$ [22a]	1.917 - 1.932	1.923
$(4\text{-}C_6H_4FNAlMe)_4$ [62]	1.922 - 1.951	1.934
$(PhNAlPh)_4$ [63]	1.900 - 1.930	1.914
$(n\text{-}PrNAlH)_6$ [22b]	1.884 - 1.972	1.913
$(p\text{-}CF_3C_6H_4CH_2NalH)_6$ [20b]	1.880 - 1.980	1.919
$(PhCH_2NalH)_6$ [20b]	1.886 - 1.974	1.918
$(PhNAlMe)_6$ [64]	1.902 - 1.951	1.925
$(MeNAlMe)_7$ [49]	1.810 - 1.970	1.910
$(1\text{-}AdCH_2NAlH)_7$ *	1.900 - 1.980	1.930
$(n\text{-}PrNAlH)_8$ [22b]	1.878 - 1.947	1.916

* this work



Scheme 6

Scheme 6 shows a sector of the general structure of compound $(RNAlR')_n$ (n = 4, 6 and 7). With longer d (d is the distance between R and R′ groups) the interaction between R and R′ groups decreases. The steric interaction in $(RNAlR')_n$ is significant for larger R and R′ groups. The number n for compounds $(RNAlR')_n$ is highly dependent on the bulkiness of the R and R′ groups, for large R and R′ groups small n values are found (see the compounds listed in Table 6 and some other compounds such as $(ArNAlPh)_4$ (Ar = 3-MeC_6H_4, 4-XC_6H_4

(X = Me, OMe, Cl or I))[65] and (tBuNAlEt)$_4$.[50] In compounds (RNAlX)$_n$ (X = H, F, Br) X is smaller compared to the R′ group of (RNAlR′)$_n$. Therefore compounds with large R groups form bigger Al-N cores due to a minimum interaction of R with the X atom. For different sizes of n it is quite difficult to evaluate the steric interaction between two R groups using a simple model. Therefore we report herein on a heptamer (R = 1-adamantyl) less common than a hexamer. If the Ph groups in (PhCH$_2$NAlH)$_6$[20b] are replaced by 1-adamantyl groups, calculations give a minimum C···C distance of 2.95 Å for two adjacent 1-adamantyl groups. Compared with the van der Waals radius for carbon (1.7 Å), however, the distance of 2.95 Å is obviously too short. Consequently the formation of a heptameric compound **9** instead of the corresponding hexamer is observed.

Single crystals of **10** were obtained from the reaction mixture in toluene. **10** crystallises in the triclinic space group $P\bar{1}$ with one molecule of toluene in the unit cell. The molecular structure of **10** is depicted in Figure 8. From the structure it is seen that the Al_7N_7 core is retained. The X-ray analysis of compound **10** was refined with an occupancy factor of 53 % for F(1), F(2) and F(3), while the other four fluorine atoms F(20), F(21), F(22) and F(23) have each an occupancy factor of 17 %. The remainder are non-replaced hydrogen atoms. Selected bond lengths and angles for **10** are listed in Table 7. The Al-F bond distances are 1.63 Å for F(1), F(2), and F(3), and 1.52 Å for F(20), F(21), F(22) and F(23). Both are shorter than the Al-F bonds (terminal) in [(Me$_3$Si)$_3$CAlF$_2$]$_3$ (1.657 - 1.681 Å)[54] due to the incomplete fluorination of **10**. The average Al-N bond length of 1.920 Å is shorter than that in **9** presumably due to the strong electron-withdrawing capability of the fluorine atoms.

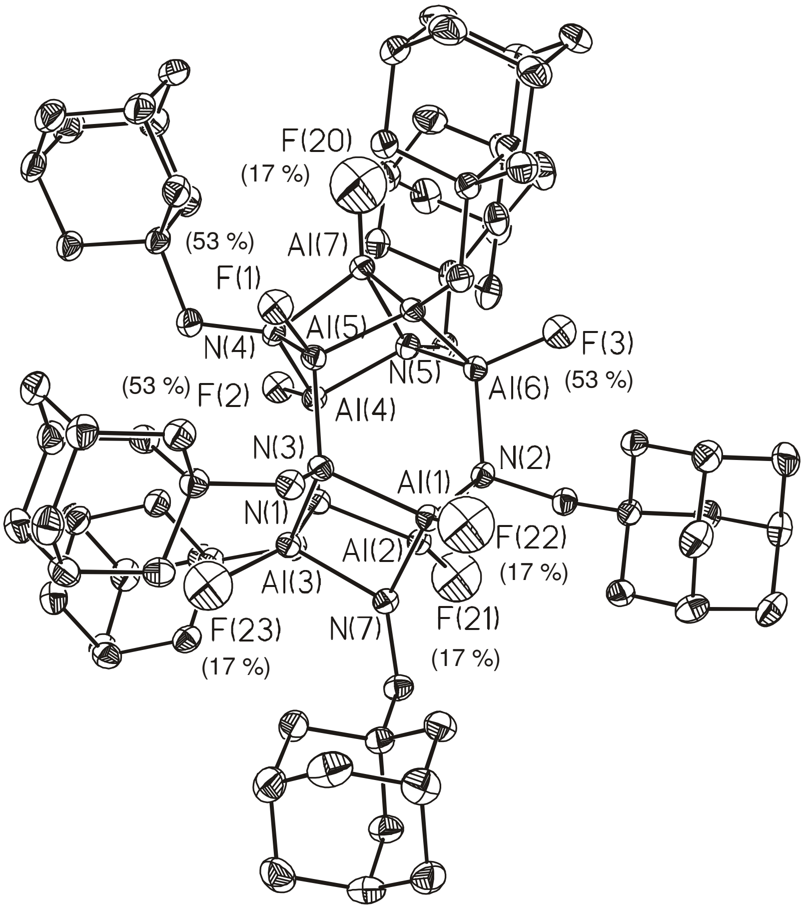
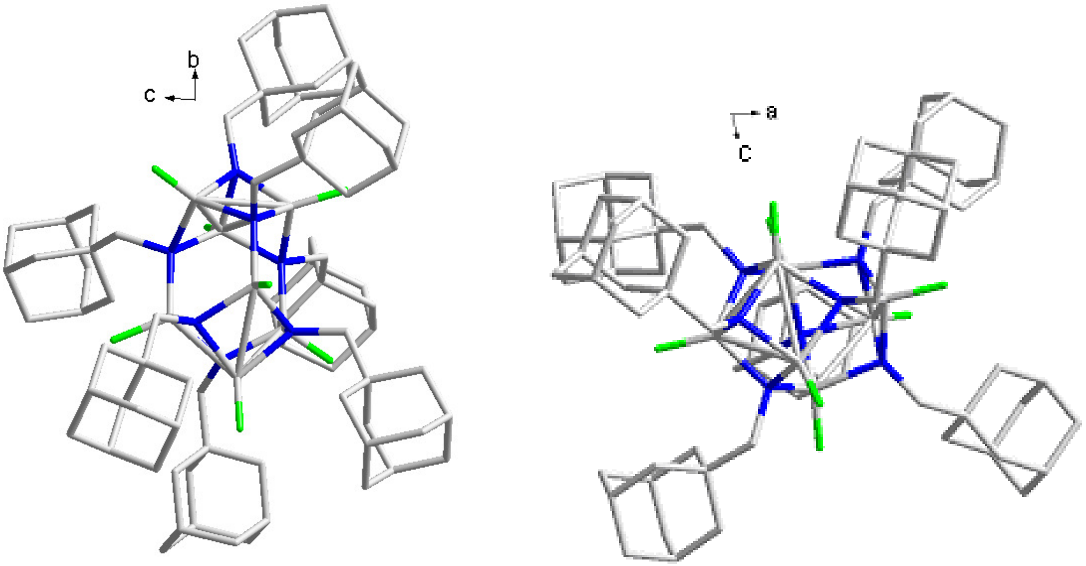


Figure 8. Molecular structure of **10** in the crystal (50% probability). Hydrogen atoms and toluene molecule have been omitted for clarity.



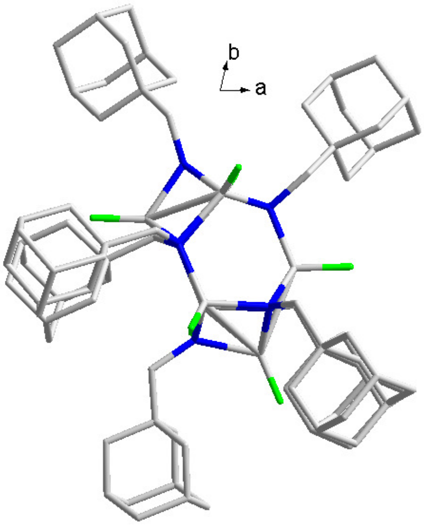


Figure 9. Core structure of **10** viewed along a, b, c directions.

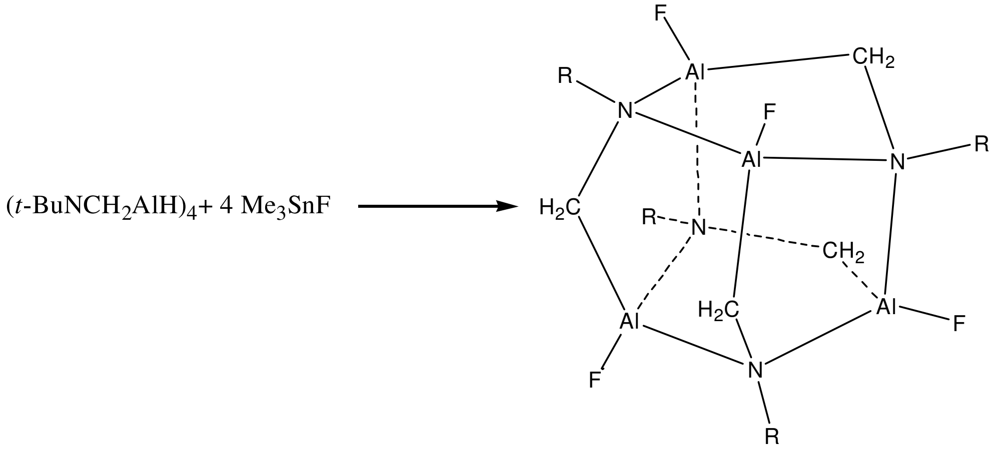
Table 7. Selected bond lengths (Å) and angles (°) for **10**.

Al(1)-F(22)*	1.506(13)	N(2)-Al(1)-N(3)	109.18(7)
Al(1)-N(7)	1.919(2)	F(3)-Al(6)-N(2)	110.84(11)
Al(1)-N(2)	1.942(2)	N(2)-Al(6)-N(6)	114.34(8)
Al(6)-F(3)	1.616(3)	N(6)-Al(6)-N(5)	90.96(8)
Al(6)-N(2)	1.883(2)	F(3)-Al(6)-N(6)	113.76(11)
Al(6)-N(6)	1.891(2)	F(20)-Al(7)-N(6)	123.9(6)
Al(7)-F(20)	1.475(16)	N(6)-Al(7)-N(5)	89.06(7)
Al(7)-N(5)	1.934(2)	Al(4)-N(1)-Al(3)	122.98(9)
N(1)-C(15)	1.539(2)	Al(3)-N(1)-Al(2)	86.65(7)
N(4)-C(17)	1.500(3)	C(15)-N(1)-Al(4)	110.04(13)
N(7)-C(8)	1.492(3)	Al(4)-N(4)-Al(5)	112.37(9)
F(22)-Al(1)-N(7)	127.4(5)	Al(4)-N(4)-Al(7)	88.46(8)
F(22)-Al(1)-N(2)	123.0(5)	Al(1)-N(7)-Al(3)	89.23(8)
N(7)-Al(1)-N(2)	91.54(7)	C(8)-N(7)-Al(3)	128.13(14)

* the occupancy of F(1), F(2) and F(3) was refined as 53 %, while the other four fluorine atoms F(20), F(21), F(22) and F(23) have each an occupancy of 17 %.

2.3.3. Preparation and X-ray structural analysis of 11

Consequently, the metathesis reaction of **9** to **10** using Me_3SnF was applied to the cluster (tBuNCH$_2$AlH)$_4$[20a] to yield the corresponding tetrafluoro compound **11**. The reaction proceeds smoothly at room temperature (Scheme 7). Compound **11** crystallises in the monoclinic space group $P2_1/n$. The molecular structure of **11** is shown in Figure 10. The selected bond lengths and angles are listed in Table 8. The $Al_4C_4N_4$ core with four F atoms in place of the four H atoms is retained in the tetrafluoro derivative as shown in Figure 10. The four Al atoms form a distorted tetrahedron with D_{2d} symmetry (distorted by compression of the tetrahedron along one of the C_2 axis). The four shorter Al-Al edges are each bridged by a N atom and every N atom is connected to another Al atom by a CH_2 group. Moreover every N atom binds to a *t*Bu group, while each Al atom bears a terminal F atom. The terminal Al-F bond lengths (1.659 - 1.666 Å) are in agreement with those reported in literature ([$(Me_3Si)_3CAlF_2$]$_3$ (1.657 - 1.681 Å),[54] $(nBu_4N)_2(PhPO_3AlF_2)_2$ (1.659 Å), $(nBu_4N)_2(tBuPO_3AlF_2)_2$ (1.666 Å).[56] A comparison of



R = *t*Bu **11**

Scheme 7

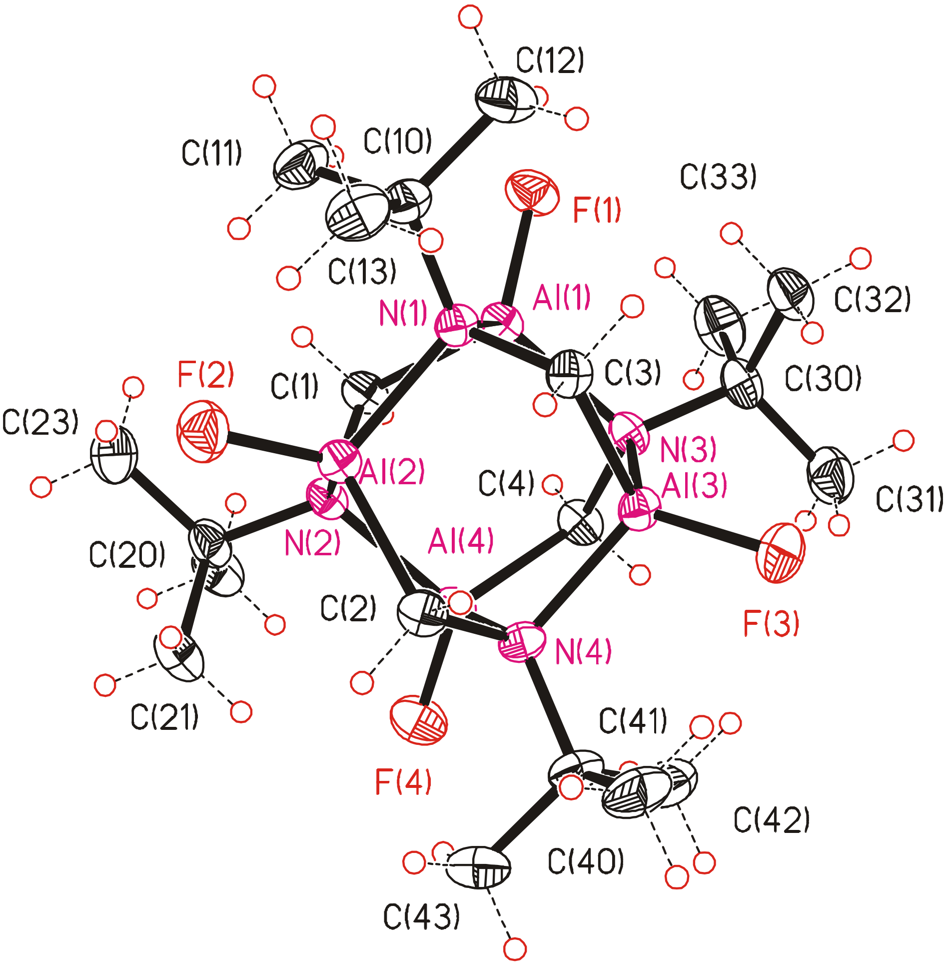
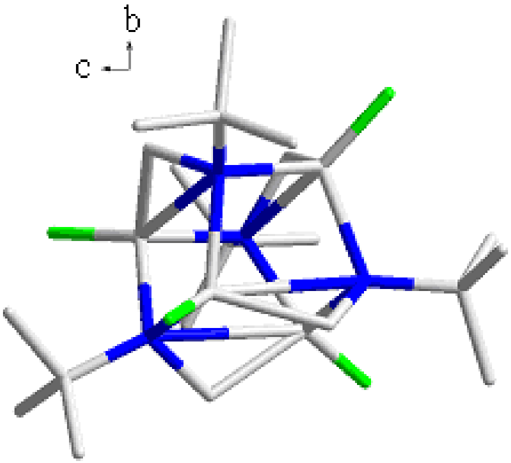
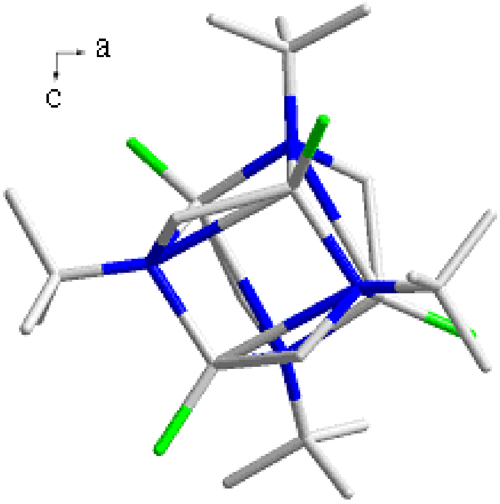


Figure 10. Molecular structure of **11** in the crystal (50 % probability).





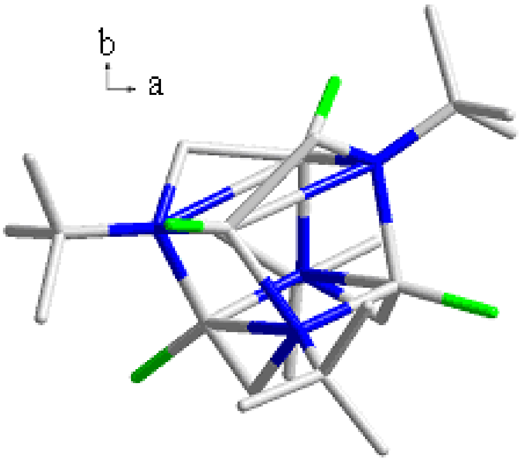


Figure 11. Core structure of **11** viewed along a, b, c directions.

Table 8. Selected bond lengths (Å) and angles (°) for **11**.

Al(1)-F(1)	1.6657(10)	N(1)-Al(1)-N(3)	105.05(6)
Al(2)-F(2)	1.6586(13)	F(1)-Al(1)-C(1)	114.21(6)
Al(3)-F(3)	1.6632(12)	N(1)-Al(1)-C(1)	99.56(7)
Al(4)-F(4)	1.6655(11)	N(3)-Al(1)-C(1)	108.21(7)
Al(1)-N(1)	1.952(14)	F(1)-Al(1)-N(3)	114.31(6)
Al(1)-N(3)	1.959(16)	C(3)-N(1)-C(10)	112.65(12)
Al(1)-C(1)	1.980(17)	C(3)-N(1)-Al(1)	106.55(10)
N(1)-C(3)	1.526(2)	C(10)-N(1)-Al(1)	115.73(10)
N(1)-C(10)	1.541(2)	Al(1)-N(1)-Al(2)	101.56(6)
F(1)-Al(1)-N(1)	114.14(6)	N(2)-C(1)-Al(1)	109.06(10)

the ^{19}F NMR shifts of compounds having only terminal Al-F bonds is given in Table 9. The chemical shifts for the ^{19}F NMR of **10** (-163.9, -162.8, -162.2 ppm) and **11** (-155.7 ppm) are in the range of compounds with terminal fluorine atoms which values range from -145.9 to -180.0 ppm.

Table 9. ^{19}F NMR spectra of terminal Al-F bonds

Compound	^{19}F
$(Me_3Si)_3CAlF_2 \cdot THF$[52]	-159.2
$(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)AlF_2 \cdot THF$[53a]	-178.1
$(2,6\text{-}Me_2C_6H_3)N\{Si(t\text{Bu})Me_2\}AlF_2 \cdot THF$[53a]	-175.0
$(n\text{Bu}_4N)_2(PhPO_3AlF_2)_2$[58]	-180.0
$(n\text{Bu}_4N)_2(t\text{BuPO}_3AlF_2)_2$[58]	-179.5
$(n\text{Bu}_4N)(RMeAlF_2)$ (R = Me)[59]	-154.8
$(n\text{Bu}_4N)(RMeAlF_2)$ (R = $(Me_3Si)_3C$)[59]	-145.9
$(Me_4N)(i\text{Bu}_2AlF_2)$[60]	-149.4
$(Ph_4P)(i\text{Bu}_2AlF_2)$[60]	-151.7
$(1\text{-}AdCH_2NAl)_7F_{2.26}H_{4.74}$*	-163.9, -162.8, -162.2
$(t\text{BuNCH}_2AlF)_4$ *	-155.7

* this work

2.4. Reactions of monomeric organoaluminum(I) compounds

LAl^I (**12**) (L = $HC(CMeNAr)_2$, Ar = $2,6\text{-}i\text{Pr}_2C_6H_3$)[31] with its non-bonding lone pair of electrons at aluminum indicates a singlet carbene-like character. It could be used in carbene type reactions, as a Lewis base, and as a reducing reagent, which may show remarkable and unprecedented chemical reactions. However, the yield of **12** is low (21 %), in order to improve the yield we tried a more bulky β-diketiminato ligand $[HC(CPhNAr)_2]H$[66a] within the backbone of Ph substituents in place of Me groups for the preparation of Al(I) compound.

2.4.1. Preparation and structural analysis of $[HC(CPhNAr)_2]AlMe_2$ (Ar = $2,6\text{-}i\text{Pr}_2C_6H_3$) (13)

Since the disclosure by K. Ziegler et al. of the "aufbau" reaction, alkylaluminum compounds have been known as olefin oligomerisation catalysts, because of the displacement reaction competing with a "smooth stepwise addition of ethylene".[66b] In 1992 H. Martin and H. Bretinger demonstrated that the growth reaction of ethylene at bis(dichloroaluminum)ethane and trialkylaluminum produces with low activity polyethylene of high molecular weight and thermoplastic character.[66c] More recently, A. Sen et al. reported that simple alkylaluminum compounds, after reaction with the activators commonly used in the homogeneous olefin polymerisation catalysis {i.e. $B(C_6F_5)_3$, $[(C_6H_5)_3C][B(C_6F_5)_4]$}, are able to catalyse the polymerisation of ethylene and propene, although with low activity.[66d]

Compound **13** was synthesised from the reaction of $AlMe_3$ with ligand $[HC(CPhNAr)_2]H$ in refluxing toluene in a 1:1 ratio. When the reaction was carried out at 0 ºC or room temperature it did not proceed completely, and the proton of the NH group of the ligand was observed in the ^1H NMR spectrum. Compound **13** was characterised by NMR and elemental analysis as well as by X-ray structural analysis. The ^1H NMR spectrum exhibits the expected set of ligand proton signals and a high-field singlet for the Al-Me protons (δ -0.76 ppm, s). Treatment of **13** with an equivalent or excess of I_2 at room temperature or heating did not lead to the expected product $[HC(CPhNAr)_2]AlI_2$. The $[HC(CMeNAr)_2]H$ ligand is easier prepared and possesses better solubility, therefore we selected **12** as the starting material for the following reactions.

The X-ray crystal structure of **13** is given in Figure 12. Compound **13** crystallises in the monoclinic space group $P2/c$. The symmetry of **13** is C_s. Selected bond lengths and angles are given in Table 10. The Al-N distances (1.933(4) and 1.932(4) Å) are comparable with those of

[HC(CMeNAr)$_2$]AlMe$_2$ (1.922(2) and 1.935(2) Å).[43] The Al-Me distances (1.961(7) and 1.982(7) Å) are slightly longer than those of [HC(CMeNAr)$_2$]AlMe$_2$ (1.958(3) and 1.970(3) Å).[43] The bond angles of N-Al-N (95.99(19)º) and C-Al-C (115.7(3)º) are similar to those of [HC(CMeNAr)$_2$]AlMe$_2$ (96.18(9) and 117.40(13)º).[43] Thus we conclude that the substituents on the backbone at the C atoms do not affect much the bond lengths and bond angles. The six-membered ring of L is not in one plane any more: the dihedral angle of Al(1) – N(2)–C(5)–C(4) is 23.28(64)°. This distortion may originate from significant steric repulsion between two adjacent phenyl rings. The shortest H···H distance between two phenyl rings is only 2.192(15) Å, which is close to the sum of their van der Waals radii. If the six-membered ring is not distorted this distance will be even shorter, and gives significant steric repulsion.

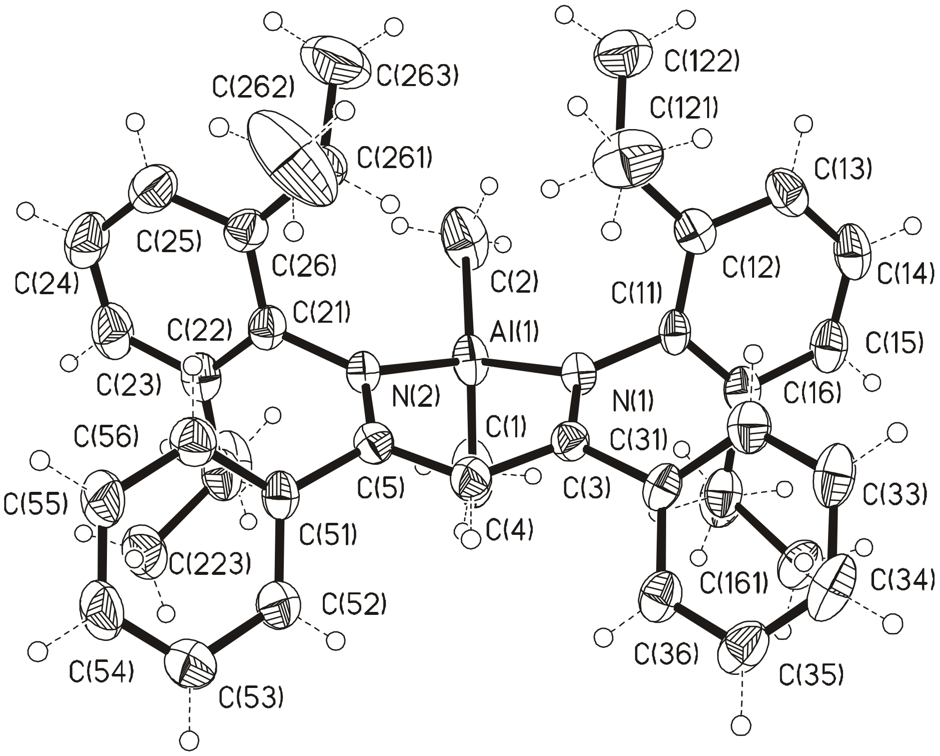


Figure 12. Molecular structure of **13** in the crystal.

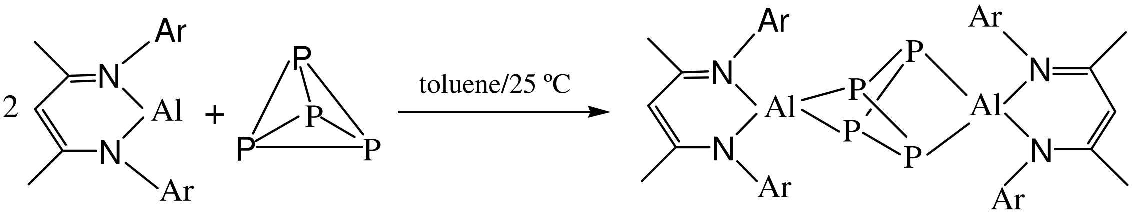
Table 10. Selected bond lengths (Å) and angles (°) for **13**.

Al(1)-N(2)	1.933(4)	N(1)-Al(1)-C(2)	115.3(3)
Al(1)-N(1)	1.932(4)	N(2)-Al(1)-C(1)	109.6(3)
Al(1)-C(2)	1.961(7)	N(1)-Al(1)-C(1)	107.2(3)
Al(1)-C(1)	1.982(7)	C(2)-Al(1)-C(1)	115.7(3)
N(2)-C(5)	1.346(7)	C(3)-N(1)-Al(1)	118.0(4)
C(4)-C(5)	1.390(8)	C(5)-N(2)-Al(1)	116.5(3)
N(1)-C(3)	1.338(6)	N(2)-C(5)-C(4)	122.4(5)
C(3)-C(4)	1.421(7)	N(1)-C(3)-C(4)	121.3(5)
N(2)-Al(1)-N(1)	95.99(19)	C(5)-C(4)-C(3)	129.7(5)
N(2)-Al(1)-C(2)	111.3(3)		

2.4.2. Preparation of $[HC(CMeNAr)_2]_2Al_2P_4$ (Ar = 2,6-*i*$Pr_2C_6H_3$) (14) with a formal P_4^{4-} charged species

The chemistry of white phosphorus has gained great interest over the past decades due to its tetrahedral structure and variable bonding modes. Organophosphorus compounds are used as reagents[67] and ligands for a cornucopia of complexes in catalytic processes.[68] Reactions of transition-metal complexes with white phosphorus have been extensively studied and have resulted in a large variety of P_x complexes with unpredicted structures.[69] Among them, only one compound $[Cp_2^*(CO)_2Co_2P_4]$[70] with a P_4^{4-} species has been reported. Reactions of the P_4 molecule with main group metal complexes were limited to a few examples, $[(AlCp^*)_6P_4]$ ($Cp^* = C_5Me_5$),[28] $[(GaR)_3P_4]$ (R = $(SiMe_3)_3C$),[71a] and $[Ga_2P_4t Bu_6]$.[71b] Compounds containing the heavy elements of group 13 and 15 were used as models in bonding theory[72] and as precursor for semi conducting materials.[73] Herein we report the reaction of **12** with white phosphorus to yield the first main group complex of composition [$(LAl)_2P_4$] (**14**) containing the P_4^{4-} species.

Treatment of two equivalents of **12** with white phosphorus at room temperature leads to **14** in good yield (Scheme 8). In contrast, the reaction of the tetrahedral aluminum(I) compound $(AlCp^*)_4$ ($Cp^* = C_5Me_5$)[24] with white phosphorus gave the electron deficient



12 **14**

Scheme 8

cage compound $(AlCp^*)_6P_4$,[28] which consists of two face-sharing heterocubanes with two opposite corners unoccupied, as well as four P atoms from the complete cleavage of the P_4 molecule. Therefore we reacted **12** and P_4 in a 4:1 ratio to explore the possibility of complete cleavage of all P-P bonds, however we obtained **14** and unreacted **12** based on ^1H and ^{31}P NMR investigations. Obviously the bulky ligand L prevents the arrangement of a larger number of LAl moieties around the P atoms. When the reaction was carried out in a ratio of 1:1 between **12** and P_4, **14** and unreacted P_4 together with some byproducts were obtained due to the results of ^1H and ^{31}P NMR investigations. Compound **14** is air sensitive and decomposes at 145 ºC. **14** is sparingly soluble in pentane and hexane, but readily soluble in benzene, toluene and diethylether. In $CDCl_3$ we observed the decomposition of **14**.

Compound **14** was characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy using benzene-d$_6$ as the solvent, by EI mass spectrometry and elemental analysis. The EI mass spectrum shows the molecular ion of **14**. The ^{31}P NMR spectrum of **14** (78.6 ppm) exhibits a strong chemical shift difference compared to that of the free P_4 molecule (-519 ppm). No resonances were observed in C_6D_6 solution for the ^{27}Al NMR of **14**, thus the measurement in solid state was carried out and signals in a range of 50 - 120 ppm were found which are comparable to those for four coordinated Al(III) compounds, but much different from the resonance for LAl^I (**12**) (590 ± 40 ppm, $\upsilon_{1/2}$ = 30 000Hz).[74] In the ^{1}H NMR pattern of **14**, only one set of resonances for the L ligand was detected indicating that the two L ligands are in the same chemical environment.

2.4.3. Molecular structure of 14

The X-ray single-crystal structural analysis confirms the composition of **14** (Figure 13). **14** crystallises in the orthorhombic space group $P2_12_12_1$ with one molecule of pentane. As shown in Figure 13, compound **14** contains an Al_2P_4 core, and the four-membered P_4 ring is attached to two LAl moieties. Selected bond lengths and angles are listed in Table 11. The Al-P bond length (av. 2.37 Å) of **14** is in the range of those in $(AlCp^*)_6P_4$ (2.31 to 2.42 Å).[28] The P-P bond length (av. 2.29 Å) is slightly longer than that in $Cp_2^*(CO)_2Co_2P_4$ (av. 2.23 Å).[70] The distances between P(1)-P(3) and P(2)-P(4) in **14** (3.049(2) and 3.063(2) Å) are distinctly longer than those in $Cp_2^*(CO)_2Co_2P_4$ (2.560(2), 2.597(2) Å),[70] which shows the

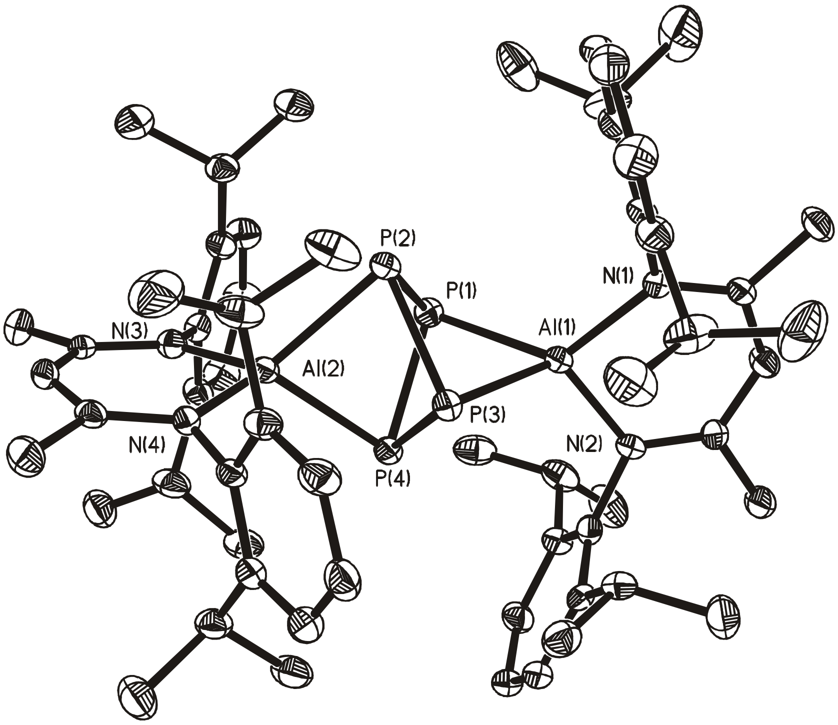


Figure 13. The crystal structure of **14**. The hydrogen atoms of the C-H bonds are omitted for clarity.

cleavage of two P-P bonds within the P_4 molecule. The Al-N bond lengths (av. 1.90 Å) are in the range of other aluminum derivatives bearing the ligand L.[19a] The average P-Al-P bond angle is 80.27 °. The symmetry of the compound is roughly D_{2d}, which means the two L ligand planes are vertical.

2.4.4. Theoretical calculations for 14

DFT calculations with RI-BP86/TZVP within TURBOMOLE[44,45] were carried out to investigate the electronic structure of **14**. The calculated Mulliken charges on the P atoms (-0.22) show a significant charge transfer from the Al atoms to the P_4 unit, which indicates the formation of ionic Al-P bonds. The bond order (shared electrons between two P atoms) of P-P bonds (0.01) supports the complete cleavage of the P(1)-P(3) and P(2)-P(4) bonds.

Table 11. Selected bond lengths (Å) and angles (°) for **14**.

Al(1)-P(1)	2.377(2)	P(3)-Al(1)-P(1)	80.16(7)
Al(1)-P(3)	2.359(2)	P(2)-P(1)-P(4)	83.98(7)
P(1)-P(2)	2.287(2)	P(3)-P(2)-P(1)	83.69(8)
P(1)-P(4)	2.292(2)	P(2)-P(3)-P(4)	83.96(8)
P(2)-P(3)	2.284(2)	P(1)-P(4)-P(3)	83.34(8)
P(3)-P(4)	2.295(2)	P(2)-P(1)-Al(1)	81.64(8)
P(1)···P(3)	3.049(2)	P(4)-P(1)-Al(1)	77.60(7)
P(2)···P(4)	3.063(2)	P(2)-P(3)-Al(1)	82.07(8)
Al(1)-N(1)	1.897(5)	P(4)-P(3)-Al(1)	77.91(7)
Al(1)-N(2)	1.912(5)	N(1)-Al(1)-N(2)	95.5(2)
N(1)-C(2)	1.355(7)	N(1)-Al(1)-P(3)	118.18(16)
C(2)-C(3)	1.411(8)	C(2)-N(1)-Al(1)	124.1(4)
C(3)-C(4)	1.383(8)	N(1)-C(2)-C(3)	122.7(5)
N(2)-C(4)	1.339(7)	C(4)-C(3)-C(2)	127.5(5)

The calculated binding energy [E($(LM)_2$-P_4) − 2*E(L-M) − E(P_4)/2.0] (36.4 kcal/mol) shows the strong interaction between the P_4 unit and the Al atoms.

In the uncoordinated P_4 molecule the average P-P distance lies around 2.21 Å. Herein we use PH_2-PH_2 as an example to study how much the P-P bond loses energy during its extension.[75] The energy curve of PH_2-PH_2 for the P-P distance (1.7 to 3.6 Å) is given in Figure 14. It shows that near the minimum the curve is quite flat. At r(P-P) > 3.0 Å, most of the bond energy is lost and the bond order is about zero.

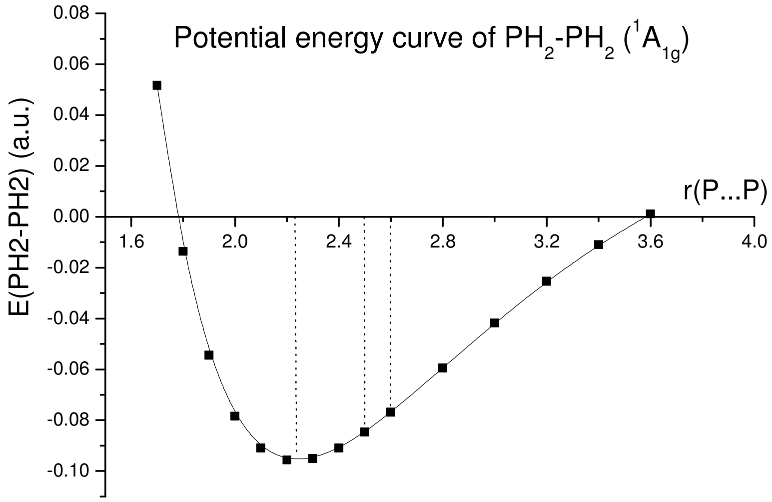


Figure 14. Potential energy curve of PH_2-PH_2 (0 means no binding energy for two PH_2 radicals).

In conclusion, both the charge calculation and the P-P bond analysis support the ionic Al-P_4 bond for **14**. Therefore in **14** the P_4 moiety is carrying formally four negative charges.

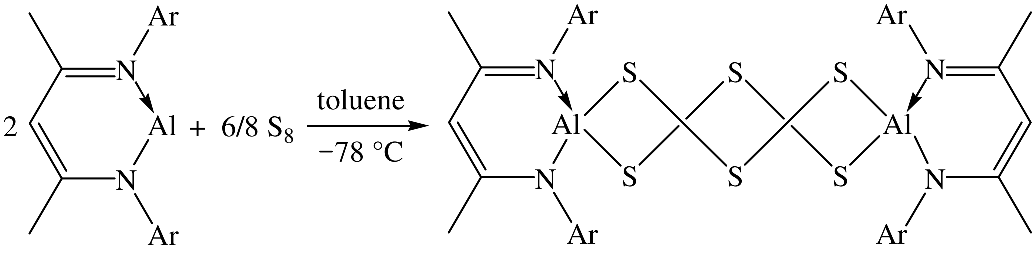
In summary, the reaction of LAl^I (**12**) with white phosphorus yields the first main group complex $(LAl)_2P_4$ (**14**) containing the P_4^{4-} species, in which two P-P edges of the P_4 tetrahedron are opened and each is bridged by a LAl moiety.

2.4.5. Preparation of a bimetallic derivative of the sulphur crown S_8: $LAl(\mu\text{-}S_3)_2AlL$ (L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) (15)

Metal polysulfides, synthesized by a variety of methods using various reagents as sulphur source, such as S_8, M_2S_n (M = alkali metal), P_4S_{10}, H_2S and organic polysulfanes, have attracted much attention not only regarding their structure and reactivity but also due to their potential uses.[76] Metal polysulfide complexes[76b] may be viewed as derivatives of the S_x^{2-}

(x ≥ 2) ion. Transition metal polysulfides have attracted interest as catalysts and intermediates in enzymatic processes and in catalytic reactions of industrial importance such as the hydrodesulphurisation (HDS) of fossil fuels.[77] Furthermore, the metal polysulfides can be used as precursor for metal-sulphur clusters. In contrast, such complexes containing heavier main group elements such as Group 13, 14, and 15 metals have been much less explored.[76a,76d] The examples are: Tbt(R)ME_4 (M = Si, Ge, Sn, Pb; E = S, Se; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; R = aryl group).[76d] Among the numerous investigations of the metal polysulfides, complexes with the (μ-S_3) chain were rarely reported. The most common examples are those of transition metal complexes $[(\eta^5\text{-RC}_5\text{H}_4)_2\text{Ti}(\mu\text{-S}_3)]_2$ (R = H, Me)[78] and $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{PPh}_3)(\mu\text{-S}_3)]_2$[79] which were obtained by treatment of $(\eta^5\text{-RC}_5\text{H}_4)_2\text{TiS}_5$ (R = H, Me) with PPh_3, and $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{PPh}_3)_2\text{S}]_2[\text{SbF}_6]_2$ with $(\text{NBu}_4)_2\text{S}_6$ respectively. The tetrameric Al(I) compound $(\text{Cp*Al})_4$[24] can be oxidized with Se and Te to afford heterocubanes $(\text{Cp*Al})_4\text{E}_4$ (E = Se, Te).[29] However no reaction was carried out between S and $(\text{Cp*Al})_4$.[24] Herein we describe the synthesis and structural characterisation of $\text{LAl}(\mu\text{-S}_3)_2\text{AlL}$ (**15**) containing two (μ-S_3) chains.

Compound **15** was synthesised by the reaction of **12** with sulphur in a molar ratio of 2:6 (the ratio corresponds to the stoichiometry of S) (Scheme 10). Cold toluene was added to the mixture of **12** and sulphur at -78 ºC. After several minutes a suspension was obtained which was kept at -78 ºC for 2 h. Subsequently, the suspension was slowly warmed to room temperature under formation of more precipitate. Compound $\text{LAl}(\mu\text{-S})_2\text{AlL}$[35b] was isolated from the precipitate and characterized by its characteristic melting point and EI mass spectrum. Pale yellow crystals of **15** were obtained from the concentrated filtrate at 4 ºC, as



12 **15**

Ar = 2,6-*i*$Pr_2C_6H_3$

Scheme 10

well as at room temperature. It is noted that even when the above reaction was employed in a molar ratio of 2:3 (the ratio corresponds to the stoichiometry of S), the isolated product is also **15**, however in low yield (about 10 %). Compound **15** was characterised by ^{1}H, ^{13}C NMR spectroscopy, EI mass spectrometry, and elemental analysis. The most intense peak in the EI mass spectrum of **15** appears at *m/z* 508 $[M - LAlS_4]^+$. The signals at 540 (38 %) and 572 (15 %) are assigned to the $[M - LAlS_3]^+$ and $[M - LAlS_2]^+$ fragments respectively. **15** is sparingly soluble in benzene-d$_6$, and the solubility does not improve even when heated, it does not dissolve in hexane and pentane. When the reaction mixture or the isolated compound is exposed to traces of moisture, the free ligand LH can be detected by ^{1}H NMR investigation.

2.4.6. Molecular structure of 15

Single crystals of **15** suitable for X-ray structural analysis were obtained in toluene at 4 °C. Compound **15** crystallises in the monoclinic space group $P2_1/n$ with two molecules of toluene. Figure 15 shows the molecular structure of **15**. Two (μ-S_3) chains are connecting two Al atoms to form an aluminum polysulfide with an Al_2S_6 eight-membered ring. The two L ligands are almost coplanar. The symmetry of the structure is *Ci*. Compared to the S_8 structure,[80] the two S_3 units in the S_8 structure are eclipsed, while in **15** they are staggered, thus we cannot simply argue that the two Al atoms are replacing the corresponding S atoms in S_8. Selected bond lengths and angles are shown in Table 12. The S-S bonds (av. 2.08 Å) are slightly longer than those of S_8 (av 2.05 Å),[80] $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Ti}(\mu\text{-S}_3)]_2$ (av. 2.06 Å)[78] and $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{PPh}_3)(\mu\text{-S}_3)]_2$ (av. 2.05 Å).[79] The Al-S bonds (av. 2.24 Å) are comparable with those of dimeric $\text{LAl}(\mu\text{-S})_2\text{AlL}$ (av 2.24 Å)[35b] and LAl(SH)_2 (av. 2.22 Å).[36] The Al-N bond length (av. 1.89 Å) falls within the range of those in aluminum derivatives bearing the L ligand.[19a] The S-S-S angle (104.7°) is close to those found in $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Ti}(\mu\text{-S}_3)]_2$ (109.1°)[78] and $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{PPh}_3)(\mu\text{-S}_3)]_2$ (105.2°).[79]

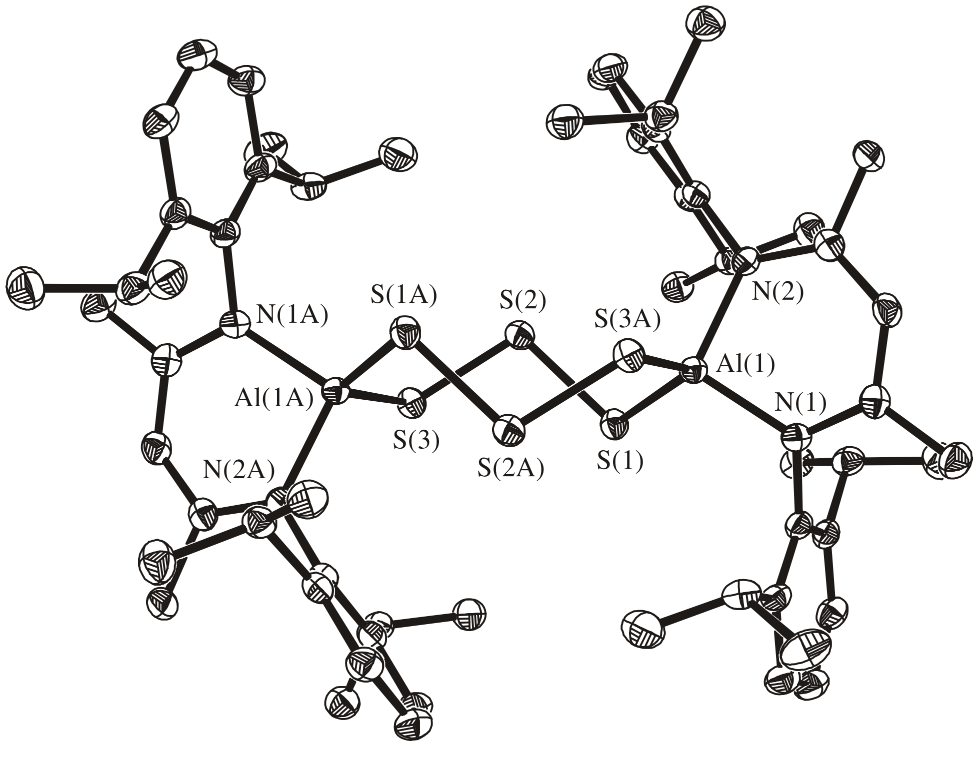


Figure 15. Thermal ellipsoids plot of **15** showing the atoms at the 50 % probability level. H atoms and solvent molecules are omitted for clarity.

Table 12. Selected bond lengths (Å) and angles (°) for **15**.

Al(1)-N(1)	1.882(2)	S(1)-Al(1)-S(3A)	116.9(1)
Al(1)-N(2)	1.904(2)	N(2)-Al(1)-S(1)	117.33(6)
Al(1)-S(1)	2.223(1)	N(1)-Al(1)-S(3A)	112.39(6)
Al(1)-S(3A)	2.248(1)	N(2)-Al(1)-S(3)	104.93(5)
S(1)-S(2)	2.095(1)	S(3)-S(2)-S(1)	104.7(1)
S(2)-S(3)	2.073(1)	S(2)-S(1)-Al(1)	98.0(1)
N(1)-C(2)	1.351(3)	S(2)-S(3)-Al(1A)	107.18(3)
C(2)-C(3)	1.389(3)	C(2)-N(1)-Al(1)	119.92(13)
C(3)-C(4)	1.402(3)	N(1)-C(2)-C(3)	122.47(18)
N(2)-C(4)	1.337(3)	C(2)-C(3)-C(4)	128.0(2)
N(1)-Al(1)-N(2)	97.7(1)	N(2)-C(4)-C(3)	122.99(19)
N(1)-Al(1)-S(1)	106.17(6)	C(4)-N(2)-Al(1)	119.95(13)

2.4.7. Theoretical calculation for 15

The S_8 ring can have different cleavage patterns and thus forms various types of structures.[76a] For $L_2Al_2S_n$ species the product with n = 2 is already known,[35b] and herein compound **15** has n = 6. The theoretical calculation was carried out to estimate the relative stability of the compounds with n = 2-8. The method used is RI-BP86/TZVP within the TURBOMOLE[45] program. The optimised structure of $L_2Al_2S_6$ is in good agreement with the X-ray values for **15** (mean deviation < 0.04 Å), which shows the reliability of the selected theoretical method. In the calculation the $CHMe_2$ groups of the ligand L were replaced by H atoms. The relative stability of $L_2Al_2S_n$ was estimated by the reaction energy of 2 LAl + n/8 $S_8 \rightarrow L_2Al_2S_n$. The calculated reaction energies are listed in Table 13. All reactions are exothermic. Compound $L_2Al_2S_2$[35b] is the most stable one. However, there are quite a few conformations with only a little smaller reaction energies, and thus thermodynamically they are all possible. Most $L_2Al_2S_n$ species prefer only one bridging S atom, while all the other S atoms are arranged in the second bridge (Table 13). We could isolate **15** but not the (theoretically favored) S1 S5 isomer, this might be due to the very low solubility of the latter species.

Table 13. The reaction energy of $L_2Al_2S_n$ (n = 2-8) is obtained from $E(L_2Al_2S_n) - 2\ E(LAl) - n/8\ E(S_8)$. The notes below the energies show the conformations. For example, S3 S4 means one bridge has three S atoms, while the other one has four S atoms.

n	2	3	4	5	6	7	8
Reaction Energy (kJ/mol)	-648.7 S1 S1	-641.6 S1 S2	-644.9 S1 S3 -571.7 S2 S2	-602.0 S1 S4 -581.8 S2 S3	-621.5 S1 S5 -608.9 S3 S3	-594.6 S1 S6 -408.5 S3 S4	-609.2 S1 S7 -257.0 S4 S4

Therefore, the theoretical work shows that all $L_2Al_2S_n$ (n = 2 - 8) species have rather stable conformations (can be more than one).[81] They may coexist in the product, and under different reaction conditions another species may be preferentially formed. To obtain a single crystal out of such a mixture is difficult except for n = 2 where one can use excess of **12** to react with sulphur.

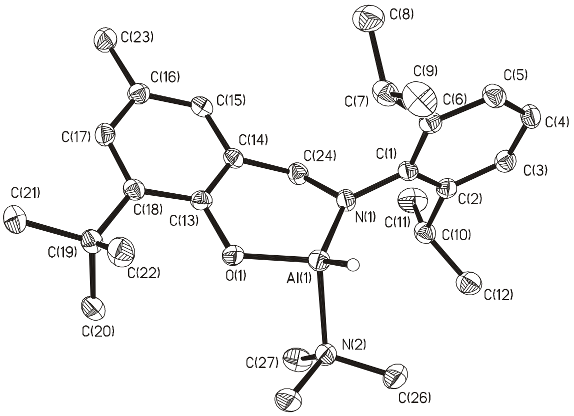
In summary, we report herein the first compound of Group 13 with two (μ-S_3) chains connecting two aluminum atoms under formation of an eight-membered Al_2S_6 ring. Studies of other possible conformations of $L_2Al_2S_n$ estimated by calculation are currently under investigation in our laboratory.

3. Summary and Outlook

3.1 Summary

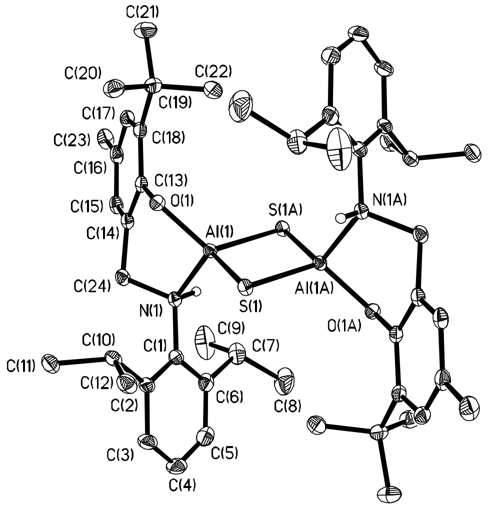
The focus of the work reported here has been on the synthesis, structures and reactions of aluminum(I) and aluminum(III) compounds with organic species. In this thesis bulky bidentate salicylaldiminato, β-diketiminato, tert-butyl and adamantyl groups have been employed as supporting moieties for aluminum compounds. The experimental results demonstrate that steric bulk and intramolecular hydrogen bond can stabilise some unusual organoaluminum compounds.

The first aluminum monohydride (3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$) AlH(NMe_3) (**2**) bearing a bidentate [N,O] ligand has been prepared from the salicylaldimine [3-*t*Bu-5-Me-2-(OH)C_6H_2CH=N-2,6-*i*$Pr_2C_6H_3$] (**1**) and $AlH_3 \cdot NMe_3$. Noteworthy, during the formation of **2** in addition to the elimination of hydrogen a hydrogen migration from the aluminum center to the ligand backbone occurred at the CH=N double bond to yield a CH_2N single bond.

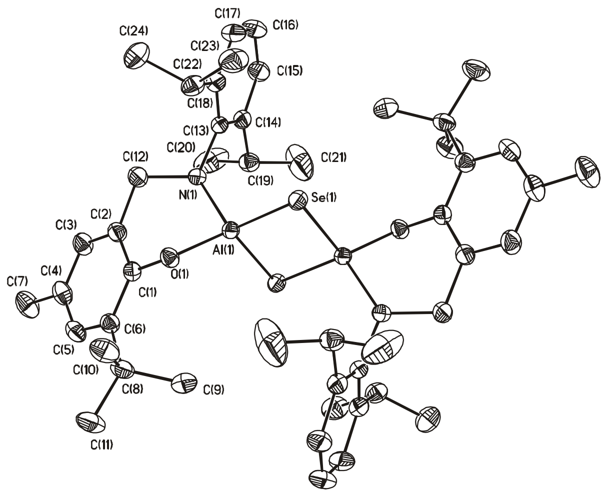


Structure of 2

2 reacts with elemental S and Se respectively to afford the dimeric chalcogenide [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(μ-E)]$_2$ [E = S (**3**), Se (**4**)]. A possible reaction mechanism is discussed. We assume that during the formation of **3** and **4** a reactive intermediate [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(EH)(NMe_3)] (E = S, Se) is formed which dimerises to [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(μ-EH)]$_2$ with elimination of NMe_3. The unstable [(3-*t*Bu-5-Me-2-(O)$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)Al(μ-EH)]$_2$ is converted to **3** and **4** under heating. The molecular structures of **3** and **4** show that both of them have a dimeric structure featuring a fused planar four-membered ring with a central Al_2E_2 core. Attempts to obtain single crystals from the reaction of **2** with Te was unsuccessful.

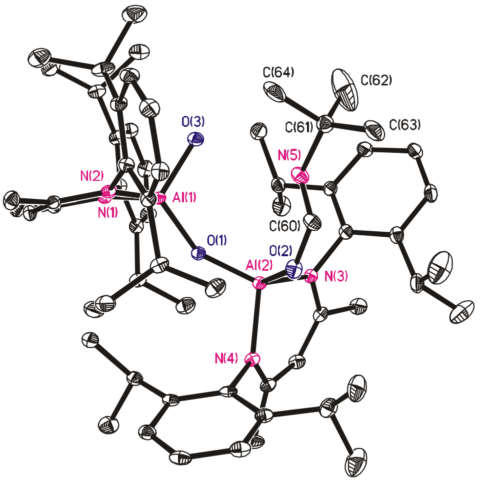


Structure of 3



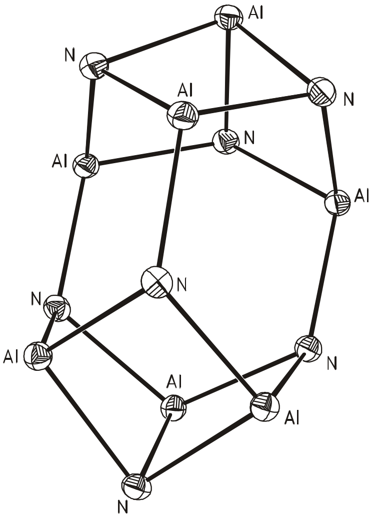
Structure of 4

The reaction of aluminum dihydride $LAlH_2$ (L = $HC(CMeNAr)_2$, Ar = 2,6-*i*$Pr_2C_6H_3$) (**5**) and *tert*-butylisocyanate in the presence of trace amounts of water and from **5** and LAlH(OCH=N-*t*Bu) (**6**) with water, respectively, afforded the first aluminoxane hydroxide LAl(OH)OAlL(OCH=N-*t*Bu) (**8**). The important point is to control strictly the amount of water during the reaction, an excess of water will decompose product **8**. The intramolecular hydrogen bond and the bulky L ligand at the aluminum center stabilise **8** to be a binuclear aluminoxane with terminal OH group. Treatment of **5** with *tert*-butylisocyanate in a ratio of 1:1 or 1:2 gave the nucleophilic addition product **6** or LAl(OCH=N-*t*Bu)$_2$ (**7**).

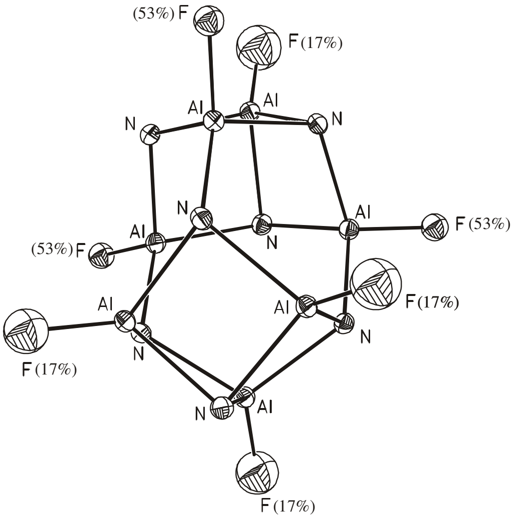


Structure of 8

The heptameric aluminum imide (RCH$_2$NAlH)$_7$ **(9)** was isolated from the reaction of the bulky nitrile RCN (R = 1-adamantyl) with AlH$_3$·NMe$_3$ in boiling toluene. **9** is the first heptameric aluminum imide with Al-H bonds, and the second imide with an Al$_7$N$_7$ core. Nitriles with less bulky R groups led to the formation of hexameric imides. The possible reason of this phenomenon is discussed.

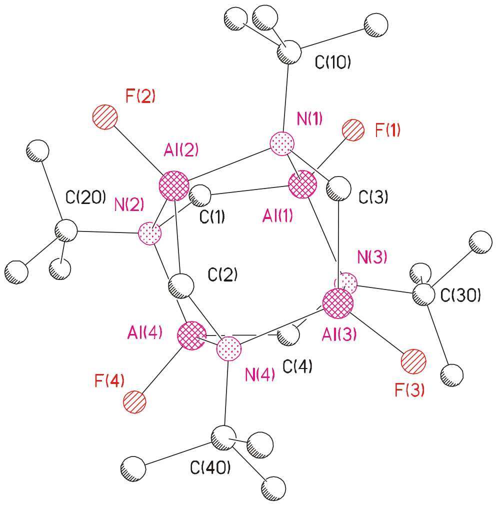


Core structure of 9

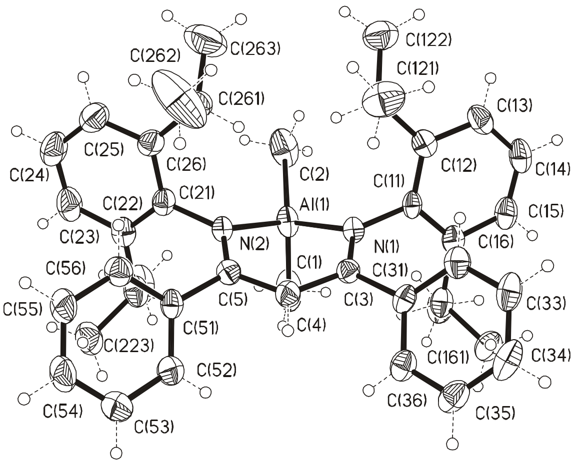


Core structure of 10

Fluorination of **9** with Me_3SnF was carried out at room temperature in CH_2Cl_2 or refluxing toluene to obtain a partially fluorinated compound $(RCH_2NAl)_7F_{2.26}H_{4.74}$ (R = 1-adamantyl) (**10**). The reaction of **9** with Me_3SiCl and Me_3SiBr both afforded also partially substituted products. The fluorination reaction using Me_3SnF was applied to the cluster (tBuNCH$_2$AlH)$_4$ to yield the corresponding tetrafluoro compound (t-BuNCH$_2$AlF)$_4$ (**11**). **10** and **11** are the first two aggregates containing only terminal Al-F bonds.



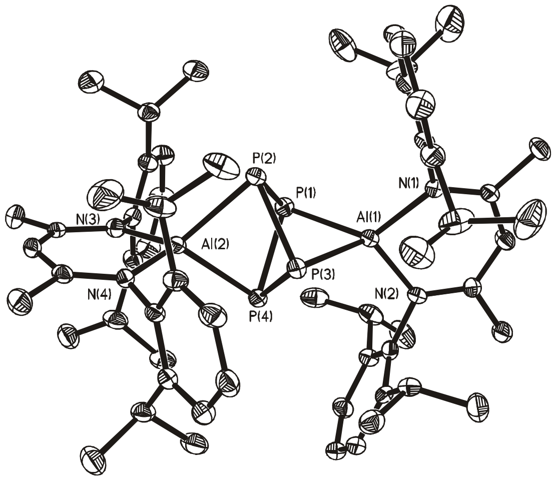
Structure of 11



Structure of 13

Compound **13** was synthesised from the reaction of $AlMe_3$ with $[HC(CPhNAr)_2]H$ in refluxing toluene in a 1:1 ratio. **13** was characterised by NMR and elemental analyses as well as X-ray structural analyses.

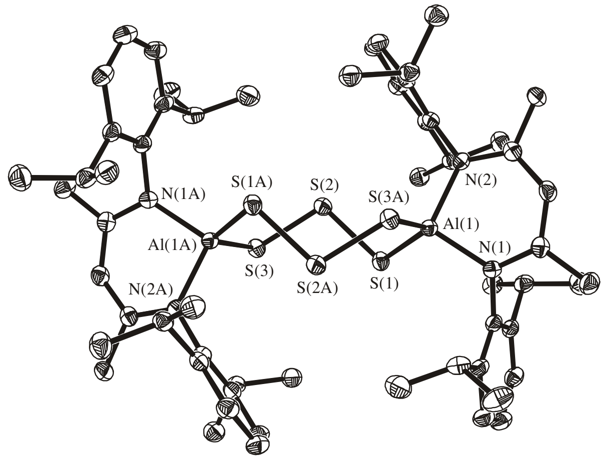
The reactive monomeric aluminum(I) compound LAl^I (L = $HC(CMeNAr)_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) (**12**) was reacted with white phosphorus to yield the first main group complex of composition $[HC(CMeNAr)_2]_2Al_2P_4$ (**14**) with a formal P_4^{4-} charged species. **14** was characterized by ^1H, ^{13}C, ^{27}Al, ^{31}P NMR spectroscopy as well as structural analyses. It is sensitive to air and moisture and well soluble in diethyl ether, benzene and toluene. The crystal structure shows that **14** contains an Al_2P_4 core in which two P-P edges of the P_4 tetrahedron are opened and each is bridged by a LAl moiety. The DFT calculations show that a significant charge transfer from the Al atoms to P_4 occurs and the aluminum is oxidised to +3 from +1. The ^{27}Al NMR also supports this point.



Structure of 14

Reaction of **12** with elemental sulfur at -78 °C affords a bimetallic derivative of the sulfur crown S_8: $LAl(\mu\text{-}S_3)_2AlL$ (**15**). **15** is extremely sensitive to air and moisture, and it is the first example of a main group cyclic bimetallic compound of the trisulfide ion. Two (μ-S_3) chains are connecting two Al atoms to form an aluminum polysulfide with an Al_2S_6 eight-membered ring. The two ligands are almost coplanar. The symmetry of the structure is *Ci*. Compared to the S_8 structure, the two S_3 units in the S_8 structure are eclipsed, while in **15** they are staggered. The theoretical work shows that all $L_2Al_2S_n$ (n = 2-8) species from the reaction $2\ LAl + n/8\ S_8 \rightarrow L_2Al_2S_n$ have rather stable conformations (can be more than one).

These compounds may coexist in the product, and under different reaction conditions other species may be preferentially formed.



Structure of 15

3.2. Outlook

This thesis reports the synthesis and characterisaton of organoaluminum(I) and aluminum(III) compounds. A more general extension of this work would be:

1. The aluminoxane hydroxide can react with other less bulky organometallic compounds in solution, which provides the possibility for the synthesis of aluminum containing homo- or heteroorganometallic compounds and their application for the polymerisation of olefins.
2. The monomeric aluminum(I) is a reactive starting material which can be used as reducing agent to react with group 15 and 16 elements.
3. As a two-electron donor the monomeric aluminum(I) can react with metal carbonyl complexes to replace the carbonyl groups under formation of Al-metal bonds.

4. Experimental Section

4.1. General procedures

All experimental manipulations, unless otherwise stated, were carried out in oxygen-free dry dinitrogen atmosphere using Schlenk glassware and techniques.[82] The handling of solids and the preparation of samples for spectral measurements were carried out inside a MBraun LABMASTER-130 dry-box where the O_2 and H_2O levels were normally kept below 1 ppm. The glassware used in all the manipulations were oven-dried at 150 °C for a minimum of 14 h, assembled hot, and cooled under high vacuum prior to use. Commercial grade solvents were purified and freshly distilled following conventional procedures prior to use.[83] For the use of highly air- and moisture-sensitive reactions, the solvents were freshly trap-to-trap distilled.

4.2. Physical measurements

Melting points of all new compounds were measured on a Büchi melting point B-540 apparatus in sealed capillaries and are uncorrected.

IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer (only characteristic absorptions are reported) and the samples were prepared as Nujol mulls between KBr plates.

NMR spectra were recorded on Bruker Avance 200, AM 300, MSL 400 (CP-MAS), and Bruker Avance 500 NMR spectrometers. Chemical shifts are reported in ppm external referenced by $SiMe_4$ for ^1H, ^{13}C nuclei, $CFCl_3$ for ^{19}F, and 85 % H_3PO_4 for ^{31}P nuclei. Downfield shifts from the reference are quoted positive, upfield shifts are assigned negative values. All the NMR grade solvents were dried prior to use and the samples for the measurements were freshly prepared in a dry-box. Heteroatom NMR spectra were recorded ^{1}H decoupled.

Mass spectra were obtained on Finnigan MAT system 8230 or Varian MAT CH5 mass spectrometers by EI-MS methods.

Elemental analysis were performed at the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

Crystal structure determination: Intensity data for compounds **2**, **3** and **15** were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector, for **4**, **8, 9**, **10** and **14** on a Stoe IPDS II two-circle diffractometer, and for **11** and **13** on a Siemens-Stoe AED2 four-circle instrument. The data for all the compounds were collected at low temperatures. All structures were solved by direct methods (SHELXS-97)[84] and refined with all data by full-matrix least-squares methods on F^2.[85] The non-hydrogen atoms were refined anisotropically, except those of the highly disordered toluene molecules in **4** which were refined isotropically. The hydrogen atoms were included at geometrically idealized positions and refined with the riding model, except for the Al-H and N-H hydrogen atoms which were located by difference Fourier synthesis and refined isotropically. The toluene molecules in **2** were disordered over two positions and refined with distance restraints and restraints for the anisotropic displacement parameters. Crystal data, data collection details, structural solution and refinement procedures for all compounds are summarized in the tables of section 6.

4.3. Starting Materials

Commercially available chemicals were purchased from Fluka or Aldrich and used as received. The other compounds used in this thesis were prepared according to published procedures: Me_3SnF,[86] $AlH_3{\cdot}NMe_3$,[38] (t-$BuNCH_2AlH)_4$,[20a] $LAlH_2$ (L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$),[19a] 4-methyl-6-tertbutylsalicylaldehyde,[5] $[HC(CPhNAr)_2]H$ (Ar = 2,6-$i$$Pr_2C_6H_3$),[66a] $[HC(CMeNAr)_2]_2Al$ (Ar = 2,6-$i$$Pr_2C_6H_3$) (**12**).[31]

4.4. Synthesis

4.4.1. [3-*t*Bu-5-Me-2-(OH)C_6H_2CH=N-2,6-*i*$Pr_2C_6H_3$] (1)

2,6-Diisopropylaniline (4.88 mL, 25.9 mmol) was added *via* syringe to a solution of 4-methyl-6-tertbutylsalicylaldehyde (4.97 g, 25.9 mmol)[5] in EtOH (100 mL). Formic acid (5 drops) was added to the resulting solution, and the solution was refluxed for 20 h. After cooling to room temperature the solution was dried over $MgSO_4$ and finally filtered. The volatiles were removed under *vacuo*. The residue was extracted with *n*-hexane (15 mL) and stored at -20 °C overnight to afford a pure yellow solid. Yield: 90 % (8.18 g).

M.p.: 97 - 98 °C; IR (nujol): $\tilde{\nu}$ = 3400 cm^{-1} (br, O-H stretch), 1620 cm^{-1} (C=N stretch); ^1H NMR (200.13 MHz, C_6D_6,): δ 1.06 (d, 12 H, J = 6.8 Hz, $CH(CH_3)_2$), 1.60 (s, 9 H, $C(CH_3)_3$), 2.14 (s, 3 H, (CH_3)), 3.03 (sept, 2 H, J = 6.8 Hz, $CHMe_3$), 6.73 (d, 1 H, J = 2.2 Hz, OAr-*H*), 7.13 (m, 3 H, NAr-*H*), 7.26 (d, 1 H, J = 2.2 Hz, OAr-*H*), 8.03 (s, 1 H, C*H*=N), 13.89 (s, 1 H, -O*H*); EI-MS (70 eV): *m*/z (%): 351 (100) M^+; Elemental analysis for $C_{24}H_{33}NO$ (351.52): Calcd. C, 82.00; H, 9.46; N, 3.98; Found C, 81.67; H, 9.45; N, 4.24 %.

4.4.2. (3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-N-2,6-*i*$Pr_2C_6H_3$)AlH·NMe_3 (2)

$AlH_3·NMe_3$ (17.2 mL of a 0.8 M solution in toluene, 13.76 mmol) was added at 0 °C to a solution of **1** (3.14 g, 8.95 mmol) in toluene (40 mL). The reaction mixture was slowly warmed to room temperature and stirred for additional 15 h. The volatiles were removed in *vacuo*. The crude product was recrystallised from toluene, and the filtrate was kept at -20 °C to obtain colourless crystals. Yield: 79 % (3.10 g).

M.p.: 109 - 112 °C; IR (nujol): $\tilde{\nu}$ = 1837 cm^{-1} (Al-H stretch); ^1H NMR (300.13 MHz, C_6D_6,): δ 1.02 (d, 3 H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.19 (d, 3 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.43 (d, 6 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.72 (s, 9 H, C(C*H*$_3$)$_3$), 1.79 (s, 9 H, N(C*H*$_3$)$_3$), 2.26 (s, 3 H, (C*H*$_3$)), 3.72 (sept, 2 H, *J* = 6.8 Hz, C*H*Me$_2$), 3.86 (d, 1 H, *J* = 14.6 Hz, C*H*$_2$N), 4.69 (d, 1 H, *J* = 14.6 Hz, C*H*$_2$N), 6.65 (d, 1 H, *J* = 1.7 Hz, OAr-*H*), 6.99-7.18 (m, 4 H, NAr-*H*, OAr-*H*); EI -MS (70 eV): *m*/z (%) only CH fragments; Elemental analysis for $C_{27}H_{43}AlN_2O$ (438.62): Calcd. C, 73.93; H, 9.88; N, 6.39; Found: C, 74.29; H 9.51; N, 5.53 %.

4.4.3. [(3-*t*Bu-5-Me-2-O-$C_6H_2CH_2$-NH-2,6-*i*$Pr_2C_6H_3$)Al(μ-S)]$_2$ (3)

Toluene (20 mL) was added to a mixture of **2** (0.56 g, 1.28 mmol) and S_8 (0.04 g, 1.28 mmol), and the resulting solution was warmed to 60 °C and stirred for 15 h. After cooling to room temperature the yellow-green solution was filtered and the filtrate was concentrated to ca. 8 mL. Yellow crystals were obtained after storing the resulting solution at -20 °C for 5 days. Yield: 62 % (0.72 g).

M.p.: 121 °C dec; IR (nujol): $\tilde{\nu}$ = 3175 cm^{-1} (N-H stretch); ^1H NMR (300.13 MHz, C_6D_6,): δ 0.88, 0.92, 1.09, 1.14 (d, 24 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.52 (s, 2 H, N*H*), 1.45, 1.71

(s, 18 H, C(C*H*$_3$)$_3$), 2.10, 2.18 (s, 6 H, (C*H*$_3$)), 3.15, 3.25, 3.41, 3.57 (sept, 4 H, J = 6.8 Hz, C*H*Me$_2$), 4.58, 4.64 (d, 4 H, J = 6.8 Hz, C*H*$_2$N), 5.8 (d, 1 H, J = 10.4 Hz, OAr-*H*), 6.01 (d, 1 H, J = 10.4 Hz, OAr-*H*), 6.40 (d, 1 H, J = 1.7 Hz, OAr-*H*), 6.51 (d, 1 H, J = 1.8 Hz, OAr-*H*), 7.01-7.15 (m, 6 H, NAr-*H*); EI-MS (70 eV): *m*/*z* (%) 822 (12) (M - H)$^+$, 162 (100) (*i*Pr$_2$C$_6$H$_4$); Elemental analysis for $C_{48}H_{68}Al_2N_2O_2S_2$ (823.16): Calcd. C, 70.04; H, 8.33; N, 3.40; Found C, 70.75; H, 8.46; N, 3.50 %.

4.4.4. [(3-*t*Bu-5-Me-2-O-C$_6$H$_2$CH$_2$-NH-2,6-*i*Pr$_2$C$_6$H$_3$)Al(μ-Se)]$_2$ (4)

Toluene (30 mL) was added to a mixture of **2** (0.77g, 1.75 mmol) and Se (0.28g, 3.54 mmol). The solution was refluxed for 2 h, unreacted Se was removed by filtration. The filtrate was concentrated to ca. 8 mL and kept at 0 °C to obtain yellow crystals. Yield: 60 % (1.06 g).

M.p.: 118 °C dec; IR (nujol): $\tilde{\nu}$ = 3220 cm^{-1} (N-H stretch); ^{1}H NMR (300.13 MHz, C$_6$D$_6$,): δ 0.87, 0.94, 1.14, 1.44 (d, 24 H, J = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.50, 1.56 (s, 18 H, C(C*H*$_3$)$_3$), 1.88 (s, 2 H, N*H*), 2.10, 2.15 (s, 6 H, (C*H*$_3$)), 2.64, 3.25, 3.43, 3.57 (sept, 4 H, J = 6.6 Hz,C*H*Me$_2$), 4.35, 4.39 (d, 4 H, J = 6.8 Hz, C*H*$_2$N), 6.05 (d, 1 H, J = 7.8 Hz, OAr-*H*), 6.21 (d, 1 H, J = 7.9 Hz, OAr-*H*), 6.33 (d, 1 H, J = 1.8 Hz, OAr-*H*), 6.47 (d, 1 H, J = 1.9 Hz, OAr-*H*), 7.01-7.15 (m, 6 H, NAr-*H*); EI-MS (70 eV): *m*/*z* (%) 916 (4) (M - H)$^+$, 162 (100) (*i*Pr$_2$C$_6$H$_4$); Elemental analysis for $C_{62}H_{84}Al_2N_2O_2Se_2$ (1101.23) (**4**·2C$_7$H$_8$): Calcd. C, 67.62; H, 7.69; N, 2.54; Found C, 67.25; H, 7.81; N, 2.72 %.

4.4.5. LAlH(OCH=N-*t*Bu) (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (6)

Tert-butylisocyanate (0.14 mL, 1.2 mmol) was added by syringe to LAlH$_2$(0.55 g, 1.25

mmol) (**5**) in toluene (20 mL). The solution was refluxed for 1 h. After removal of all the volatiles the residue was recrystallised from pentane. The resulting solution was concentrated to ca 5 mL and kept at 0 ºC to afford colourless crystals. Yield: 68 % (0.44 g).

M.p.: 141-143 ºC; IR (nujol): $\tilde{\nu}$ = 1868 cm^{-1} (Al-H stretch); ^1H NMR (300.13 MHz, C_6D_6): δ1.07 (s, 9 H, tC_4H_9), 1.12 (d, 6 H, J = 6.9 Hz, $CH(CH_3)_2$), 1.18 (d, 6 H, J = 6.8 Hz, $CH(CH_3)_2$), 1.28 (d, 6 H, J = 6.7 Hz, $CH(CH_3)_2$), 1.38 (d, 6 H, J = 6.8 Hz, $CH(CH_3)_2$), 1.55 (s, 6 H, (CH_3)), 3.41 (sept, 4 H, C*H*Me$_2$), 5.09 (s, 1 H, γ-*H*), 7.12-7.15 (m, 6 H, Ar-*H*), 7.54 (s, 1H, C*H*=N); EI-MS: *m/z* (%) 545 (38) M^+, 544 (100) (M - H)$^+$; Elemental analysis for $C_{34}H_{52}AlN_3O$ (545.78): Calcd. C, 74.82; H, 9.60; N, 7.70; Found C, 75.03; H, 9.51; N, 7.83 %.

4.4.6. LAl(OCH=N-*t*Bu)$_2$ (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (7)

Tert-butylisocyanate (0.30 mL, 2.90 mmol) was added by syringe to $LAlH_2$(0.620 g, 1.39 mmol) (**5**) in toluene (20 mL). The solution was refluxed for 2.5 h. After removal of all the volatiles the residue was recrystallised from pentane. The concentrated resulting solution was kept at 0 ºC to afford colourless crystals. Yield: 80 % (0.72 g).

M.p.: 175-176 ºC; ^1H NMR (300.13 MHz, C_6D_6): δ 0.98 (s, 18H, *tBu*), 1.40 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, $CH(CH_3)_2$), 1.54 (s, 6H, (CH_3)), 1.66 (d, 12H, $^3J_{H-H}$ = 6.8 Hz, $CH(CH_3)_2$), 3.42 (sept, 4H, C*H*Me$_2$), 5.13 (s, 1H, γ-*H*), 7.12-7.15 (m, 6H, Ar-*H*), 7.45 (s, 2H, C*H*=N); EI-MS: *m/z* (%) 644 (2) [M^+], 587 (16) [M - *t*Bu]$^+$, 544 (100) (M - HOCH=N*t*Bu)$^+$; Elemental analysis for $C_{39}H_{61}AlN_4O_2$ (644.91): Calcd. C, 72.63; H, 9.53; N, 8.69; Found C, 72.53; H, 9.84; N, 8.27 %.

4.4.7. LAl(OH)OAlL(OCH=N-*t*Bu) (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (8)

Method 1: The procedure is the same as that for the preparation of **6**, except that the ratio of the reagents is 1:2, and the resulting concentrated pentane solution reacted with water when it was stored at 0 ºC to obtain **8** in 18 % yield. Method 2: A solution of H_2O (0.07 mL, 3.9 mmol) in THF (70 mL) was added dropwise to the solution of $LAlH_2$ (**5**) (0.87 g, 1.95 mmol) and **6** (1.06 g, 1.95 mmol) in THF (20 mL) at -30 °C. The resulting solution was warmed slowly to room temperature and stirred for additional 12 h. All volatiles were removed under reduced pressure. The residue was extracted with pentane (8 mL). After filtration the solution was concentrated and kept at 0 ºC. Colourless crystals were obtained. Yield: 20 % (0.40 g).

M.p.: 185 ºC dec; IR (nujol): $\tilde{\nu}$ = 3458 cm^{-1} (br, O-H stretch); ^{1}H NMR (300.13 MHz, C_6D_6): δ -0.30 (s, 1 H, O*H*), 0.73 (d, 6 H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 0.82 (d, 6 H, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 0.87 (s, 3 H, *t*C$_4$*H*$_9$), 1.09 (s, 6 H, *t*C$_4$*H*$_9$), 1.14 (d, 15 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.20 (d, 3 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.35 (d, 12 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.41 (d, 6 H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.45 (s, 3 H, (C*H*$_3$)), 1.50 (s, 3 H, (C*H*$_3$)), 1.54 (s, 3 H, (C*H*$_3$)), 1.57 (s, 3 H, (C*H*$_3$)), 3.12 (sept, 2 H, *J* = 6.6 Hz, C*H*Me$_2$), 3.24 (sept, 2 H, *J* = 6.8 Hz, C*H*Me$_2$), 3.46 (sept. 1 H, *J* = 6.8 Hz, C*H*Me$_2$), 3.57 (sept, 1 H, *J* = 6.7 Hz, C*H*Me$_2$), 3.73 (sept, 2 H, *J* = 6.8 Hz, C*H*Me$_2$), 4.86 (s, 1 H, γ-*H*), 4.91 (s, 1 H, γ-*H*), 7.25-7.00 (m, 12 H, Ar-*H*), 7.81 (s, 1 H, C*H*=N); EI-MS: *m/z* (%) 1021 (40) M^+, 604 (100) (M - L)$^+$; Elemental analysis for $C_{68}H_{104}Al_2N_5O_3$ (1093.52) (**8**·C_5H_{12}): Calcd. C, 74.69; H, 9.59; N, 6.40; Found C, 73.81; H, 9.58; N, 6.31 %.

4.4.8. (RCH$_2$NAlH)$_7$ (R = 1-adamantyl) (9)

$AlH_3 \cdot NMe_3$ (6.2 mL, 0.8 M solution in toluene, 4.96 mmol) was added under stirring to a solution of RC≡N (0.53 g, 3.29 mmol) in toluene (15 mL) at -78 °C. The mixture was kept at this temperature for 1 h before it was slowly warmed to room temperature, and then refluxed until gas evolution ceased. After cooling the solution to room temperature it was filtered to remove the insoluble precipitate. Finally the volatiles were removed *in vacuo* from the filtrate to yield product **9**. Single crystals suitable for X-ray diffraction analysis were obtained from toluene at room temperature. Yield: 51 % (0.32 g).

M.p.: > 340 °C; IR (nujol): 1916, 1896, 1867, 1851 cm^{-1} (Al-H strech); ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.56, 1.66, 1.87, 1.99 (105 H, *1-adamantyl*), 2.76, 2.79, 3.05 (14 H, CH_2); EI-MS (70 eV): *m/z* (%) 1337 (11) $(M - H)^+$, 1203 (100) $(M$ - 1-adamantyl$)^+$; Elemental analysis for $C_{84}H_{134}Al_7N_7$ (1430.88) (**9**$\cdot C_7H_8$): Calcd. C, 70.51; H, 9.44; N, 6.85; Found C, 68.87; H, 9.24; N, 6.66 %.

4.4.9. $[(RCH_2NAl)_7H_{4.74}F_{2.26}]$ (R = 1-adamantyl) (10)

To a mixture of **9** (0.50 g, 0.37 mmol) and Me_3SnF (0.47 g, 2.60 mmol) toluene (30 mL) was added at room temperature. The resulting solution was refluxed for 2 h and then filtered. The solvent from the filtrate was removed *in vacuo* to yield compound **10**. Single crystals suitable for X-ray diffraction analysis were obtained from toluene at room temperature. Yield: 47 % (0.24 g).

M.p.: 190 °C dec; IR (nujol): 1895 cm^{-1} (Al-H strech); ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.55, 1.66, 1.68, 1.85, 1.88, 1.99 (105 H, *1-adamantyl*), 2.76, 2.78, 2.80, 3.02, 3.03, 3.08 (14 H, CH_2); ^{19}F NMR (188.28 MHz, $CDCl_3$): -163.89, -162.77, -162.15; EI-MS (70 eV): The mass spectrum only shows CH fragments; Elemental analysis for $C_{84}H_{131.74}Al_7F_{2.26}N_7$ (1466.73) (**10**·C_7H_8): Calcd. C, 68.56; H, 9.23; N, 6.66; F, 2.92; Found C, 67.20; H, 9.02; N, 6.30; F, 2.81 %.

4.4.10. (tBuNCH$_2$AlF)$_4$ (11)

To a mixture of (t-BuNCH$_2$AlH)$_4$ (0.467g, 1 mmol) and Me_3SnF (0.779g, 4.3 mmol) CH_2Cl_2 (50 mL) was added at room temperature. The resulting solution was stirred at room temperature for 3 d and a suspension was obtained. The suspension was filtered and the volatiles were removed *in vacuo* from the filtrate. The resulting residue was dissolved in toluene to afford colourless crystals at 0 °C. Yield: 67 % (0.35 g).

M.p.: 288 - 289 °C; ^1H NMR (300.13 MHz, $CDCl_3$): δ 1.32, 1.50 (br, 36 H, tC_4H_9), 1.74 (d, 4 H, J = 13.0 Hz, CH_2), 1.93 (d, 4 H, J = 13.1 Hz, CH_2); ^{19}F NMR (188.28 MHz, $CDCl_3$): -155.74; EI-MS (70 eV): m/z (%) 509 (4) (M - Me)$^+$, 467 (100) ([M - tBu]$^+$; Elemental analysis for $C_{20}H_{44}Al_4F_4N_4$ (524.51): Calcd. C, 45.80; H, 8.46; N, 10.68; F, 14.49; Found C, 45.96; H, 8.40; N, 10.57; F, 14.11 %.

4.4.11. [HC(CPhNAr)$_2$]AlMe$_2$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) (13)

$AlMe_3$ (1.5 mL, 2.0 M solution in toluene, 3 mmol) was added under stirring to a solution of [HC(CPhNAr)$_2$]H (1.62g, 3 mmol) in toluene (30 ml) at 0 °C. The mixture was slowly warmed to room temperature and then refluxed for 1 h. After cooling to room temperature the resulting solution was concentrated to ca. 8 mL and kept at –20 ºC to afford yellow-green crystals. Yield: 60 % (1.07 g).

M.p.: 235 - 237 °C; ^{1}H NMR (500.13 MHz, $CDCl_3$): δ -0.76 (s, 6 H, Al-(C*H*$_3$)), 0.86 (d, 12 H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.22 (d, 12 H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 3.31 (sept, 4 H, *J* = 6.7 Hz, C*H*Me$_2$), 5.59 (s, 1 H, γ-*H*), 7.03-7.25 (m, 16 H, Ar-*H*); EI-MS (70 eV): *m/z* (%) 583 (100) (*M* - Me)$^+$; Elemental analysis for $C_{41}H_{51}AlN_2$ (598.84): Calcd. C, 82.23; H, 8.58; N, 4.68; Found: C, 82.50; H, 8.40; N, 4.82 %.

4.4.12. [HC(CMeNAr)$_2$]$_2$Al$_2$P$_4$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (14)

Toluene (30 mL) was added to a mixture of **12** (0.445 g, 1 mmol) and P_4 (0.062 g, 0.5 mmol). The resulting solution was stirred at room temperature for one week. After removal of the solvent the residue was recrystallised from a mixture of hexane and pentane at room temperature to afford red crystals. Yield: 79 % (0.40 g).

M.p.: 145 ºC dec; ^{1}H NMR (300.13 MHz, C_6D_6): δ 1.13 (d, 24 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$) 1.15 (d, 24 H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.70 (s, 12 H, (C*H*$_3$)), 3.61 (sept, 8 H, *J* = 6.8 Hz, C*H*Me$_2$), 5.03 (s, 2 H, γ-*H*), 7.15-7.02 (m, 12 H, Ar-*H*); ^{13}C NMR (125.77 MHz, C_6D_6): δ 169.97 (*C*N), 143.94, 142.07, 124.14 (*Ar*), 97.79 (γ-*C*), 29.26 (*C*HMe$_2$), 25.43(CH(*C*H$_3$)$_2$), 24.57 (CH(*C*H$_3$)$_2$), 23.86 ((*C*H$_3$)); ^{27}Al NMR (600 MHz, 26 KHz, MAS, $AlCl_3$): δ = 50-120 ppm; ^{31}P NMR (121.5 MHz, C_6D_6): δ 78.6 ppm; EI-MS: *m/z* (%) 1012 (30) M^+, 429 (100) (LAl - Me)$^+$; Elemental analysis for $C_{63}H_{94}Al_2N_4P_4$ (1085.26) (**14**·C_5H_{12}): Calcd. C, 69.72; H, 8.73; N, 5.16; Found C, 69.88; H, 8.12; N, 5.76 %.

4.4.13. LAl(μ-S$_3$)$_2$AlL (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (15)

Toluene (30 mL) was added to a mixture of **12** (0.580 g, 1.3 mmol) and S_8 (0.125 g, 3.9

mmol) at -78 ºC. The resulting suspension was stirred at this temperature for 2 h and slowly warmed to room temperature. The mixture was stirred for additional 15 h. After removal of the precipitate by filtration, the concentrated solution was kept at room temperature for 3 days to afford pale yellow crystals of **2**. Yield: 22 % (0.150 g).

M.p.: 185 ºC dec; ^{1}H NMR (500.13 MHz, C_6D_6): δ 1.00 (d, 24 H, J = 6.8 Hz, CH(CH_3)$_2$), 1.37 (d, 24 H, J = 6.8 Hz, CH(CH_3)$_2$), 1.50 (s, 12 H, (CH_3)), 3.30 (sept, 8 H, J = 6.8 Hz, CHMe$_2$), 4.72 (s, 2 H, γ-H), 7.20-6.90 (m, 12 H, Ar-H); ^{13}C NMR (125.77 MHz, C_6D_6): δ 23.55 ((CH$_3$)), 23.93 (CH(CH$_3$)$_2$), 25.45 (CH(CH$_3$)$_2$), 28.92 (CHMe$_2$), 97.74 (γ-C), 145.74, 143.69, 128.20, 123.83 (Ar), 171.78 (CN); EI-MS: m/z (%) 508 (100) (M - LAlS$_4$)$^+$, 540 (38) (M - LAlS$_3$)$^+$, 572 (15) (M - LAlS$_2$)$^+$; Elemental analysis for $C_{58}H_{82}Al_2N_4S_6$ (1081.66) (**15**·2C_7H_8): Calcd. C, 64.40; H, 7.64; N, 5.18; Found C, 64.65; H, 7.88; N, 4.76 %.

5. Handling and Disposal of Solvents and Residual Waste

1. The recovered solvents were distilled or condensed into cold-traps under vacuum and collected in halogen-free or halogen-containing solvent containers, and stored for disposal.
2. Used NMR solvents were classified into halogen-free and halogen-containing solvents and were disposed as heavy metal wastes and halogen-containing wastes, respectively.
3. The heavy metal residues were dissolved in nitric acid and after neutralisation stored in the containers for heavy metal wastes.
4. Drying agents such as KOH, $CaCl_2$, and P_4O_{10} were hydrolyzed and disposed as acid or base wastes.
5. Whenever possible, sodium metal used for drying solvents was collected for recycling.[87] The non-reusable sodium metal was carefully hydrolysed in cold ethanol and poured into the base-bath used for cleaning glassware.
6. Ethanol and acetone used for cold-baths were subsequently used for cleaning glassware.
7. The acid-bath used for cleaning glassware was neutralized with Na_2CO_3 and the resulting NaCl solution was washed-off in the communal water drainage.
8. The residue of the base-bath used for glassware cleaning was poured into the container for base wastes.

Amounts of various types of disposable wastes generated during the work:

Metal containing wastes	10 L
Halogen-containing solvent wastes	5 L
Halogen-free solvent wastes	35 L
Acid wastes	10 L
Base wastes	20 L

6. Crystal Data and Refinement Details

Table CD1. Crystal data and structure refinement for 2·C_7H_8.

Empirical formula	$C_{34}H_{51}AlN_2O$
Formula weight	530.75
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.100(1) Å
	b = 9.632(1) Å, β = 96.65(1)°
	c = 36.703(1) Å
Volume	3195(1) Å^3
Z	4
Calculated density	1.103 Mg/m^3
Absorption coefficient	0.746 mm^{-1}
F(000)	1160
θ range for data collection	2.42 – 58.94°
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-40 \leq l \leq 40$
Reflections collected	13836
Independent reflections	4447 [R(int) = 0.0327]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4447 / 0 / 361
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0338, $wR2$ = 0.0845
R indices (all data)	$R1$ = 0.0413, $wR2$ = 0.0886
Largest difference peak and hole	0.169 and -0.243 e·Å^{-3}

Table CD2. Crystal data and structure refinement for $3 \cdot 2C_7H_8$.

Empirical formula	$C_{62}H_{84}Al_2N_2O_2S_2$
Formula weight	1007.39
Temperature	100(2)
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 12.149(1) Å, α = 108.94(1)°
	b = 12.345(1) Å, β = 118.62(1)°
	c = 12.554(1) Å, γ = 97.75(1)°
Volume	1465(1) Å^3
Z	1
Calculated density	1.142 Mg/m^3
Absorption coefficient	1.431 mm^{-1}
F(000)	544
θ range for data collection	4.04 – 58.97°
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$
Reflections collected	11561
Independent reflections	4107 [R(int) = 0.0299]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4107 / 249 / 394
Goodness-of-fit on F^2	1.047
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0324, $wR2$ = 0.0859
R indices (all data)	$R1$ = 0.0369, $wR2$ = 0.0891
Largest difference peak and hole	0.200 and -0.232 e·Å^{-3}

Table CD3. Crystal data and structure refinement for $4 \cdot 2C_7H_8$.

Empirical formula	$C_{62}H_{82}Al_2N_2O_2Se_2$
Formula weight	1101.19
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.0480(4) Å, α = 77.061(3)°
	b = 12.4855(5) Å, β = 68.039(3)°
	c = 13.1473(6) Å, γ = 89.284(3)°
Volume	1486.23(11) $Å^3$
Z	1
Calculated density	1.230 Mg/m^3
Absorption coefficient	1.315 mm^{-1}
$F(000)$	580
θ range for data collection	1.68 – 24.82°
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	50725
Independent reflections	5105 [R(int) = 0.0437]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5105 / 0 / 292
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0345, $wR2$ = 0.0878
R indices (all data)	$R1$ = 0.0367, $wR2$ = 0.0891
Largest difference peak and hole	0.920 and -0.633 $e \cdot Å^{-3}$

Table CD4. Crystal data and structure refinement for 8·C_5H_{12}

Empirical formula	$C_{68}H_{104}Al_2N_5O_3$
Formula weight	1093.52
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.128(3) Å
	b = 21.500(4) Å, β = 98.01(3)°
	c = 22.083(4) Å
Volume	6642(2) Å^3
Z	4
Calculated density	1.093 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	2388
θ range for data collection	1.74 – 24.87°
Index ranges	$-16 \leq h \leq 16$, $-23 \leq k \leq 25$, $-26 \leq l \leq 26$
Reflections collected	39741
Independent reflections	11408 [R(int) = 0.1377]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11408 / 2 / 770
Goodness-of-fit on F^2	0.722
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0484, $wR2$ = 0.0935
R indices (all data)	$R1$ = 0.1009, $wR2$ = 0.1035
Largest difference peak and hole	0.254 and -0.252 e·Å^{-3}

Table CD5. Crystal data and structure refinement for 9·C_7H_8.

Empirical formula	$C_{84}H_{134}Al_7N_7$
Formula weight	1430.88
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 13.254(3)$ Å, $\alpha = 82.71(3)°$
	$b = 15.305(3)$ Å, $\beta = 75.80(3)°$
	$c = 20.996(4)$ Å, $\gamma = 75.50(3)°$
Volume	3987.7(14) Å^3
Z	2
Calculated density	1.186 Mg/m^3
Absorption coefficient	0.140 mm^{-1}
$F(000)$	1542
θ range for data collection	1.63 – 24.84°
Index ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 18$, $-24 \leq l \leq 24$
Reflections collected	28395
Independent reflections	12367 [R(int) = 0.0524]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12367 / 0 / 852
Goodness-of-fit on F^2	0.939
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0441$, $wR2 = 0.1194$
R indices (all data)	$R1 = 0.0582$, $wR2 = 0.1241$
Largest difference peak and hole	0.716 and -0.371 e·Å^{-3}

Table CD6. Crystal data and structure refinement for 10·C_7H_8.

Empirical formula	$C_{84}H_{127}Al_7F_{2.26}N_7$
Formula weight	1466.73
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 13.254(3) Å, α = 82.75(3)°
v	b = 15.216(3) Å, β = 75.89(3)°
	c = 21.059(4) Å, γ = 75.38(3)°
Volume	3976.2(14) $Å^3$
Z	2
Calculated density	1.225 Mg/m^3
Absorption coefficient	0.146 mm^{-1}
$F(000)$	1583
θ range for data collection	1.39 – 24.90°
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 17$, $-24 \leq l \leq 24$
Reflections collected	62662
Independent reflections	13754 [R(int) = 0.0858]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13754 / 0 / 879
Goodness-of-fit on F^2	0.829
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0397, $wR2$ = 0.0954
R indices (all data)	$R1$ = 0.0586, $wR2$ = 0.0993
Largest difference peak and hole	0.689 and -0.353 e·$Å^{-3}$

Table CD7. Crystal data and structure refinement for 11·C_7H_8.

Empirical formula	$C_{20}H_{44}Al_4F_4N_4$
Formula weight	524.51
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.5158(16) Å
	b = 13.447(2) Å, β = 91.094(14)°
	c = 17.086(3) Å
Volume	2645.3(8) $Å^3$
Z	4
Calculated density	1.317 Mg/m^3
Absorption coefficient	0.220 mm^{-1}
$F(000)$	1120
θ range for data collection	3.51 – 25.03°
Index ranges	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-20 \leq l \leq 20$
Reflections collected	9300
Independent reflections	4650 [R(int) = 0.0573]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4650 / 0 / 301
Goodness-of-fit on F^2	1.062
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0383$, $wR2 = 0.1019$
R indices (all data)	$R1 = 0.0403$, $wR2 = 0.1043$
Largest difference peak and hole	0.522 and -0.330 e·$Å^{-3}$

Table CD8. Crystal data and structure refinement for 13.

Empirical formula	$C_{41}H_{51}AlN_2$
Formula weight	598.82
Temperature	200(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2/n$
Unit cell dimensions	a = 18.100(4) Å
	b = 12.568(3) Å, β = 100.14(3)°
	c = 31.973(6) Å
Volume	7160(2) Å^3
Z	8
Calculated density	1.111 Mg/m^3
Absorption coefficient	0.086 mm^{-1}
$F(000)$	2592
θ range for data collection	3.53 – 22.53°
Index ranges	$-19 \le h \le 19$, $-2 \le k \le 13$, $-1 \le l \le 34$
Reflections collected	9366
Independent reflections	9365 [R(int) = 0.0930]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9365 / 0 / 814
Goodness-of-fit on F^2	1.152
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0743, $wR2$ = 0.1910
R indices (all data)	$R1$ = 0.1144, $wR2$ = 0.2122
Largest difference peak and hole	0.300 and -0.297 e·Å^{-3}

Table CD9. Crystal data and structure refinement for 14·C_5H_{12}.

Empirical formula	$C_{63}H_{94}Al_2N_4P_4$
Formula weight	1085.26
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_1/n$
Unit cell dimensions	a = 13.8751(7) Å
	b = 14.3627(8) Å
	c = 31.8580(16) Å
Volume	6348.8(6) $Å^3$
Z	4
Calculated density	1.135 Mg/m^3
Absorption coefficient	0.186 mm^{-1}
$F(000)$	2344
θ range for data collection	1.28 – 22.63°
Index ranges	$-12 \leq h \leq 14$, $-15 \leq k \leq 15$, $-34 \leq l \leq 34$
Reflections collected	25400
Independent reflections	8387 [R(int) = 0.0983]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8387 / 0 / 652
Goodness-of-fit on F^2	1.063
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0618$, $wR2 = 0.1372$
R indices (all data)	$R1 = 0.0847$, $wR2 = 0.1490$
Largest difference peak and hole	0.491 and -0.410 $e \cdot Å^{-3}$

Table CD10. Crystal data and structure refinement for 15·2C_7H_8.

Empirical formula	$C_{72}H_{98}Al_2N_4S_6$
Formula weight	1265.86
Temperature	100(2)
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 14.277(1) Å
	b = 16.387(1) Å, β = 109.66(1)°
	c = 15.786(1) Å
Volume	3478(1) Å^3
Z	2
Calculated density	1.209 Mg/m^3
Absorption coefficient	2.386 mm^{-1}
F(000)	1360
θ range for data collection	3.62 – 58.92°
Index ranges	$-15 \leq h \leq 14$, $-17 \leq k \leq 16$, $-17 \leq l \leq 17$
Reflections collected	15352
Independent reflections	4907 [R(int) = 0.0363]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4907 / 0 / 394
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0328, $wR2$ = 0.0836
R indices (all data)	$R1$ = 0.0385, $wR2$ = 0.0868
Largest difference peak and hole	0.619 and -0.263 e·Å^{-3}

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