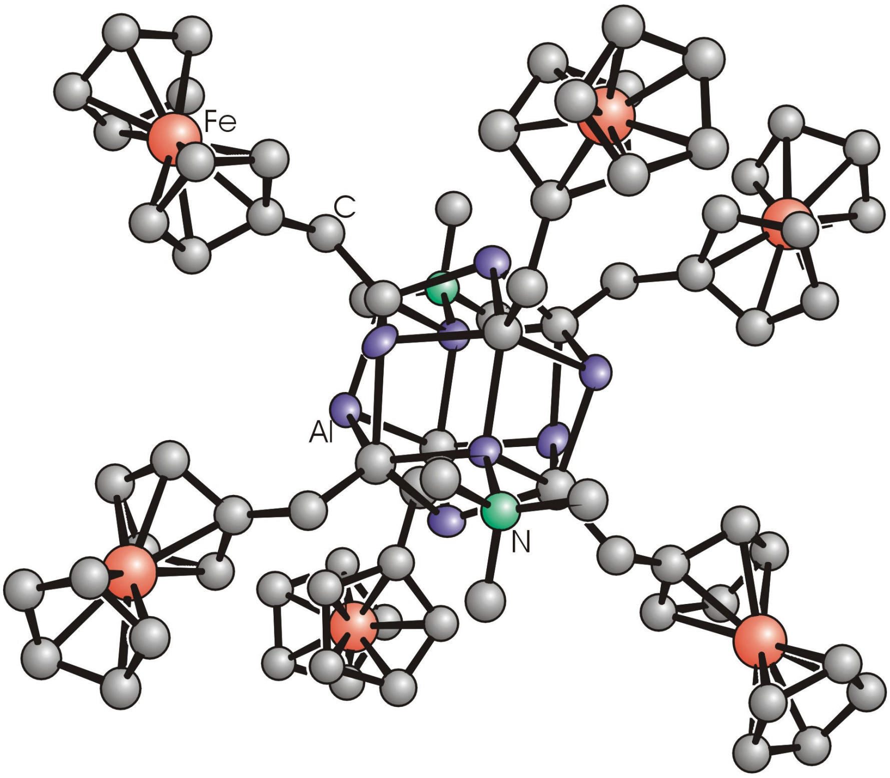
Shravan Kumar Srisailam

SYNTHESIS, STRUCTURAL CHARACTERIZATION AND REACTIVITY OF HOMO- AND HETEROBIMETALLIC IMIDOALANES AND CARBAALANES, ALUMINUM HYDRAZIDE AND ALUMINUM PEROXIDE COMPOUNDS



SYNTHESIS, STRUCTURAL CHARACTERIZATION AND REACTIVITY OF HOMO- AND HETEROBIMETALLIC IMIDOALANES AND CARBAALANES, ALUMINUM HYDRAZIDE AND ALUMINUM PEROXIDE COMPOUNDS

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Dedicated to my parents

for their love and affection

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Abbreviations

av.	average
br	broad
^{i}Bu	*iso*-butyl
^{t}Bu	*tert*-butyl
cis	cisoid
Cp	cyclopentadienyl
CVD	chemical vapor deposition
d	doublet, day
δ	chemical shift
C	Celsius
decomp.	decomposition
Do	donor
EI	electron impact ionization
Et	ethyl
eV	electron Volts
Fc	ferrocenyl
HOMO	highest occupied molecular orbital
IR	infrared
J	coupling constant
L	ligand
K	Kelvin
KHz	Kilo Hertz
η	heptacity

λ	wavelength
LUMO	lowest unoccupied molecular orbital
m	multiplet, medium
M	metal
M^+	molecular ion
m/Z	mass/charge
MAS	magic angle spinning
Me	methyl
MHz	Mega Hertz
M.p.	melting point
MS	mass spectrometry
μ	absorption coefficient, bridging
NMR	nuclear magnetic resonance
$\tilde{v}$	wave number
Ph	phenyl
^{i}Pr	*iso*-propyl
q	quartet
R, R’	organic substituent
rt	room temperature
s	singlet
sept	septet
SAW	sound acoustic wave application
t	triplet
tert	tertiary
trans	transoid

TMS	tetramethylsilane
Z	number of molecules in the unit cell
w	weak

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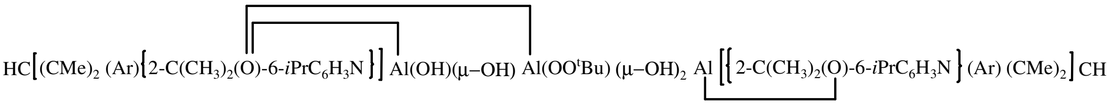


$$HC[(CMe)_2(Ar)\{2\text{-}C(CH_3)_2(O)\text{-}6\text{-}iPrC_6H_3N\}]Al(OH)(\mu\text{-}OH)Al(OO^tBu)(\mu\text{-}OH)_2Al[\{2\text{-}C(CH_3)_2(O)\text{-}6\text{-}iPrC_6H_3N\}(Ar)(CMe)_2]CH$$

1. Introduction

In the last half a century, a significant amount of work was carried out on boron hydride chemistry and a large number of distinct boron hydrides were identified, characterized[1-3] and employed.[4,5] Hydroboration of unsaturated systems like linear and branched alkenes using borane leads not only to the formation of mono-, di- or trialkylboron species but also plays an effective role in the synthesis of many enantiomerically pure natural products. Controlled hydroboration to synthesize mono-, di-, and trialkyl boranes can be carried out under extremely mild conditions as well as by using sterically hindered alkenes. The chirality present in the alkylboron compounds can be induced in the synthesis of natural products. In hydroboration reactions the electrophilic nature of the reagent used, stoichiometry and the regio- and the stereoselectivity play a vital role. Moreover, the boron-hydrogen bond not only adds effectively to the alkenes and acetylenes but also to the carbon-oxygen double and carbon-nitrogen double and triple bonds. However, the hydrides of group 13 metals (Al, Ga and In) are considerably less documented. It is noteworthy to observe that although AlH_3 has been known for almost 60 years[6] it is limited only to the nonvolatile, polymeric and solid trihydride $(AlH_3)_n$ compound under normal conditions,[3,7,8] whereas the GaH_3 has only been well characterized in the last decade.[9] Nonetheless, in recent years there has been a gradual upsurge in this area due to various aspects of their chemistry and applications.[10-16]

The field of aluminum hydride chemistry improved when Stecher and Wiberg synthesized AlH_3 as an impure solid in 1942.[6] It was obtained by thermolysis of crystalline $AlH_3{\cdot}NMe_3$, which itself was obtained by fractional crystallization of NMe_3 solution of the residue from glow-discharge reactions of mixtures of $(Me_3Al)_2$ and H_2. Subsequently, the synthesis of $LiAlH_4$ by Schlesinger[17] introduced aluminum hydrides as new, powerful reducing agents for organic and inorganic chemistry. The selectivity of the desired product could be modified by substituting some of the hydrides on aluminum by amides, alkoxides, alkyls, aryls etc. Similar to the hydroboration reactions, the electrophilic nature of the reagent drives the mode of addition to the alkene and acetylene systems. Although there has been wide application of hydroboration reactions, only recently the corresponding hydroalumination reactions have found application both in industry as well as in the academics.[18-24] Following sections describes about the development of imidoalanes, carbaalanes, aluminum hydrazides and (alkylperoxo)aluminum chemistry.

1.1. Imidoalanes

The bonding between the group 13 and 15 elements has received considerable interest as their properties are comparable to the isoelectronic carbon group 14 element derivatives. Group 13 metal nitrides AlN,[25] GaN[26] and InN, as well as their alloys $Al_xGa_yIn_{1-x-y}N$[27] can be used for micro- and optoelectronic devices[28-35] whose physical and chemical properties depend on their purity as well as on their composition. Among all the group 13 metal nitrides, aluminum nitride is considered to be one of the best electrical insulators for microelectronic applications.[36-40] Imidoalanes and amidoalanes were studied extensively as they are potential precursor for the chemical vapor deposition of aluminum nitride.[41-44] They are also very important from the academic point of view due to their complex structural features.[45-52] They received much less attention[53] in comparison to the analogous boron nitrogen compounds despite of their importance as active polymerization co-catalyst.[54]

Compounds containing Al–N bonds have been investigated[53-55] and employed in catalysis,[56] as reducing agents[57-59] and as synthetic intermediates.[60-62] Monomeric amidoalanes were investigated by Sheldrick et al.[63] and by Power and co- workers.[64,65] The di- and tri-meric amidoalanes were synthesized by decomposition of molecular species under elimination of hydrogen or organic substituents.[66] Besides neutral compounds, anionic,[67,68] and cationic[69,70] complexes are known and they are of interest from the perspective of multiple bonding between aluminum and nitrogen. Amidoalanes can serve as the precursors for the preparation of imidoalanes $(RAlNR')_n$, formed by alkane elimination in amidoalanes due to the presence of N–H and Al–R units. The thermolysis of amidoalanes results in the formation of interesting imidoalanes and the degree of association, which leads to the formation of rings,[46,71] chains,[72] cubes and complex cages[51,69] depends largely on the bulkiness of the R and R' groups present on the aluminum and nitrogen atoms. Few amidoalanes like *trans*-$[Me_2Al(\mu\text{–}NHMes^*)]_2$ ($Mes^* = 2,4,6\text{–}{}^tBu_3C_6H_2$) undergo orthometalation instead of methane evolution due to the presence of the bulky *tert*-butyl group at the ortho position and intramolecular condensation via C–H bond activation.[73]

Polyaluminum imidoalane was first synthesized by Wiberg and May[74] when the reaction was carried out between equimolar amounts of aluminum trihydride and methylamine in diethylether/dioxane to yield an insoluble polymeric substance $(HAlNR)_n$. Laubengayer et al. synthesized these frameworks from (a) methylamine hydrochloride and triethylaluminum, (b) methylamine and diethylaluminum chloride and (c) triphenylaluminum and methylamine or dimethylamine respectively.[75,76] Fetter et al.[77] prepared imidoalanes from hydrazine and trimethylamino alane and Paterson and Onyszchuk[78] from hydrazine and aluminum trichloride. The work with the hydrazine-aluminum compounds was hampered by their shock sensitivity. Woods and McCloskey[79] reported the substituted imidoalanes by the reaction of triethylaluminum and borazines but the polymeric materials were not examined. Later, Ehrlich and co-workers[80] prepared compounds containing aluminum-nitrogen backbones by the reactions of (a) trialkylamino alane with ethylamine, acetonitrile or ethyleneamine or (b) lithiumtetra hydroaluminate with ethylamine hydrochloride. The first structurally characterized tetramer $(PhAlNPh)_4$ was reported in 1963[81] and thereafter imidoalanes involving tetramers,[82] hexamers,[47,83-85] heptamers,[86] and an octamer[84] having four coordinated aluminum and nitrogen centers were reported.[51,87] Lower aggregates $(CpAlNAr)_2$ (Cp = C_5H_5; Ar = 2,6–$^iPr_2C_6H_3$),[88] $(Mes^*AlNPh)_2$ (Mes* = 2,4,6–$^tBu_3C_6H_2$),[89] and $(RAlNR')_3$ (R = Me; R' = 2,6–$^iPr_2C_6H_3$)[45,90] are also known where both the aluminum and nitrogen atoms are three coordinated. Power et al. recently described a monomeric imidoalane RAlNR' (R = HC{(2,6–$^iPr_2C_6H_3N$)(CMe)}$_2$; R' = 2,4,6–$^iPr_3C_6H_2$)[91] with both the aluminum and nitrogen having the coordination number two.

1.2. Carbaalanes

It is known that the carboranes or carbaboranes[92-95] are compounds having carbon (C) and boron (B) as the basic structural unit, which are arranged on the vertices of triangulated polyhedron. These compounds are in general synthesized by the reaction of polyboranes and unsubstituted or substituted acetylenes where one or more boron atoms are replaced by the carbon atoms.[94] They obey the electronic rules given for boranes and are known in *closo*, *nido* and *arachno* structures. In each carborane B–H and C–H group donates two and three electrons to the framework respectively. The replacement for a BH fragment i.e., a species which can provide three orbitals and two electrons similar to BH or the replacement for a CH fragment by a species which has three orbitals and three electrons by the isolobal fragments of the main group and the transition metals leads to the formation of interesting metallacarborane derivatives.

Quite contrary to these boron polyhedral compounds, only few examples in the area of aluminum chemistry have been reported. The polyhedral aluminum cluster $[Al_{12}{}^iBu_{12}]^{2-}$ (**1**) was first isolated by Uhl et al. in low yield. It was synthesized by the reduction of di(isobutyl)

-aluminum chloride with elemental potassium.[96]

Carbaalanes were inferred for the first time by Wilke and Schneider[97] by hydroalumination reactions involving trialkylaluminum or dialkylaluminum hydrides with dialkylaluminum acetylides but they did not succeed in isolating and characterizing polyhedral carbaalanes. They proposed ‘pseudo-alumino-adamantane’ and ‘alumino-adamantane’ kind of structures for these compounds. Only recently the field of polyaluminum chemistry became the subject of detailed research and in this pursuit Uhl and co-workers reported for the first time structurally characterized polyhedral carbaalane $[(AlMe)_8(CCH_2Ph)_5H]$ (**2**) by carrying out the hydroalumination reaction between excess of dimethylaluminum hydride and dimethylaluminum phenylacetylide.[98,99] It was formed by the repeated hydroalumination of the aluminum acetylide and by the condensation reaction with the simultaneous release of trimethylalane. The bridging hydrogen atom was introduced by a hydroalumination step with $MeAlH_2$, which is formed by dismutation of Me_2AlH. When dimethylaluminum phenylacetylide was treated with Me_2AlH in 1:2 molar ratio under less drastic conditions $[(AlMe)_8(CCH_2Ph)_5(C{\equiv}CPh)]$ (**3**) was isolated.[100] Similarly, treatment of diethylaluminum phenylacetylide with slight excess of diethylaluminum hydride yielded $[(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H]$ (**4**),[101] which was transformed to $[(AlEt)_8(CCH_2Ph)_5H]$ (**5**) [100] and $[(AlEt)_7(CCH_2Ph)_4(C{\equiv}CPh)H]$ (**6**).[101] This approach was followed also on aliphatic derivatives to generate $[(AlMe)_8(CCH_2Me)_5H]$ (**7**),[102] the THF adduct $[(AlMe)_8(CCH_2Me)_5H]\cdot 2THF$ (**8**),[102] $[(AlMe)_7(CCH_2Me)_4H_2]$ (**9**)[100] and $[(AlMe)_8(CCH_2Me)_5(C{\equiv}CMe)]$ (**10**).[102] In addition to the synthesis of these carbaalanes, they were functionalized with halides in the synthesis of $[(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3(\mu_3{-}F)]$ (**11**) and $[(AlCl)(AlMe)_7(CCH_2Ph)_5H]$ (**12**).[103]

1.3. Heterobimetallic clusters containing aluminum

Compounds containing multi-metallocenyl assemblies especially multi-ferrocenyl assemblies[104,105] have gained importance in recent years due to their chemical, electrical, optical and magnetic properties. These compounds are electron-rich and can be considered as efficient material for the modification of electrodes, ion sensors, or as materials for electronic devices.[106-108] Although most work has been undertaken to understand the redox properties of ferrocene containing dendrimers[109-112] only recently transition metal containing aluminum compounds have gained attention as they can serve as the single source precursor for the mixed-metal thin films.[113,114] Moreover, organometallic complexes containing certain combinations of main group elements and transition metals in the same molecular unit are of interest due to the different reactivities of the metal centers as well as their relationship toward materials and solid state chemistry. This kind of molecules reported involve either direct bonds between the metals[115-118] or are bridged by a spacer in M–X–M species,[119-126] where X is O, NR, or PR. CO as a spacer group is not an ideal choice for the thin film deposition due to the contamination by C and O by the dissociation of the CO unit. Obtaining transition metal containing thin films via Al–C bond cleavage was also discouraged as it leads to contamination by hydrocarbon impurities of the film due to incomplete Al–C cleavage. Only few compounds with direct transition metal-aluminum bonds were reported.[115-118,127,128] Fischer and Priermeier[127] reported M–Al bond formation by salt elimination reactions. For example, the reaction between the aluminum halide compounds $X–Al[(CH_2)_3NMe_3](R)$ and $Y–Al(X_2)(Do)$ (X, Y = H, Cl, Br; R = Cl, Br, ^iBu, $CH_2{}^tBu$; Do = NMe_3, quinuclidine, THF) and $[L(CO)_nM][K]$ (M = Fe, Ru, Co; L = CO, PMe_3, $\eta^5–C_5H_5$; n =1-3) gave transition metal–aluminum bonds containing molecules $L(CO)_nM–Al[(CH_2)_3NMe_3](R)$ and $L(CO)_nM–Al(X_2)(Do)$.

1.4. Aluminum hydrazides

Until now much of the aluminum structural chemistry was focused on the synthesis of amidoalanes and imidoalanes as they have shown to be suitable precursor for aluminum nitride,[41-44] which in combination with CVD formed diamond film is a promising piezoelectric material for acoustic wave (SAW) application.[129] Fetter et al. [77,130] reported the reaction between hydrazine and trimethylamine alane but were unsuccessful in the synthesis of aluminum hydrazides. Further work with hydrazine-aluminum compounds was hampered by their shock sensitivity. Only in the past few years there has been a gradual upsurge in the synthesis of hydrazine derivatives of aluminum[131-146] as they can be considered as potential precursor not only in the formation of aluminum and nitrogen containing rings and cages[131-135] but also in the formation of aluminum nitride by CVD methods or by thermolysis of macroscopic samples. The hydrazine derivatives have been prepared either by treatment of hydrazines with trialkylaluminum compounds, which eliminates alkanes[131,133,139,140] or by reactions of hydrazines with dialkylaluminum hydrides[134] or $LiAlH_4$,[136] which eliminates hydrogen. Furthermore, they can be prepared by reactions of lithiated hydrazines with dialkylaluminum chlorides[136,137] or by hydroalumination of azobenzene with an arylaluminum dihydride.[138] The above methods have been employed to obtain aluminum hydrazides in higher yields and they have been found to be relatively stable even at higher temperatures and moreover no hazardous properties were reported. As mentioned above, these hydrazides due to their bidentate nature adopt different geometries. Dialkylaluminum hydrazides having terminal hydrazido groups exist as monomers in the presence of ether molecules or hydride ions due to the saturation of fourth coordination of aluminum atom. In the absence of the Lewis bases dimers containing a four-membered Al_2N_2,[131,132,137,139,141] five-membered Al_2N_3,[138] and a six-membered Al_2N_4 heterocycle[136,140,145] are formed. These dimers exist not only as *cis* and *trans* isomers (Al_2N_2) but also adopt *chair*- and *twist-boat* conformations (Al_2N_4) and the five-membered (Al_2N_3) heterocycle has one endo- and one exocyclic N–N bond.

1.5. (Alkylperoxo)aluminum compounds

Considerable work has been reported on transition metal peroxo compounds, but organoperoxo aluminum compounds have received much less attention as they are highly unstable due to the high reactivity of R–O–O–Al group with respect to carbon-aluminum bond and in most cases aluminum alkoxides are formed.[147] Alkylperoxo aluminum compounds are postulated as intermediates in the oxidation of organoaluminum compounds.[148,149] There are few reports where organic peroxides were employed directly on aluminum alkyls to prepare alkylperoxo aluminum compounds but they were not structurally characterized and in general they decomposed. A monomeric aluminum peroxide $ROOAl(OEt)_2$ (R = cumyl, ^tBu) was reported by Anisimov et al. from the reaction of cumyl and *tert*-butyl hydroperoxide with diethoxyaluminum chloride in the presence of ammonia.[150] Dimeric $PhC(Me)_2OOAl(OEt)_2$ was obtained by Razuvaev et al. from diethoxyaluminum chloride with sodium salt of cumyl hydroperoxide.[151] Similarly, Davies and Hall synthesized tris(decahydro-9-naphthylperoxy)aluminum from decahydro-9-naphthyl hydroperoxide and aluminum *tert*-butoxide, which decomposed after the removal of solvent.[147] Pasynkiewicz et al. observed the rearrangement of unstable $PhC(Me)_2OOAlCl_2$ to $PhOAlCl_2 \cdot O{=}C(Me)_2$ when methylaluminum dichloride was treated with cumyl hydroperoxide in 1,2-dimethoxyethane.[152]

In addition to the direct treatment of aluminum alkyls with organic peroxides, attempts were made to synthesize alkylperoxo aluminum compounds by investigating the interaction of dioxygen and aluminum alkyls. A complex mixture of aluminum alkoxides was obtained when aluminum alkyls were treated with dioxygen.[148] Only recently alkylperoxo gallium and indium compounds $\{[({}^tBu)_2M(\mu\text{–}OO{}^tBu)]_2$; M = Ga,[153] In[154]$\}$ were successfully isolated by carrying out the autoxidation reactions on gallium and indium alkyls. A similar reaction with $Al{}^tBu_3$ resulted in the formation of $[({}^tBu)_2Al(\mu\text{–}O{}^tBu)]_2$.[155] These reactions proceed via interaction of molecular oxygen and three-coordinated metal alkyls. In 1996 Lewiński et al. isolated and characterized the first alkylperoxo aluminum compound $[({}^tBuOO)({}^tBuO)Al(\mu\text{–}O{}^tBu)_2Al(mesal)_2]$ by the oxidation of di-*tert*-butylaluminum compound $({}^tBu)_2Al(mesal)$ (mesal = methyl salicylate), which contains a four- and six-coordinated aluminum center.[156,157] Its formation was described to proceed via an intermediate penta-coordinated aluminum center.[157b]

1.6. Objectives of this work

Polyaluminum compounds have gained importance as they are efficient chelating Lewis acids in phase transfer processes or in the recognition of anions.[158] In retrospect of their utility, hydroalumination reactions have gained significance. On the basis of the aforementioned discussion in the sections **1.1 - 1.5** we can say that the Al–H bond containing compounds are very important in the synthesis of aluminum-nitrogen containing imidoalanes and aluminum-hydrazide compounds, aluminum-carbon containing carbaalanes and alkylperoxo aluminum compounds having aluminum-oxygen bonds.

The objective of the present work was (a) to demonstrate the facile synthesis of imidoalanes by carrying out hydroalumination reaction with nitriles, (b) to synthesize and structurally characterize carbaalanes obtained by hydroalumination reactions of mono-substituted acetylenes and metalacetylide, (c) to fix transition metal containing ligands on both imidoalane and carbaalane, and study their electrochemical behavior, (d) to explore the reactivity of Al–H bonds toward hydrazine derivatives in the synthesis of aluminum-hydrazide compounds, and (e) to synthesize alkylperoxo aluminum compounds by treating organic peroxides directly with Al–H bond containing compounds.

2. Results and Discussion

2.1. Imidoalanes

The reduction of nitriles by aluminum hydride was first reported in 1957[159-161] and is a well known procedure in organic synthesis but intermediates have not been isolated. Cucinella et al. have synthesized and reported the crystal structures of few polyaluminum imidoalanes by treating alkylamines with trimethylamine adduct of aluminum trihydride or an amine hydrochloride with lithium aluminum hydride[162] but could not structurally characterize the imidoalanes obtained from the reaction between nitrile and $AlH_3 \cdot NMe_3$ in diethylether as shown in reaction 3 (Scheme 1). Wehmschulte and Power reported the orthometalated dimers, *cis*- and *trans*-$[\overline{AlC_6H_2\text{-}2,4\text{-}{}^tBu_2\text{-}6\text{-}CMe_2\text{-}C}H_2\{\mu_2\text{-}N(H)CH_2R\}]_2$ when the bulky alane $[Mes^*AlH_2]_2$ ($Mes^* = 2,4,6\text{–}{}^tBu_3C_6H_2$) was reacted with the nitriles RCN (R = Me, ^{t}Bu, Mes) instead of an imidoalane. One of the *tert*-butyl groups present on the Mes* undergoes orthometalation and the nitriles were reduced to an amide ligand (Scheme 2). They also described the reactions with the isonitriles, H_2NCH_2Mes and H_2NSiPh_3.[163]

Scheme 1

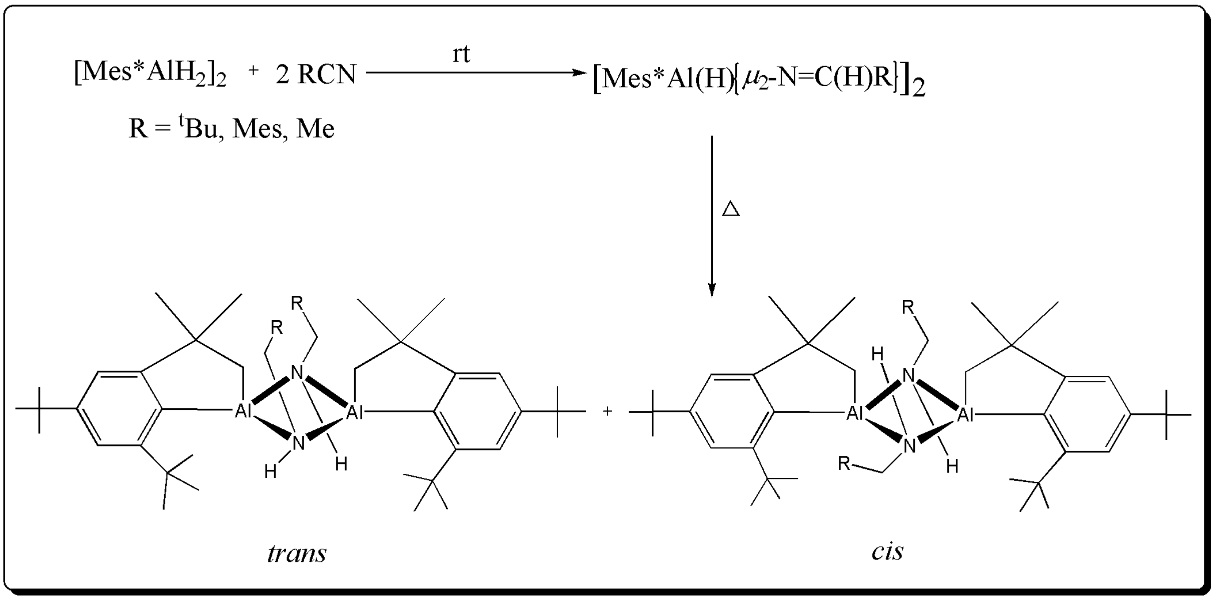
$$AlH_3 \cdot NMe_3 \quad + \quad RNH_2 \xrightarrow{Et_2O} (HAlNR)_n + H_2 + NMe_3 \qquad (1)$$

$$LiAlH_4 \quad + \quad RNH_2 \cdot HCl \xrightarrow{Et_2O} 1/n(HAlNR)_n + H_2 + LiCl \qquad (2)$$

$$AlH_3 \cdot NMe_3 \quad + \quad RCN \xrightarrow{Et_2O} 1/n(HAlNCH_2R)_n + H_2 + NMe_3 \qquad (3)$$

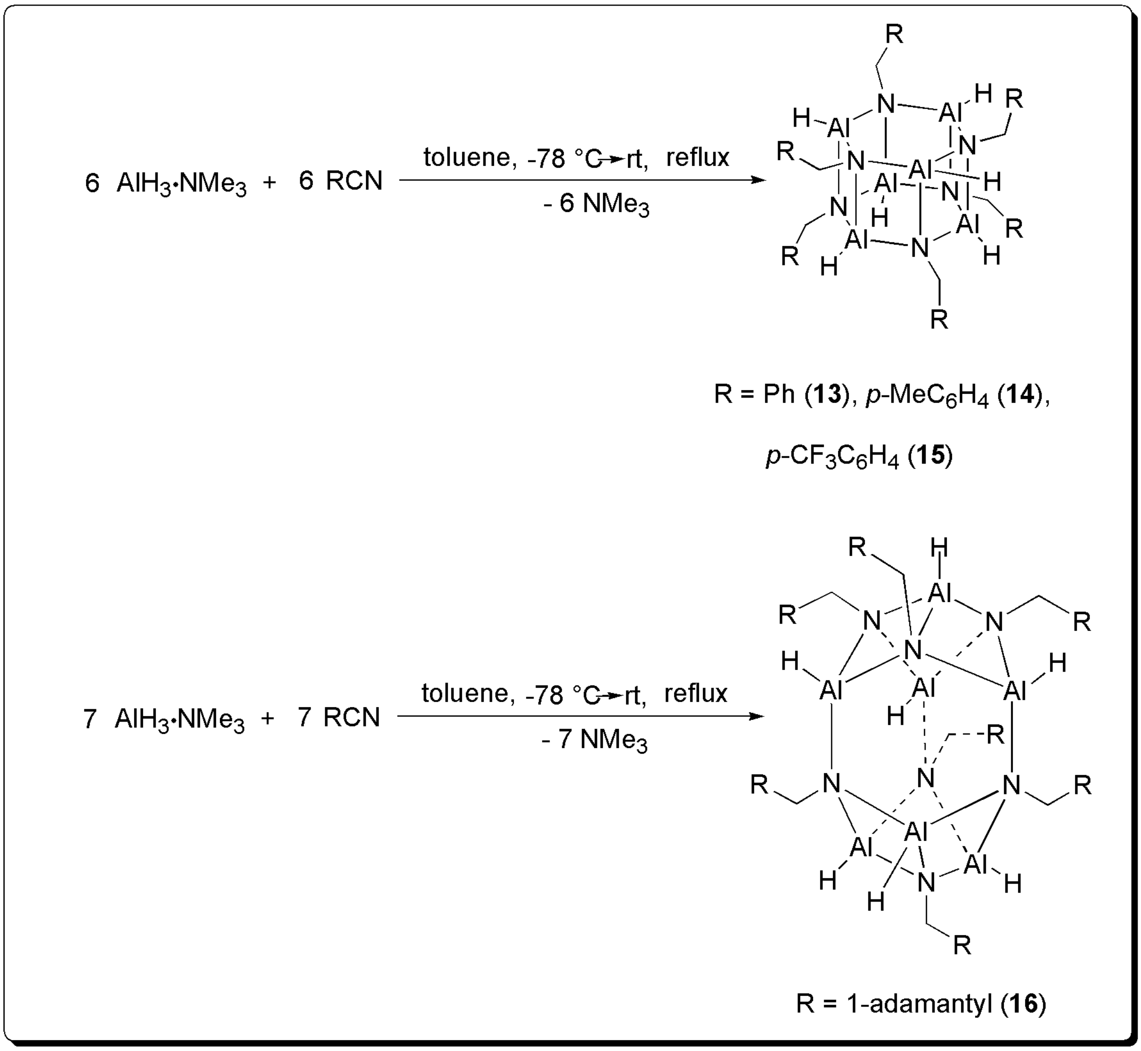
Roesky et al.[164-166] demonstrated the facile synthesis and structural characterization of the hexameric imidoalanes $[HAlNCH_2R]_6$ (R = Ph (**13**), p–MeC_6H_4 (**14**), and p–$CF_3C_6H_4$ (**15**)[164]) and the heptameric imidoalane $[HAlNCH_2R]_7$ (R = 1–adamantyl (**16**)[165])

Scheme 2



by the treatment of PhCN, *p*–MeC_6H_4CN, *p*–$CF_3C_6H_4CN$ and 1–adamantylnitrile, respectively with a slight excess of trimethylamine adduct of aluminum trihydride (Scheme 3). Addition of $AlH_3{\cdot}NMe_3$ to the respective nitrile in toluene at –78 °C and refluxing the resulting solutions until the evolution of NMe_3 had ceased gave the imidoalanes **13** - **16**. The mechanism of the reaction was studied on the basis of IR and NMR spectral analysis on **13** and it is not yet understood completely. A pale yellow product that was obtained when $AlH_3{\cdot}NMe_3$ was added to PhCN at room temperature showed two absorptions (1653 cm^{-1} and 1791 cm^{-1}) corresponding to the ν(C=N) and ν(Al–H) in addition to the absorptions of **13**. In the ^1H NMR spectrum three doublet resonances (δ 7.31, 7.41, and 7.65 ppm) assignable to an unsaturated intermediate species, $PhCH{=}N{-}AlH_2{\cdot}NMe_3$ were observed in the lowfield region along with the multiplet related to **13** (δ 7.14 ppm) and they diminish at 30 °C. Upon heating formation of the imidoalane **13** takes place followed by the elimination of NMe_3.

Scheme 3



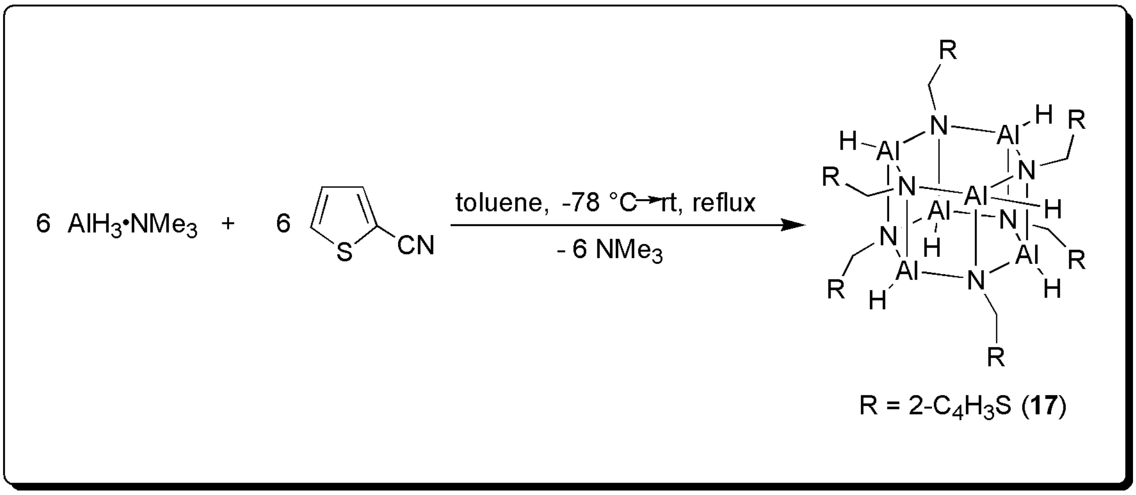
R = Ph (**13**), *p*-MeC$_6$H$_4$ (**14**), *p*-CF$_3$C$_6$H$_4$ (**15**)

R = 1-adamantyl (**16**)

2.1.1. Synthesis of the hexameric imidoalane [HAlNCH$_2$(C$_4$H$_3$S)]$_6$ (17)

An interesting feature of the structure of **13** is the orientation of the benzyl groups. Three of them are aligned in one direction while the remaining three are projected in another direction. This observation prompted us to take up the task of synthesizing a hexadentate, tridentate on each side of the cluster core, hexameric imidoalane and we have chosen 2-cyanothiophene for this purpose. Addition of a slight excess of AlH$_3$·NMe$_3$ to 2-cyanothiophene in toluene at –78 °C and refluxing the resulting solution until the evolution

Scheme 4



of NMe_3 had ceased gave colorless crystals of $[HAlNCH_2(C_4H_3S)]_6$ (**17**) in good yield (Scheme 4).[167] Varying the stoichiometry of the reactants drastically decreased the yield. Six thienyl groups dangling over the Al–N network make **17** hexameric. A thorough literature search on this type of compounds having donor atoms revealed one hexameric imidoalane with six NMe_2 groups.[168]

Compound **17** was fully characterized by means of mass, IR, NMR spectra and elemental analysis data. It has a melting point of 238 - 240 °C. Under electron impact ionization, the cluster core of the hexameric imidoalane remained intact and a molecular ion peak was observed at *m/z* 834. The smaller fragments observed are due to the loss of thienyl groups. A strong absorption band at 1860 cm^{-1} in the IR spectrum of **17** can be attributed to ν(Al–H).[169-170] The absence of any ν(C≡N) frequency indicates the complete hydroalumination of the 2-cyanothiophene. The ^1H NMR spectral data of **17** is in agreement with the X-ray crystal structure. A single resonance was observed for the methylene protons (CH_2) at δ 4.31 ppm. The protons present on the thienyl ring resonate between δ 6.74 and 7.04 ppm. In the ^{13}C NMR spectrum the methylene carbon atoms (CH_2) resonate at δ 44.07 ppm.

2.1.2. X-ray crystal structure of [HAlNCH$_2$(C$_4$H$_3$S)]$_6$ (17)

The molecular structure of [HAlNCH$_2$(C$_4$H$_3$S)]$_6$ (**17**) in the solid state was determined by X-ray crystal structure analysis on colorless crystals obtained from a saturated toluene solution at ambient temperature. Compound **17** crystallizes in the trigonal space group $R\overline{3}$ with one sixth of the molecule in the asymmetric unit. An ORTEP plot of **17** is shown in Figure 1.

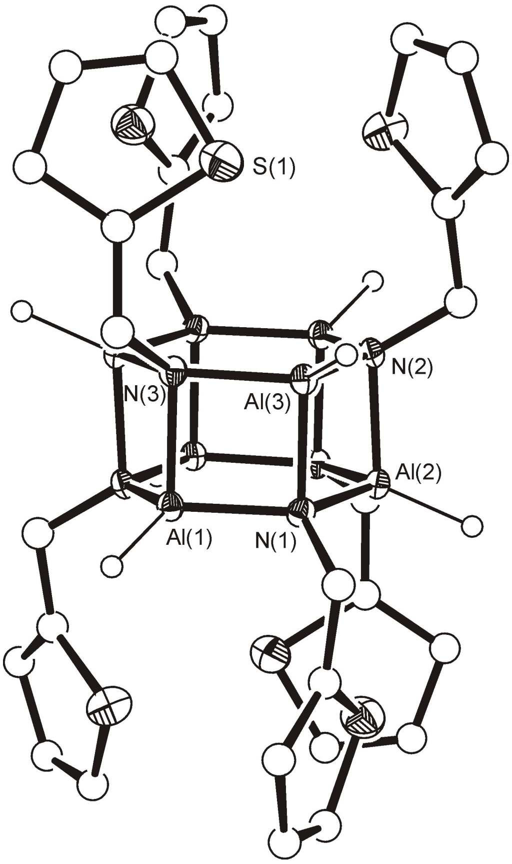


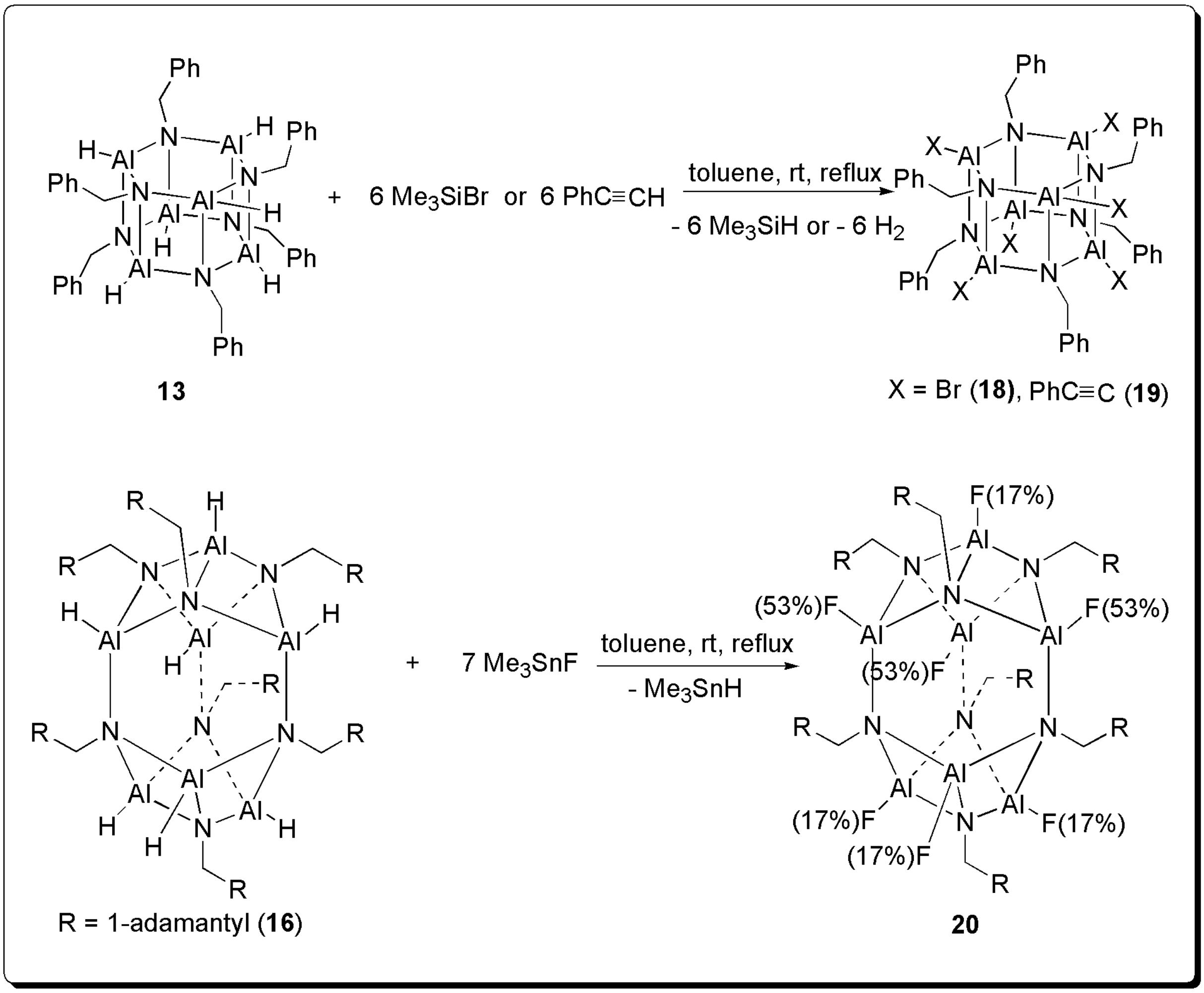
Figure 1*. Crystal structure of compound [HAlNCH$_2$(C$_4$H$_3$S)]$_6$* (**17**) *with 50 % ellipsoid probability. All hydrogen atoms except those on Al are excluded for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Al(1) 1.892(3), N(3)–Al(1) 1.974(3), N(3)–Al(3) 1.894(3); N(3)–Al(1)–N(1) 90.83(13), N(3)–Al(3)–N(1) 90.89(13), N(3)–Al(3)–N(2) 115.38(15), Al(1)–N(1)–Al(2) 124.33(15), Al(1)–N(1)–Al(3) 89.00(12), Al(1)–N(3)–Al(3) 88.94(12).*

The central core of the structure is comprised of an Al–N network containing six aluminum atoms and six nitrogen atoms in alternate positions forming a hexagonal prism. The hexagonal prism is made of two six-membered $(AlN)_3$ rings, which are interlinked by Al–N bonds. As studied earlier,[164] the interlinking Al–N bond distances (Al(1)–N(3) 1.974(3) Å) are longer than the covalent Al–N ones (Al(1)–N(1) 1.892(3) Å) present within the six-membered rings. Three of the six thienylmethylene groups dangling over one of the hexagonal faces of the polyhedron are oriented in one direction while those on the other hexagonal face are oriented in the opposite direction. The thienyl rings are oriented in such a way that the sulfur atoms are slightly tilted toward the center of the respective six-membered rings.

2.2. Reactivity of 17 toward Me_3SiX (X = Br, Cl)

The reactivity of the Al–H bonds on compounds **13** and **16** was studied by Roesky et al. by treating **13** and **16** with nucleophilic reagents like Me_3SiBr, PhC≡CH and Me_3SnF, respectively.[164,165] The hydrides in compound **13** were replaced by bromide and phenylacetylide groups by carrying out reactions with Me_3SiBr and PhC≡CH to give $[BrAlNCH_2Ph]_6$ (**18**) and $[PhC{\equiv}CAlNCH_2Ph]_6$ (**19**) whereas reaction between a stoichiometric amount of Me_3SnF and the heptameric imidoalane **16** in refluxing toluene gave a partially substituted compound $[(1\text{–adamantyl}CH_2NAl)_7H_{4.74}F_{2.26})]$ (**20**)[165] (Scheme 5).

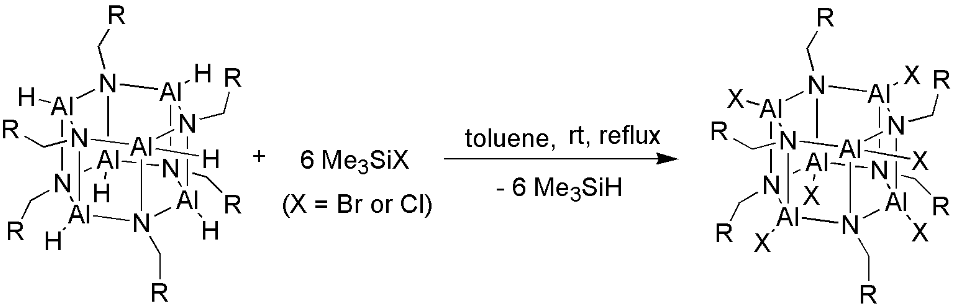
Scheme 5



2.2.1. Synthesis of $[BrAlNCH_2(C_4H_3S)]_6$ (21) and $[ClAlNCH_2(C_4H_3S)]_6$ (22)

In order to further explore the reactivity of Al–H bonds in compound **17** metathesis reactions were carried out by the treatment with the nucleophilic reagents Me_3SiBr and Me_3SiCl. Treatment of **17** with an excess of Me_3SiBr or Me_3SiCl in toluene under refluxing conditions resulted in the formation of $[BrAlNCH_2(C_4H_3S)]_6$ (**21**) and $[ClAlNCH_2(C_4H_3S)]_6$ (**22**), respectively. In both the reactions the color of the reaction mixture changed to light yellow and it sustained during the course of the reaction. Compounds **21** and **22** were the only isolable products of the respective reactions (Scheme 6).[167]

Scheme 6



R = 2-C_4H_3S (**17**)

R = 2-C_4H_3S, X = Br (**21**), Cl (**22**)

Compounds **21** and **22** were fully characterized by means of mass, IR, NMR spectra and elemental analysis data. They have a melting points of 284 - 287 °C and 218 - 223 °C, respectively. The EI mass spectra of **21** and **22** showed molecular ion peaks at *m/z* 1308 and 1040, respectively. The absence of Al–H stretching frequencies in the IR spectra of both compounds indicates complete substitution. NMR spectra of compounds **21** and **22** could not be recorded due to their poor solubility.

2.2.2. X-ray crystal structure of [BrAlNCH$_2$(C$_4$H$_3$S)]$_6$ (21)

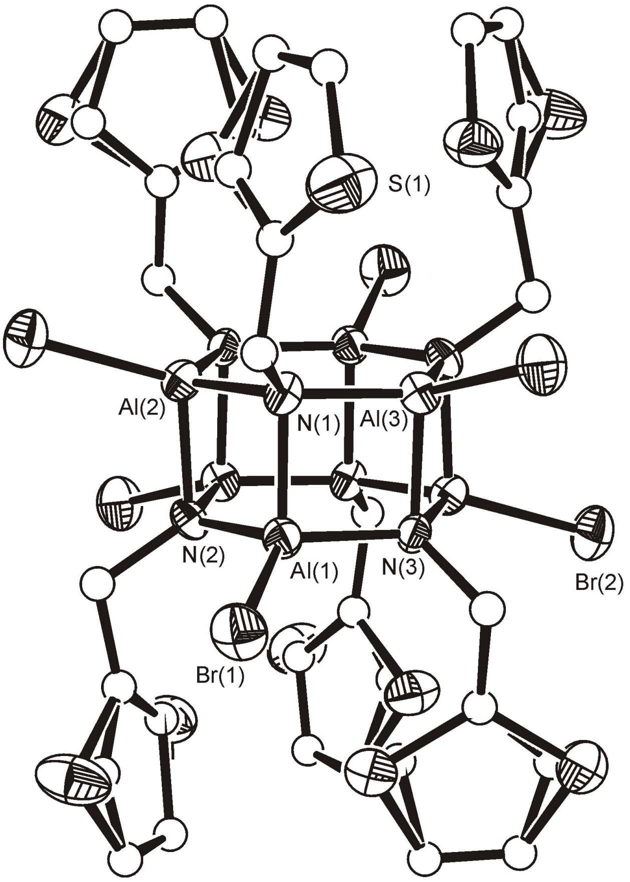


***Figure 2**. Crystal structure of compound [BrAlNCH$_2$(C$_4$H$_3$S)]$_6$* (**21**) *with 50 % ellipsoid probability. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Al(1) 1.963(8), N(1)–Al(2) 1.873(8), N(1)–Al(3) 1.876(8), Al(1)–Br(1) 2.253(3); Al(1)–N(3)–Al(3) 88.6(3), Al(2)–N(1)–Al(3) 124.7(4), Al(3)–N(1)–Al(1) 88.5(3), N(3)–Al(1)–N(1) 91.2(3), N(3)–Al(1)–N(2) 114.8(4), N(3)–Al(3)–N(1) 91.3(3), Br(1)–Al(1)–N(1) 111.0(2), Br(1)–Al(1)–N(3) 119.3(3).*

Single crystals of **21** suitable for an X-ray diffraction analysis were grown from saturated solution in toluene at 0 °C. Compound **21** crystallizes in the cubic space group $Pa\bar{3}$ with one sixth of the molecule in the asymmetric unit. An ORTEP plot depicting the spatial arrangement of the atoms in compound **21** is shown in Figure 2. The orientation of the thienyl groups is similar to that of **17**. Comparison of bond parameters reveals that the cluster core of compound **21** is similar to that of **17** and the cage structure is not disturbed by the presence of large bromine atoms. The sulfur atom of the thienyl group is disordered with an occupancy of 0.628(12).

2.2.3. X-ray crystal structure of $[ClAlNCH_2(C_4H_3S)]_6$ (22)

From a saturated solution in toluene at 0 °C single crystals of $[ClAlNCH_2(C_4H_3S)]_6$ (**22**) suitable for X-ray crystal structural analysis were obtained. Compound **22** crystallizes in the triclinic space group $P\bar{1}$ with one half of the molecule in the asymmetric unit. An ORTEP plot depicting the spatial arrangement of the atoms in compound **22** is shown in Figure 3. The bond parameters and the orientation of the thienyl groups are similar to that of the starting material **17**. The sulfur atom of the thienyl group is disordered with an occupancy of 0.719(4).

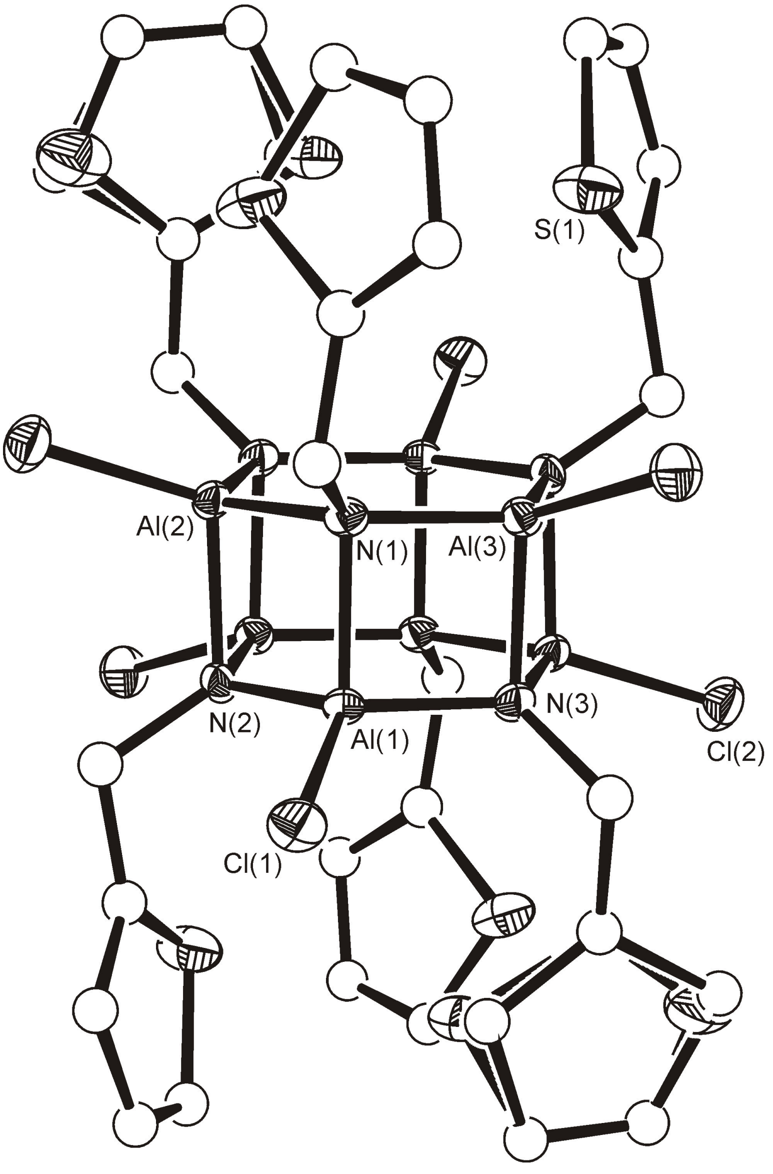


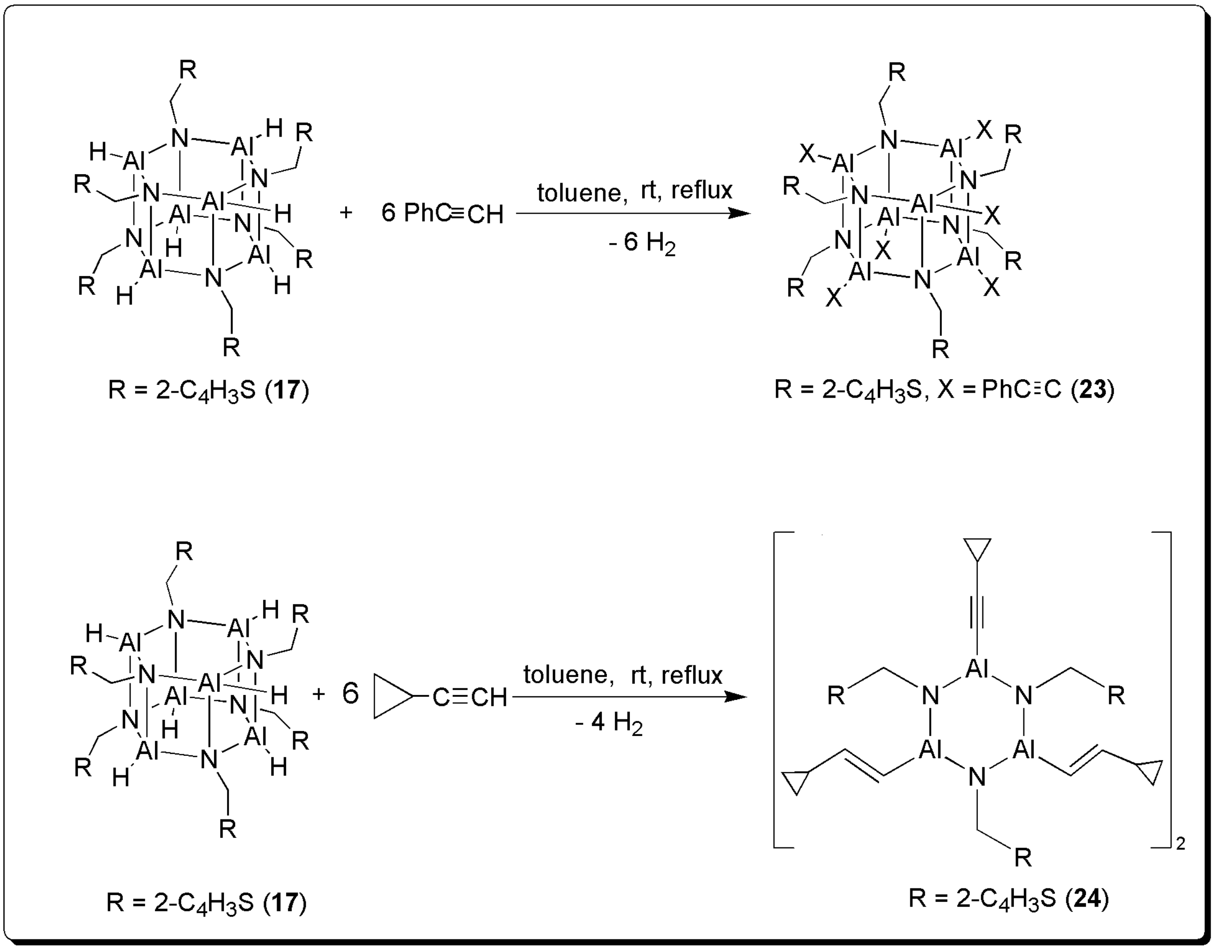
***Figure 3**. Crystal structure of compound* $[ClAlNCH_2(C_4H_3S)]_6$ (**22**) *with 50 % ellipsoid probability. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Al(1) 1.972(3), N(1)–Al(2) 1.880(3), N(1)–Al(3) 1.884(3), Al(1)–Cl(1) 2.099(1); Al(1)–N(3)–Al(3) 88.41(12), Al(2)–N(1)–Al(3) 124.64(15), Al(3)–N(1)–Al(1) 88.42(11), N(3)–Al(1)–N(1) 91.47(12), N(3)–Al(1)–N(2) 115.67(12), N(3)–Al(3)–N(1) 91.80(13), Cl(1)–Al(1)–N(1) 112.38(9), Cl(1)–Al(1)–N(3) 118.75(9).*

2.3. Reactivity of 17 toward PhC≡CH and $C_3H_5C{\equiv}CH$

2.3.1. Synthesis of $[PhC{\equiv}CAlNCH_2(C_4H_3S)]_6$ (23) and $[(C_3H_5C{\equiv}CAlNCH_2C_4H_3S)_2(C_3H_5CH{=}CHAlNCH_2C_4H_3S)_4]$ (24)

As shown in Scheme 5, compound **13** reacts with PhC≡CH to give phenylacetylide substituted imidoalane **19**. Similarly, **17** was reacted with PhC≡CH and cyclopropylacetylene under boiling conditions in the synthesis of **23** and **24**. The reaction pathway involved in the formation of **23** and **24** is completely different. Compound **17** when treated with PhC≡CH in boiling toluene conditions afforded $[PhC{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**23**) under evolution of

Scheme 7



H_2 (Scheme 7).[167] During the reaction the color of the reaction mixture changed to orange and it sustained during the course of the reaction. Compound **23** decomposes at 270 °C. In the EI-MS of **23** only fragments are observable. Its IR spectrum shows a sharp band of strong intensity at 2129 cm^{-1} corresponding to the C≡C stretch.[171] In the ^1H NMR spectrum, a single resonance was observed for the methylene protons (CH_2) at δ 4.68 ppm. In the ^{13}C NMR spectrum, the carbon atoms bound to aluminum (Al–*C*) resonate at δ 67.98 ppm whereas the other carbon atoms of the acetylide unit (Al–C≡*C*) resonates at δ 83.15 ppm.

From the reaction of cyclopropylacetylene and **17** we expected the formation of hexa-substituted imidoalane cluster similar to that of **23**, instead $[(C_3H_5C{\equiv}CAlNCH_2C_4H_3S)_2(C_3H_5CH{=}CHAlNCH_2C_4H_3S)_4]$ (**24**) was obtained. In this reaction four of the six Al–H bonds undergo *cis* addition on the acetylene bond of the cyclopropylacetylene to generate four alkylidene units and the remaining two hydrides were completely replaced by two cyclopropylacetylide units. The mechanism involved in the formation of **24** is not clear. Cyclopropylacetylene was added to a toluene solution of **17** at room temperature. The reaction mixture was stirred for an hour before refluxing it until the evolution of H_2 had ceased. During the reaction the color of the solution slowly changes to light yellow. Partial removal of the solvent and storage at 0 °C afforded colorless crystals of **24**. The composition of compound **24** was confirmed by elemental and spectral analysis. In the IR spectrum, bands corresponding to C≡C and C=C bonds were observed at 2136 and 1583 cm^{-1}, respectively. In addition to these two bands, a weak band at 1835 wave numbers was identified which can be assigned to a C–C bond having a bond order between two and three. In the mass spectrum we did not observe a molecular ion peak rather a peak (*m/z* 1228) corresponding to $[(M+2H)^+]$ was detected. Fragments at *m/z* 1160, 1092, 1063, 995, 927 and 860 were found which involve the successive loss of cyclopropylethylene units. NMR spectra could not be recorded due to its poor solubility.

2.3.2. X-ray crystal structure of $[PhC{\equiv}CAlNCH_2(C_4H_3S)]_6$ (23)·2PhMe

X-ray diffraction study of $[PhC{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**23**)·2PhMe was performed with crystals obtained by recrystallization from toluene at 0 °C. Compound **23** crystallizes in the triclinic space group $P1$ with two molecules of toluene in the asymmetric unit. An ORTEP plot depicting the spatial arrangement of the atoms in compound **23** is shown in Figure 4. The bond parameters of the cluster core are similar to that of **17**. Although the orientation of thienyl groups is similar to that of **17**, **21** and **22** there is a slight variation in the C≡C–Al bond angles. The bond angles deviate from the ideal 180° and vary significantly from each other ((C(5)–C(4)–Al(3) 143.19(7)°, C(8)–C(7)–Al(4) 158.06(6)°, C(2)–C(1)–Al(2) 169.23(5)°). Similarly, C≡C–C bond angles show deviation (C(1)–C(2)–C(3) 170.52(7)°, C(4)–C(5)–C(6) 149.92(8)°, C(7)–C(8)–C(9) 160.28(8)°).

2.3.3. X-ray crystal structure of

$[(C_3H_5C{\equiv}CAlNCH_2C_4H_3S)_2(C_3H_5CH{=}CHAlNCH_2C_4H_3S)_4]$ (24)·PhMe

The molecular structure of **24** in the solid state was determined by X-ray crystal structure analysis on colorless crystals obtained from a saturated toluene solution at ambient temperature. Compound **24** crystallizes in the triclinic space group $P\bar{1}$ with one half of the molecule and a toluene molecule in the asymmetric unit. An ORTEP plot of **24** is shown in Figure 5. The cyclopropylacetylide and cyclopropylalkylidene groups are projected away from the cluster. The six 2-$C_4H_3SCH_2$ units are oriented around the cluster where the sulfur atom has an occupancy of 0.75. Although the bond parameters of the drum-shaped Al–N core are similar to that of compound **17** there is a significant variation in the bond lengths and angles of cyclopropyl units. The two cyclopropylacetylide units bound to the aluminum center have a bond lengths of 1.13(7) Å (C(1)–C(2)) for the C≡C bond and a bond angle of 162.4(6)° for C(2)–C(1)–Al(1) unit. These bond parameters are typical for the *sp* hybridized carbon atom. A bond distance of 1.28(6) Å (C(7)–C(8)) and a bond angle of 132(4)° (C(8)–C(7)–Al(3)) can be noticed for the two CH=CH units, which are formed by the *cis* addition of Al–H hydrogens to the acetylene bond. The bond parameters of the cyclopropylalkylidene units are of sp^2 hybridized carbon atoms with a slight deviation from the planarity (132°). The bond lengths and bond angles of the remaining two cyclopropylacetylide units are an average of double and triple bonds (C(4)–C(5) 1.172(7) Å and C(5)–C(4)–Al(2) 146.9(6)°).

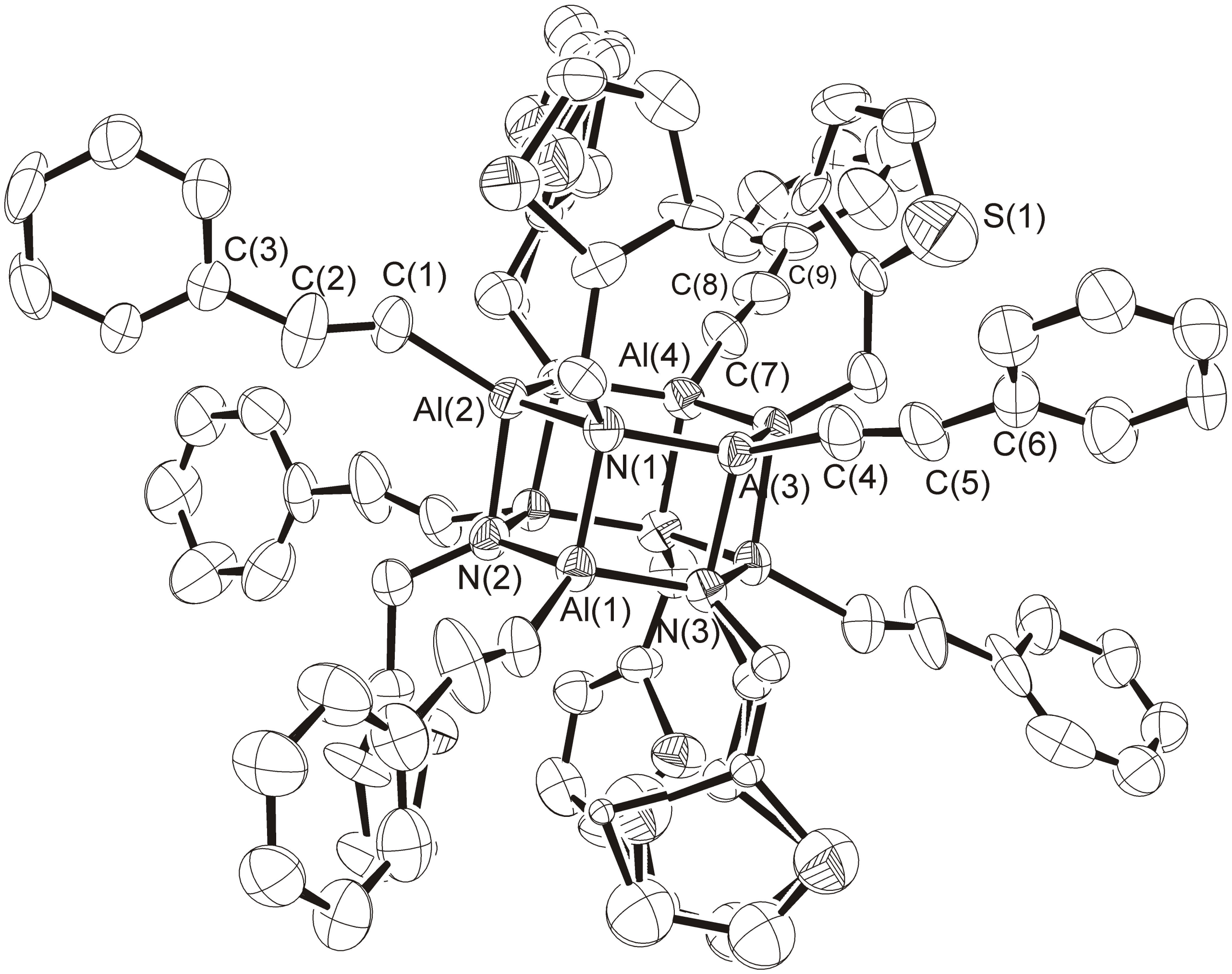


***Figure 4**. Crystal structure of compound [PhC≡CAlNCH$_2$(C$_4$H$_3$S)]$_6$* (**23**)*·2PhMe with 50 % ellipsoid probability. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.959(6), Al(1)–N(2) 1.912(5), Al(1)–N(3) 1.890(5), Al(3)–C(4) 1.950(6), C(4)–C(5) 1.185(8), C(5)–C(6) 1.460(8); C(2)–C(1)–Al(2) 169.23(5), C(5)–C(4)–Al(3) 143.19(7), C(8)–C(7)–Al(4) 158.06(6), C(1)–C(2)–C(3) 170.52(7), C(4)–C(5)–C(6) 149.92(8), C(7)–C(8)–C(9) 160.28(8), N(1)–Al(1)–N(2) 90.29(2), N(3)–Al(1)–N(2) 116.47(8), N(1)–Al(3)–C(4) 118.14(2), Al(1)–N(1)–Al(2) 89.60(2), Al(2)–N(1)–Al(3) 125.28(2).*

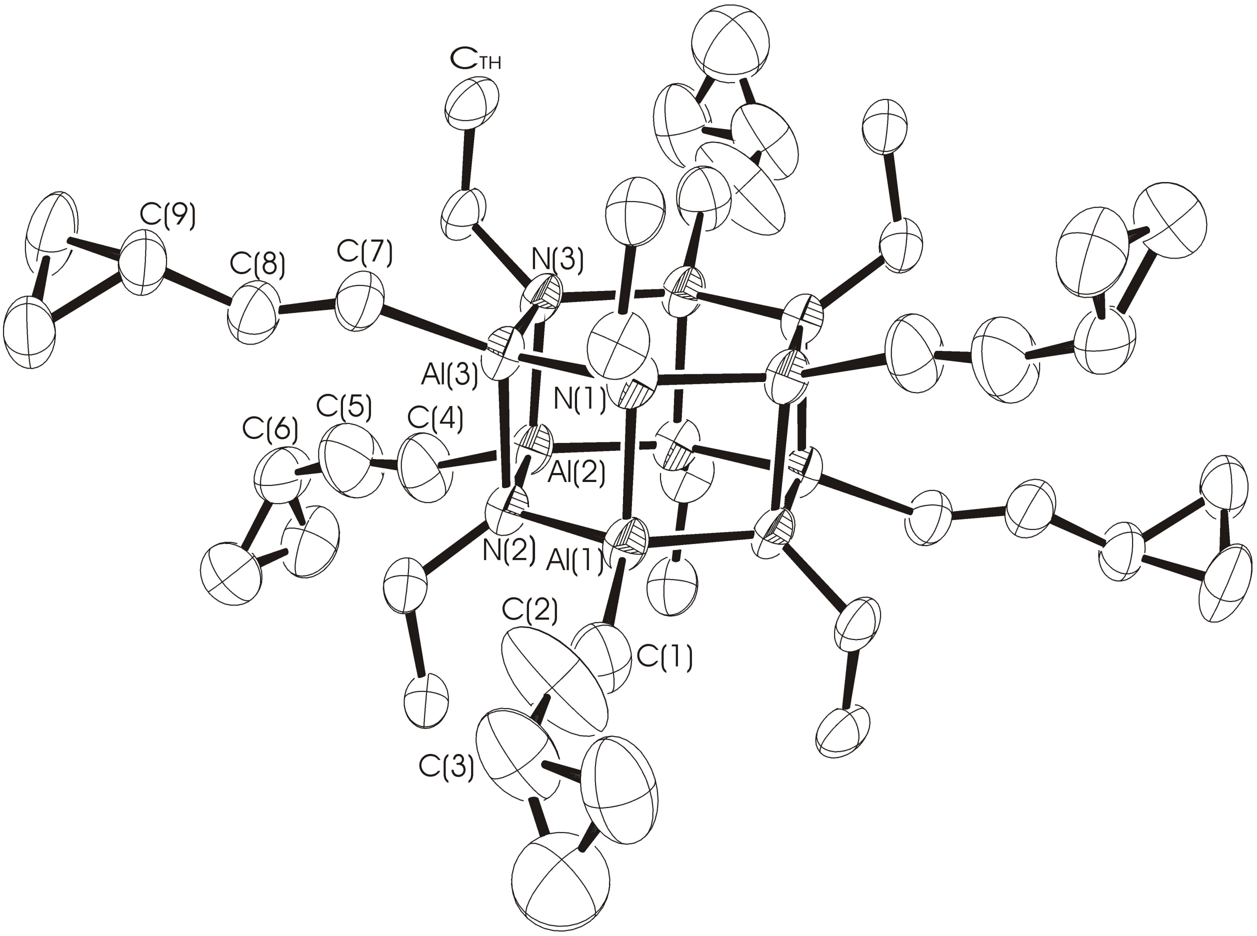


***Figure* 5**. *Crystal structure of compound [($C_3H_5C{\equiv}CAlNCH_2C_4H_3S$)$_2$-($C_3H_5CH{=}CHAlNCH_2C_4H_3S$)$_4$]* (**24**)*·PhMe with 50 % ellipsoid probability. C_{TH} = 2-C_4H_3S. 2-C_4H_3S groups, toluene molecule and the hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.974(3), Al(1)–N(2) 1.895(3), Al(1)–C(15) 1.930(4), C(1)–C(2) 1.130(7), C(4)–C(5) 1.172(7), C(7)–C(8) 1.280(6); C(2)–C(1)–Al(1) 162.4(6), C(5)–C(4)–Al(2) 146.9(6), C(8)–C(7)–Al(3) 132.0(4), C(1)–C(2)–C(3) 158.9(8), C(4)–C(5)–C(6) 159.0(9), C(7)–C(8)–C(9) 131.4(5), N(1)–Al(1)–N(2) 91.31(13), N(3)–Al(1)–N(2) 114.75(13), Al(1)–N(1)–Al(3) 88.40(13), Al(2)–N(2)–Al(1) 125.13(15).*

2.4. Reactivity of PhSH toward imidoalanes 13 and 17

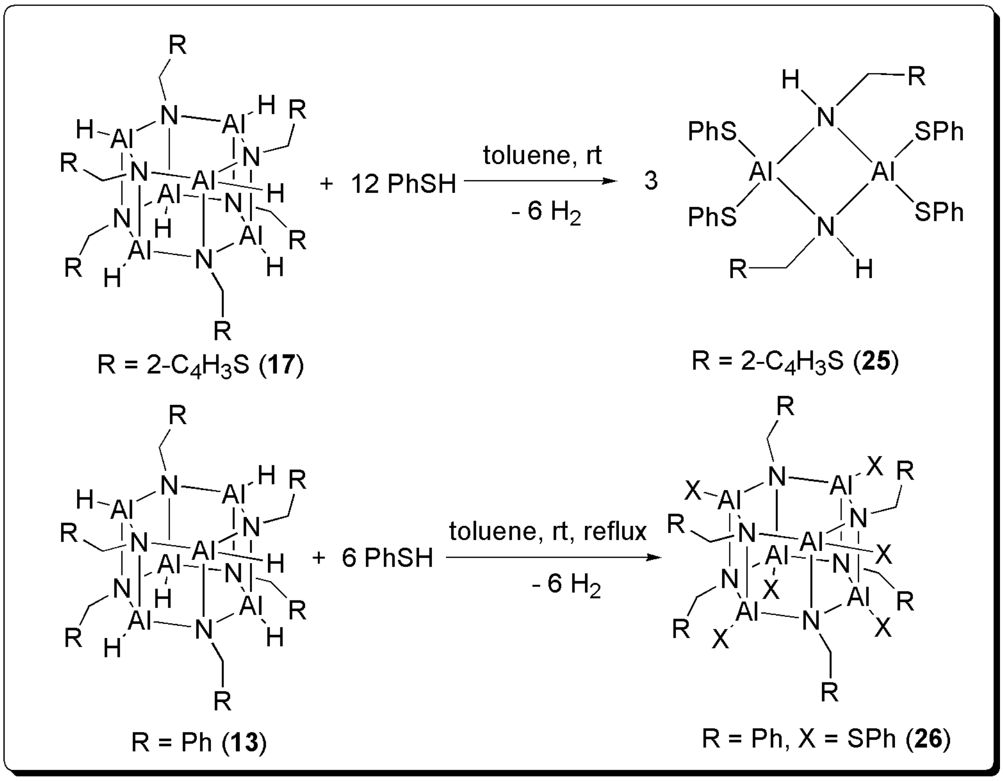
2.4.1. Synthesis of $[(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (25) and $[PhSAlNCH_2Ph)]_6$ (26)

When compound **17** was treated with stoichiometric amount of PhSH at room temperature vigorous evolution of H_2 was observed. The reaction mixture was stirred at room temperature for 1 d and it was crystallized followed by filteration to obtain colorless crystals of $[(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (**25**).[167] The Al–N cluster was degraded to form a four-membered ring system (Al_2N_2). In this reaction, migration of a proton from sulfur to nitrogen was observed (Scheme 8). Although several four-membered Al–N ring compounds have been described in the literature, none of them carries as many as six sulfur atoms. Hence, compound **25** is the first four-membered imidoalane carrying six sulfur atoms of which four are directly connected to the ring aluminum atoms. To compare the stability of the cores of **17** and **13**, the latter was similarly treated with PhSH in toluene. No reaction was observed at room temperature but under reflux conditions the reaction proceeds under evolution of H_2. The reaction mixture was refluxed until the evolution of H_2 had ceased. The solution was filtered and crystallized at room temperature to yield colorless crystals of the hexameric product $[PhSAlNCH_2Ph]_6$ (**26**). The Al–N network of **13** remained intact in contrast to the reaction between **17** and PhSH.[167] The difference in the reactivity can be attributed to the relative stability of imidoalanes with respect to thiophenol.

Compounds **25** and **26**, characterized by MS, IR, NMR spectra and elemental analysis, have melting points of 143 - 153 °C and 220 - 223 °C, respectively. In the EI-MS of **25** the peak corresponding to the molecular ion was observed at *m/z* 714, only small fragments were found for compound **26**. Evidence for the presence of N–H bonds in compound **25** is seen in its IR spectrum showing a sharp band at 3248 cm^{-1}. The ^1H NMR spectrum of

26 shows a resonance for the N–*H* proton at *δ* 4.68 ppm whereas the NMR spectrum of **26** is similar to that of **13**, but without Al–H resonances.

Scheme 8



2.4.2. X-ray crystal structure of $[(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (25)

Single crystals of **25** suitable for an X-ray diffraction study were obtained from a saturated solution in toluene at 0 °C. Compound **25** crystallizes in the monoclinic space group *P*2$_1$/*c* with one half of the molecule in the asymmetric unit. Figure 6 shows the molecular structure of **25**. The two thienylmethylene groups are trans to each other and the phenyl groups on the same side of the plane of the Al–N ring are oriented in the same direction. The average Al–N bond distance (1.940(2) Å) is comparable to **17** and is in accordance with those reported in the literature.[164] The sulfur atoms S(1) and S(2) are slightly tilted away from the vertical axis of the four-membered Al_2N_2 ring with an obtuse angle at the aluminum centers ((S(2)–Al(1)–N(2) 112.2(6)° and S(1)–Al(1)–N(2) 104.4(6)°).

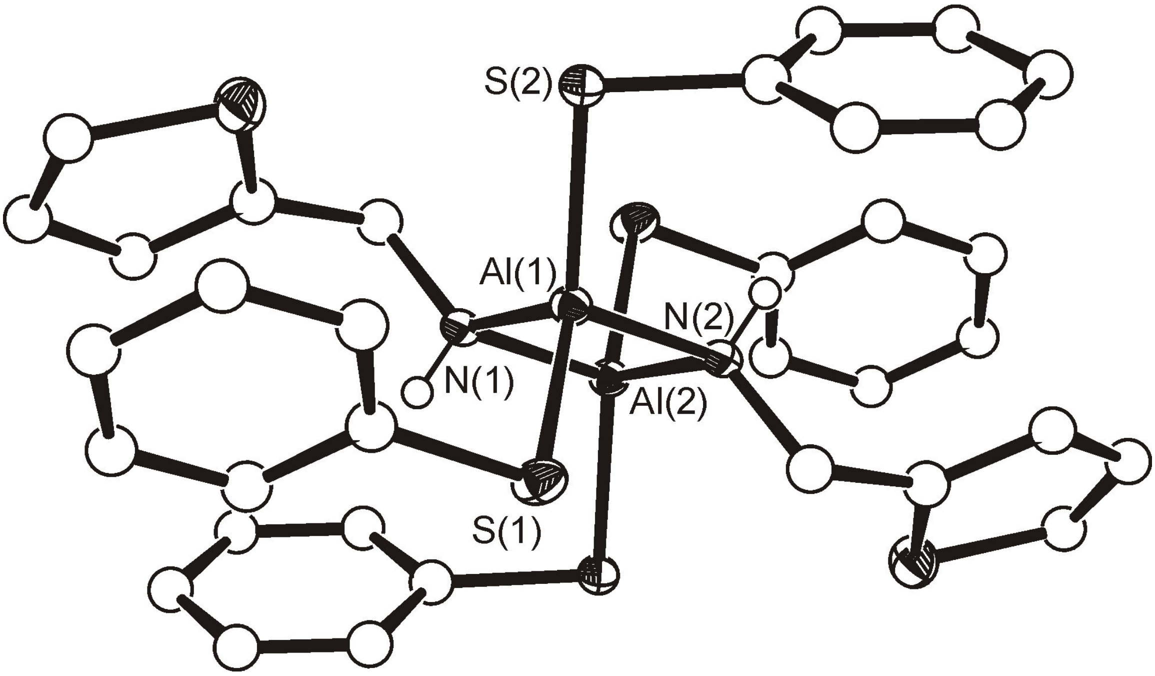


Figure 6. *Crystal structure of compound* $[(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (**25**) *with 50 % ellipsoid probability. All hydrogen atoms except those on N are excluded for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Al(1) 1.933(2), N(1)–Al(2) 1.946(2), S(1)–Al(1) 2.209(1), S(2)–Al(1) 2.220(1); Al(1)–N(1)–Al(2) 90.62(7), N(1)–Al(2)–N(2) 89.38(7), S(1)–Al(1)–S(2) 123.81(3), S(1)–Al(1)–N(2) 104.4(6), S(2)–Al(1)–N(1) 104.40(6), S(2)–Al(1)–N(2) 112.2(6).*

2.4.3. X-ray crystal structure of $[PhSAlNCH_2Ph]_6$ (26)·PhMe

Colorless crystals of **26** suitable for X-ray crystal structure analysis were obtained from a toluene solution at room temperature. Compound **26** crystallizes in the monoclinic space group *C*2/*c* with one half of the molecule and one half of a toluene molecule in the asymmetric unit. Figure 7 shows the ORTEP plot of **26**. The Al–N polyhedron is completely surrounded by organic moieties. While the bond lengths are similar to those of

13, the bond angles between the interlinking Al–N bonds and the Al–S bonds in **26** vary significantly from each other (S(2)–Al(2)–N(1) 120.86(4)°, S(3)–Al(3)–N(2) 111.75(5)°).

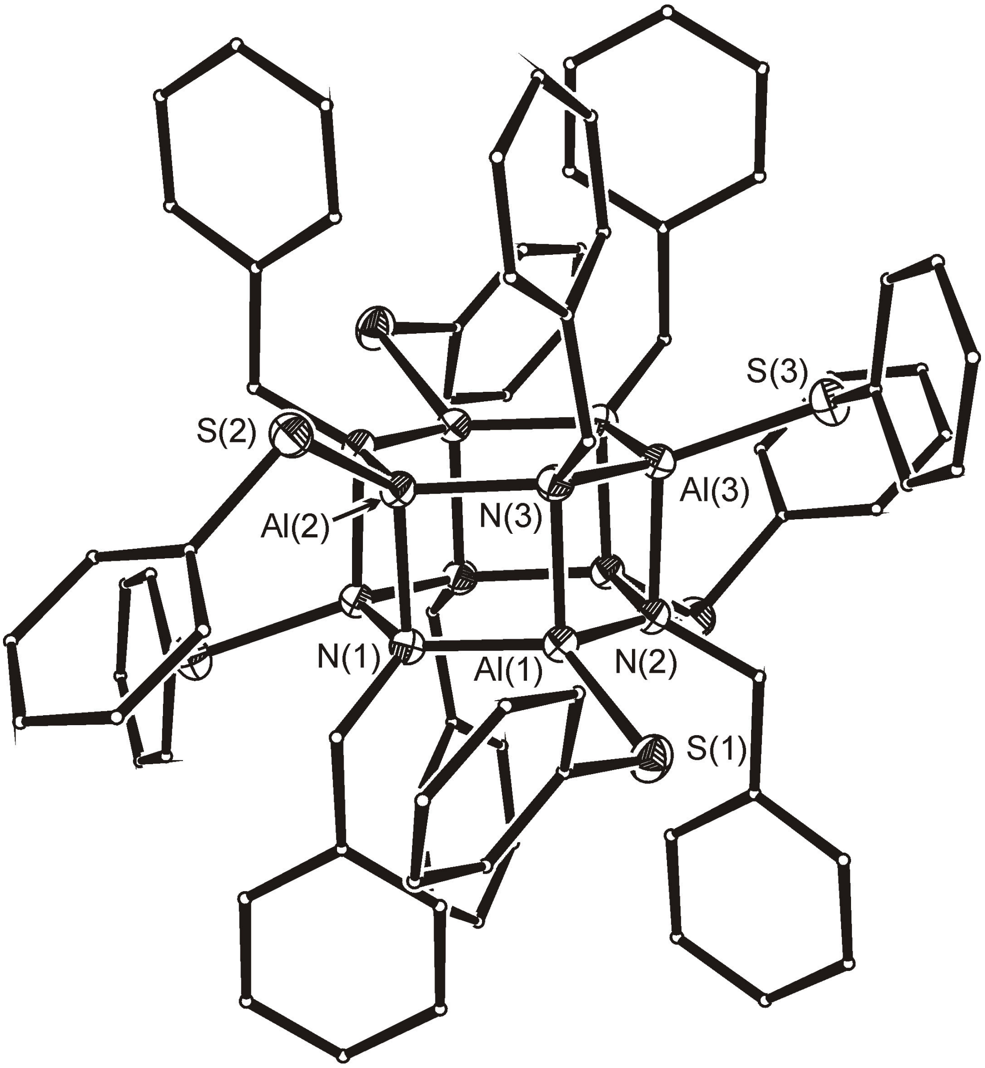


***Figure** 7. Crystal structure of compound* $[PhSAlNCH_2Ph]_6$ (**26**)*·PhMe with 50 % ellipsoid probability. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Al(1) 1.890(2), N(1)–Al(2) 1.975(2), N(3)–Al(1) 1.973(2), N(3)–Al(2) 1.902(2), Al(1)–S(1) 2.220(1); Al(1)–N(3)–Al(3) 88.34(6), Al(2)–N(3)–Al(3) 125.10(7), N(1)–Al(1)–N(2) 115.86(6), N(1)–Al(1)–N(3) 91.65(6), S(1)–Al(1)–N(1) 117.24(5), S(2)–Al(2)–N(1) 120.86(4), S(3)–Al(3)–N(2) 111.75(5).*

2.5. Reactivity of 17 toward metal alkyls

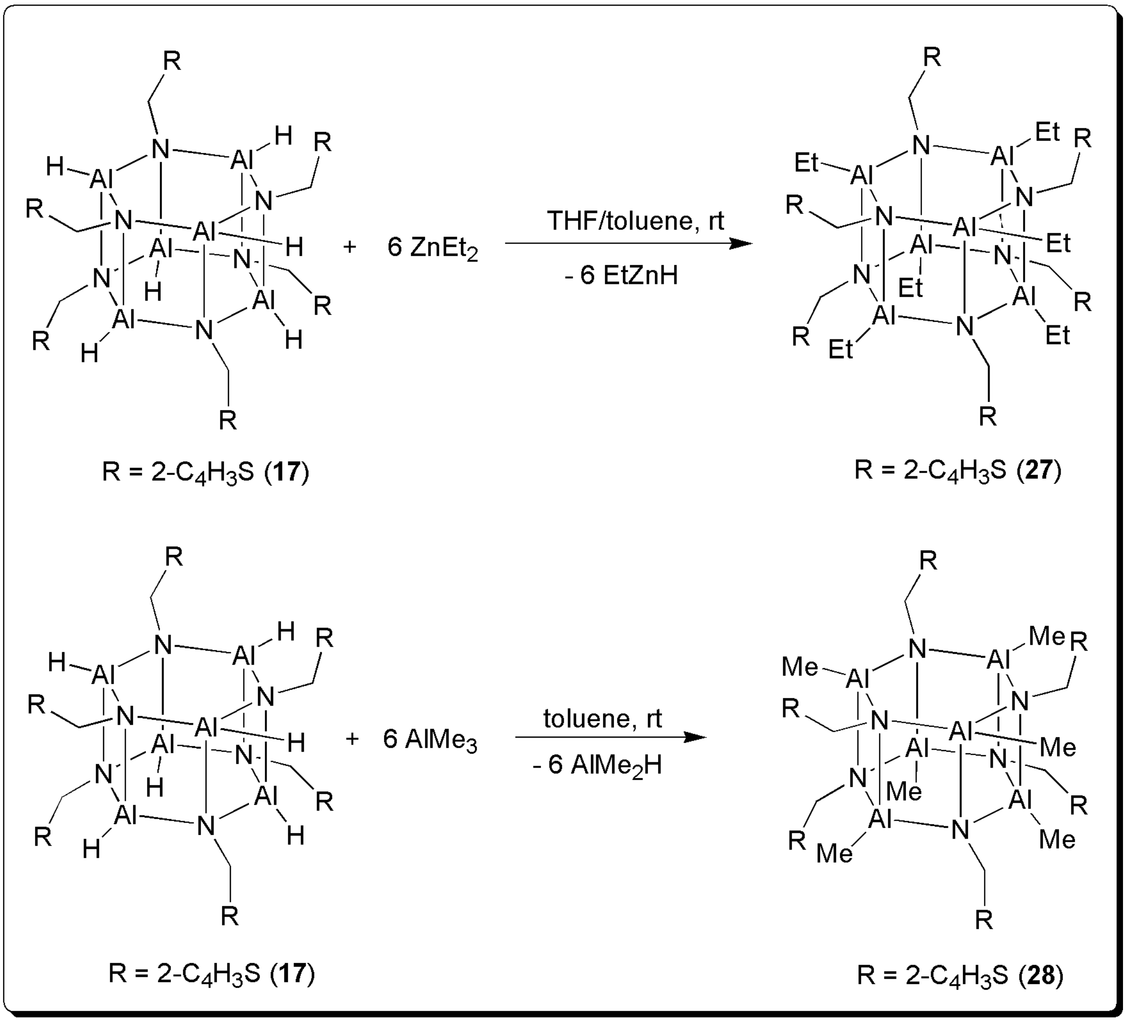
The substitution of hydridic hydrogens of hexameric imidoalanes, prepared from aluminum hydrides and primary amines, with alkyl groups was performed in the 1970's. Partially or fully alkylated species were isolated from reactions with AlR_3 (R = Me, Et) but not structurally characterized.[172] Only one structurally characterized alkylated imidoalane, $(MeAlN^iPr)_6$, has been reported in the literature. It was obtained by the replacement of hydrides of $(HAlN^iPr)_6$ with the methyl groups of $AlMe_3$. The substitution reactions were observed upon treatment of imidoalanes with AlR_3 (R = Me, Et) without any degradation of the cages or clusters. Methyl substituted imidoalanes prepared from primary amines and $AlMe_3$ at elevated temperatures often show different degrees of oligomerization depending on the size of the organic groups.[90] A prominent example is the planar alumazene.[45]

2.5.1. Synthesis of $[EtAlNCH_2(C_4H_3S)]_6$ (27) and $[MeAlNCH_2(C_4H_3S)]_6$ (28)

The metathesis reaction were carried out on **17** with $ZnEt_2$ and $AlMe_3$. With an excess of $ZnEt_2$ in a THF/toluene at room temperature all the hydrides have been replaced by ethyl groups giving rise to $[EtAlNCH_2(C_4H_3S)]_6$ (**27**).[167] With increasing reaction time the color of the solution changes to gray. We assume that gray zinc formed as a byproduct is due to the disproportionation of EtZnH into Et_2Zn and H_2. The yield of the product in this reaction was not quantitative. We observed no coordination of diethylzinc to the sulfur atom of the thienyl groups. In a similar fashion, **17** was treated with $AlMe_3$ in toluene at room temperature. The reaction mixture was stirred overnight at room temperature and filtered. The filtrate was reduced in volume and stored at 0 °C for several days to obtain colorless crystals of the methylated imidoalane $[MeAlNCH_2(C_4H_3S)]_6$ (**28**) (Scheme 9).[173] $AlMe_2H$ was formed as a by-product and undergoes dimerization to give more stable dimers and trimers via bridging hydrides.[174]

Both compounds were characterized by means of analytical and spectral techniques. Compounds **27** and **28** decompose at 262 and 246 °C, respectively. The EI mass spectra of both show peaks corresponding to the loss of one alkane group at *m/z* 973 [$(M\text{-}C_2H_6)^+$] and 903 [$(M\text{-}CH_4)^+$], respectively. No Al–H stretching frequency in the IR spectra of **27** and **28** are observable. In the ^{1}H NMR spectrum, a multiplet was found for the methylene protons of Al–CH_2–CH$_3$ of **27** (δ 0.20 ppm) whereas a singlet is observable for the methyl protons (Al–

Scheme 9



CH_3) of **28** at δ –0.52 ppm. In the ^{13}C NMR spectra, the CH_2 unit of the ethyl groups bound to aluminum (Al–CH_2–CH_3) in **27** resonates at δ –1.09 ppm and the methylide (Al–CH_3) carbon atom in **28** resonates at δ –7.20 ppm. The NMR resonances for both the compounds are in complete agreement with their composition.

2.5.2. X-ray crystal structure of [EtAlNCH$_2$(C$_4$H$_3$S)]$_6$ (27)

Suitable single crystals of **27** for an X-ray crystal structure analysis were obtained from toluene solution at ambient temperature. Compound **27** crystallizes in the cubic space group $Pa\overline{3}$ with one sixth of a molecule in the asymmetric unit. Figure 8 shows the molecular structure of **27**. The orientation of the thienyl groups in compound **27** is quite different from others. The sulfur atoms in **27** point away from the vertical axis whereas they are tilted toward the vertical axis in compounds **17**, **21** and **22**. Bond parameters of the Al–N network in compound **27** are similar to that of **17**.

2.5.3. X-ray crystal structure of [MeAlNCH$_2$(C$_4$H$_3$S)]$_6$ (28)

The molecular structure of **28** in the solid state was determined by X-ray crystal structure analysis on colorless crystals obtained from a saturated toluene solution at room temperature. Compound **28** crystallizes in the triclinic space group $P\overline{1}$ with one half of a molecule in the asymmetric unit. Figure 9 shows the molecular structure of **28**. One thienyl group is distorted and two positions of the thienyl ring were refined for S(1) with an occupancy of 0.661(7). The core structure is nearly identical to its starting material. The Al–C bond lengths for the methyl groups range from 1.937(4) Å to 1.978(5) Å in **28**.

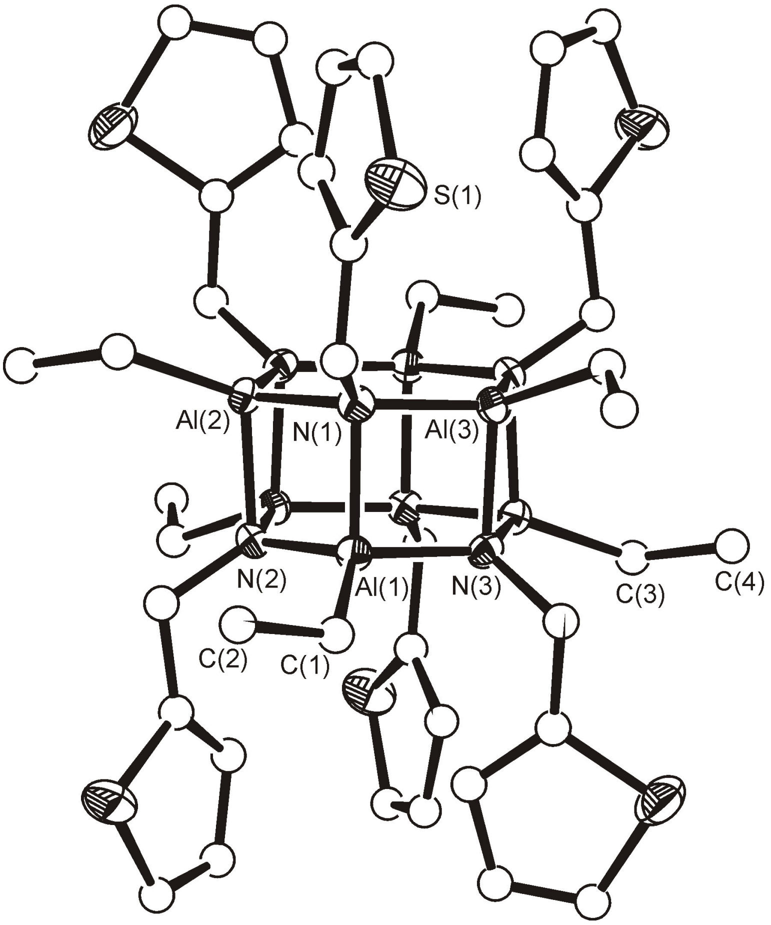


Figure 8. *Crystal structure of compound* $[EtAlNCH_2(C_4H_3S)]_6$ (**27**) *with 50 % ellipsoid probability. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: N(1)–Al(1) 1.987(3), N(1)–Al(2) 1.897(3), N(1)–Al(3) 1.898(3), Al(1)–C(1) 1.940(4); Al(1)–N(3)–Al(3) 88.40(10), Al(2)–N(1)–Al(3) 125.32(13), N(3)–Al(1)–N(2) 114.12(14), N(3)–Al(3)–N(1) 91.36(11), C(1)–Al(1)–N(1) 114.38(15), C(1)–Al(1)–N(2) 122.20(15), C(1)–Al(1)–N(3) 115.80(14).*

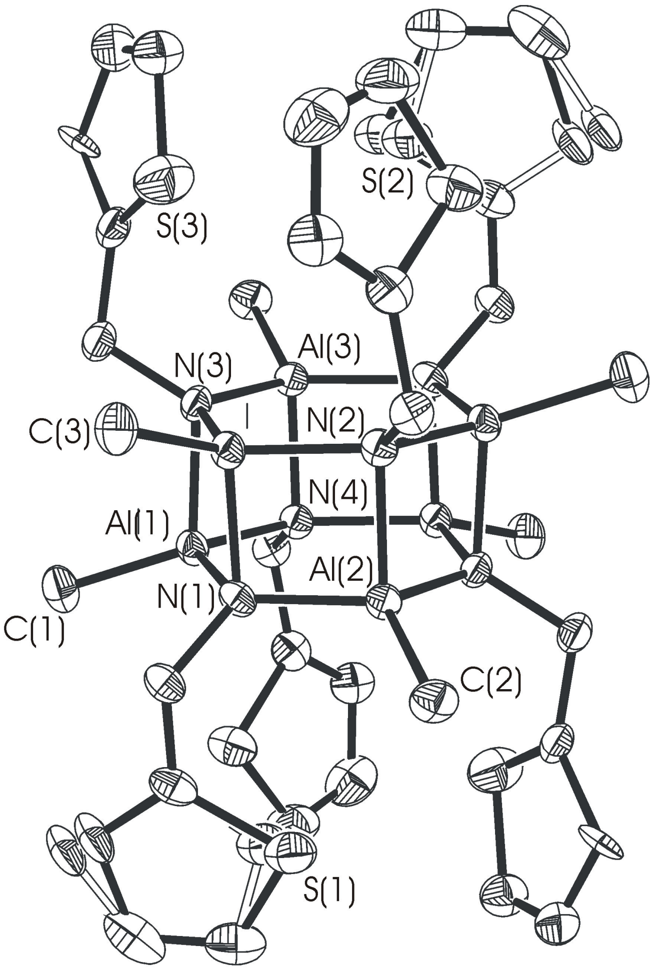


Figure 9. *Crystal structure of compound [MeAlNCH$_2$(C$_4$H$_3$S)]$_6$* (**28**) *with 50 % ellipsoid probability. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.886(4), Al(1)–N(3) 1.986(3), Al(2)–N(1) 1.877(3), Al(2)–N(2) 1.982(3), Al(3)–N(1) 1.986(3), Al(3)–N(3) 1.879(3), Al(1)–C(1) 1.978(5), Al(2)–C(2) 1.937(4), Al(3)–C(3) 1.94(1); N(1)–Al(1)–N(3) 91.3(2), N(4)–Al(1)–N(1) 113.8(2), N(1)–Al(1)–C(1) 119.3(2).*

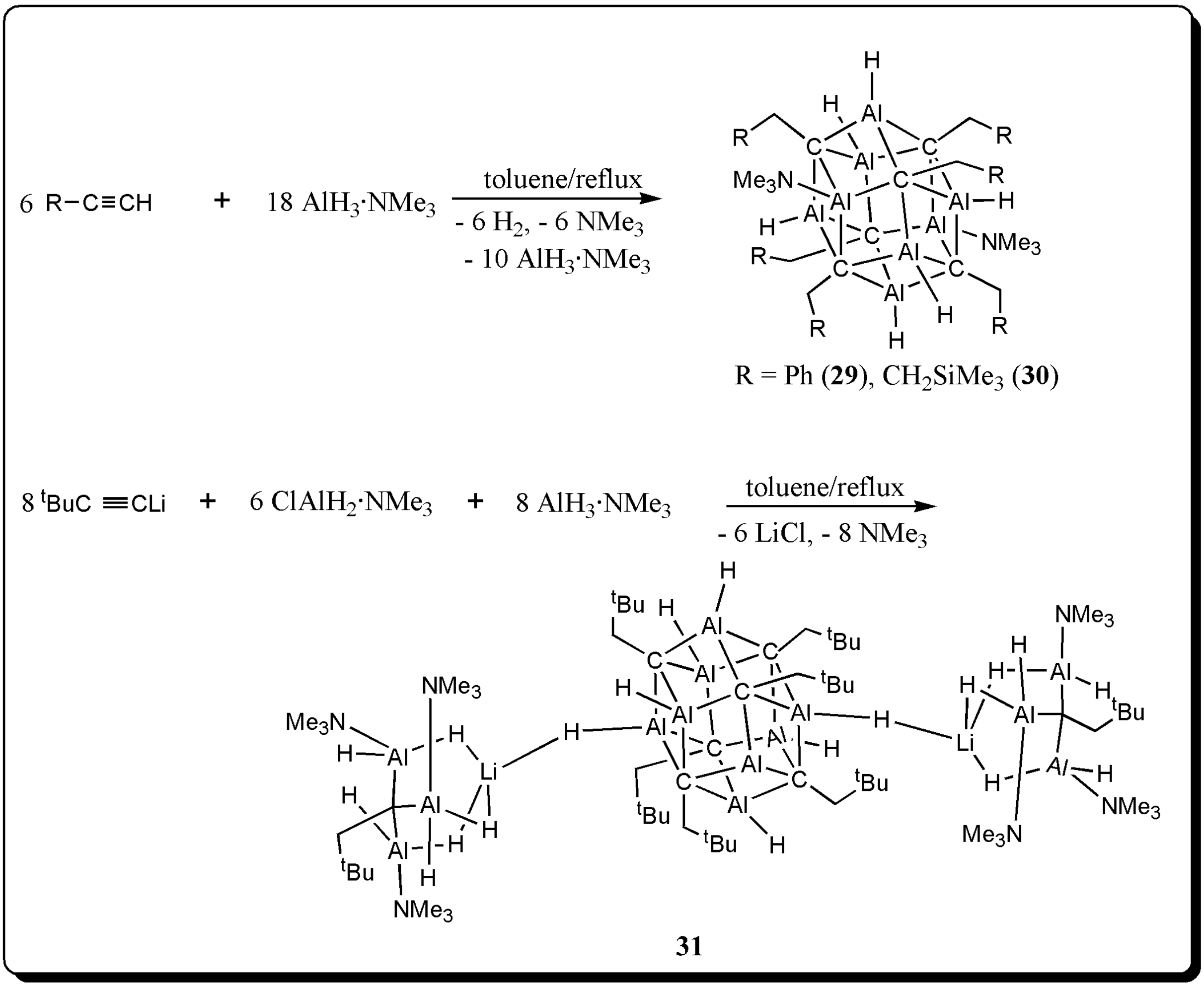
2.6. Carbaalanes

In contrast to the method employed by Uhl et al., Roesky et al. synthesized the carbaalanes by treating monosubstituted acetylenes with $AlH_3 \cdot NMe_3$. Reaction of acetylenes $PhC{\equiv}CH$ and $Me_3SiCH_2C{\equiv}CH$ with an excess of $AlH_3 \cdot NMe_3$ in boiling toluene led to the formation of carbaalanes $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**29**), and $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**30**) (Scheme 10).[175] The mechanism of hydroalumination of acetylenes proceeds via the deprotonation of the acidic acetylene hydrogen atom followed by the elimination of H_2. Subsequent regioselective hydroalumination reaction on this intermediate leads to the formation of $RCH_2C(AlH_2 \cdot NMe_3)_3$ (R = Ph, CH_2SiMe_3), which can undergo condensation reaction to afford the carbaalanes **29** and **30** (Scheme 10). The reactive Al–H bonds in **29** and **30** underwent substitution reactions with nucleophilic reagents to yield $[(AlX)_6(AlNMe_3)_2(CCH_2R)_6]$ (R = Ph, CH_2SiMe_3 and X = F, Cl, Br, I, Me).[173,175,176] A carbaalanate $[\{^tBuCH_2C(AlH_2 \cdot NMe_3)_3Li\}_2\{(AlH)_8(CCH_2{}^tBu)_6\}]$ (**31**) was also reported by the treatment of $^tBuC{\equiv}CLi$ with equivalent amounts of $AlH_3 \cdot NMe_3$ and $ClH_2Al \cdot NMe_3$ (Scheme 10).[177]

2.6.1. Synthesis of $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (29) and $[(AlH)_6(AlNMe_3)_2(CCH_2C_3H_5)_6]$ (32)

As said above, the aluminum-carbon cluster compound $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**29**) was prepared by treatment of $PhC{\equiv}CH$ with an excess of $AlH_3 \cdot NMe_3$ in refluxing toluene. It could also be prepared by carrying out hydroalumination reaction on aluminum trisphenylacetylide $[(PhC{\equiv}C)_3Al \cdot NMe_3]$ (**33**).[178] To a solution of $[(PhC{\equiv}C)_3Al \cdot NMe_3]$

Scheme 10



R = Ph (**29**), CH_2SiMe_3 (**30**)

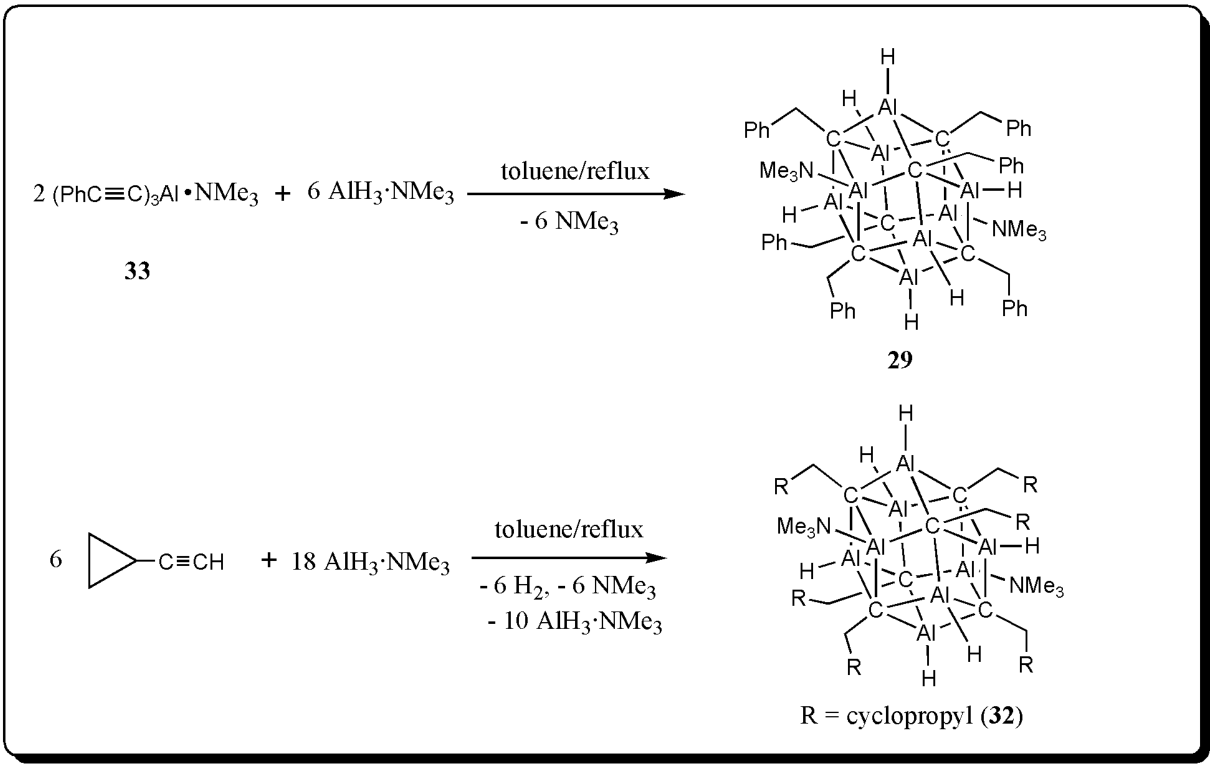
31

(**33**) in toluene was added an excess of 0.5 M solution of $AlH_3{\cdot}NMe_3$ in toluene at room temperature. The reaction mixture was stirred at room temperature for 0.5 h before refluxing it until the evolution of NMe_3 had ceased (Scheme 11). The resulting solution was filtered and the product was crystallized at room temperature to afford colorless crystals of **29** in good yield. Thus, the hydroalumination reaction was efficient on aluminum trisphenylacetylide. Similar reactions on the trisphenylacetylides of the heavier elements (Ga, In) resulted in the deposition of the metal. Hydroalumination reaction was also carried out on cyclopropylacetylene. Refluxing conditions were employed in the preparation of cyclopropyl-

-methylene substituted carbaalane $[(AlH)_6(AlNMe_3)_2(CCH_2C_3H_5)_6]$ (**32**), which precipitates during the course of the reaction. The compound is highly insoluble in any solvent and thus it could not be recrystallized.

Compounds **29** and **32** were characterized by means of spectral and analytical data. Both decompose at 280 - 282 °C and >300 °C, respectively. No molecular ion peak was observed in the mass spectrum of **29** whereas in **32** a peak (*m/z* 742) corresponding to the molecular ion was identified. In the IR spectrum of **29** a broad Al–H stretching frequency was found at 1822 cm^{-1} and in **32** at 1776 wave numbers. Due to poor solubility of **29** only ^1H NMR spectrum was recorded. The protons of the methylene group (CH_2) resonates at δ 2.04 ppm. A singlet for the protons of NMe_3 groups was found at δ 2.10 ppm and at δ 4.0 ppm a very broad resonance for Al–*H* protons was noticed. Owing to the poor solubility of **32**, the ^1H and

Scheme 11



^{13}C NMR spectrum was not recorded.

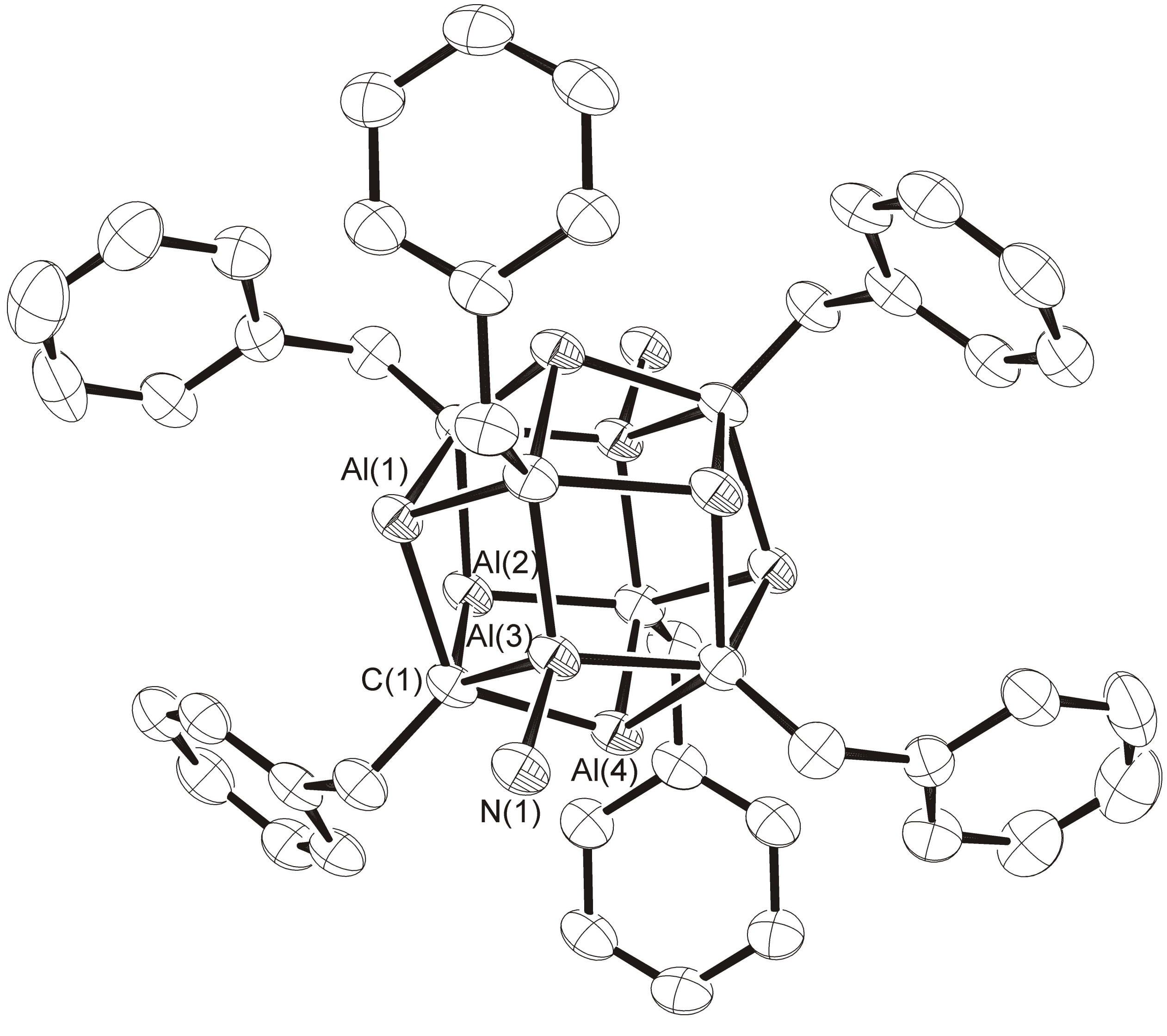


***Figure 10**. Crystal structure of compound* $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**29**)*·2PhMe with 50 % ellipsoid probability. Toluene molecules, methyl groups and hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–Al(2) 2.670(2), Al(3)–Al(4) 2.582(1), Al(4)–N(1) 1.986(3); Al(3)–C(1)–Al(4) 77.29(17), Al(4)–C(1)–Al(1) 123.85(2).*

2.6.2. X-ray crystal structure of $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (29)·2PhMe

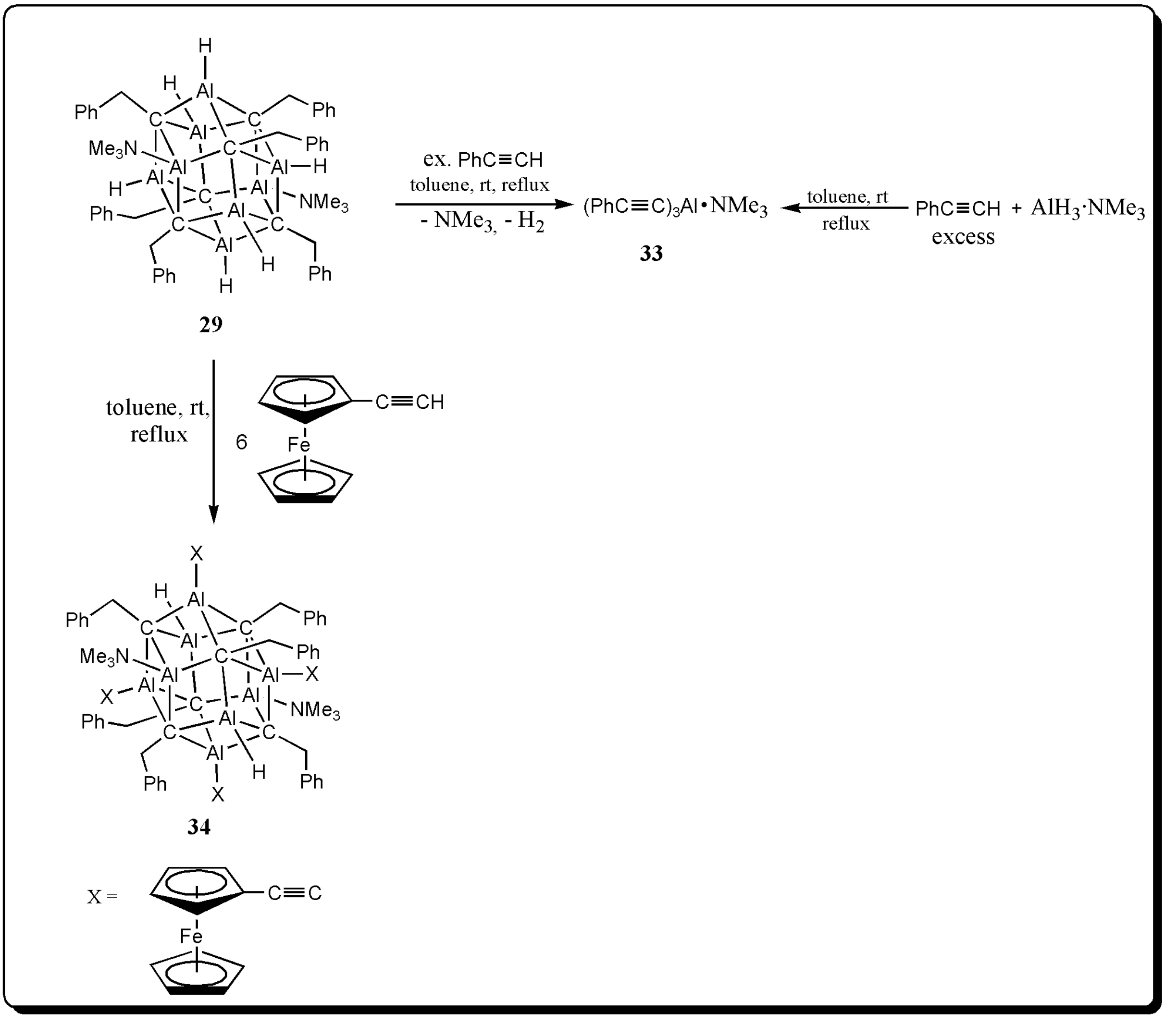
Crystals of $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**29**)·2PhMe suitable for X-ray diffraction study were obtained at room temperature from toluene solution. Compound **29** crystallizes in the triclinic space group $P\bar{1}$ with one half of the molecule and a toluene molecule in the asymmetric unit. An ORTEP plot of **29** is shown in Figure 10. The cluster core is a rhombic dodecahedron with eight aluminum atoms at the corners of the cube and six carbon atoms, bound to the benzyl groups, cap the faces of each cube. The carbon atoms present in the cluster are connected to three Al–H units and one $AlNMe_3$ unit. This results in a closed carbaalane with D_{3h} symmetry. Of the eight aluminum atoms six are bound to the hydrogen atoms and the other two are coordinatively bonded to one NMe_3 group respectively. Two $AlNMe_3$ groups are positioned anti to each other. The average distances between the aluminum atoms bonded to the NMe_3 groups and the closest cluster carbon atoms (2.037(3) Å, 2.034(3) Å) are significantly shorter than the corresponding distances from the aluminum atoms bonded to the hydrogen atoms (2.109(4) Å, 2.082(3) Å, 2.099(4) Å). Similarly, the average distances between the aluminum atoms coordinated to the NMe_3 groups and the aluminum atoms bonded to the hydrogen atoms (2.582(1) Å, 2.590(1) Å) are shorter than the corresponding distances between the aluminum atoms bearing the hydrogen atoms (2.647(2) Å, 2.650(2) Å). These aluminum-aluminum distances are comparable with those of the dimeric aluminum trimethyl.[180] The average bond angles are found to be similar to the reported carbaalanes[98-103,175,179] (Al(4)–C(1)–Al(1) 123.85(2)°, Al(1)–C(1)–Al(3) 77.29(17)°). Theoretical calculations[175] were done on **29** to understand the surface aromaticity and the nature of bonding within the core. The geometry of the structure was modified to $[(AlH)_6(AlNH_3)_2(CMe)_6]$ and the calculations were performed using RHF and DFT methods. On the basis of these *ab initio* calculations the orbital scheme localized at one cubic face has an orbital sextet with a large HOMO - LUMO gap of 8.8 eV, which is consistent with the criteria of aromaticity. The qualitative valence bond theory also describes the nature of bonding within the core. In carbaalane **29**, the capped carbon atoms and the aluminum atoms donate electrons to each face of the cube leading to the strong delocalization of electrons resulting in the formation of a *hyper-closo* type structure analogous to that of $C_6B_8H_{14}^{2-}$, which obeys the 6*m*+2*n* electron counting rule where *m* denotes the number of faces larger than triangles and *n* denotes the number of triangles.[181]

2.7. Reactivity of 29 toward phenyl- and ferrocenylacetylene

2.7.1. Synthesis of [(PhC≡C)$_3$Al·NMe$_3$] (33) and [(AlH)$_2$(FcC≡CAl)$_4$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$] (34)

Addition of phenylacetylene to a suspension of **29** in toluene was done at room temperature. After stirring it for an hour at room temperature the reaction mixture was refluxed until the evolution of NMe$_3$ and H$_2$ had ceased and aluminum trisphenylacetylide [(PhC≡C)$_3$Al·NMe$_3$] (**33**) was isolated (Scheme 12).[178] In order to assess whether the

Scheme 12



cluster **29** was undergoing any decomposition in solution, as a control experiment, we heated it without any other reagent. The cluster retained its integrity even after refluxing it for 5 hours. Compound **33** was the only isolable product when the reaction was carried out either in a 1:6 stoichiometric ratio or even when an excess of phenylacetylene was used. The yield of **33** has been optimized in this reaction to 68 %. It is of interest to note that **33** was originally prepared by the reaction of an excess of phenylacetylene with $AlH_3 \cdot NMe_3$ in boiling hexane.[182]

Compound **33** was fully characterized using spectral and elemental analysis data. It decomposes at 183 °C. In the mass spectra a peak corresponding to the molecular ion was not observed rather a peak *m/z* 391 [$(M+2H)^+$] was noticed. A stretching frequency at 2125 wave numbers in the IR spectrum can be attributed to the acetylide bond. In the ^1H NMR spectrum the protons of the methyl groups (NMe_3) resonate at δ 2.80 ppm whereas in ^{13}C NMR spectrum the carbon atom of the Al–*C*≡C unit resonates at δ 101.2 ppm.

The reaction of **29** with six equivalents of ferrocenylacetylene in refluxing toluene proceeds with the evolution of hydrogen and affords $[(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6]$ (**34**) (Scheme 12).[178] Compound **34** was formed from **29** as a result of the substitution of four Al–H bonds (out of a total of six). It was not possible to obtain any other product even when the reaction was carried out (a) with an excess of ferrocenylacetylene (b) in higher boiling solvents such as *p*-xylene and mesitylene. The characterization of **34** is based on its analytical data as well as solid-state NMR and IR spectra. Absorption bands at 2115 cm^{-1} and 1808 cm^{-1} in the IR spectrum of **34** can be assigned to ν(C≡C) and ν(Al–H) stretching frequencies. The solid-state ^{27}Al NMR resonances for **34** showed a weak resonance at δ 40 ppm and a strong one at δ 130 ppm. The ^{13}C NMR spectrum exhibits a broad resonance at δ 40 ppm which can be designated to N*Me*$_3$. The ferrocene moieties and the phenyl groups resonate at δ 65 ppm and δ 120 - 130 ppm, respectively. In the ^{1}H NMR spectrum the presence of a broad signal at δ 4 ppm is due to the presence of unreacted Al–H bonds and the resonances corresponding to CCH_2, NMe_3, $C_5H_4FeC_5H_5$ and C_6H_5 groups are observed at δ 1.9, 2.7 - 3.0, 4.5 and 7.2 ppm, respectively. Although, the precise reasons for the difference in reactivity between FcC≡CH and PhC≡CH elude us, it is possible that the steric requirements of ferrocenylacetylene do not allow the reaction to proceed beyond **34**.

2.7.2. X-ray crystal structure of [(PhC≡C)$_3$Al·NMe$_3$] (33)

Suitable colorless single crystals of [(PhC≡C)$_3$Al·NMe$_3$] (**33**) for X-ray structural analysis were grown from toluene solution at –20 °C. Compound **33** crystallizes in the monoclinic space group $P2_1/n$. An ORTEP plot of **33** is shown in Figure 11. In the asymmetric unit one full molecule of this compound is found. X-ray crystal analysis of compound **33** shows that the aluminum center is bound to three phenylacetylide groups and one NMe_3 group. A distorted tetrahedral geometry is observed around the aluminum center, which is quite contrary to the trigonal pyramidal geometry observed in the $H_3Al·NMe_3$. The C–Al–N bond angles are smaller (104.0(3)°) than the C–Al–C bond angle (C(1)–Al–C(4) 109.7(1)°, C(4)–Al–C(7) 115.9(1)°, C(7)–Al–C(1) 112.8(9)°). The reason for the distortion in the tetrahedral geometry around the aluminum center can be attributed to the rapprochement of an ideal sp^2 hybridization with the donation of a lone pair of electrons by the NMe_3 group to the high energy p orbital of aluminum or a weaker coordinate bond is preferred by the utilization of higher energy p orbital (Bent's rule).[183,184] Compound **34** crystallizes in the triclinic space group $P\overline{1}$. The crystal structure of this compound could not be determined completely due to severe disorder between the ferrocenylacetylide units and toluene molecules.

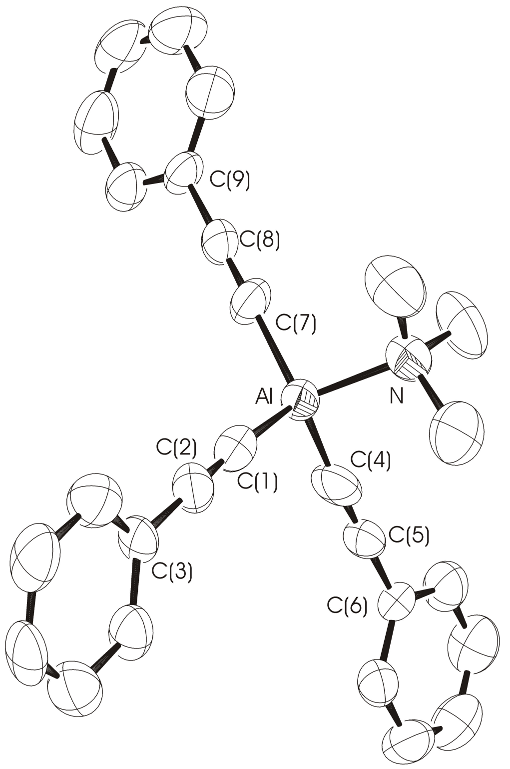


Figure 11. *Crystal structure of compound [(PhC≡C)$_3$Al·NMe$_3$]* (**33**) *with 50 % ellipsoid probability. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [°]: Al–C(1) 1.940(2), Al–C(4) 1.943(2), Al–C(7) 1.939(3); Al–C(1)–C(2) 171.7(2), Al–C(4)–C(5) 176.0(2), Al–C(7)–C(8) 171.3(2), C(1)–Al–C(4) 109.7(1), C(4)–Al–C(7) 115.9(1), C(7)–Al–C(1) 112.8(9), C(1)–C(2)–C(3) 177.8(8), C(4)–C(5)–C(6) 178.7(9), C(7)–C(8)–C(9) 176.29(8), C(1)–Al–N 104.0(3).*

2.7.3. Cyclo voltammetric studies of $[(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6]$ (34)

Complex **34** exhibits a considerably broadened wave with shoulders preceding the main anodic and cathodic peak (Figures 12a and 12b). The $\Delta E_{p/2}$ and ΔE_p values are distinctly larger than those of the decamethylferrocene standard at all sweep rates. Figures 13 and 14 display a typical voltammogram and a differential pulse voltammogram of **34** in the presence of decamethylferrocene, which clearly show the broadening. Essentially the same results were obtained in THF/Bu_4NPF_6 as the electrolyte. Such behavior is typical of a weak interacting system. Effects like solvent reorganization and increasing Columbic repulsion upon adding further positive charges are likely similar for all compounds. We therefore assign the observed wave broadening to weak electronic interactions between the individual ferrocenyl sites in **34**. These are presumably transmitted by the ethynyl spacers and transanular or through bond interactions within the four-membered $(Al{-}C{\equiv}CFc)_2(CCH_2Ph)_2$ rings. From the broadening of the wave, and, after accounting for Ohmic drop, the half wave potentials of the individual ferrocenyl entities was determined. This was done under the premise that there are two independent pairs of weakly interacting ferrocene sites with no interaction between the two $(Al{-}C{\equiv}CFc)_2(CCH_2Ph)_2$ entities of **34**. The individual redox potentials were then assessed by digital simulation. A satisfactory fit over the range of sweep rates employed in this study (0.05 V/s to 1 V/s) was obtained by assuming a 65 mV difference between the individual half wave potentials (see Table 1).

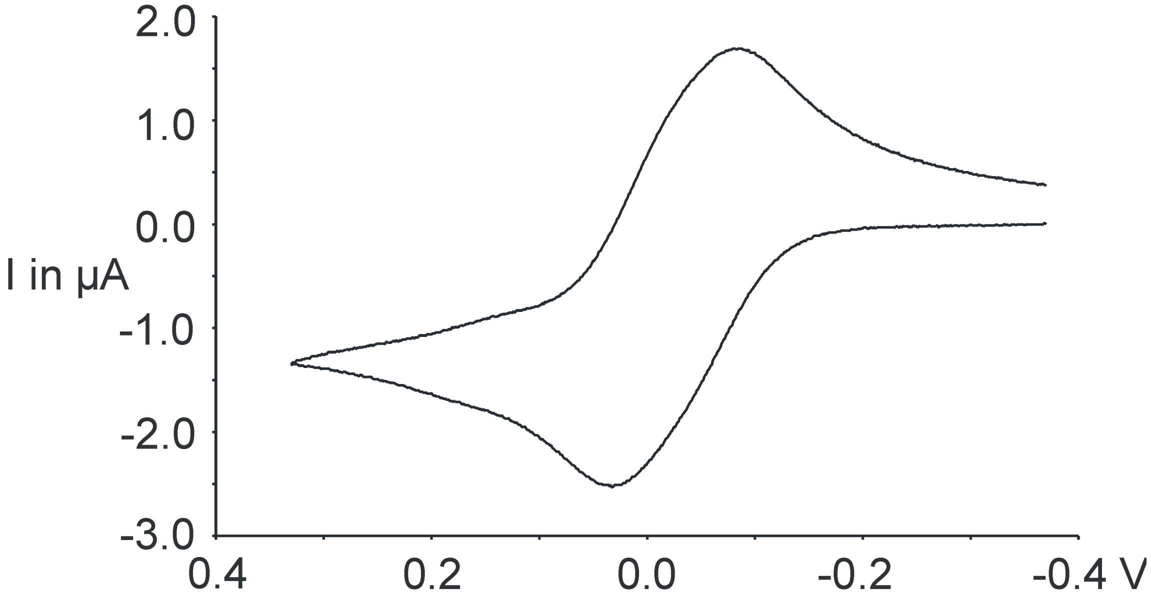


Figure 12a. *Cyclic voltammogram of compound* $[(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6]$ (**34**) *in* CH_2Cl_2/Bu_4NPF_6 *(0.2* M*) at v = 0.05 V/s.*

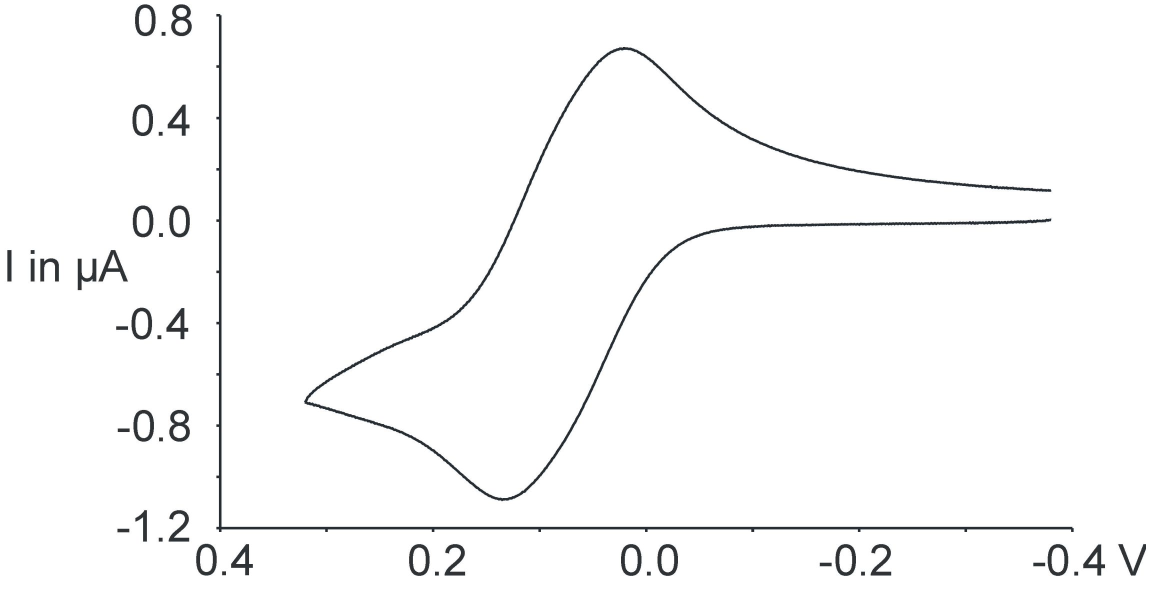


Figure 12b. *Cyclic voltammogram of compound* $[(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6]$ (**34**) *in* THF/Bu_4NPF_6 *(0.2* M*) at v = 0.05 V/s.*

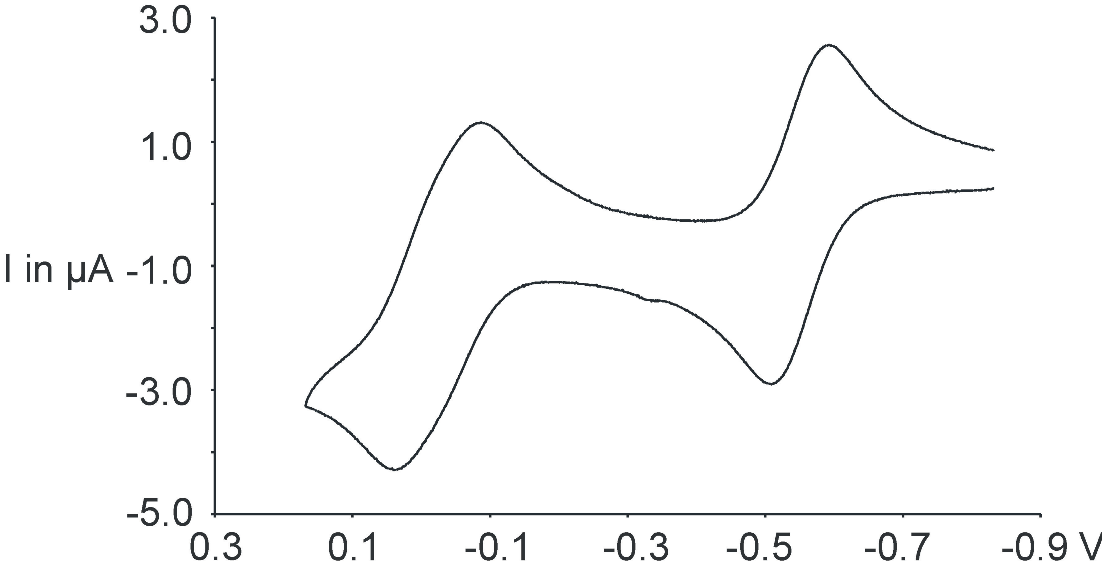


Figure 13. *Cyclic voltammogram of compound [(AlH)$_2$(FcC≡CAl)$_4$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$]* (**34**) *in CH$_2$Cl$_2$/Bu$_4$NPF$_6$ (0.2* M*) in the presence of internal decamethylferrocene at v = 0.05 V/s.*

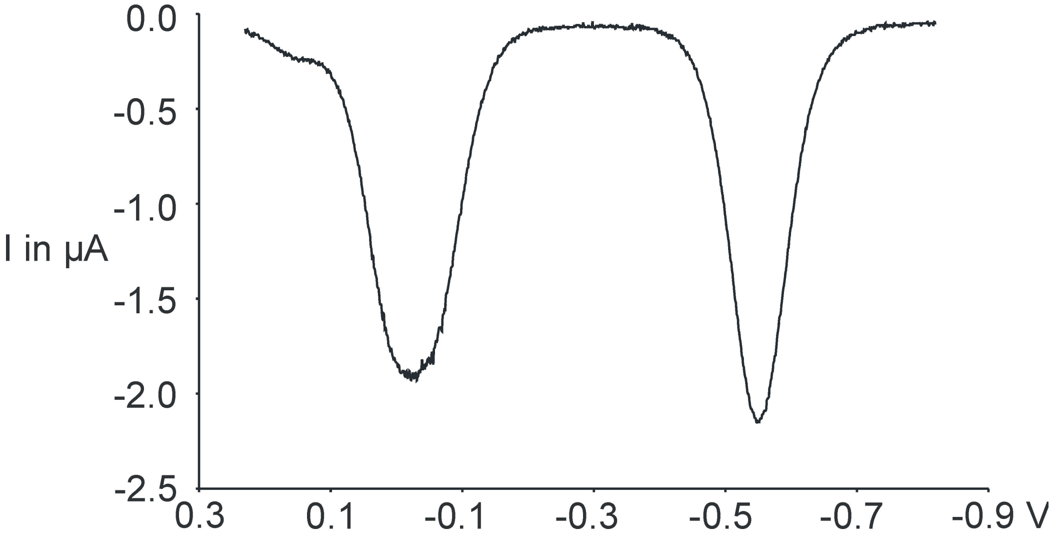
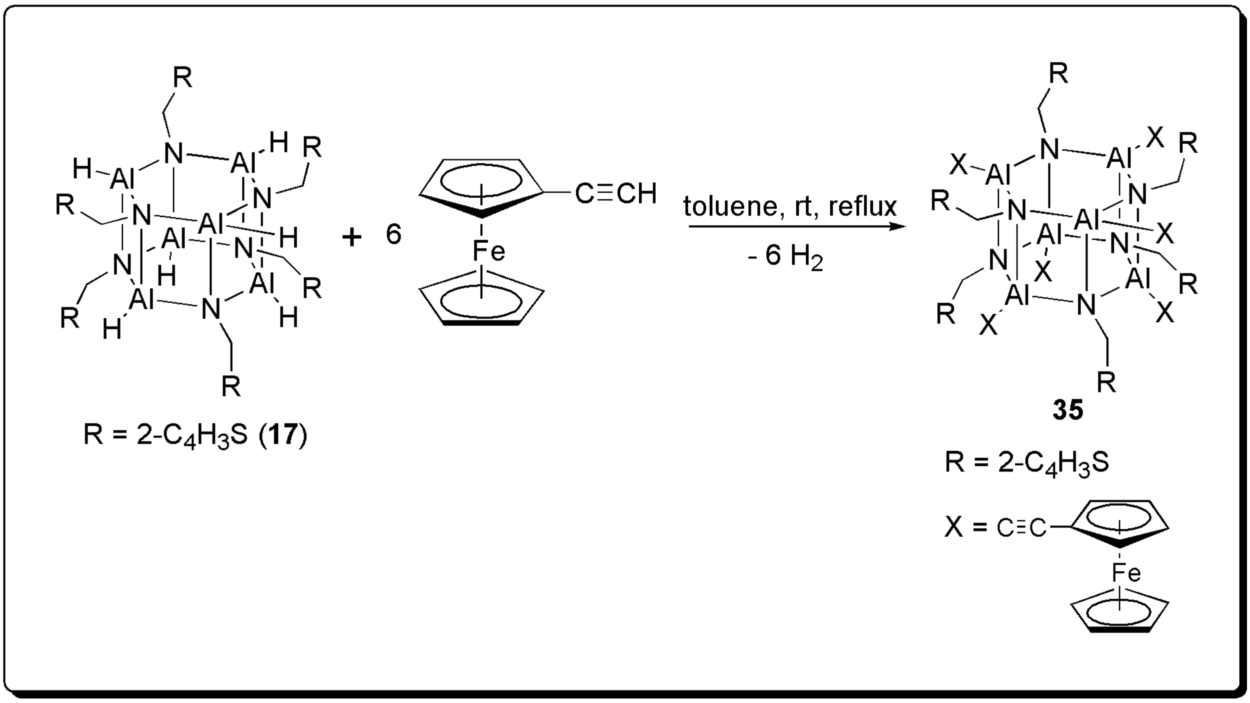


Figure 14. *Differential pulse voltammogram of [(AlH)$_2$(FcC≡CAl)$_4$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$]* (**34**) *at v = 5 mV/s in in CH$_2$Cl$_2$/Bu$_4$NPF$_6$ (0.2* M*) in the presence of internal decamethylferrocene.*

2.8. Heterobimetallic clusters containing aluminum

In the literature ferrocene derivatives of the group 13 organometallic compounds are reported of the ((dimethylamino)methyl)ferrocene adduct of BH_3,[185] $(OH)_2BF$,[186] AlH_3[187] and $AlMe_3$.[187] A few ferrocenylacetylene cluster compounds containing transition metals like mono nuclear complex $[PtH(C{\equiv}CFc)(PPh_3)_2]$,[188] dinuclear complex $[Ru_2(CO)_6(C_4H_2Fc)_2]$[189] and trinuclear complexes $[Co_3(CO)_9(CC{\equiv}CFc)]$[190] and $[Os_3H(CO)_{10}(CH{=}CHFc)]$[191] were reported in the literature and have been investigated by electron spectroscopy and cyclic voltammetry, however, there are no reports where ferrocenyl units are assembled on an aluminum nitride and aluminum carbide surfaces using C≡C and CH_2 spacers respectively.

Scheme 13



2.8.1. Synthesis of [CpFe$C_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$ (35)

The reaction between stoichiometric amounts of compound **17** and ferrocenylacetylene under refluxing conditions leads to the formation of compound **35** (Scheme 13). The reaction mixture was refluxed till the evolution of H_2 had ceased.[192] The resulting solution was kept at 0 °C to obtain reddish brown crystals of **35**. It is the only isolable compound. All the six hydridic hydrogens were replaced by six ferrocenylacetylide moieties. The Al–N framework remained intact during the substitution. Compound **35** is air and moisture sensitive and was characterized by multinuclear NMR, mass spectrometry, IR and elemental analysis. A strong absorption band at 2119 cm^{-1} in the IR spectrum can be designated to ν(C≡C)[171] stretching frequency. The lack of absorption bands at 1860 cm^{-1} and 3313 cm^{-1} indicates the absence of Al–H and C≡*C–H* bonds respectively. No molecular ion peak was found in the EI mass spectrum rather fragments were observed.

2.8.2. X-ray crystal structure of

[CpFe$C_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$ (35)·4PhMe

The molecular structure of **35** in the solid state was determined by single crystal X-ray structural analysis. Compound **35** crystallizes in the triclinic space group $P\bar{1}$ with one half of the molecule and two molecules of toluene in the asymmetric unit. An ORTEP plot of **35** is shown in Figure 15. The polyhedron contains an Al–N framework in which the aluminum and nitrogen atoms are positioned alternatively. The molecule has a center of symmetry and two of the ferrocenyl moieties are oriented toward the central core while the rest is projected away. The bond parameters are similar to the previously studied structures and the Al–N bond lengths forming the hexagonal faces are significantly shorter than the interlinking Al–N bonds. It is to be noted that the C≡C–Al bond angles deviate from the expected 180° similar to that of compounds **19** and **23** and vary significantly from each other (C(2)–C(1)–Al(1) 170.82(7)°, C(5)–C(4)–Al(2) 166.88(6)°, C(8)–C(7)–Al(3) 169.11(5)°). In a similar fashion,

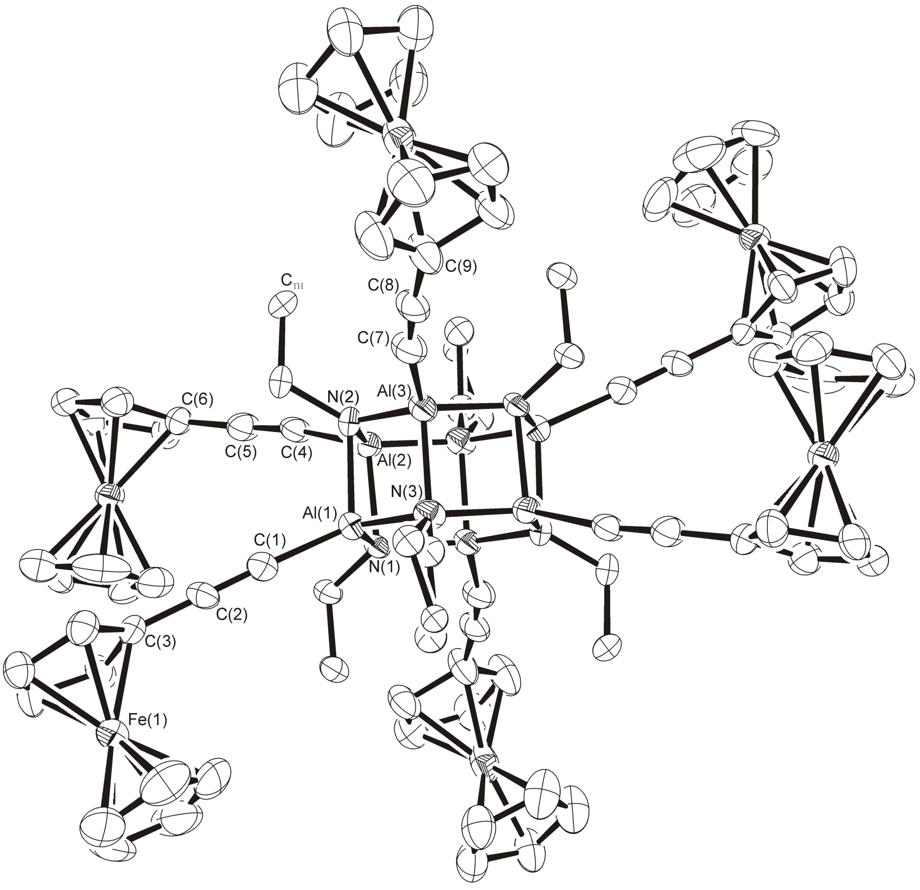


***Figure 15**. Crystal structure of compound* $[CpFeC_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**35**)$\cdot$*4PhMe in the crystal with 50 % ellipsoid probability.* C_{TH} = $2\text{-}C_4H_3S$. $2\text{-}C_4H_3S$ *groups, toluene molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–N(1) 1.887(6), Al(1)–N(2) 1.981(5), Al(1)–N(3) 1.882(5), Al(1)–C(1) 1.893(6), C(1)–C(2) 1.222(8), C(2)–C(3) 1.444(8); C(2)–C(1)–Al(1) 170.82(7), C(5)–C(4)–Al(2) 166.88(6), C(8)–C(7)–Al(3) 169.11(5), C(1)–C(2)–C(3) 174.9(8), C(4)–C(5)–C(6) 174.70(7), C(7)–C(8)–C(9) 176.90(8), N(1)–Al(1)–N(2) 92.01(2), N(3)–Al(1)–N(1) 115.79(8), Al(1)–N(1)–Al(2) 87.56(2), Al(2)–N(2)–Al(3) 123.91(2), N(2)–Al(1)–C(1) 115.00(2), N(3)–Al(1)–C(1) 121.17(3).*

the C≡C–C bond angles also deviate from linearity (C(4)–C(5)–C(6) 174.70(7)°, C(7)–C(8)–C(9) 176.90(8)°, C(1)–C(2)–C(3) 174.9(8)°).

2.8.3. Cyclo voltammetric studies of $[CpFeC_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$ (35)

The electrochemistry of **35** was investigated in CH_2Cl_2 solution. Only one single oxidation wave was observed within the solvent window (Figure 16). This was fully reversible even at sweep rates as low as 25 mV/s and displayed a half wave potential of +0.16 V when calibrated against the ferrocene/ferrocenium couple. The forward peak width at half height and the peak-to-peak separation were identical to those measured for the internal ferrocene[193,194] and decamethylferrocene[195,196] standards, which were added in concentrations that can provide peak currents identical to those of compound **35**. The same overall behavior was found in Differential Pulse and Osteryoung Square Wave Voltammetry

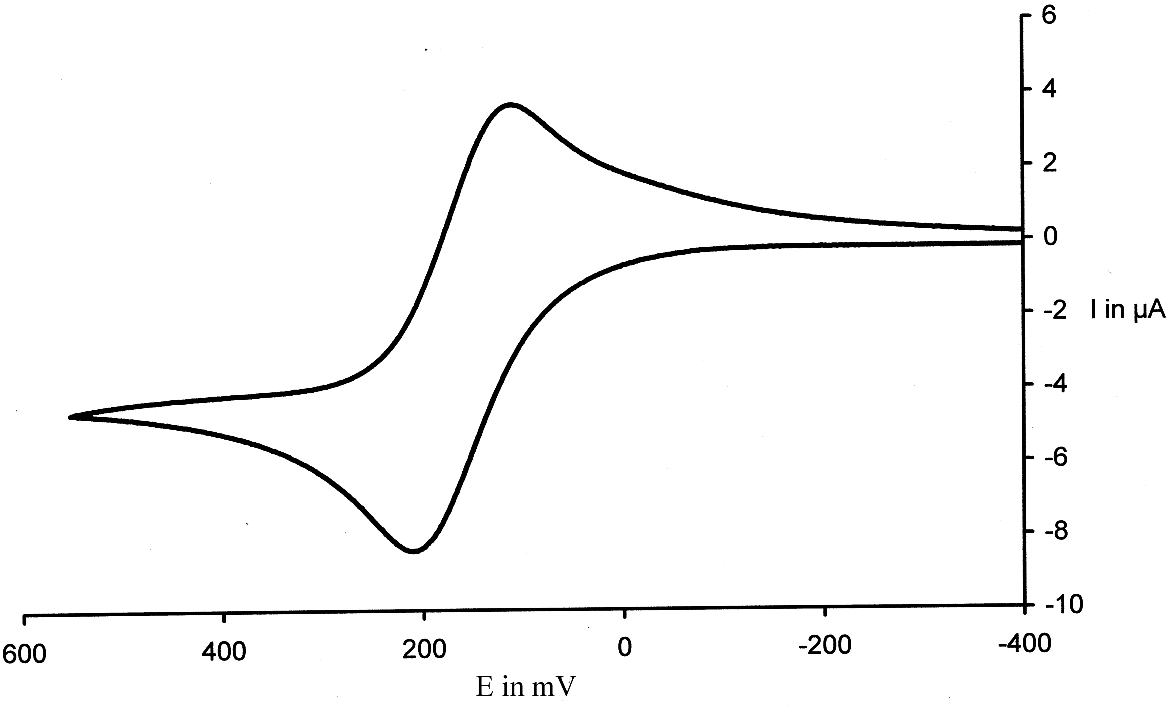


Figure 16. *Cyclic voltammogram of compound* $[CpFeC_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**35**) *in* CH_2Cl_2 *in the presence of* Cp_2Fe *and decamethylferrocene as internal standards.*

(Figure 17). Here the peak widths at half height fully agreed with those of both the internal standards. From this we conclude that all the six equivalent ferrocenyl subunits present in **35** are oxidized at the very same potential. The reversible electrochemical behavior of compound **35** shows that this compound is perfectly stable and robust even in the oxidized state. These results argue against any kind of electronic interactions between the individual ferrocenyl subunits. In diferrocenylacetylene and related systems ethynyl spacers have been found to provide a pathway for at least some degree of electronic coupling between the bridged sites.[197] Since no coupling between the ferrocenyl subunits is detected in compound **35** the nitrogen atoms at the other end of the acetylene spacer are probably well insulated from each other by the interspersed RAl bridges.

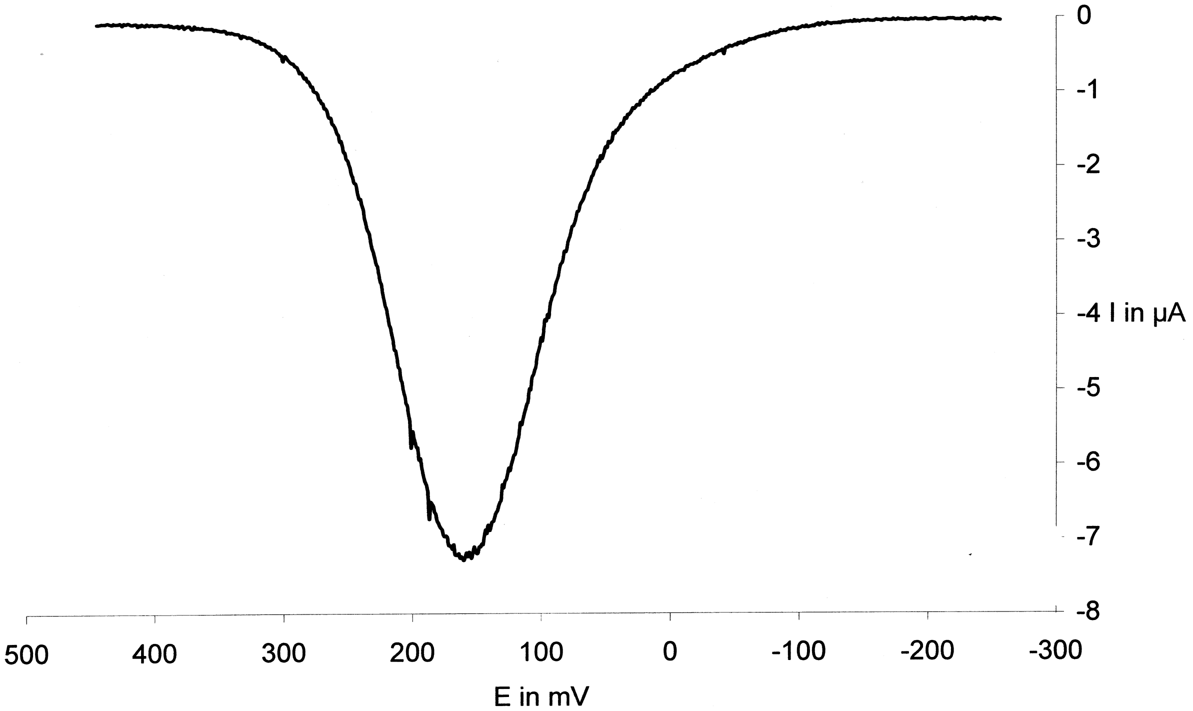
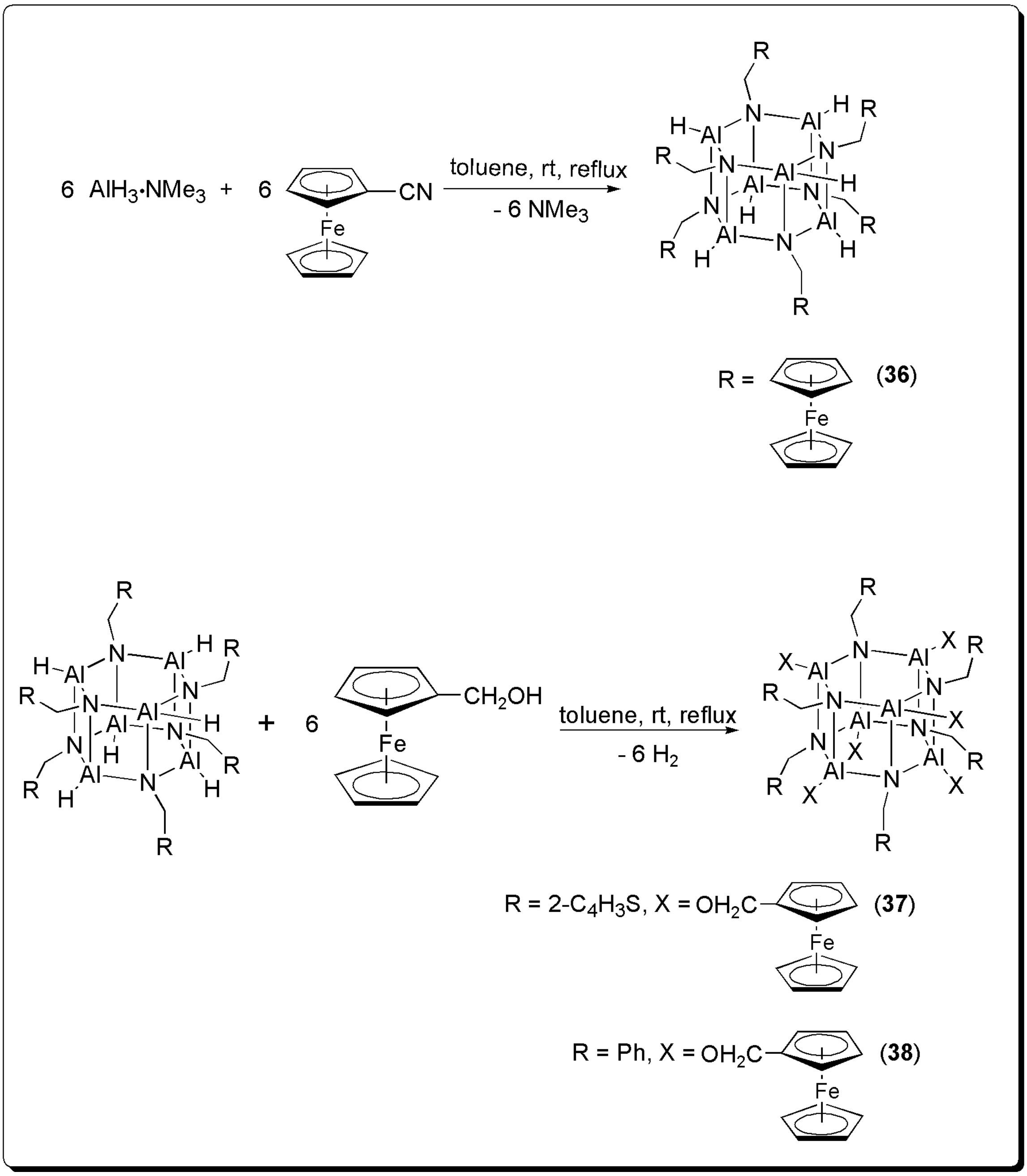


***Figure 17**. Differential Pulse and Osteryoung Square Wave Voltammetry of compound* $[CpFeC_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**35**).

2.8.4. Synthesis of $[HAlNCH_2C_5H_4FeCp]_6$ (36), $[CpFeC_5H_4CH_2OAlNCH_2(C_4H_3S)]_6$ (37), and $[CpFeC_5H_4CH_2OAlNCH_2Ph]_6$ (38)

To a toluene solution of ferrocenylnitile was added an excess amount of $AlH_3 \cdot NMe_3$ at room temperature. The reaction mixture was stirred at ambient temperature for 0.5 h and refluxing the resulting solution till the evolution of NMe_3 had ceased gave $[HAlNCH_2C_5H_4FeCp]_6$ (**36**) in good yield (Scheme 14). The experimental conditions employed in the synthesis of $[CpFeC_5H_4CH_2OAlNCH_2(C_4H_3S)]_6$ (**37**) and $[CpFeC_5H_4CH_2OAlNCH_2Ph]_6$ (**38**) are similar to that of compound **35**. The reaction between stoichiometric amount of ferrocenylmethanol and $[HAlNCH_2(C_4H_3S)]_6$ (**17**), ferrocenylmethanol and $[HAlNCH_2Ph]_6$ (**13**) under refluxing toluene conditions yielded the compounds **37** and **38** in quantitative yield.[198] All the compounds were completely analyzed by means of spectral and elemental analysis. Compound **36** exhibits a characteristic Al–H bond stretching frequency correspondingly at 1845 cm^{-1} in the IR spectrum, which is absent in the compounds **37** and **38**. The solid-state ^1H NMR spectra resonances for the protons of the ferrocenyl units appear at δ 4.3 ppm for **36** and at δ 4.1 ppm for **37** and **38**. The protons of OCH_2 units in **37** and **38** resonate in the downfield region at δ 3.6 ppm and δ 3.3 ppm whereas singlets were observed for NCH_2 protons in the upfield region (δ 2.4 ppm for **37** and δ 3.1 ppm for **38**). In the solid-state ^{13}C NMR spectra the carbon atoms of the ferrocenyl units resonate at δ 68.0, 67.0 and 68.0 ppm, respectively for **36**, **37** and **38** and the carbon atom of the OCH_2 unit in **37** and **38** appear at δ 59.0 ppm and δ 60.0 ppm. The resolution of the spectra in ^1H-^{13}C 2D HETCOR (Heteroatom Correlation Spectra) showed this observation more clearly.

Scheme 14


6 AlH3·NMe3 + 6
CN
Fe
toluene, rt, reflux
- 6 NMe3
R =
(36)
+ 6
CH2OH
toluene, rt, reflux
- 6 H2
R = 2-C4H3S, X = OH2C
(37)
R = Ph, X = OH2C
(38)

2.8.5. Cyclo voltammetric studies of [$HAlNCH_2C_5H_4FeCp]_6$ (36), [$CpFeC_5H_4CH_2OAlNCH_2(C_4H_3S)]_6$ (37), and [$CpFeC_5H_4CH_2OAlNCH_2Ph]_6$ (38)

All compounds in this study are chemically and electrochemically reversible and oxidized at nearly the same potential as the ferrocene/ferrocenium standard. In compounds **36, 37** and **38** the oxidation of the individual ferrocene sites gives rise to only a single wave with basically the same characteristics as that of the internal decamethylferrocene standard. Thus, the measured peak widths at half height, $\Delta E_{p/2}$ for the anodic (forward) peak and peak potential differences, ΔE_p are just a few mV larger than the values measured for decamethylferrocene present at concentrations that rendered similar peak currents as that of the analyte. The same holds for differential pulse voltammetry. This signals that any interactions between the individual ferrocene entities are, at best, very weak. In these compo-

Table 1. Electrochemical data of compounds **34**, and **36** - **38**

Compound	$E_{1/2}$ in V[a)]	ΔE_p in mV[b)]	$E_{p/2}$ in mV[b)]
34	0.010, -0.060	100	92
36	-0.010	64	63
37	-0.010	66	63
38	-0.025	62	60

[a)] Half-wave potentials are referenced versus the ferrocene/ferrocenium standard.

[b)] The experimental values of decamethylferrocene were set equal to the theoretical value of 59 mV (ΔE_p) or 57 mV ($E_{p/2}$)[199] to account for Ohmic drop.

-unds the ferrocenyl substituents are attached to the imidoalane cores through insulating methylene (CH_2) or methyleneoxy (OCH_2) spacers, which interrupts any interactions between them. All data are compiled in Table 1 and Figures 18-20 display the voltammograms of the individual compounds at a scan rate of 50 mV/s.

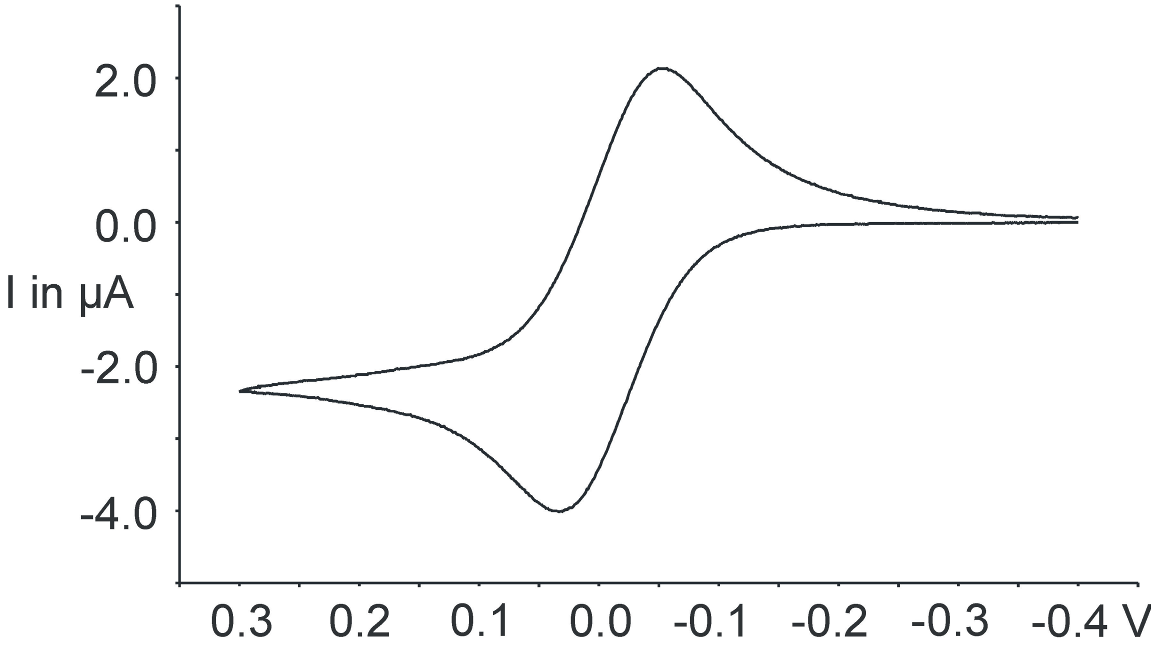


Figure 18. *Cyclic voltammogram of compound* $[HAlNCH_2C_5H_4FeCp]_6$ (**36**) *in* CH_2Cl_2/Bu_4NPF_6 *(0.2* M*) at* $v = 0.05$ *V/s.*

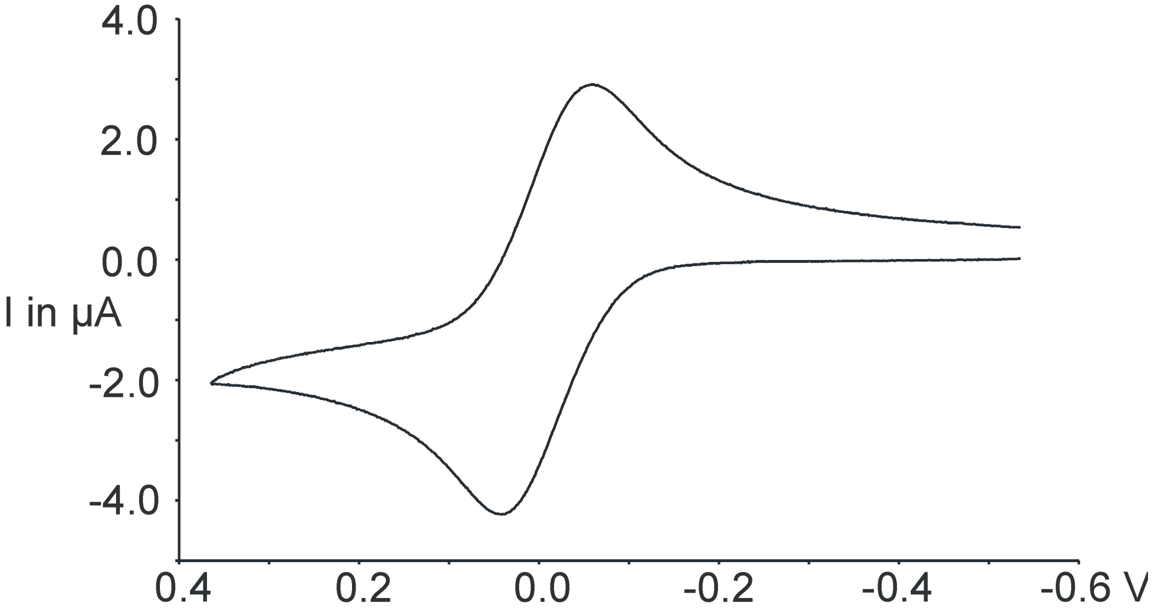


Figure 19. *Cyclic voltammogram of compound* $[CpFeC_5H_4CH_2OAlNCH_2(C_4H_3S)]_6$ (**37**) *in* CH_2Cl_2/Bu_4NPF_6 *(0.2* M*) at v = 0.1 V/s.*

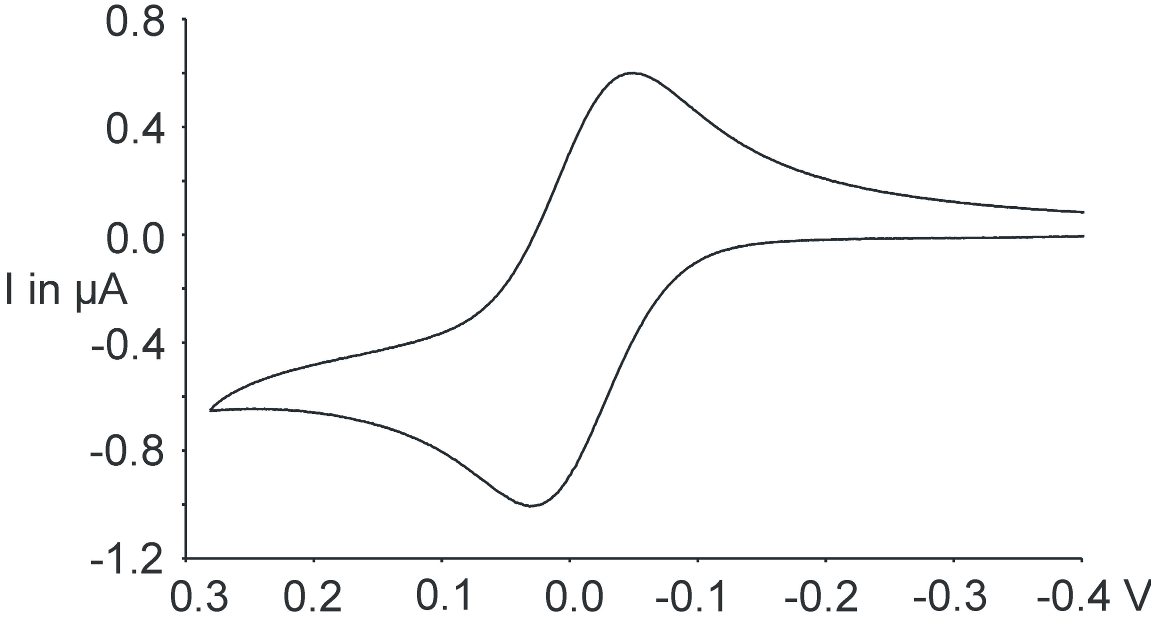
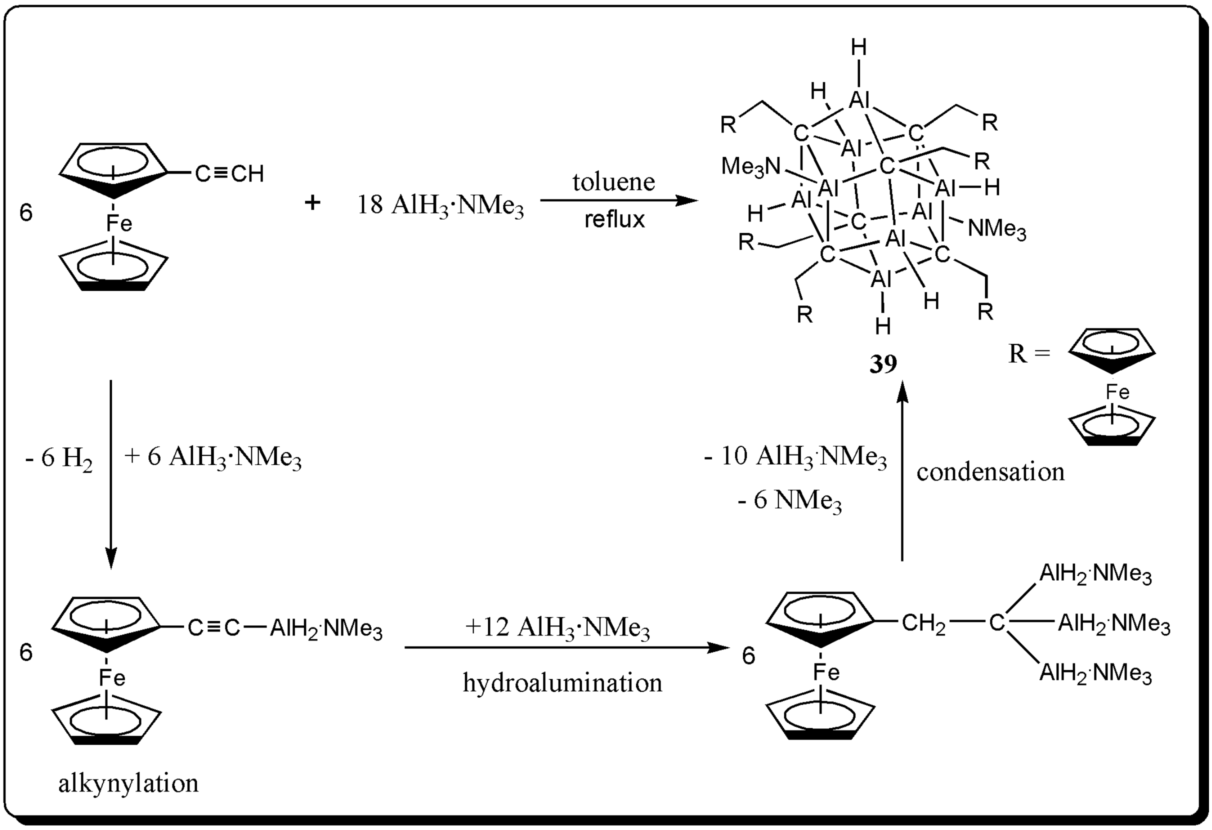


Figure 20. *Cyclic voltammogram of compound* $[CpFeC_5H_4CH_2OAlNCH_2Ph]_6$ (**38**) *in* CH_2Cl_2/Bu_4NPF_6 *(0.2* M*) at v = 0.05 V/s.*

2.8.6. Synthesis of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeCp)_6]$ (39)

The reaction of ferrocenylacetylene with an excess of $AlH_3{\cdot}NMe_3$ in refluxing toluene resulted in the formation of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeCp)_6]$ (**39**) (Scheme 15).[178] During the reaction evolution of NMe_3 and H_2 was observed. Reddish brown crystals of compound **39** were obtained as the only isolable product when the reaction mixture was kept for crystallization at room temperature after the heating period. The mechanism of hydroalumination of ferrocenylacetylene is believed to be similar to that of $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**29**).[175] Thus, as shown in Scheme 15 the first step is envisaged as the formation of $FcC{\equiv}C{-}AlH_2{\cdot}NMe_3$ (Fc = ferrocenyl) accompanied by the elimination of H_2. Subsequent hydroalumination reaction on this intermediate would lead to the formation of $FcCH_2C(AlH_2{\cdot}NMe_3)_3$, which can undergo condensation reaction to afford

Scheme 15



the carbaalane **39**. Compound **39** is an air/moisture sensitive solid that was characterized by single crystal X-ray structural analysis, IR spectroscopy and elemental analysis. ^{1}H and ^{13}C NMR spectra of **39** in solution could not be recorded due to its very poor solubility in benzene, toluene, acetonitrile and THF, respectively. Also, **39** decomposes in trichloromethane. Although there are two chemically different aluminum atoms, the solid-state ^{27}Al NMR spectrum of compound **39** shows only one prominent broad resonance at δ 140.0 ppm. The solid-state ^{27}Al NMR spectrum of **39** is shown in Figure 21. It was difficult to further quantify the quadrupolar sites due to the significant degree of structural disorder. The solid-state ^{13}C NMR resonances of the cluster carbon and N*Me*$_3$ appear at δ 28.0 ppm and δ 44.0 ppm, respectively. In the solid-state ^{1}H NMR spectrum of **39** the methylene protons of the cluster resonates at δ 1.9 ppm and the methyl protons of N*Me*$_3$ are observed at δ 2.7 ppm. Further resolution of the spectra in ^{1}H-^{13}C 2D HETCOR (Heteroatom Correlation Spectra)

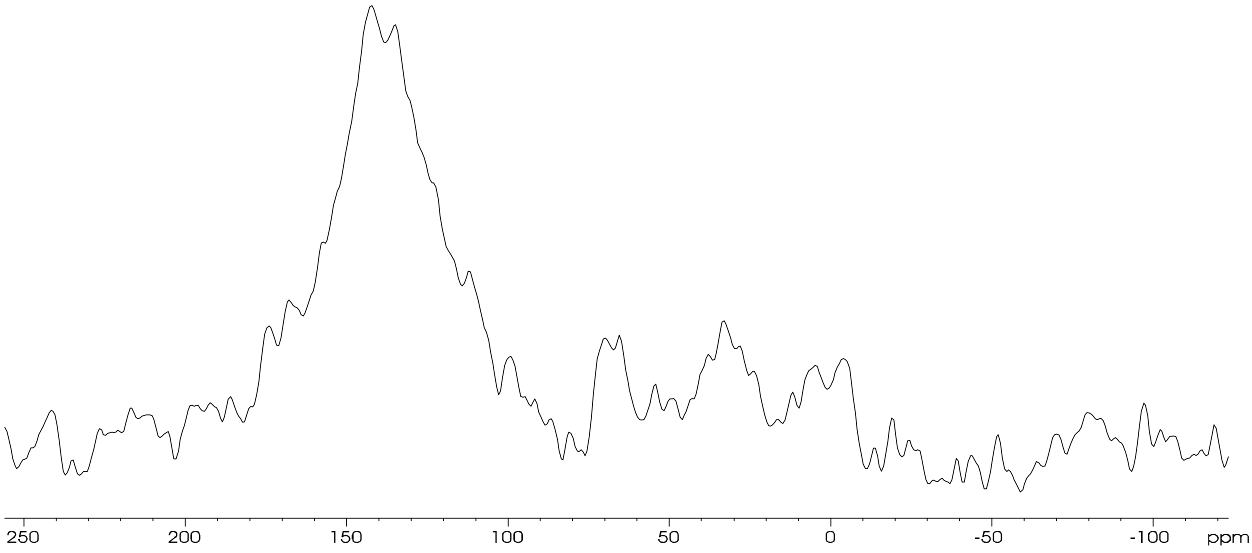


Figure 21. *Magic Angle Spinning spectra of ^{27}Al in solid state for compound* **39** *recorded at 600 MHz (1H) and 23 KHz.*

showed this observation more clearly. A correlation typical for the methyl group could be found at $^{1}H = \delta$ 2.7 ppm and $^{13}C = \delta$ 44 ppm. Similarly, the correlation ($^{1}H = \delta$ 5.0 ppm and $^{13}C = \delta$ 65 ppm) could be attributed to the ferrocenyl subunit. The absence of a strong absorption band at 2119 cm^{-1} in the IR spectrum indicates the absence of ν(C≡C) [171] stretching frequency. The presence of a broad absorption band at 1802 cm^{-1} can be assigned to the Al–H bond. We could not explore the electrochemical studies and reactivity of Al–H bonds of **39** due to its very poor solubility.

2.8.7. X-ray crystal structure of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeCp)_6]$ (39)·2.5PhMe

The molecular structure of **39** in the solid state was determined by single crystal X-ray structural analysis on reddish brown crystals obtained from saturated toluene solution at ambient temperature. **39** crystallizes in the triclinic space group $P\bar{1}$ with two halves of the molecule and 2.5 molecules of toluene in the asymmetric unit. In one cluster molecule all Fe units are disordered (nearly 60:40). An ORTEP plot of **39** is shown in Figure 22. The carbaalane polyhedron contains an Al–C framework with eight aluminum atoms occupying the corners of the rhombic cube while the six carbon atoms bearing the ferrocenylmethylene groups cap the faces of the cube. Six of the eight aluminum atoms carry a hydrogen atom and the remaining two, which are positioned opposite to each other in the cluster, are bonded to the NMe_3 groups. The opposite pairs of ferrocenylmethylene groups are trans to each other. The average distances between the aluminum atoms bonded to the NMe_3 groups and the closest cluster carbon atoms (2.017(5) Å, 2.025(5) Å, 2.032(5) Å) are significantly shorter than the corresponding distances from the aluminum atoms bonded to the hydrogen atoms

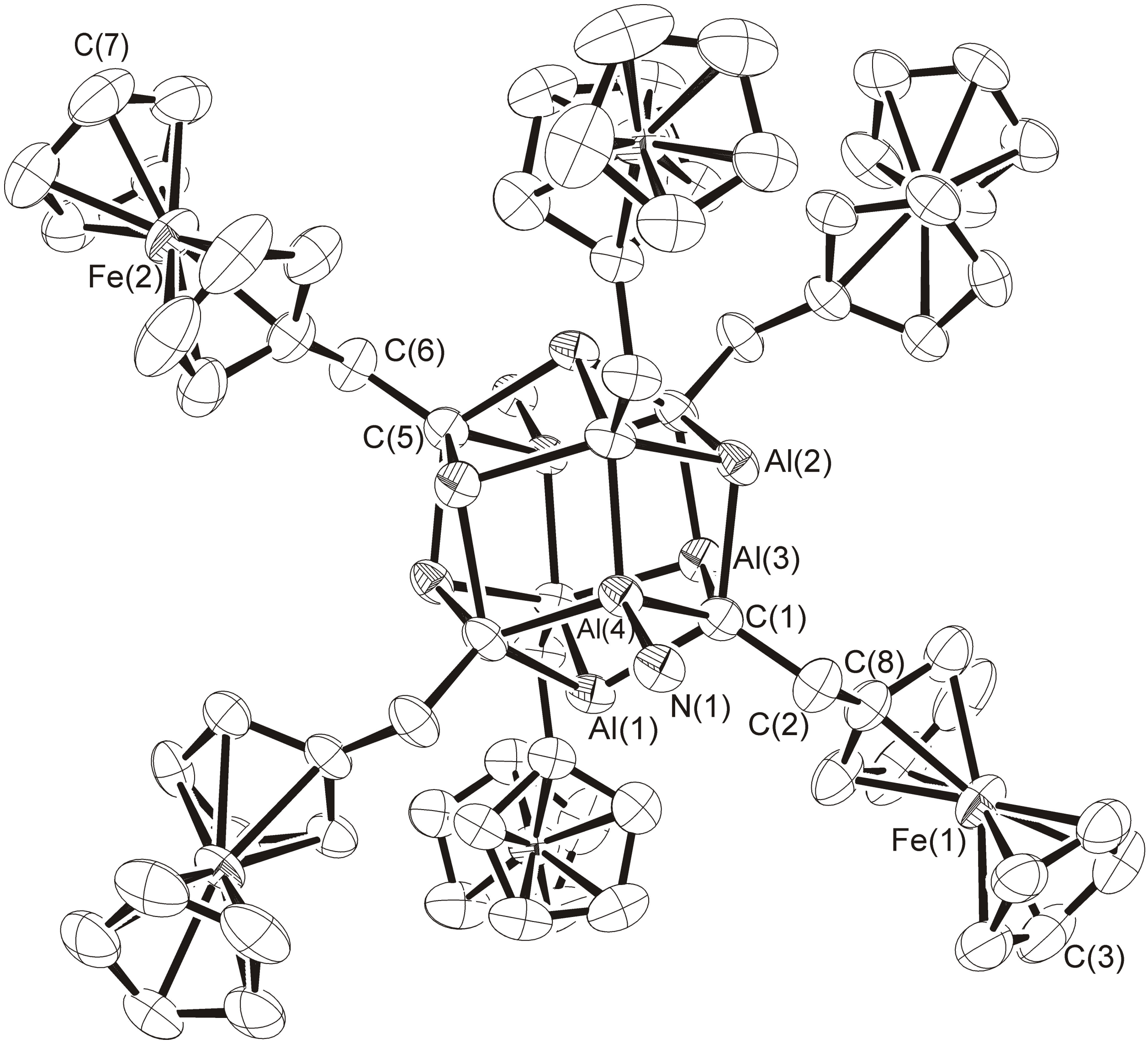


Figure 22. *Crystal structure of compound [$(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$]* (**39**) *·2.5PhMe with 50 % ellipsoid probability without disordered positions. Toluene molecules, methyl groups and hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [°]: Al(1)–Al(3) 2.645 (2), Al(1)–Al(4) 2.584 (2), Al(4)–N(1) 2.001 (4); Al(4)–C(1)–Al(2) 77.97 (17), Al(4)–C(1)–Al(3) 123.83 (1), Al(1)–C(1)–Al(2) 127.34 (2), Al(2)–C(1)–Al(3) 78.37 (17).*

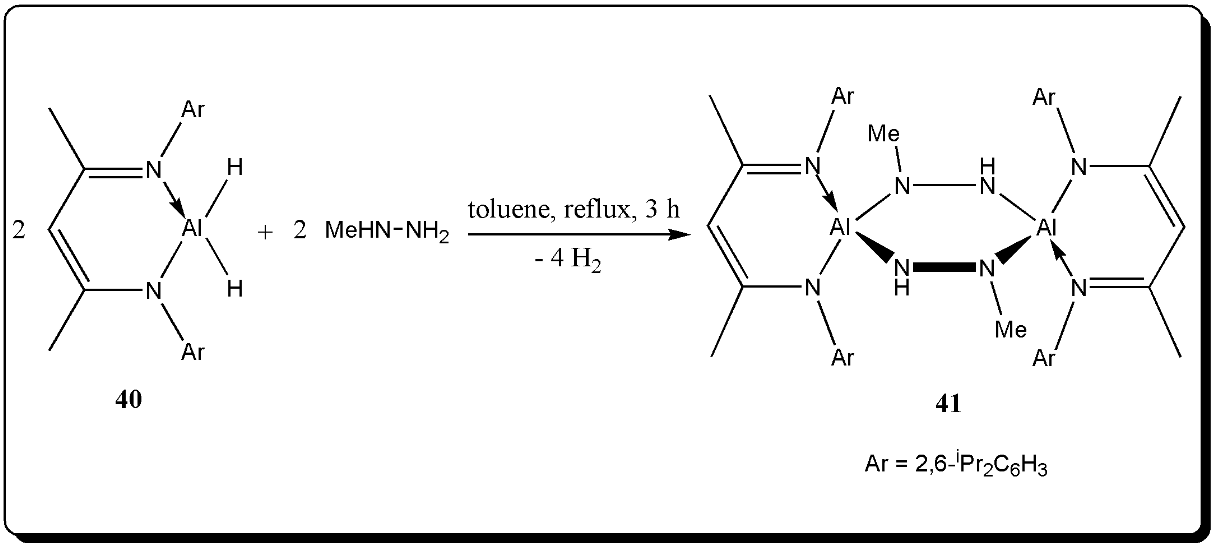
(2.076(5) Å, 2.094(5) Å, 2.099(5) Å). Similarly, the average distances between the aluminum atoms coordinated to the NMe_3 groups and the Al atoms bonded to the hydrogen atoms (2.578(2) Å, 2.584(2) Å) are shorter than the corresponding distances between the aluminum atoms bearing the hydrogen atoms (2.645(2) Å, 2.641(2) Å). These aluminum-aluminum distances are comparable with those of the dimeric aluminum trimethyl.[180] The average bond angles are found to be similar to the reported carbaalane[175] (Al(4)–C(1)–Al(3) 123.83(2)°, Al(1)–C(1)–Al(2) 127.34(2)°, Al(2)–C(1)–Al(3) 78.37(17)°). The diameter of the cluster measured between two ferrocenylmethylene groups of the cluster, which are trans to each other, is 1.648 nm (C(7)–C(3)). All the bond parameters are comparable to that of compound **29**.

2.9. Aluminum hydrazides

2.9.1. Synthesis of a planar dimeric six-membered spirane aluminum hydrazide $[LAlN(Me)NH]_2$ (41); [L = $HC\{(2,6\text{–}^{i}Pr_2C_6H_3N)(CMe)\}_2$]

The reaction between stoichiometric amounts of $LAlH_2$ (**40**) and methylhydrazine in toluene under refluxing conditions leads to the formation of compound **41** with elimination of H_2 (Scheme 16). During the reaction the color of the solution changed from colorless to reddish brown and this color was sustained throughout the reaction period. All the volatiles were removed in vacuo and the residue was extracted with *n*-hexane (20 mL). The resulting solution was kept at 0 °C to obtain reddish brown crystals of **41**. Compound **41** was the only isolable compound. No reaction was observed when the reaction was carried out at room temperature. The air and moisture sensitive compound **41** has a melting point of 297 - 299 °C and was characterized by multinuclear NMR, mass spectrometry, IR, and elemental analysis. In the ^1H NMR spectrum the N*Me* protons resonate at δ 2.10 ppm and the N*H* proton at δ 0.21 ppm. Compound **41** is centrosymmetric and has two septets corresponding to the C*H* proton of the isopropyl groups (δ 3.46 and 3.25 ppm). In the EI mass spectrum the most intense peak

Scheme 16



40

41

Ar = 2,6-$^iPr_2C_6H_3$

(*m/z* 976) corresponds to the dimer, which is indicative of the stability of the Al_2N_4 ring, and a small peak related to the monomer appears at *m/z* 488. In the IR spectrum a weak band was observed at 3440 cm^{-1}, which can be attributed to the N–H stretching frequency.[200]

2.9.2. X-ray crystal structure of $[LAlN(Me)NH]_2$ (41)·C_6H_{14}

X-ray crystal structural analysis of $[LAlN(Me)NH]_2$ (**41**)·C_6H_{14} was perfomed using reddish brown crystals obtained by slow crystallization from saturated hexane solution at 0 °C. An ORTEP plot of **41** is shown in Figure 23. Compound **41** crystallizes in the triclinic space group $P\overline{1}$ with one half of the molecule and one half of the *n*-hexane molecule in the asymmetric unit. It is a spirane molecule in which the six-membered Al_2N_4 ring is connected by *β*-diketiminato ligands at each of the aluminum centers. Compound **41** has a planar Al_2N_4 ring. It contains a centrosymmetric dimer with an inversion center. The aromatic groups are dangling above and below the six-membered ring and they are slightly inclined towards the vertical axis of the six-membered ring. The aluminum atom is tetracoordinate, connected to the four nitrogen atoms in a distorted tetrahedral array. Two methyl groups present on N(1) and N(3) are anti-periplanar to each other. The hydrogen atoms on two nitrogen atoms were freely refined on two split positions with half occupancy. The Al–N bond lengths (Al(1)–N(1) 1.787(2) Å, N(2)–Al(2) 1.804(2) Å) within the planar Al_2N_4 ring of **41** are shorter in comparison to those of $[Me_2AlN(SiMe_3)–N(^tBu)H]_2$ (1.874(2) Å and 2.016(2) Å),[136] $[(Me_3C)_2AlN(SiMe_3)NH_2]_2$ (1.867(2) Å and 2.004(1) Å),[140] $[(Me_3C)_2AlNHNH_2]_2$ (1.951(2) Å)[145] and $[(Me_3C)_2AlNHNH]_2[\mu–Al(CMe_3)_2]_2$ (1.941(7) Å to 1.970(6) Å).[145] The sum of the bond angles of N(1) and N(3), which are bonded to the methyl groups is 359.99°, indicating the trigonal planar geometry. For N(2) and N(4) the sum of the bond angles is 337.45° showing clearly the pyramidal arrangement.

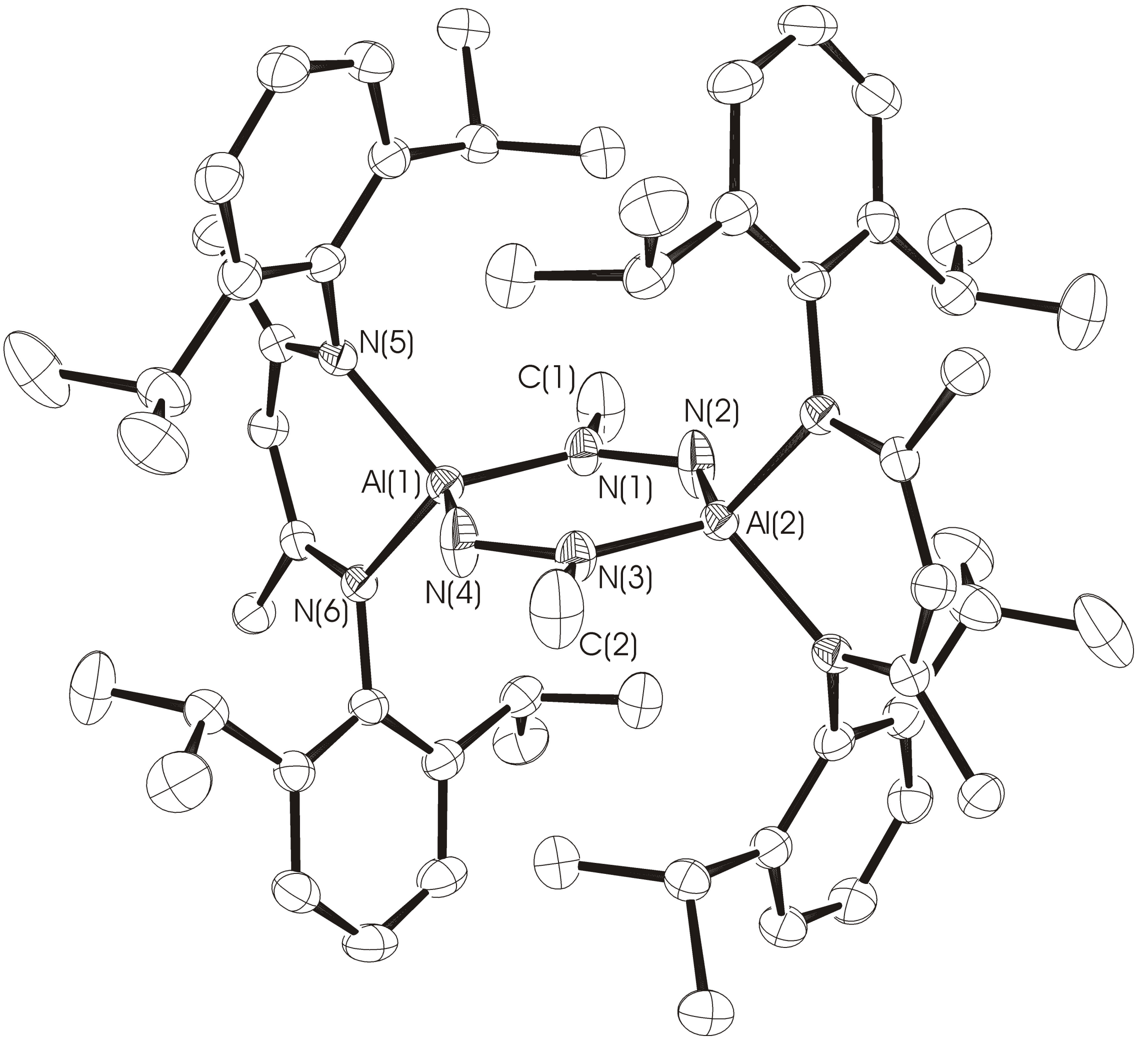


Figure 23. *Crystal structure of compound [LAlN(Me)NH]$_2$ (**41**)·C$_6$H$_{14}$ with 50 % ellipsoid probability without disordered positions. All hydrogen atoms are excluded for clarity. Selected bond lengths [Å] and angles [º]: Al(1)–N(1) 1.787(2), Al(1)–N(5) 1.939(2), N(1)–N(2) 1.445(2), N(2)–Al(2) 1.804(2); N(1)–Al(1)–N(4) 109.79(8), N(5)–Al(1)–N(1) 112.23(8), N(6)–Al(1)–N(5) 93.92(7), Al(1)–N(1)–N(2) 126.66(13), Al(1)–N(1)–C(1) 124.61(15), C(1)–N(1)–N(2) 108.72(17), N(1)–N(2)–Al(2) 123.54(13).*

2.9.3. Theoretical calculations of $[LAlN(Me)NH]_2$ (41)

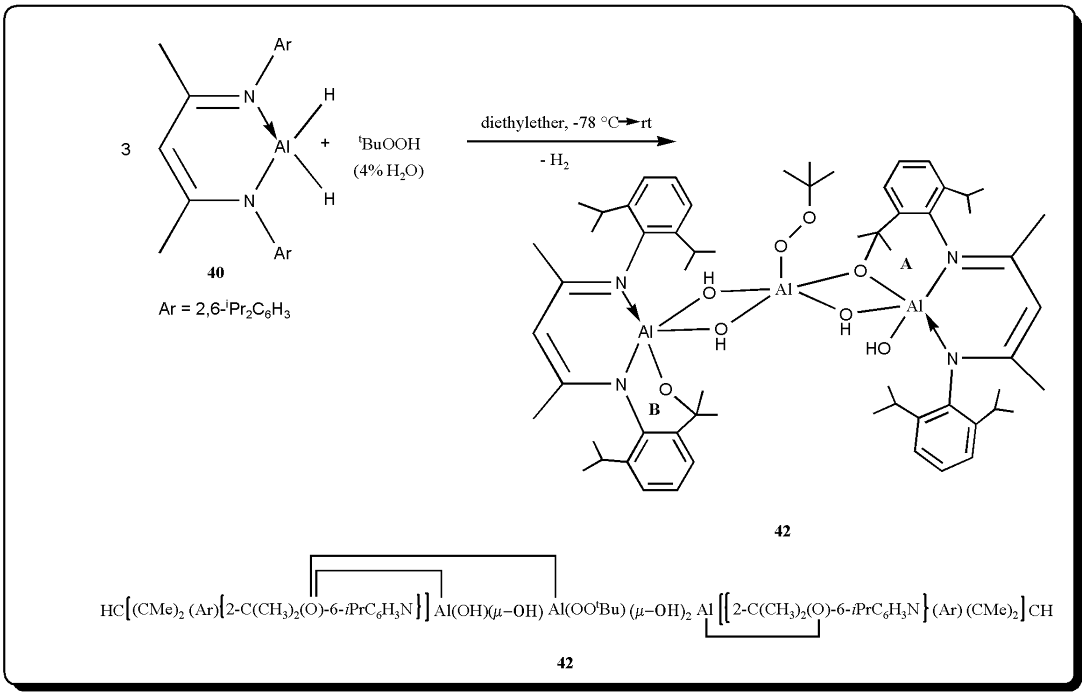
The theoretical calculations were carried out to explain the planarity of the nitrogen centers in the Al_2N_4 ring of compound **41**. The DFT-B3LYP method was employed within the Gaussian 98[201] selecting 6-311g(d,p) as basis sets unless otherwise specified. The geometry of compound **41** was optimized (6-311g for phenyl, and $CHMe_2$ in L was replaced by H). The planar nitrogen center and other structural parameters were successfully reproduced and the average bond length deviation is less than 0.02 Å, thus showing the reliability of the theoretical method. According to the classical chemical bond theory and VSEPR model, nitrogen with its coordination number three adopts a pyramidal geometry. However, in compound **41** there are two planar Al–N(Me)N centers. Several model molecules ($AlH_2(H_2O)(NH_2)$, $AlH_2(H_2O)(NMe_2)$, $AlH_2(H_2O)N(NH_2)_2$, $AlCl_2(H_2O)(NHNH_2)$) were studied theoretically in order to find the reason for the planarity of the nitrogen centers in **41**. It was observed that the geometry optimization gives a planar nitrogen center. These results show that the nitrogen center forms a triangular planar arrangement when bonded to aluminum and two other atoms. Thus the planar nitrogen center in **41** is due to the Al–N bond character rather than the presence of the sterically bulky ligands and other steric interactions. Moreover we also calculated the curve when the planar nitrogen center in $AlH_2(H_2O)N(NH_2)_2$ is distorted artificially (torsion angle 180°) to a pyramidal conformation (torsion angle 130°). The total energy change is only 0.95 kcal/mol, which is small compared with that of a hydrogen bond interaction. This may explain the pyramidal geometry at the Al–NHN center in compound **41** as the steric interaction prefers a staggered NH–NMe conformation rather than an eclipsed one.

2.10. Alkylperoxo aluminum compounds

2.10.1. Synthesis of penta-coordinated *tert*-butylperoxo aluminum compound (42)

To a solution of $LAlH_2$[202] (**40**) in diethylether (30 mL) was added drop wise two equivalents of $^{t}BuOOH$ (5 - 6 M solution in decane) at –78 °C. The $^{t}BuOOH$ solution in decane contains approximately 4 % water. After the addition, the reaction mixture was slowly warmed to room temperature and stirred overnight at this temperature. During the reaction the color of the solution changed to light yellow and this color was sustained during the course of the reaction. The volume of the solution was reduced to 15 mL and then stored at 0 °C. The expected four-coordinated aluminum di-*tert*-butylperoxide, $LAl(OO^{t}Bu)_2$ was not formed instead colorless crystals of **42** were obtained after one week (Scheme 17). The reaction pathway involved in the formation of **42** is not clear but we presume that the intermediate *tert*-butyl aluminumperoxide formed in the reaction medium might have activated C–H bond

Scheme 17



$$HC\left[(CMe)_2\,(Ar)\left[2\text{-}C(CH_3)_2(O)\text{-}6\text{-}iPrC_6H_3N\right\}\right]Al(OH)(\mu\text{-}OH)\,Al(OO^{t}Bu)\,(\mu\text{-}OH)_2\,Al\left[\left[2\text{-}C(CH_3)_2(O)\text{-}6\text{-}iPrC_6H_3N\right\}(Ar)\,(CMe)_2\right]CH$$

42

of the isopropyl group resulting in C–O–Al formation. During the course of reaction two C*H* protons (out of total of 8 CH protons) of the isopropyl groups of the *β*-diketiminato ligand were activated leading to the formation of two six-membered heterocyclic rings **A** and **B**. Both rings possess one Al–O bond.[203]

Compound **42** is stable in solution. Complete characterization of **42** after its isolation from the mother liquor was not possible due to its decomposition under formation of the *β*-diketimine ligand. The latter compound was confirmed by spectral analysis.

2.10.2. X-ray crystal structure of 42·Et$_2$O

The molecular structure of **42** in the solid state was determined by X-ray crystal structural analysis. An ORTEP plot of **42** is shown in Figure 24. Compound **42** crystallizes in the triclinic space group $P\overline{1}$ with a diethylether molecule in the asymmetric unit. It has two four-membered Al_2O_2 rings connected by *β*-diketiminato ligand at aluminum centers Al(1) and Al(2). Each aluminum atom is five coordinated. The aluminum atom Al(3) present at the center of the molecule has a distorted trigonal bipyramidal geometry, in which three oxygen atoms occupy the basal sites with bond angles of O(3)–Al(3)–O(5) 106.82(10)°, O(3)–Al(3)–O(7) 120.30(11)°, and O(5)–Al(3)–O(7) 132.85(10)°. It is bound to *tert*-butyl peroxide group with a Al(3)–O(7) bond length of 1.764(2) Å. The O(7)–O(8) bond length of 1.487(3) Å is slightly longer than that of peroxo bond distance of [(^{t}BuOO)(^{t}BuO)Al(μ–O^{t}Bu)$_2$Al(mesal)$_2$] [156] and those of transition metal peroxides.[204,205] In addition, the bond angles of Al(3)–O(7)–O(8) and O(7)–O(8)–C(3) (112.07(14)° and 106.97(18)°, respectively) slightly deviate from those of the alkylperoxo bond angles of [(^{t}BuOO)(^{t}BuO)Al(μ–O^{t}Bu)$_2$Al(mesal)$_2$].[156] Al(3) lies above the plane of Al(1) and Al(2) with a bond angle of Al(1)–Al(3)–Al(2) 109.42(4)°. The average Al–Al distance is 2.872 Å. Al(3) is connected to Al(1) through two

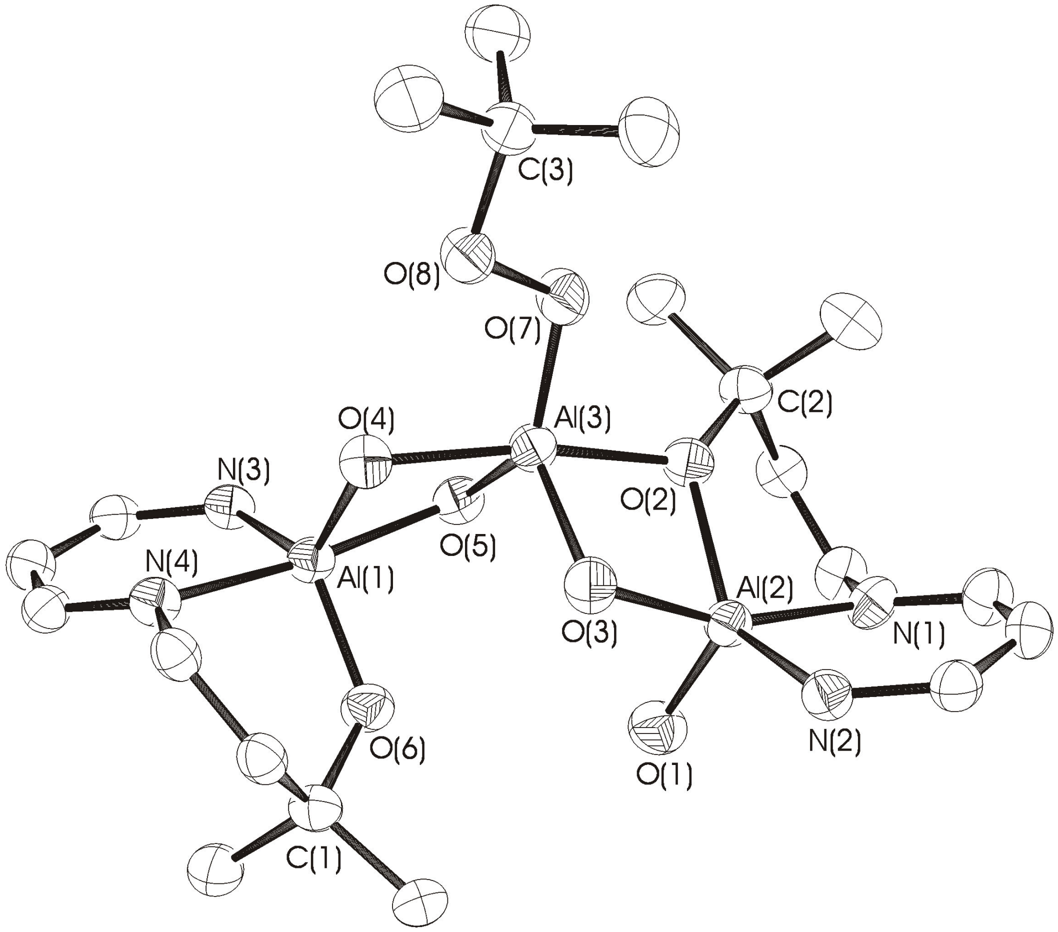


Figure 24. *Molecular structure of* **42**·Et$_2$O *with 50 % ellipsoid probability. Only core of the molecule is shown. Selected bond lengths [Å] and angles [º]: Al(1)–O(4) 1.826(2), Al(1)–O(5) 1.894(2), Al(1)–O(6) 1.757(2), Al(2)–O(1) 1.732(2), Al(2)–O(2) 1.891(2), Al(2)–O(3) 1.888(2), Al(3)–O(2) 1.874(2), Al(3)–O(3) 1.803(2), Al(3)–O(4) 1.871(2), Al(3)–O(5) 1.836(2), Al(3)–O(7) 1.764(2), Al(1)–N(3) 1.934(2), Al(1)–Al(3) 2.873(1), Al(2)–Al(3) 2.871(1), O(7)–O(8) 1.487(3), C(1)–O(6) 1.434(3), C(2)–O(2) 1.463(3); Al(1)–O(4)–Al(3) 101.97(11), Al(1)–O(6)–C(1) 126.07(17), O(4)–Al(1)–O(5) 75.69(9), Al(1)–Al(3)–Al(2) 109.42(4), Al(2)–O(2)–Al(3) 99.40(9), Al(3)–O(2)–C(2) 130.64(16), Al(3)–O(7)–O(8) 112.07(14), O(7)–O(8)–C(3) 106.97(18), O(3)–Al(3)–O(5) 106.82(10)°, O(3)–Al(3)–O(2) 78.79(19).*

bridging hydroxyl groups (O(4)H and O(5)H) whereas Al(2) and Al(3) are bridged by an oxo- (O(2)) and a hydroxyl group (O(3)H). The bridging Al–OH bond has an average bond length of 1.864 Å.

Aluminum atoms Al(1) and Al(2), which are planked by *β*-diketiminato ligands have distorted trigonal bipyramidal geometry. Al(2) has a terminal hydroxyl group with a bond length of Al(2)–O(1) 1.732(2) Å and it is similar to the reported terminal aluminum hydroxide.[205-207] The two six-membered rings **A** and **B** have similar bond parameters and are highly puckered in nature. The rings almost lie perpendicular to the plane of the *β*-diketiminato ligand. The carbon atom adjacent to the oxygen atom in rings **A** and **B** has two methyl groups. One methyl group in each ring is projected over the plane of the *β*-diketiminato ligand whereas the second methyl group is projected away. The oxygen atom O(2) present in **A** has a coordination number three, which results in the elongation of Al(2)–O(2) bond whereas the oxygen atom O(6) in **B** has a coordination number of two. The Al(2)–O(2) bond (1.891(2) Å) present in four- and six-membered ring (**A**) is longer in comparison to the Al(1)–O(6) bond length (1.751(2) Å) of ring **B**.

3. Summary and Outlook

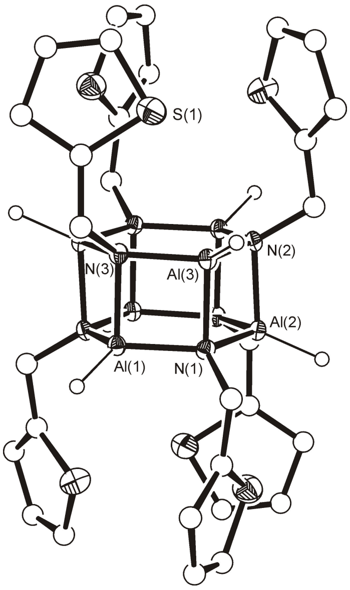
3.1. Summary

Hydroalumination reactions on nitriles and monosubstituted acetylenes have resulted in the synthesis of structurally characterized homo- and heterobimetallic imidoalanes and carbaalanes. They can be considered as intermediates in the synthesis of saturated hydrocarbons. The reaction pathway involved in the synthesis of these aluminum clusters is different due to the difference in the reactivity of the acetylene and nitrile.

In the synthesis of the imidoalane $[HAlNCH_2(C_4H_3S)]_6$ (**17**), aluminum trihydride primarily forms an adduct with 2-cyanothiophene and subsequently the adduct undergoes hydroalumination under boiling conditions to give imidoalane with the complete loss of NMe_3. The X-ray crystal structure shows the imidoalane with an open framework built up by two six-membered rings, which in turn are interlinked by an Al–N coordinate bond where the lone pair of electrons present on the nitrogen atom is donated to the electron deficient aluminum center. The stability of the imidoalane is due to the cross-linkage of the rings. The interlinked Al–N bonds are found to be longer than the Al–N bonds present in the six-membered rings.

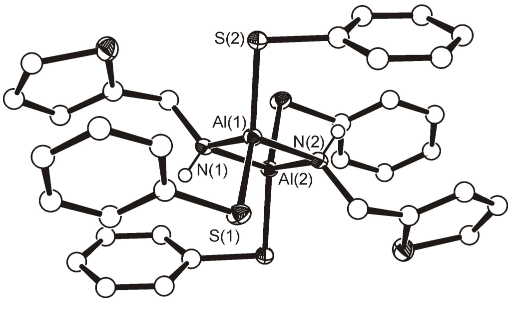
Hydroalumination of monosubstituted acetylenes involves deprotonation of the acidic acetylene hydrogen atom. Subsequent regioselective hydroalumination reaction on the intermediate, $RC{\equiv}C{-}AlH_2{\cdot}NMe_3$, and condensation reaction leads to the formation of carbaalanes. A closed rhombic dodecahedron framework can be observed in the case of carbaalanes. The carbon atoms caps a cube made of eight aluminum atoms. The electrons donated by the capping carbon atoms and the aluminum atoms result in surface aromaticity.

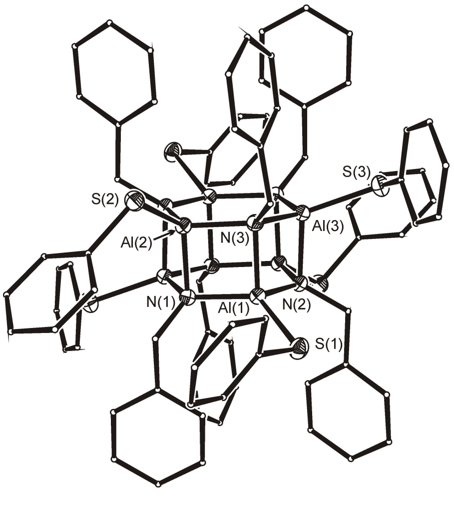
The hydrides present on both clusters were effectively replaced by nucleophilic moieties and in most cases the integrity of the core was maintained. The imidoalane **17** has been



Molecular Structure of ***17***

used for metathesis reactions by the substitution of the hydrides with halides and the acetylides to yield functionalized derivatives **21** – **24** ($[BrAlNCH_2(C_4H_3S)]_6$ (**21**), $[ClAlNCH_2(C_4H_3S)]_6$ (**22**), $[PhC{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**23**) $[(C_3H_5C{\equiv}CAlNCH_2C_4H_3S)_2(C_3H_5CH{=}CHAlNCH_2C_4H_3S)_4]$ (**24**)). The core of the cluster was retained in these reactions. The reactivity of the imidoalanes **13** and **17** toward PhSH





Molecular Structure of ***25***

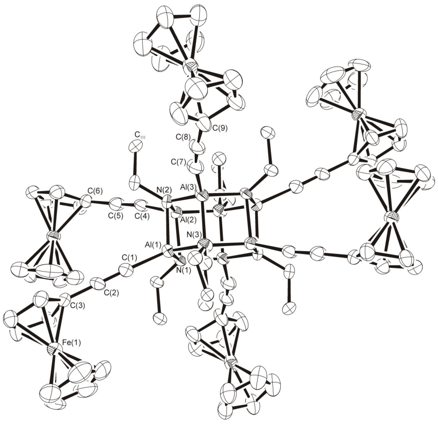
Molecular Structure of ***26***

is different than what we expected. The imidoalane **13** having benzyl units undergoes a smooth reaction under boiling conditions with PhSH giving rise to thiophenoxide-substituted imidoalane $[PhSAlNCH_2Ph]_6$ (**26**).

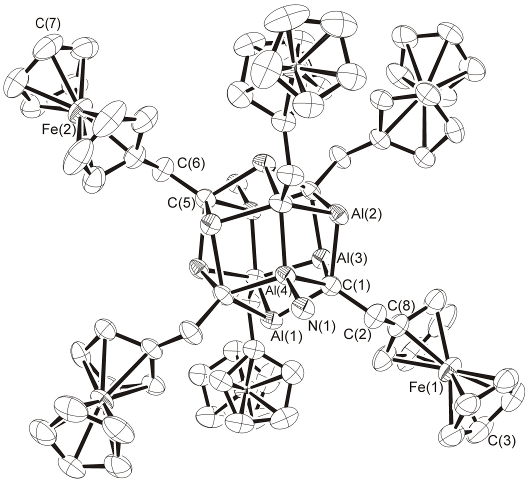
In contrast, the imidoalane **17** bearing thienylmethylene units degrades to the four-membered amidoalane $[(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (**25**) upon treatment with PhSH at room temperature. Nucleophilic substitution reactions of the imidoalane framework **17** using metal alkyls like $ZnEt_2$ and $AlMe_3$ were done successfully to obtain ethyl- and methyl- substituted imidoalanes $[EtAlNCH_2(C_4H_3S)]_6$ (**27**) and $[MeAlNCH_2(C_4H_3S)]_6$ (**28**), respectively.

Carrying out hydroalumination reactions with aluminum trisphenylacetylide as a different strategy to hydroalumination reaction with phenylacetylene generates the carbaalane $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**29**). Similar hydroalumination reactions on gallium and indium trisphenylacetylide resulted in the deposition to their respective metals, gallium and indium. Cyclopropylacetylene was hydroaluminated at elevated temperature to give the corresponding carbaalane $[(AlH)_6(AlNMe_3)_2(CCH_2C_3H_5)_6]$ (**32**). The reactivity and the stability of the carbaalane **29** was examined in the presence of phenyl- and ferrocenylacetylene. Reaction with phenylacetylene leads to the formation of the aluminum trisphenylacetylide $[(PhC{\equiv}C)_3Al{\cdot}NMe_3]$ (**33**), whereas only four ferrocenylacetylide units were incorporated in the synthesis of $[(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6]$ (**34**) when the reaction was carried out with ferrocenylacetylene. The difference in the reactivities can be attributed to steric factors.

The objective to fix organometallic substituents like transition metal containing moieties on nitride and carbide surfaces was also achieved. Ferrocenylacetylide has been successfully fixed on the imidoalane **17** to generate $[CpFeC_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**35**). It is the first model compound exhibiting the fixation of a metal containing ligands on an imidoalane. The electrochemical behavior of this compound shows a single reversible oxidation wave, which suggests the electrochemical equivalence of all the six-ferrocenylacetylide units. At higher temperatures ferrocenylacetylene was hydroaluminated in the synthesis of the ferrocenylmethylene substituted carbaalane $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeCp)_6]$ (**39**).

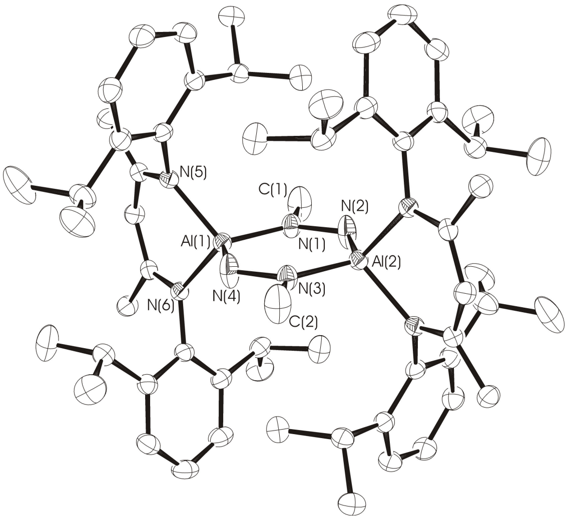


Molecular structure of ***35***



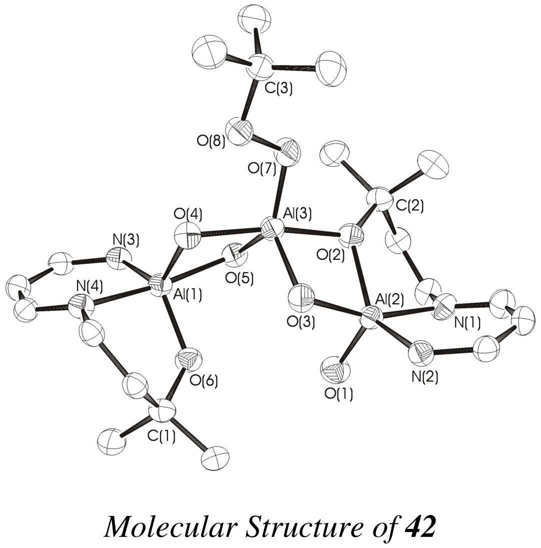
Molecular structure of ***39***

Besides the hydroalumination reactions, the reactivity of Al–H bonds of the *β*-diketiminato stabilized aluminum dihydride toward methylhydrazine and *tert*-butylperoxide has been investigated. The reaction between stoichiometric amounts of the *β*-diketiminato stabilized aluminum dihydride $LAlH_2$ (**40**) and methylhydrazine in boiling toluene afforded reddish brown crystals of the planar dimeric spirane aluminum hydrazide complex $[LAlN(Me)NH]_2$ (**41**). To explain the planarity and the stability of the six-membered Al_2N_4 ring in **41** theoretical studies were performed using DFT-B3LYP method, which demonstrated that the planarity at the nitrogen centers in **41** is due to the Al–N bond character rather than the presence of the sterically bulky ligands and other steric interactions. The pyramidal geometry at the Al–NHN unit in compound **41** is due to the preferred staggered NH–NMe



Molecular Structure of ***41***

conformation rather than an eclipsed one. Upon treatment of $LAlH_2$ (**40**) with ^{t}BuOOH the penta-coordinated *tert*-butylperoxo aluminum compound **42** was obtained. This was the first attempt to directly treat *tert*-butyl hydroperoxide on Al–H bonds in the synthesis of penta-coordinated *tert*-butylperoxo aluminum compound. The complete characterization was not possible as the compound decomposes after the isolation.



Molecular Structure of ***42***

3.2. Outlook

The reactivity of carbaalanes and imidoalanes as an interesting class of compounds has gained significance and its application in catalytic processes seems possible. In the future outlook, similar to silicates these clusters can be considered as solid supports in catalytic applications. In order to achieve this goal, methods should be employed (a) to transform the Al–H bonds of both the clusters to the AlXH bonds (X = O, NR, PR and S). The presence of acidic protons in AlXH bonds can be useful in generating interesting carbaalane and imidoalane clusters containing reactive sites, (b) to synthesize carbaalane derivatives similar to the metallacarboranes where the carbon atom capping the face of each cube can be replaced by the isolobal species of main group and transition elements, and (c) to synthesize more stable aluminum peroxide compounds using aluminum alkyl compounds and organic peroxides and to study their behavior in oxidation reactions in organic chemistry synthesis.

4. Experimental Section:

4.1. General remarks:

All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk glassware and high vacuum techniques. The samples for spectral measurements were prepared in a dry box where the O_2 and H_2O levels are normally maintained below 1 ppm. The glassware used in all the reactions and manipulations were dried in an oven at 150 °C and were used after cooling under high vacuum with intermittent flushing with nitrogen. Solvents were purified according to conventional procedures and were freshly distilled prior to use. [208]

4.2. Physical measurements:

The *melting point*s of the compounds synthesized were measured in sealed capillaries on Büchie B540 apparatus and are reported uncorrected.

Infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as nujol mulls between NaCl and KBr plates.

^{1}H and ^{13}C *NMR spectra* were recorded on a Bruker AM 200, 300 and 500 instruments and the chemical shifts are reported with reference to TMS. Downfield shifts from the reference are quoted positive and the upfield shifts are reported negative. The solvents for NMR measurements were dried over CaH_2 and trap-to-trap distilled before use. Solid-state NMR spectra for the nuclei ^{1}H, ^{13}C, and ^{27}Al were recorded on a Bruker Avance DMX at 600 MHz proton frequency at the Max-Planck-Institut für Biophysikalische Chemie, Göttingen, Germany. ^{27}Al NMR chemical shifts are reported referenced to $AlCl_3$.

Mass spectra were obtained on Finnigan MAT 8230 or Varian MAT CH 5 instruments by EI and FAB-MS techniques.

Elemental analysis were performed on solvent free samples at the analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

Cyclic Voltammetry: The electrochemical studies were performed at the Anorganische Chemie der Universität Stuttgart, Stuttgart, Germany. The measurement for **35** was conducted in CH_2Cl_2 solution employing 0.1 M Bu_4NPF_6 as the supporting electrolyte. Cyclic voltammetric investigations on compounds **34**, **36**, **37**, and **38** were conducted in CH_2Cl_2/Bu_4NPF_6 (0.2 M) at ambient temperature, compound **34** was also studied in THF/Bu_4NPF_6 (0.2 M). The electrochemical experiments were performed in a home-built cylindrical vacuum-tight compartment cell. A spiral-shaped Pt wire and a Ag wire as the counter electrodes and reference electrodes were sealed directly into opposite sides of the glass wall while the respective working electrode (Pt or glassy carbon 1.1 mm polished with 0.25 μm diamond paste (Buehler-Wirtz) before each experiment series) were introduced via a teflon screw cap with a suitable fitting. The cell was attached to a conventional Schlenk line via two sidearms equipped with teflon screw valves. All other details were as described previously.[209] CH_2Cl_2 and THF were obtained from Fluka (Burdick&Jackson Brand) and freshly distilled from CaH_2 (CH_2Cl_2) or Na (THF) before use. Bu_4NPF_6 was used as the supporting electrolyte. Compounds **34**, **36**, **37**, and **38** oxidized at nearly the same potential as ferrocene such that decamethylferrocene had to be employed as the internal standard for potential calibration. Referencing against the ferrocene/ferrocenium scale was then performed by determining the half-wave potential of decamethylferrocene ($E_{1/2}$ = –0.55 V) against the ferrocene/ferrocenium standard in a separate set of experiments but under otherwise identical conditions and recalculating the observed $E_{1/2}$ values of the respective analyte relative to the ferrocene/ferrocenium scale. Assessment of the individual half-wave potentials of **34** was performed as follows: first, the experimental wave of the ferrocene couple was simulated. Values of D ($2.40\ cm^2s^{-1}$)^{52}, k_s ($6.8 \cdot 10^6\ cm \cdot s^{-1}$) and α (0.49) were taken from the literature.[210] Ohmic drop was included such that the experimental peak-to-peak separation of the $Cp_2Fe^{0/+}$ couple was reproduced over a range of sweep rates ranging from v = 0.05 to 1 V/s. Next, the wave of the analyte was analyzed by adjusting the individual $E_{1/2}$ values until good agreement between simulated and experimental CVs was obtained over the entire range of sweep rates. Digital simulations of experimental CVs were performed with DigiSim® (version 3.0a) available from BAS.

X-ray Structure Determinations: A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data for **21** were collected on a Siemens-STOE AED2 four-circle instrument, and for **17**, **22 – 29**, **33**, **35**, **39**, **41**, and **42** the data were collected on a STOE IPDS II diffractometer. All measurements were made with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[211] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[212] All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors (including anomalous scattering) were taken from *International Tables for X-ray Crystallography*.[213] Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. The crystal data for the compounds mentioned along with structure factors and refinement parameters are tabulated in Section.

4.3. Starting materials:

$AlH_3 \cdot NMe_3$,[49] **13**,[164] ferrocenylacetylene,[214,215] and ferrocenylnitrile[216] were prepared as described in the literature. 2-Cyanothiophene, Me_3SiBr, Me_3SiCl, PhSH, $ZnEt_2$, $AlMe_3$, PhC≡CH, cyclopropylacetylene (70 % in toluene), $^{t}BuOOH$, and $FcCH_2OH$ (Fc = ferrocenyl) were purchased from Aldrich and used as received. Methylhydrazine (Aldrich) was distilled over NaOH prior to use.

4.4. Synthesis and functionalization of the hexameric imidoalane

4.4.1. Synthesis of [HAlNCH$_2$(C$_4$H$_3$S)]$_6$ (17): AlH$_3$·NMe$_3$ (30 mL, 0.5 M solution in toluene) was added to a solution of 2-cyanothiophene (1.50 g, 13.74 mmol) in toluene (30 mL) at –78 °C whilst stirring. The reaction mixture was allowed to come to room temperature and refluxed until the evolution of NMe$_3$ had ceased. Storing the resultant solution overnight at room temperature afforded colorless crystals of **17**. Yield: 1.23 g (64 %). M.p. 238 - 240 °C. IR (KBr, nujol mull): $\tilde{\nu}$ = 1860 (s, Al–H), 1718, 1648, 1596, 1528, 1339, 1269, 1216, 1156, 1075, 1040, 1013, 969, 854, 819, 753, 723, 693, 658, 637, 621, 529, 481, 438, 413 cm^{-1}. ^{1}H NMR (200.13 MHz, CDCl$_3$, 25 °C, TMS): δ = 4.31 (s, 12 H, CH_2), 6.83 (m, 18 H, C$_4H_3$S) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$, 25 °C): δ = 44.07 (CH$_2$), 124.35, 125.28, 127.23, 146.95 (C_4H$_3$S) ppm. EI-MS (70 eV): *m/z* (%) = 834 (20) [M$^+$], 737 (28) [(M-CH$_2$C$_4$H$_3$S)$^+$], 653 (36) [(M-CH$_2$C$_4$H$_3$S-C$_4$H$_4$S)$^+$], 113 (100) [H$_2$NCH$_2$C$_4$H$_3$S$^+$]. Elemental analysis C$_{30}$H$_{36}$Al$_6$N$_6$S$_6$ (834.89) (%): Calcd. C 43.16, H 4.35, N 10.07. Found C 43.2, H 4.5, N 9.4.

4.4.2. Synthesis of [BrAlNCH$_2$(C$_4$H$_3$S)]$_6$ (21): To a suspension of **17** (0.73 g, 0.87 mmol) in toluene (30 mL) was added Me$_3$SiBr (1.07 g, 6.99 mmol) at room temperature. The reaction mixture was stirred overnight at room temperature and refluxed for an hour. The solution was filtered and cooled to room temperature to obtain colorless crystals of **21**. Yield: 0.77 g (68 % with respect to **17**). M.p. 284 - 287 °C. IR (KBr, nujol mull): $\tilde{\nu}$ = 1887, 1780, 1714, 1647, 1602, 1532, 1433, 1335, 1272, 1226, 1216, 1162, 1135, 1074, 1043, 977, 891, 850, 826, 757, 723, 655, 617, 562, 520, 504, 465, 435 cm^{-1}. EI-MS (70 eV): *m/z* (%) = 1308 (5) [M$^+$], 113 (16) [H$_2$NCH$_2$C$_4$H$_3$S$^+$]. Elemental analysis C$_{30}$H$_{30}$Al$_6$Br$_6$N$_6$S$_6$ (1308.30) (%): Calcd. C 27.54, H 2.31, N 6.42. Found C 27.2, H 2.9, N 6.2.

4.4.3. Synthesis of [ClAlNCH$_2$(C$_4$H$_3$S)]$_6$ (22): A reaction between **17** (0.50 g, 0.60 mmol) and Me$_3$SiCl (0.45 g, 4.14 mmol) was carried out similar to that of **21** in the synthesis of **22**. Yield: 0.44 g (71 % with respect to **17**). M.p. 218 - 223 °C. IR (NaCl, nujol mull): $\tilde{\nu}$ = 1889, 1797, 1724, 1650, 1594, 1531, 1495, 1435, 1341, 1272, 1219, 1158, 1135, 1074, 1042, 972, 896, 855, 824, 753, 728, 685, 653, 622, 593, 564, 540 cm^{-1}. EI-MS (70 eV): *m/z* (%) = 1040 (10) [M$^+$], 943 (10) [(M-CH$_2$C$_4$H$_3$S)$^+$], 97 (100) [CH$_2$C$_4$H$_3$S$^+$]. Elemental analysis C$_{30}$H$_{30}$Al$_6$Cl$_6$N$_6$S$_6$ (1041.54) (%): Calcd. C 34.59, H 2.90, N 8.07. Found C 33.6, H 3.5, N 7.6.

4.4.4. Synthesis of [PhC≡CAlNCH$_2$(C$_4$H$_3$S)]$_6$ (23): To a suspension of **17** (0.50 g, 0.60 mmol) in toluene (30 mL) was added PhC≡CH (0.42 g, 4.11 mmol) at room temperature. The reaction mixture was stirred for half an hour at room temperature before refluxing it until the evolution of H$_2$ had ceased. The resulting dark brown solution was filtered and kept for crystallization at room temperature to obtain colorless crystals of **23**. Yield: 0.55 g (64 % with respect to **17**). M.p. 270 °C (decomp.). IR (NaCl, nujol mull): $\tilde{\nu}$ = 2129 (m, C≡C), 2030, 1951, 1880, 1801, 1675, 1653, 1594, 1572, 1540, 1486, 1341, 1276, 1214, 1175, 1156, 1098, 1068, 1044, 1025, 996, 971, 915, 894, 851, 817, 799, 755, 726, 690, 647, 610, 565, 535 cm^{-1}. ^{1}H NMR (200.13 MHz, CDCl$_3$, 25 °C, TMS): δ = 4.68 (s, 12 H, CH_2), 6.95 (m, 18 H, C$_4$$H_3$S), 7.27 (m, 18 H, *m*– and *p*–C$_6$$H_5$), 7.46 (m, 12 H, *o*–C$_6$$H_5$) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$, 25 °C): δ = 41.28 (CH$_2$), 67.98 (Al–C), 83.15 (Al–C≡C), 122.14, 128.30, 128.77, 132.14 (C_6H$_5$), 125.30, 128.23, 129.04, 137.88 (C_4H$_3$S) ppm. In the mass spectrum only small fragments were found. Elemental analysis C$_{78}$H$_{60}$Al$_6$N$_6$S$_6$ (1434.21) (%): Calcd. C 65.26, H 4.21, N 5.85. Found C 64.9, H 4.8, N 5.8.

4.4.5. Synthesis of [$(C_3H_5C{\equiv}CAlNCH_2C_4H_3S)_2(C_3H_5CH{=}CHAlNCH_2C_4H_3S)_4$] (24): To a suspension of **17** (1.67 g, 2 mmol) in toluene (40 mL) was added $C_3H_5C{\equiv}CH$ (70 % in toluene, 1.5 mL, 14 mmol) at room temperature. The reaction mixture was stirred for half an hour at room temperature before refluxing it until the evolution of H_2 had ceased. Partial removal of the solvent from the light brown solution and storage at 0 °C afforded colorless crystals of **24**. Yield: 1.87 g (76 % with respect to **17**). M.p. 246 °C (decomp.). IR (NaCl, nujol mull): $\tilde{\nu}$ = 2136 (m, C≡C), 1835, 1583 (C=C), 1367, 1264, 1218, 1153, 1124, 852 cm^{-1}. EI-MS (70 eV): *m/z* (%) = 1228 (28) [$(M+2H)^+$], 1160 (60) [$(M+2H-C_3H_5CH{=}CH_2)^+$], 1093 (40) [$(M+2H-2C_3H_5CH{=}CH_2)^+$], 995 (100) [$(M+2H-3C_3H_5CH{=}CH_2)^+$], 927 (72) [$(M+2H-4C_3H_5CH{=}CH_2)^+$], 860 (24) [$(M+2H-5C_3H_5CH{=}CH_2)^+$]. Elemental analysis $C_{60}H_{68}Al_6N_6S_6$ (1226.27) (%): Calcd. C 58.71, H 5.58, N 6.85. Found C 58.5, H 5.6, N 6.8.

4.4.6. Synthesis of [$(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (25): To a suspension of **17** (0.50 g, 0.60 mmol) in toluene (30 mL) was added PhSH (0.46 g, 4.17 mmol) slowly at room temperature. Evolution of H_2 was observed during the addition. The reaction mixture was stirred overnight and filtered. Colorless crystals of **25** were obtained by storage of the filtrate at room temperature. Yield: 0.63 g (84 % based on PhSH). M.p. 143 - 153 °C. IR (KBr, nujol mull): $\tilde{\nu}$ = 3248 (br, N–H), 3231, 3160, 1954, 1882, 1655, 1579, 1473, 1436, 1380, 1326, 1303, 1257, 1205, 1147, 1082, 1066, 1043, 1023, 971, 907, 864, 828, 740, 709, 691, 647, 574, 554, 530, 492, 483, 472 cm^{-1}. ^1H NMR (200.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.80 (s, 2 H, N*H*), 3.90 (s, 4 H, CH_2), 6.82 (m, 4 H, C_4H_3S), 7.21 (m, 14 H, C_6H_5S, C_4H_3S), 7.55 (m, 8 H, C_6H_5S) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 41.38 (CH_2), 123.95, 125.63, 127.17, 137.07 (C_4H_3S), 125.63, 129.07, 129.46, 130.74 (C_6H_5S) ppm. EI-MS (70 eV): *m/z* (%) = 714 (5) [M^+], 605 (68) [$(M-PhSH)^+$], 110 (100) [$PhSH^+$]. Elemental analysis $C_{34}H_{32}Al_2N_2S_6$

(714.94) (%): Calcd. C 57.12, H 4.51, N 3.92. Found C 56.8, H 4.6, N 3.7.

4.4.7. Synthesis of [PhSAlNCH$_2$Ph]$_6$ (26): To a suspension of **13** (0.52 g, 0.65 mmol) in toluene (30 mL) was added PhSH (0.50 g, 4.54 mmol) at room temperature. The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of H_2 had ceased. The solution was filtered and kept for crystallization at room temperature to obtain colorless crystals of **26**. Yield: 0.66 g (70 % with respect to **13**). M.p. 220 - 223 °C. IR (KBr, nujol mull): $\tilde{\nu}$ = 1579, 1496, 1437, 1367, 1300, 1282, 1260, 1198, 1156, 1079, 1066, 1031, 1023, 1003, 974, 810, 735, 693, 667, 547, 524, 480, 459, 439 cm^{-1}. ^{1}H NMR (200.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.22 (s, 12 H, CH_2), 6.95 (m, 24 H, *o*–C_6H_5 and *o*–SC_6H_5), 7.22 (m, 36 H, *m*–, *p*–C_6H_5 and *m*–, *p*–SC_6H_5) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 29.70 (CH_2), 126.97 (*p*–C_6H$_5$), 127.16 (*m*–C_6H$_5$), 127.56 (*o*–C_6H$_5$), 137.06 (CH$_2$–*C*), 128.49 (*p*–SC_6H$_5$), 128.59 (*m*–SC_6H$_5$), 129.06 (*o*–SC_6H$_5$), 130.74 (S–*C*) ppm. In the mass spectrum only small fragments were found. Elemental analysis $C_{85}H_{80}Al_6N_6S_6$ (**26**·PhMe) (1539.79) (%): Calcd. C 66.30, H 5.24, N 5.46. Found C 66.7, H 5.4, N 5.2.

4.4.8. Synthesis of [EtAlNCH$_2$(C$_4$H$_3$S)]$_6$ (27): To a solution of **17** (0.85 g, 1.02 mmol) in THF (20 mL) was added drop wise a solution of $ZnEt_2$ (15 mL, 1.1 M solution, 16.5 mmol) in toluene. The resultant mixture was stirred overnight at room temperature and filtered. The filtrate was reduced to 15 mL and stored at 0 °C to obtain colorless crystals of **27**. Yield: 0.81 g (79 % with respect to **17**). M.p. 262 °C. IR (NaCl, nujol mull): $\tilde{\nu}$ = 1337, 1269, 1225, 1199, 1157, 1125, 1072, 1006, 990, 973, 927, 848, 823, 767, 717, 696, 636 cm^{-1}. ^{1}H NMR (200.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.20 (m, 12 H, AlCH_2), 1.11 (t, 18 H, CH_3), 4.38 (s, 12 H, NCH_2), 6.79 (m, 18 H, C$_4H_3$S) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = -1.09 (Al–

*C*H$_2$), 9.81 (*C*H$_3$), 43.45 (N*C*H$_2$), 123.63, 124.88, 126.72, 147.37 (*C*$_4$H$_3$S) ppm. EI-MS (70 eV): *m/z* (%) = 974 (45) [(M-C$_2$H$_5$)$^+$], 973 (100) [(M-C$_2$H$_6$)$^+$]. Elemental analysis C$_{42}$H$_{60}$Al$_6$N$_6$S$_6$ (1003.20) (%): Calcd. C 50.28, H 6.03, N 8.38. Found C 50.6, H 6.0, N 8.0.

4.4.9. Synthesis of [MeAlNCH$_2$(C$_4$H$_3$S)]$_6$ (28): To a solution of **17** (0.50 g, 0.60 mmol) in toluene (20 mL) was added dropwise a solution of AlMe$_3$ (2.7 mL, 2.0 M solution, 5.4 mmol) in heptane at room temperature. The resultant mixture was stirred overnight at room temperature and filtered. The filtrate was reduced to 20 mL and stored at 0 °C for several days to obtain colorless crystals of **28**. Yield: 0.40 g (73 % with respect to **17**). M.p. 206 °C (decomp.). IR (NaCl, nujol mull): $\tilde{\nu}$ = 1340, 1254, 1210, 1167, 1059, 1014, 980, 965, 943, 848, 747, 734, 683 cm^{-1}. ^{1}H NMR (200.13 MHz, CDCl$_3$, 25 °C, TMS): δ = -0.52 (s, 18 H, Al–*Me*), 4.28 (s, 12 H, NC*H*$_2$), 6.80 (m, 18 H, C$_4$*H*$_3$S) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$, 25 °C): δ = -7.20 (Al–*Me*), 43.50 (N*C*H$_2$), 123.78, 124.98, 127.52, 148.37 (*C*$_4$H$_3$S) ppm. EI-MS (70 eV): *m/z* (%) = 903 (10) [(M-CH$_4$)$^+$], 835 (16) [C$_{30}$H$_{36}$Al$_6$N$_6$S$_6^+$], 113 (5) [CH$_2$C$_4$H$_3$SNH$_2^+$], 97 (24) [CH$_2$C$_4$H$_3$S$^+$]. Elemental analysis C$_{36}$H$_{48}$Al$_6$N$_6$S$_6$ (919.04) (%): Calcd. C 47.05, H 5.26, N 9.14. Found C 46.5, H 4.9, N 9.0.

4.5. Synthesis and functionalization of carbaalane

4.5.1. Synthesis of [(AlH)$_6$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$] (29): AlH$_3$·NMe$_3$ (10 mL, 0.50 M solution in toluene) was added to a solution of [(PhC≡C)$_3$Al·NMe$_3$] (**33**) (0.60 g, 1.54 mmol) at room temperature. The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of NMe$_3$ had ceased. The resulting solution was filtered and kept for crystallization at 0 °C to obtain colorless crystals of **29**. Yield: 0.50 g (72 % with respect to **33**). M.p. 280 - 282 °C. IR (KBr, nujol mull): $\tilde{\nu}$ = 1822 (m, Al–H), 1262, 1091, 976, 802, 756, 721, 681, 563, 509 cm^{-1}. ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, TMS): $\delta = 2.04$ (s, 12 H, CH_2), 2.10 (s, 18 H, NMe_3), 4.0 (s, 6 H, Al–H), 6.96 - 7.15 (m, 30 H, C_6H_5) ppm. In the mass spectrum only small fragments were found. Elemental analysis $C_{54}H_{66}Al_8N_2$ (958.97) (%): Calcd. C 67.63, H 6.94, N 2.92. Found C 66.4, H 7.0, N 2.9.

4.5.2. Synthesis of [$(AlH)_6(AlNMe_3)_2(CCH_2C_3H_5)_6$] (32): $AlH_3 \cdot NMe_3$ (65 mL, 1 M solution in toluene, 60 mmol) was added to a solution of cyclopropylacetylene (70 % in toluene, 2 mL, 20 mmol) in toluene (30 mL) at room temperature whilst stirring. The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of NMe_3 had ceased. After cooling the resulting solution a white colored suspension of **32** precipitates from the mother liquor. Yield: 0.65 g. M.p. >300 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu} = 1776$ (m, Al–H), 1408, 1291, 1262, 1106, 1002, 917 cm^{-1}. EI-MS (70 eV): *m/z* (%) = 742 (4) [M$^+$], 700 (2) [$(M\text{-}C_3H_6)^+$], 42 (100) [$C_3H_6^+$]. Elemental analysis $C_{36}H_{66}Al_8N_2$ (742.77) (%): Calcd. C 58.21, H 8.96, N 3.77. Found C 87.9, H 8.6, N 3.5.

4.5.3. Reaction of 29 with PhC≡CH to [$(PhC{\equiv}C)_3Al{\cdot}NMe_3$] (33): Compound **29** (1.00 g, 1.00 mmol) was dissolved in toluene (20 mL) and phenylacetylene (3.20 g, 30.0 mmol) was added at room temperature. The reaction mixture was heated at reflux for 1 h during which period the evolution of NMe_3 and H_2 was observed and the solution became dark-red. The volume of the solvent was reduced in vacuo to about 10 mL and the residual solution was stored overnight at –20 °C to obtain colorless crystals of **33**. The spectroscopic and analytical data of **33** prepared by the above procedure matched exactly with the authentic sample obtained in the reaction of $AlH_3 \cdot NMe_3$ with excess PhC≡CH.[182] Yield: 2.21 g (68 % with respect to **29**). M.p. 183 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu} = 2125$ (C≡C), 1594, 1570, 1378, 1212, 990, 816, 757, 693, 611 cm^{-1}. ^{1}H NMR (200.13 MHz, CDCl$_3$, 25 °C, TMS): δ = 2.80 (s, 9 H, *Me*), 7.25 (m, 9 H, *o*–, and *p*–C$_6$*H*$_5$), 7.47 (m, 6 H, *m*–C$_6$*H*$_5$) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$, 25 °C): δ = 47.4 (*Me*), 101.2 (br, Al–*C*), 107.5, (C$_6$H$_5$–*C*), 124.6, 127.7, 128.0, 132.0, (arom, *C*) ppm. EI-MS (70 eV) *m/z* (%): 391 [(M+2H)$^+$]. Elemental analysis $C_{27}H_{24}AlN$ (389.47) (%): Calcd. C 83.27, H 6.21, N 3.60. Found C 84.0, H 6.1, N 3.3.

4.5.4. Reaction of 29 with FcC≡CH to [(AlH)$_2$(FcC≡CAl)$_4$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$] (34): To a suspension of **29** (0.60 g, 0.62 mmol) in toluene (30 mL) was added ferrocenylacetylene (0.80 g, 3.80 mmol) at room temperature. The reaction mixture was stirred for 1 h at room temperature. Subsequently it was refluxed until the evolution of H_2 had ceased. The resulting solution was filtered and kept for crystallization at room temperature to obtain reddish brown crystals of **34**. Yield: 0.75 g (67 % with respect to **29**). M.p. 254 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu}$ = 2119 (m, C≡C), 1808 (Al–H), 1600, 1261, 1233, 1106, 1023, 976, 915, 801, 753, 699, 674, 582, 534 cm^{-1}. ^{1}H NMR (600 MHz, 26 KHz, MAS): δ = 1.9 (br, 12 H, C*H*$_2$), 2.7 - 3.0 (br, 18 H, N*Me*$_3$), 4.0 (br, 2 H, Al–*H*), 5.0 (br, 36 H, C$_5$*H*$_4$Fe*Cp*), 7.2 (br, 30 H, C$_6$*H*$_5$) ppm. ^{13}C NMR (600 MHz, 26 KHz, MAS): δ = 30.0 (cluster *C*, and *C*H$_2$C), 40.0 (N*Me*$_3$), 65.0 (*C*$_5$H$_4$Fe*Cp*), 120.0 - 130.0 (*C*$_6$H$_5$) ppm. ^{27}Al NMR (600 MHz, 26 KHz, MAS, AlCl$_3$): δ = 40.0 - 130.0 ppm. In the mass spectrum only small fragments were found. Elemental analysis $C_{102}H_{98}Al_8Fe_4N_2$ (1791.12) (%): Calcd. C 68.40, H 5.51, N 1.56. Found C 67.9, H 5.6, N 1.5.

4.6. Synthesis of heterobimetallic cluster compounds

4.6.1. Synthesis of [CpFeC$_5$H$_4$C≡CAlNCH$_2$(C$_4$H$_3$S)]$_6$ (35): To a suspension of **17** (0.42 g, 0.50 mmol) in toluene (30 mL) was added ferrocenylacetylene (0.64 g, 3.05 mmol) at room temperature. The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of H_2 had ceased. The resulting solution was filtered and kept for crystallization at room temperature to obtain reddish brown crystals of **35**. Yield: 0.54 g (52 % with respect to **17**). M.p. 297 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu}$ = 2119 (m, C≡C), 1411, 1261, 1235, 1223, 1150, 1106, 1079, 1001, 921, 875, 852, 819, 752, 536, 475, 452 cm^{-1}. ^1H NMR (200.13 MHz, C_6D_6, 25 °C, TMS): δ = 4.08 ppm (s, 30 H, *Cp*), 4.22 (s, 12 H, CH_2), 3.83 (t, $^3J_{HH}$ = 2 Hz, 12 H, C_5H_4), 4.33 (t, $^3J_{HH}$ = 2 Hz, 12 H, C_5H_4), 6.70 - 7.00 (br, 18 H, C_4H_3S) ppm. ^{13}C NMR (125.77 MHz, C_6D_6, 25 °C): δ = 40.28 (CH_2), 64.81 (Al–*C*), 70.26 (*Cp*), 74.09, 72.00, 68.83 (C_5H_4), 82.65 (Al–C≡*C*), 125.30, 128.20, 129.01, 137.88 (C_4H_3S) ppm. In the mass spectrum only small fragments were found. Elemental analysis $C_{102}H_{84}Al_6Fe_6N_6S_6$ (2083.15) (%): Calcd. C 58.81, H 4.06, N 4.03. Found C 57.9, H 4.4, N 4.2.

4.6.2. Synthesis of [HAlNCH$_2$C$_5$H$_4$FeCp]$_6$ (36): $AlH_3 \cdot NMe_3$ (10 mL, 0.5 M solution in toluene) was added to a solution of ferrocenylnitrile (1.50 g, 13.74 mmol) in toluene (30 mL) at room temperature whilst stirring. The reaction mixture was stirred at room temperature and subsequently refluxed until the evolution of NMe_3 had ceased. The resulting solution was cooled and upon removal of solvent orange red compound **36** was obtained. Yield: 1.25 g (73 % with respect to ferrocenylnitrile). M.p. >300 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu}$ = 1845 (br, Al–H), 1560, 1261, 1230, 1105, 1024, 898, 802, 722, 701, 481 cm^{-1}. ^1H NMR (600 MHz, 25 KHz, MAS): δ = 2.8 (s, 12 H, NCH_2), 4.3 (br, 54 H, C_5H_4FeCp) ppm. ^{13}C NMR (600 MHz, 25 KHz, MAS): δ = 42.0 (NCH_2), 68.0 (C_5H_4FeCp) ppm. In the mass spectrum only small fragments were found. Elemental analysis $C_{66}H_{72}Al_6N_6Fe_6$ (1446.28) (%): Calcd. C 54.81, H 5.02, N 5.81. Found C 55.2, H 5.7, N 6.3.

4.6.3. Synthesis of [$CpFeC_5H_4CH_2OAlNCH_2(C_4H_3S)]_6$ (37): To a suspension of **17** (0.24 g, 0.29 mmol) in toluene (30 mL) was added ferrocenylmethanol (0.38 g, 1.77 mmol) at room temperature. The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of H_2 had ceased. The resulting solution was cooled and upon removal of solvent orange red compound **37** was obtained. Yield: 0.41 g (68 % with respect to **17**). M.p. >300 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu}$ = 1637, 1261, 1230, 1105, 1021, 923, 815, 694 cm^{-1}. ^1H NMR (600 MHz, 25 KHz, MAS): δ = 2.4 (s, 12 H, NCH_2), 3.6 (s, 12 H, OCH_2), 4.1 (br, 54 H, C_5H_4FeCp), 6.8 - 7.3 (br, 18 H, C_4H_3S) ppm. ^{13}C NMR (600 MHz, 25 KHz, MAS): δ = 42.0 (NCH_2), 59.0 (OCH_2), 67.0 (C_5H_4FeCp), 124.0 - 127.0 (C_4H_3S) ppm. In the mass spectrum only small fragments were found. Elemental analysis $C_{96}H_{96}Al_6Fe_6N_6O_6S_6$ (2119.18) (%): Calcd. C 54.47, H 4.57, N 3.97. Found C 55.8, H 4.7, N 4.3.

4.6.4. Synthesis of [$CpFeC_5H_4CH_2OAlNCH_2Ph]_6$ (38): To a suspension of **13** (0.50 g, 0.63 mmol) in toluene (30 mL) was added ferrocenylmethanol (0.84 g, 3.88 mmol) at room temperature. The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of H_2 had ceased. The resulting solution was cooled and upon removal of solvent orange red compound **38** was obtained. Yield: 1.33 g (74 % with respect to **13**). M.p. >300 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu}$ = 1604, 1263, 1230, 1105, 1024, 808, 701 cm^{-1}. ^1H NMR (600 MHz, 25 KHz, MAS): δ = 3.1 (s, 12 H, NCH_2), 3.3 (s, 12 H, OCH_2), 4.1 (br, 54 H, C_5H_4FeCp), 6.6 - 7.2 (br, 30 H, C_6H_5) ppm. ^{13}C NMR (600 MHz, 25 KHz, MAS): δ = 42.0 (NCH_2), 60.0 (OCH_2), 68.0 (C_5H_4FeCp), 125.0 - 130.0 (C_6H_5) ppm. In the mass spectrum only small fragments were found. Elemental analysis $C_{108}H_{108}Al_6Fe_6N_6O_6$ (2083.01) (%): Calcd. C 62.27, H 5.23, N 4.03. Found C 62.6, H 5.8, N 4.5.

4.6.5. Synthesis of [(AlH)$_6$(AlNMe$_3$)$_2$(CCH$_2$C$_5$H$_4$FeCp)$_6$] (39): AlH$_3$·NMe$_3$ (19 mL, 0.5 M solution in toluene) was added to a solution of ferrocenylacetylene (0.60 g, 2.86 mmol) in toluene (30 mL) at room temperature whilst stirring. The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of NMe$_3$ had ceased. The resulting solution was filtered and kept for crystallization at room temperature for 24 hours to obtain reddish brown crystals of **39**. Yield: 0.51 g (67 % with respect to ferrocenylacetylene). M.p. 257 °C (decomp.). IR (KBr, nujol mull): $\tilde{\nu}$ = 1802 (br, Al–H), 1279, 1261, 1230, 1103, 1038, 1002, 977, 920, 809, 759, 728 cm^{-1}. ^{1}H NMR (600 MHz, 23 KHz, MAS): δ = 1.9 (br, 12 H, C*H*$_2$), 2.7 (br, 18 H, N*Me*$_3$), 3.8 (br, 6 H, Al–*H*), 5.0 (br, 54 H, C$_5$*H*$_4$Fe*Cp*) ppm. ^{13}C NMR (600 MHz, 23 KHz, MAS): δ = 27.6 (cluster *C*), 28.9 (*C*H$_2$C), 44.0 (N*Me*$_3$), 65.0 (*C*$_5$H$_4$Fe*Cp*) ppm. ^{27}Al NMR (600 MHz, 23 KHz, MAS, AlCl$_3$): δ = 140.0 ppm. In mass spectrum only small fragments were found. Elemental analysis C$_{78}$H$_{90}$Al$_8$Fe$_6$N$_2$ (1612.53) (%): Calcd. C 58.10, H 6.00, N 1.74. Found C 58.6, H 5.9, N 1.3.

4.7. Synthesis of an aluminum hydrazide

4.7.1. Synthesis of [LAlN(Me)NH]$_2$ (41); [L = HC{(CMe)(2,6–^{i}Pr$_2$C$_6$H$_3$N)}$_2$]: To a solution of LAlH$_2$ (**40**) (0.50 g, 1.12 mmol) in toluene (30 mL) was added dropwise a solution of methylhydrazine (0.103 g, 2.24 mmol) in toluene (10 mL) at room temperature. The resulting solution was stirred for 0.5 h before refluxing it for 3 h. During the reaction evolution of H$_2$ was observed. After the removal of all volatiles the residue was extracted with *n*-hexane (20 mL). The resulting solution was kept for crystallization at room temperature for 24 h to give reddish brown crystals of **41**. Yield: 0.41 g (76 % with respect to **40**). M.p. 297 - 299 °C. IR (KBr, nujol mull): $\tilde{\nu}$ = 3440 (w, N–H), 1622, 1552, 1261, 1096, 1020, 800, 721 cm^{-1}. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 0.21 (s, 2 H, N*H*), 1.06 (d, $^3J_{\mathrm{HH}}$ =

6.9 Hz, 12 H, CH*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH*Me*$_2$), 1.35 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH*Me*$_2$), 1.41 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, CH*Me*$_2$), 1.57 (s, 12 H, C*Me*), 2.10 (s, 6 H, N*Me*), 3.25 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 3.46 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*Me$_2$), 4.91 (s, 2 H, *γ*–C*H*), 7.17 - 7.11 (m, 12 H, Ar) ppm. ^{13}C NMR (125.13 MHz, C_6D_6, 25 °C): δ = 20.74 (*Me*), 22.99, 23.39, 25.16, 28.3 (CH*Me*$_2$), 28.6, 31.9 (*C*HMe$_2$), 45.64 (N*Me*), 94.26 (*γ*–*C*), 144.88 - 123.55 (Ar), 161.48 (*C*N) ppm. EI-MS (70 eV): *m/z* (%): 976 (100) [M$^+$], 488 (12) [(M–Al–L–N(Me)NH)$^+$]. Elemental analysis $C_{60}H_{90}Al_2N_8$ (979.39) (%): Calcd. C 73.58, H 9.47, N 11.44. Found C 73.1, H 9.2, N 11.0.

4.8. Synthesis of (alkylperoxo)aluminum compound

4.8.1. Synthesis of penta-coordinated *tert*-butylperoxo aluminum compound (42): To a solution of LAlH$_2$ (**40**) (0.50 g, 1.12 mmol) in diethylether (30 mL) was added ^{t}BuOOH (0.46 mL, 2.24 mmol, 5 - 6 M in decane, contains approximately 4 % water) dropwise at -78 °C. The solution was allowed to warm to room temperature and stirred overnight. During the reaction the color of the solution changes to light yellow. Partial removal of the solvent and storage at 0 °C for 1 week afforded colorless crystals of **42**.

5. Handling and dispose of wastes:

1. The solvents were distilled or condensed into cold traps and disposed into halogen-free or halogen-containing solvent containers.
2. The used NMR solvents were classified into halogen-free or halogen-containing solvents and disposed as heavy metal wastes and halogen containing waste respectively.
3. The heavy metal residues were dissolved in nitric acid and were stored into containers for heavy metal wastes after neutralization.
4. Drying agents (KOH, CaH_2, P_2O_5) were hydrolyzed and disposed as basic or acidic wastes.
5. Metallic sodium used for drying solvents was collected and recycled.[217] The residual sodium wastes were carefully hydrolyzed in cold ethanol and used for cleaning glassware in the alkali bath.
6. The residues of the alkali bath used for cleaning glassware were disposed into the container for basic wastes.
7. The acid bath used for cleaning glassware was neutralized with Na_2CO_3 and the resulting NaCl solution washed off in the water drainage system.
8. 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	10 L
Acid wastes	15 L
Base wastes	15 L

6. Crystal data and refinement details:

Table 1. Crystal data and structure refinement for **17**

Emperical formula	$C_{30}H_{36}Al_6N_6S_6$
Formula weight	834.89
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	$R\bar{3}$
Unit cell dimensions	a = 15.192(2) Å
	b = 15.192(2) Å
	c = 14.349(3) Å γ = 120°
Volume, Z	2868.0(8) Å^3, 3
Density (calculated)	1.450 g.cm^{-3}
Absorption coefficient	0.528 cm^{-1}
$F(000)$	1296
θ range for data collection	4.20 - 49.20
Index range	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-16 \leq l \leq 16$
Reflections collected	6025
Independent reflections	1093 [$R_{\text{int}} = 0.0898$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1093/0/77
Goodness-of-fit on F^2	1.145
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0567$, $wR2 = 0.1698$
R indices (all data)	$R1 = 0.0622$, $wR2 = 0.1773$
Largest diff. peak and hole	1.027 and –0.536 e·Å^3

Table 2. Crystal data and structure refinement for **21**

Emperical formula	$C_{30}H_{30}Al_6Br_6N_6S_6$
Formula weight	1308.30
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	$Pa\overline{3}$
Unit cell dimensions	a = 16.4721(19) Å
	b = 16.4721(19) Å
	c = 16.4721(19) Å
Volume, Z	4469.4(9) $Å^3$, 4
Density (calculated)	1.944 $g.cm^{-3}$
Absorption coefficient	0.5822 cm^{-1}
$F(000)$	2544
θ range for data collection	3.71 - 49.88
Index range	$-19 \leq h \leq 19$, $-19 \leq k \leq 19$, $-1 \leq l \leq 11$
Reflections collected	1968
Independent reflections	1311 [R_{int} = 0.1050]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1311/166/101
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0754, $wR2$ = 0.1689
R indices (all data)	$R1$ = 0.1209, $wR2$ = 0.1965
Largest diff. peak and hole	0.643, and –0.591 e·$Å^3$

Table 3. Crystal data and structure refinement for **22**

Emperical formula	$C_{30}H_{30}Al_6Cl_6N_6S_6$	
Formula weight	1041.54	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\overline{1}$	
Unit cell dimensions	a = 10.108(2) Å	α = 98.74(3)°
	b = 10.116(2) Å	β = 100.97(3)°
	c = 10.968(2) Å	γ = 98.71(3)°
Volume, Z	1069.3(4) Å^3, 1	
Density (calculated)	1.617 g.cm^{-3}	
Absorption coefficient	0.852 cm^{-1}	
F(000)	528	
θ range for data collection	3.84 - 49.54	
Index range	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-12 \leq l \leq 12$	
Reflections collected	6310	
Independent reflections	3342 [R_{int} = 0.0917]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3342/0/251	
Goodness-of-fit on F^2	0.961	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0443, $wR2$ = 0.1169	
R indices (all data)	$R1$ = 0.0535, $wR2$ = 0.1197	
Largest diff. peak and hole	0.513 and –0.545 e·Å^3	

Table 4. Crystal data and structure refinement for **23**·2PhMe

Emperical formula	$C_{92}H_{76}Al_6N_6S_6$	
Formula weight	1619.83	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P1$	
Unit cell dimensions	a = 13.315 (3) Å	α = 92.44(3)°
	b = 14.179 (3) Å	β = 113.92(3)°
	c = 14.543 (3) Å	γ = 117.87(3)°
Volume, Z	2125.2 (7) $Å^3$, 1	
Density (calculated)	1.266 $g.cm^{-3}$	
Absorption coefficient	0.272 cm^{-1}	
$F(000)$	844	
θ range for data collection	3.40 - 49.74	
Index range	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-17 \leq l \leq 16$	
Reflections collected	15324	
Independent reflections	9236 [R_{int} = 0.0947]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	9236/7/919	
Goodness-of-fit on F^2	0.875	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0677, $wR2$ = 0.1551	
R indices (all data)	$R1$ = 0.1061, $wR2$ = 0.1707	
Largest diff. peak and hole	0.694 and –0.467 $e·Å^3$	

Table 5. Crystal data and structure refinement for **24**·PhMe

Emperical formula	$C_{67}H_{74}Al_6N_6S_6$	
Formula weight	1317.56	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\overline{1}$	
Unit cell dimensions	a = 11.424 (2) Å	α = 78.52(3)°
	b = 12.377 (3) Å	β = 85.05(3)°
	c = 12.488 (3) Å	γ = 72.27(3)°
Volume, Z	1647.6 (6) Å^3, 1	
Density (calculated)	1.328 g.cm^{-3}	
Absorption coefficient	0.334 cm^{-1}	
F(000)	692	
θ range for data collection	3.32 - 49.54	
Index range	$-13 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 14$	
Reflections collected	16605	
Independent reflections	5625 [R_{int} = 0.0455]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5625/10/377	
Goodness-of-fit on F^2	1.015	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0634, $wR2$ = 0.1691	
R indices (all data)	$R1$ = 0.0795, $wR2$ = 0.1807	
Largest diff. peak and hole	0.896 and –0.467 e·Å^3	

Table 6. Crystal data and structure refinement for **25**

Emperical formula	$C_{34}H_{32}Al_2N_2S_6$
Formula weight	714.94
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.105(3) Å
	b = 9.179(18) Å β = 107.84(3)°
	c = 14.822(3) Å
Volume, Z	1697.2(6) Å^3, 2
Density (calculated)	1.399 g.cm^{-3}
Absorption coefficient	0.483 cm^{-1}
$F(000)$	744
θ range for data collection	3.26 - 49.64
Index range	$-15 \leq h \leq 15$, $-10 \leq k \leq 10$, $-17 \leq l \leq 17$
Reflections collected	13640
Independent reflections	2910 [R_{int} = 0.0992]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2910/0/203
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0342, $wR2$ = 0.0923
R indices (all data)	$R1$ = 0.0397, $wR2$ = 0.0942
Largest diff. peak and hole	0.552, and –0.396 e·Å^3

Table 7. Crystal data and structure refinement for **26**·PhMe

Emperical formula	$C_{85}H_{80}Al_6N_6S_6$
Formula weight	1539.79
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 23.525(5) Å
	b = 14.529(3) Å β = 111.16(3)°
	c = 23.911(5) Å
Volume, *Z*	7622(3) Å^3, 4
Density (calculated)	1.342 g.cm^{-3}
Absorption coefficient	0.300 cm^{-1}
F(000)	3224
θ range for data collection	3.36 - 49.58
Index range	$-25 \le h \le 27$, $-17 \le k \le 17$, $-28 \le l \le 24$
Reflections collected	21707
Independent reflections	6377 [R_{int} = 0.0464]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6377/0/462
Goodness-of-fit on F^2	0.955
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0288, $wR2$ = 0.0742
R indices (all data)	$R1$ = 0.0370, $wR2$ = 0.0763
Largest diff. peak and hole	0.399, and –0.272 e·Å^3

Table 8. Crystal data and structure refinement for **27**

Emperical formula	$C_{42}H_{60}Al_6N_6S_6$
Formula weight	1003.20
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	$Pa\overline{3}$
Unit cell dimensions	a = 16.969(2) Å
	b = 16.969(2) Å
	c = 16.969(2) Å
Volume, Z	4886.2(10) Å^3, 4
Density (calculated)	1.364 g.cm^{-3}
Absorption coefficient	0.426 cm^{-1}
$F(000)$	2112
θ range for data collection	4.16 - 49.58
Index range	$-6 \leq h \leq 18$, $-15 \leq k \leq 19$, $-19 \leq l \leq 19$
Reflections collected	9292
Independent reflections	1398 [$R_{\text{int}} = 0.0757$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1398/0/91
Goodness-of-fit on F^2	0.833
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0404$, $wR2 = 0.0791$
R indices (all data)	$R1 = 0.0791$, $wR2 = 0.0867$
Largest diff. peak and hole	0.274, and –0.256 e·Å^3

Table 9. Crystal data and structure refinement for **28**

Emperical formula	$C_{36}H_{48}Al_6N_6S_6$	
Formula weight	919.04	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinc	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.347(9) Å	α = 99.537(7)°
	b = 10.284(9) Å	β = 100.632(7)°
	c = 10.955(9) Å	γ = 101.027(7)°
Volume, Z	1099.99 (16) $Å^3$, 1	
Density (calculated)	1.387 $g.cm^{-3}$	
Absorption coefficient	0.466 cm^{-1}	
$F(000)$	480	
θ range for data collection	3.86 - 50.16	
Index range	$-12 \leq h \leq 11$, $-11 \leq k \leq 12$, $-12 \leq l \leq 12$	
Reflections collected	6421	
Independent reflections	3579 [R_{int} = 0.0431]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3579/0/254	
Goodness-of-fit on F^2	1.046	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0589, $wR2$ = 0.1574	
R indices (all data)	$R1$ = 0.0745, $wR2$ = 0.1693	
Largest diff. peak and hole	0.883, and –0.738 e·$Å^3$	

Table 10. Crystal data and structure refinement for **29**·2PhMe

Emperical formula	$C_{68}H_{82}Al_8N_2$	
Formula weight	1143.20	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.496(2) Å	α = 105.77(3)°
	b = 11.871(2) Å	β = 100.57(3)°
	c = 12.722(3) Å	γ = 101.78(3)°
Volume, Z	1582.2(5) Å^3, 1	
Density (calculated)	1.200 g.cm^{-3}	
Absorption coefficient	0.171 cm^{-1}	
F(000)	608	
θ range for data collection	3.44 - 49.48	
Index range	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-12 \leq l \leq 14$	
Reflections collected	15140	
Independent reflections	5367 [R_{int} = 0.1397]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5367/0/368	
Goodness-of-fit on F^2	0.934	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0603$, $wR2 = 0.1464$	
R indices (all data)	$R1 = 0.0857$, $wR2 = 0.1575$	
Largest diff. peak and hole	0.545 and −0.489 e·Å^3	

Table 11. Crystal data and structure refinement for **33**

Emperical formula	$C_{27}H_{24}AlN$	
Formula weight	389.45	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.905(4) Å	
	b = 11.914(3) Å	β = 94.16(4)°
	c = 13.999(5) Å	
Volume, Z	2313.1(12) Å^3, 4	
Density (calculated)	1.118 g.cm^{-3}	
Absorption coefficient	0.099 cm^{-1}	
$F(000)$	824	
θ range for data collection	3.60 - 20.35	
Index range	$-8 \leq h \leq 12$, $-11 \leq k \leq 0$, $-13 \leq l \leq 4$	
Reflections collected	2181	
Independent reflections	1751 [R_{int} = 0.0430]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1751/0/265	
Goodness-of-fit on F^2	1.112	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0890, $wR2$ = 0.2373	
R indices (all data)	$R1$ = 0.1198, $wR2$ = 0.2802	
Largest diff. peak and hole	0.351 and –0.379 e·Å^3	

Table 12. Crystal data and structure refinement for **35**·4PhMe

Emperical formula	$C_{130}H_{116}Al_6Fe_6N_6S_6$	
Formula weight	2451.63	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 13.863(3) Å	α = 75.28(3)°
	b = 14.790(3) Å	β = 87.05(3)°
	c = 16.274(3) Å	γ = 63.63(3)°
Volume, Z	2884.2(10) Å^3, 2	
Density (calculated)	1.411 g.cm^{-3}	
Absorption coefficient	0.943 cm^{-1}	
$F(000)$	1268	
θ range for data collection	3.28 - 49.72	
Index range	$-16 \leq h \leq 16$, $-16 \leq k \leq 17$, $-14 \leq l \leq 19$	
Reflections collected	21013	
Independent reflections	8734 [R_{int} = 0.1035]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8734/1/ 716	
Goodness-of-fit on F^2	0.763	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0536, $wR2$ = 0.0867	
R indices (all data)	$R1$ = 0.1339, $wR2$ = 0.1009	
Largest diff. peak and hole	0.486 and –0.444 e·Å^3	

Table 13. Crystal data and structure refinement for **39**·2.5PhMe

Emperical formula	$C_{95.50}H_{110}Al_8Fe_6N_2$	
Formula weight	1836.80	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 12.708 (5) Å	α = 91.41(3) °
	b = 14.885 (6) Å	β = 96.97(3)°
	c = 25.994 (10) Å	γ = 101.78(3)°
Volume, Z	4450.4(3) Å^3, 2	
Density (calculated)	1.371 g.cm^{-3}	
Absorption coefficient	1.078 cm^{-1}	
F(000)	1914	
θ range for data collection	1.50 - 25.00	
Index range	$-15 \leq h \leq 14$, $-17 \leq k \leq 17$, $-30 \leq l \leq 30$	
Reflections collected	85305	
Independent reflections	15545 [R_{int} = 0.0667]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	15545/0/807	
Goodness-of-fit on F^2	1.018	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0672, $wR2$ = 0.1640	
R indices (all data)	$R1$ = 0.0880, $wR2$ = 0.1774	
Largest diff. peak and hole	1.397 and –0.929 e·Å^3	

Table 14. Crystal data and structure refinement for **41**·C_6H_{14}

Emperical formula	$C_{66}H_{104}Al_2N_8$	
Formula weight	1063.53	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\overline{1}$	
Unit cell dimensions	a = 9.054(5) Å	α = 87.23(5)°
	b = 13.218(7) Å	β = 80.54(4)°
	c = 13.446(8) Å	γ = 78.99(4)°
Volume, Z	1558.04 (15) Å^3, 1	
Density (calculated)	1.134 g.cm^{-3}	
Absorption coefficient	0.092 cm^{-1}	
F(000)	582	
θ range for data collection	3.08 - 49.16	
Index range	$-10 \le h \le 10$, $-14 \le k \le 15$, $-15 \le l \le 15$	
Reflections collected	28288	
Independent reflections	5222 [R_{int} = 0.0425]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5222/0/348	
Goodness-of-fit on F^2	1.032	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0495, $wR2$ = 0.1325	
R indices (all data)	$R1$ = 0.0583, $wR2$ = 0.1388	
Largest diff. peak and hole	0.636 and –0.493 e·Å^3	

Table 15. Crystal data and structure refinement for **42**·Et_2O

Emperical formula	$C_{66}H_{103}Al_3N_4O_9$	
Formula weight	1177.46	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 13.622(9) Å	α = 89.609(4)°
	b = 14.511(8) Å	β = 80.735(5)°
	c = 18.544(10) Å	γ = 67.620(5)°
Volume, Z	3339.7(3) $Å^3$, 2	
Density (calculated)	1.171 $g.cm^{-3}$	
Absorption coefficient	0.113 cm^{-1}	
F(000)	1276	
θ range for data collection	3.14 - 49.62	
Index range	$-16 \leq h \leq 15$, $-17 \leq k \leq 17$, $-21 \leq l \leq 21$	
Reflections collected	49160	
Independent reflections	11423 [R_{int} = 0.0974]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	11423/0/776	
Goodness-of-fit on F^2	0.993	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0592, $wR2$ = 0.1402	
R indices (all data)	$R1$ = 0.0892, $wR2$ = 0.1561	
Largest diff. peak and hole	0.317 and –0.461 e·$Å^3$	

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List of Publications:

1. *Synthesis of a Hexadentate Hexameric Aluminum Imide and its Metathesis Reactions,* N. Dastagiri Reddy, **S. Shravan Kumar**, Herbert W. Roesky, Denis Vidovic, Jörg Magull, Mathias Noltemeyer, and Hans-Georg Schmidt, *Eur. J. Inorg. Chem.* **2003**, 442 - 448.

2. *Synthesis, Structure and Cyclic Voltammetric Studies of* $[CpFeC_5H_4C{\equiv}CAlNCH_2(C_4H_3S)]_6$*: The first model compound for the Fixation of Metal Containing Ligands on an Aluminum Nitride Cluster.* **S. Shravan Kumar**, N. Dastagiri Reddy, Herbert W. Roesky, Denis Vidovic, Jörg Magull, and Rainer F. Winter, *Organometallics* **2003**, *22*, 3348 - 3350.

3. *Synthesis and Reactivity of Carbaalanes* $(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$ *and* $(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6$*: X-ray Crystal Structure of* $(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$*.* **S. Shravan Kumar**, Junfeng Rong, Sanjay Singh, Herbert W. Roesky, Denis Vidovic, Jörg Magull, Dante Neculai, Vadapalli Chandrasekhar, and Marc Baldus, *Organometallics* **2004**, *23*, 3496 - 3500.

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5b. *AlHC Chemistry.* Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28 - April 1, **2004** (INOR - 473). Herbert W. Roesky, Andreas Stasch, and **S. Shravan Kumar**.

6. *Methyl Substitution of Aluminum Hydride Bonds in a Carbaalane and an Aluminum Imide.*
   Andreas Stasch, **S. Shravan Kumar**, Vojtech Jancik, Herbert W. Roesky, Jörg Magull, and Mathias Noltemeyer, *Eur. J. Inorg. Chem.* **2004**, 4056 - 4060.

7. *Hydroalumination reactions on Acetylenes and Nitriles in the Synthesis of Carbaalanes and Imidoalanes: An Overview.* (Cover page article)
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8. *Planar Dimeric Six-Membered Spirane Aluminum Hydrazide: Synthesis, X-ray Crystal Structure and Theoretical Studies of* $[LAlN(Me)NH]_2$; $[L = HC\{(2,6\text{-}^iPr_2C_6H_3N)(CMe)\}_2]$.
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