

**Aluminum Compounds with 3,5-Di-*tert*-butylpyrazolato Ligands: Syntheses,
Structures and Reactions**

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Structures and Reactions

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Dedicated to my mother,
my wife, my son,
and my other relatives
for their great love

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Abbreviations

Å	angstrom (10^{-10} meter)
av	average
br	broad
Bu	butyl
<i>i</i> -Bu, <i>t</i> -Bu	<i>iso</i> -butyl, <i>tert</i> -butyl
δ	chemical shift
°C	centigrade
d	doublet
dec.	decompose
deg.	degree
3,5- <i>t</i> Bu ₂ pz	3,5-di- <i>tert</i> -butylpyrazolato
E	O, S, Se, Te
EI	electron impact ionization
Et	ethyl
η	hapto
h	hour(s)
IR	infrared
<i>J</i> (Hz)	coupling constant (Hertz)
K	Kelvin
λ	wavelength
M	metal
M ⁺	molecular ion
Me	methyl
MS	mass spectrometry
μ	bridging
<i>m/z</i>	mass/charge
mbar	millibar
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
<i>i</i> Pr	<i>iso</i> -propyl
pz	pyrazolyl, substituted pyrazolyl

Abbreviations

R, R', R ¹ , R ²	organic ligands
rt	room temperature
<i>tert</i> , <i>t</i>	tertiary
TMS	trimethylsilane
THF	tetrahydrofuran
vs	very strong, versus
$W_{1/2}$	half-height width
X	halide
Z	number of molecules in the unit cell

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1. Introduction

Aluminum is the most common metallic element in the earth's crust having an abundance of 8.3 % by weight. It occurs predominantly in oxide or silicate minerals such as feldspars and micas. The high abundance of aluminum has resulted in a multitude of applications for the element and its compounds. Today, aluminum plays an important role as pure metal and alloys while its compounds are used extensively as structural ceramics, electrical materials, catalysts, ionic conductors, etc.^{1,2}

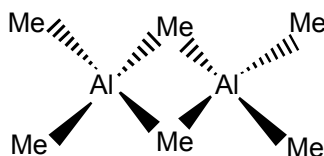
In 1859, the first organoaluminum compound $\text{Et}_3\text{Al}_2\text{I}_3$ was synthesized from elemental Al and EtI by W. Hallwachs and A. Schafarik.³ However, it took nearly one century before K. Ziegler discovered the synthetic and catalytic potential of organoaluminum compounds and the low pressure polymerization of olefins with organoaluminum/transition metal catalysts.⁴ Since then a whole new field of organometallic chemistry not only in synthetic organic chemistry and catalysis but also in the development of precursors of inorganic high-tech materials was opened up due to his pioneering work.

Some suggestions have been offered of how organoaluminum chemistry might develop in the future, where the significance of this field might include:⁵

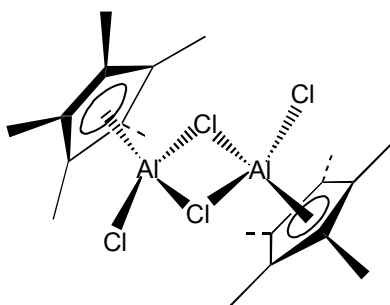
- a) Novel stoichiometric procedures for forming carbon-carbon bonds,
- b) The controlled oligomerization or polymerization of hydrocarbons,
- c) The efficient conversion of carbon monoxide into useful fuels and chemicals.

These predictions have been largely verified by extensive developments in industry and in academia.

A fundamental feature of organoaluminum chemistry is the dimeric nature of aluminum alkyls and alkylaluminum halides due to the electron-deficient character of aluminum in solution. Thus, the two Al-(CH₃)-Al fragments in trimethylalane are best described by the concept of electron-deficient three-center-two-electron 3c-2e bonding (Scheme 1).⁶ Such electron-deficient bonds in dimeric species are inherently weak and readily cleaved. The organoaluminum chemistry of the pentamethylcyclopentadienyl (Cp^{*}) ligand exhibits peculiar bonding modes. While the cores of the structures of [η^3 -Cp^{*}Al(Cl)Me]₂ and [η^3 -Cp^{*}Al(Cl)(*i*-Bu)]₂ are composed of planar and slightly asymmetric four-membered Al₂Cl₂ rings,^{7,8} the structure of the corresponding (Cp^{*}AlCl₂)₂ compound reveals η^5 -Cp^{*} interactions with the Al atoms (Scheme 2).⁹ However, monomeric aluminum compounds have been obtained by employing sterically demanding organic ligands.¹⁰⁻¹²



Scheme 1. The dimeric structure of aluminum alkyls.



Scheme 2. The structure of (Cp^{*}AlCl₂)₂.

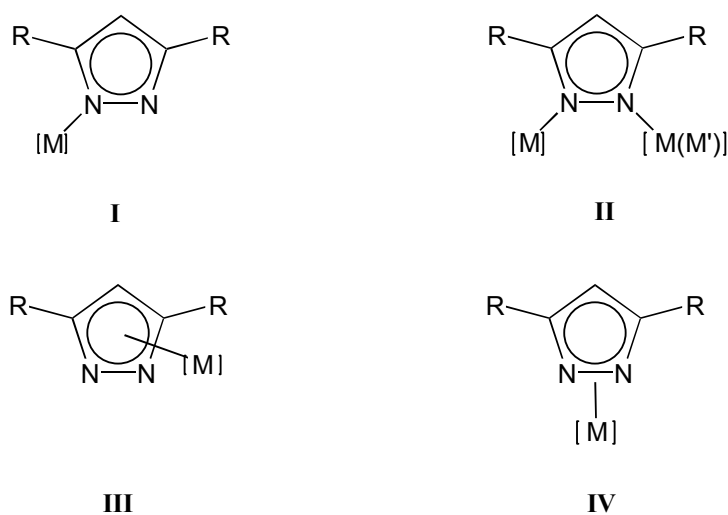
The quest of a potentially low-cost class of organoaluminum compounds has attracted the interest of especially the polymer industry, where oligomeric methylaluminoxanes (MAO) have become cocatalysts in stereoregular Ziegler-Natta alkene polymerizations.¹³ Moreover, arrays of aluminum hydrides and mixed alkyls have started to occupy a valued position in organic synthesis for the selective formation of C-E bonds, where E = C, H, O, N, or X.¹⁴ Additionally, it is well-known that aluminum halides or alkyls are extensively applied to Lewis acid-mediated reactions as reagents while aluminum acetylides hold an important role in addition reaction in organic syntheses.² Recently, research work on cationic aluminum species has led to extensive applications in organic and catalytic transformations since they possess enhanced Lewis acidity due to the positive charge on the aluminum center.¹⁵

Organoaluminum chemistry is sometimes hampered by the pyrophoric nature, the kinetic instability, and the volatility of the compounds together with a sometimes low tendency to crystallize, which makes it rather difficult to characterize the compounds completely. Recent developments in organoaluminum chemistry have overcome these difficulties by the use of bulky ancillary ligands.¹⁶

1.1. Organometallic compounds with pyrazolato ligands

Nitrogen-based ligands are attractive candidates for applications in organometallic chemistry as ancillary ligands because of the extremely strong bonds formed between these hard donor atoms and almost all metal centers. Recent examples of ligands that have been pursued in this direction include amidinates,¹⁷ and pyrazolylborates,¹⁸ and many others.¹⁹

Ligands derived from five-membered nitrogen-rich heterocycles, such as pyrazole and substituted derivatives, represent ligands for main group and early transition metals with intriguing potential, since the parent heterocycles are easily deprotonated to form monoanionic donors with flexible coordination ability. The strong metal-nitrogen bonds formed with these ligands should lead to thermodynamically robust complexes. Moreover, the degree of steric crowding about the coordination sphere could be easily controlled by choice of the organic groups attached to the carbon atoms.



Scheme 3. The known modes of complexes of transition metals with pyrazolato ligands ([M] = metal fragment).

Indeed, pyrazolato ligands have been employed in complexes of transition metals and exhibit either η^1 -bonding to a single metal ion or form a η^1, η^1 -bridge between two metal centers (Scheme 3 (I, II)).²⁰ Recently, they are enjoying a renaissance due to the discovery of η^2 - and η^5 -coordination modes with transition and lanthanoide metals (III,

IV)²⁰ such as $[\text{Ti}(\eta^2\text{-R}_2\text{pz})_4]$ (R = Me, Ph),^{21a} $[(\eta^5\text{-Cp}^*)\text{Ru}(\eta^5\text{-3,5-}t\text{Bu}_2\text{pz})]^{22}$ and a few others with unprecedented bonding modes.²³ This development has triggered the use of pyrazolato ligands for a broader investigation of various transition metals and several main group metals which to some extent have enriched the established η^1 - and η^1, η^1 -pyrazolato ligation.²⁴ These new compounds can be summarized as follows:²³

- a) $\mu_3, \eta^1, \eta^2, \eta^1$ -compounds: $[(3,5\text{-}t\text{Bu}_2\text{pz})\text{K}(\text{THF})]_6$,^{23a} $[\text{Tl}_n(\text{Ph}_2\text{pz})_n]$ (n = 3, 4) and $[\text{Tl}_4(\text{R}_2\text{pz})_3(\text{OH})]$ (R = Me, Ph),^{23b}
- b) μ, η^2, η^2 -compound: $[\text{Yb}(3,5\text{-}t\text{Bu}_2\text{pz})_2]$,^{23c}
- c) π, η^1 -(C-bonded) compounds: $[\{\text{Pd}_2(\text{R})_2(\mu_3\text{-3,5-}dm_2\text{pz})_2\text{Ag}(\eta^2\text{-}\mu\text{-ClO}_4)\}_2]$ (R = $\text{CH}_2\text{C}_6\text{H}_4\text{P}(o\text{-tolyl})_2$; 3,5-*dm*₂pz = 3,5-dimethylpyrazole),^{23d} $[\text{K}\{\text{Er}(3,5\text{-}t\text{Bu}_2\text{pz})_4\}]$,^{23e}
- d) π, η^3 -(C₂N-bonded) compound: $[\text{K}\{\text{Er}(3,5\text{-}t\text{Bu}_2\text{pz})_4\}]$,^{23e}
- e) η^5 (C₃N₂-bonded) compound: $[(\eta^5\text{-Cp}^*)\text{Ru}(\eta^5\text{-3,5-}t\text{Bu}_2\text{pz})]$,²²
- f) $\mu_3, \eta^1, \eta^1, \eta^1$ -compound: $[\text{Tl}_n(\text{Ph}_2\text{pz})_n]$ (n = 3, 4) and $[\text{Tl}_4(\text{R}_2\text{pz})_3(\text{OH})]$ (R = Me, Ph).^{23b}

Nevertheless, main group metal complexes with pyrazolato ligands are still limited, especially of group 13 elements. Due to the electron-deficient character of aluminum, unique coordination modes with the bulky Lewis basic 3,5-*tert*-butylpyrazolato ligand therefore were expected to be accessible.

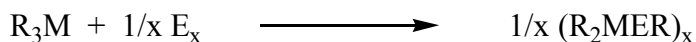
1.2. Aluminum group 16 element compounds as starting materials for semiconductors and reagents in organic synthesis

Binary group 13 - 16 organometallic compounds, where group 16 elements mainly involve S, Se and Te, have gained interest due to their potential as precursors for semiconductors, materials industry and reagents.^{25a}

Aluminum group 16 compounds are of particular interest in organic synthesis, for example, application for the transfer of aldehydes into related thio-, seleno- and telluro-esters by the reactions with $i\text{Bu}_2\text{AlER}$ ($\text{R} = \text{S}, \text{Se}, \text{Te}$).²⁶

Generally, chalcogens (S, Se, Te) can insert into M-C bonds of bulky trialkyl or triaryl group 13 organometallic compounds to form soluble group 13 element chalcogenides in most common solvents. The methods of preparing group 13 - 16 compounds in the literature are summarized as follows.²⁵

a) Reaction of triorganylmetalanes with the elemental chalcogens;



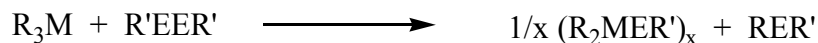
b) Reaction of lithiumchalcogenides with diorganylhalogenmetalanes;



c) Reaction of HER ($\text{E} = \text{S}, \text{Se}, \text{Te}$) with triorganylmetalanes;



d) Reaction of triorganylmetalanes with diorganodichalcogenides;

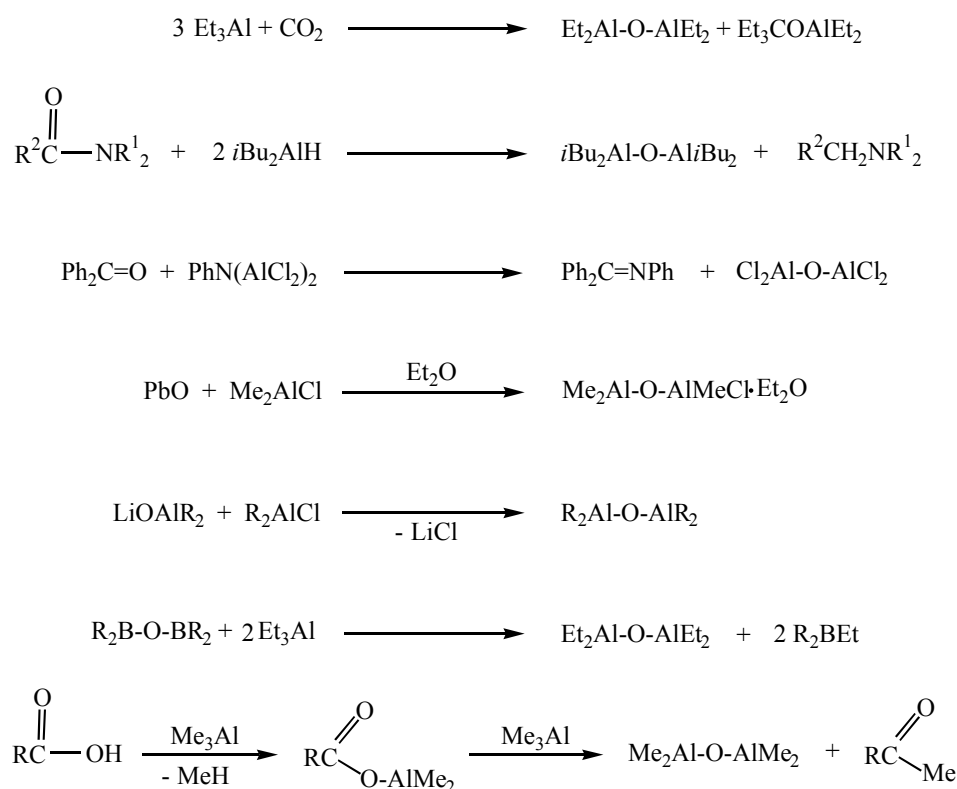


Recently an alternative route for the preparation of aluminum chalcogenides with a cubic core $(Cp^*AlE)_4$ ($E = Se, Te$; $Cp^* = C_5Me_5$) has been developed.²⁷ This type of compounds was obtained by the reactions of $(Cp^*Al)_4$ with elemental chalcogens ($E = Se, Te$).

1.3. Aluminoxanes

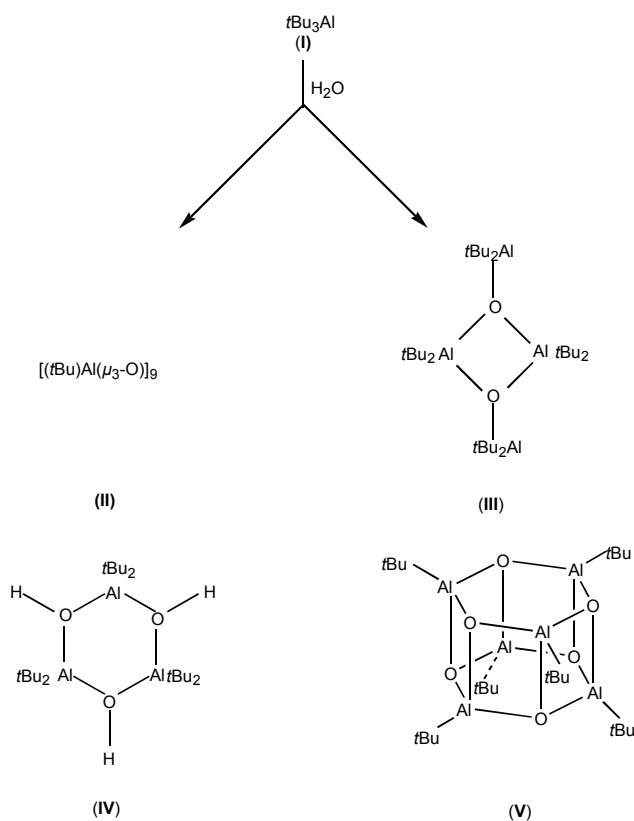
Since 1980, intense interest in alkylaluminoxanes ($R_2Al-O-AlR_2$ or $(RAIO)_n$) has been stimulated primarily by the work of H. Sinn and W. Kaminsky, who found methylaluminoxane (MAO) to be a good cocatalyst for the transition-metal catalyzed polymerization of alkenes.^{13, 28} The exploration of its properties has opened a new field since then.²⁹

Methods for the protolytic formation of aluminoxanes are well documented.³⁰ The most obvious method is the partial hydrolysis of aluminum alkyls. To obtain the related aluminoxanes, controlled amounts of water have to be introduced into a solution of R_3Al at low temperatures. Other nonprotolytic preparations of aluminoxanes are summarized in Scheme 4.⁴



Scheme 4. The nonprotolytic preparations of aluminoxanes.

Aluminoxanes easily undergo association yielding di-, tri-, tetra-, and oligoaluminoxanes. These properties of aluminoxanes make the preparation of a particular aluminoxane in a crystalline form and the determination of their crystal structures difficult. It is not surprising therefore, that the experimental data and proposed structures of aluminoxanes differ and depend on the synthetic conditions, isolation methods, solvents used and many other factors.²⁸



Scheme 5. The oligomers of tetra-*t*-butyldialuminoxane and *t*-butylaluminoxanes.³¹

The role of aluminoxanes in Ziegler-Natta catalysis is not yet clear and to understand their cocatalytic activity determination of the structures of aluminoxanes is crucial. The recent results of the Barron group on the structures of oligomers of tetra-*t*-butyldialuminoxane and *t*-butylaluminoxanes are probably best viewed in this light so far (Scheme 5).^{31a} The isolation and crystal structure determination of a number of hydrolysis products of tri-*t*-butylalane and their Lewis base adducts have provided fundamental insight into the bonding properties of $(t\text{Bu}_2\text{AlO})$ and $(t\text{BuAlO})$ units in the resulting oligomers. Furthermore, several aluminum oxide hydroxides have been successfully isolated and structurally characterized by the reaction of R_3Al ($\text{R} = \text{Me}, \text{Et}, i\text{-Bu}$) and water or and lithium hydroxide in Roesky group.^{31b-c} However, the

structure(s) and the cocatalytic activity of methylaluminoxane remain unsolved problems and represent significant challenges for future research.

1.4 Aluminum cage compounds involving Al-N and A-C cores

The reactions of alkylalanes and amines usually lead to the formation of compounds containing Al-N cores, first studied by E. Wiberg in Germany.³² The significance of these reactions are emphasized by the fact that they remain the subject focused on aluminum nitride production.³³

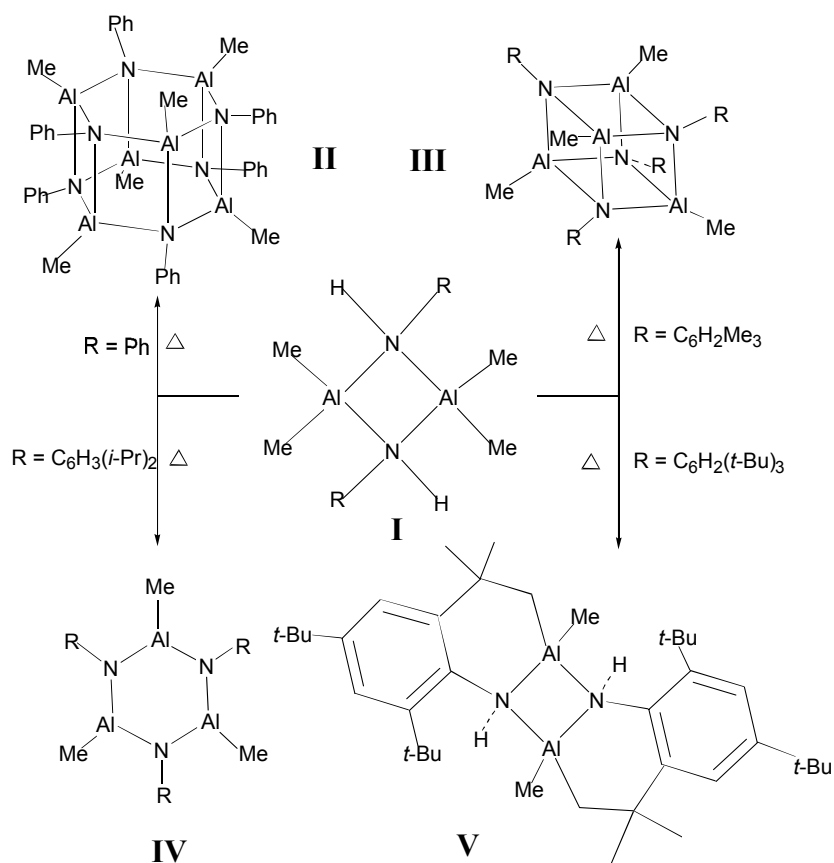
The literature reveals a series of fundamental studies performed by Smith and co-workers.³⁴ Upon initial interaction with an amine, adducts of the form $R_3Al \cdot N(H_2)R$ are the primary products. An increase in temperature proceeds through alkane evolution under formation of organoaluminum-nitrogen dimers possessing an Al_2N_2 core. For example, the reaction of Me_3Al with H_2NR affords the $(Me_2Al-NHR)_2$ dimer. These dimers offer an access to a number of aminoalanes of varying complexities.^{34e}

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

- a) Steric bulk of the alkyl group on the amine,
- b) The organic substituents coordinating to aluminum atoms,
- c) The reaction conditions.

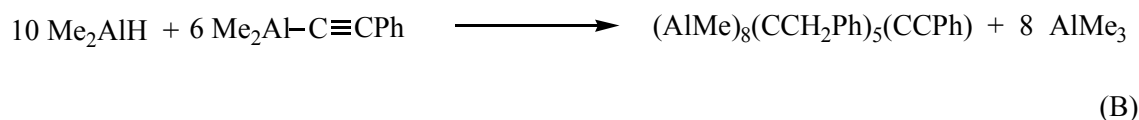
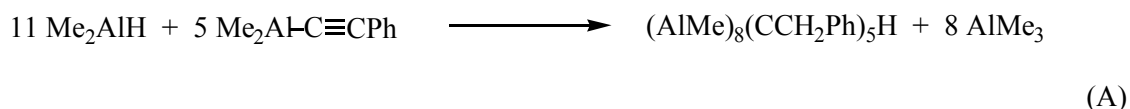
The aryl amines 2,6-diisopropylaniline, $H_2NC_6H_3(i-Pr)_2$, 2,4,6-trimethylaniline, $H_2NC_6H_2Me_3$, tri-*t*-butylaniline, $H_2NC_6H_2(t-Bu)_3$, and aniline, H_2NPh , provide an access to a series of different structures starting from $(Me_2Al-NHR)_2$. The cyclometallated dimer $[MeAl-NHC_6H_2(t-Bu)_2-\mu-(CMe_2CH_2)_2]_2$ ³⁵ is obtained with $H_2NC_6H_2(t-Bu)_3$. The quasi-aromatic $[MeAl-NC_6H_3(i-Pr)_2]_3$ trimer is the product when $H_2NC_6H_3(i-Pr)_2$ is utilized. Condensation of the $H_2NC_6H_2Me_3$ -based dimer yields the

cubane-like tetramer $(\text{MeAl-NC}_6\text{H}_2\text{Me}_3)_4$.³⁶ $(\text{Me}_2\text{Al-NHR})_2$ undergoes condensation to yield the hexamer $(\text{MeAl-NPh})_6$ in low yield,³⁷ (Scheme 6).



Scheme 6. Structures of Al-N composites generated through the influence of different substituents.

Another class of interesting aluminum cage compounds, carbaalanes, was formed by hydroalumination with aluminum acetylide compounds, synthesized and characterized only recently,^{38a-e} consisting of clusters of aluminum and carbon atoms similar to their carbaborane analogues. Their structures seem to be based on the number of electron pairs in their molecular centers in accordance with the Wade rules^{38f} (Scheme 7).



Scheme 7. Syntheses of carbaalanes.

These compounds consist of Al_8C_6 or $\text{Al}_8\text{C}_5\text{H}$ cores, respectively. The eight Al-atoms form an inner cube and the six atoms of carbon and hydrogen are located outside the surface of the inner cube in *exo* positions. However, the bonding situation of the core is still an object of discussion.

1.5 Scope and aims of this dissertation

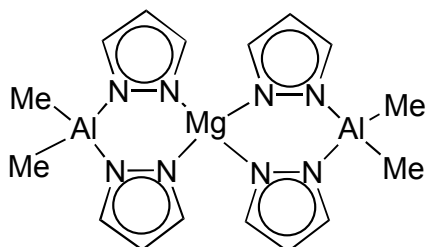
As discussed in the previous sections, organoaluminum compounds have been widely produced for catalysis, reagents as well as precursors for inorganic materials.⁵ In recent years significant progress has been made towards aluminumhydrides, low-valent aluminum species as well as aluminum-transition metal compounds.¹⁶ Additionally, cage species such as carbaalane and three-coordinated iminoalanes reflect an important role in organoaluminum chemistry. Moreover, the structure of aluminoxane is still an unresolved question although its role as a cocatalyst in Ziegler-Natta catalysis seems to be almost understood. Accordingly, this work mainly deals with the investigation of aluminum compounds with the emphasis on 3,5-di-*tert*-butylpyrazolato ligands and the main focuses are:

-
- a) Studies of the 3,5-di-*tert*-butylpyrazolato aluminum compounds with unique coordination modes,
 - b) Preparation of aluminum hydrides with 3,5-di-*tert*-butylpyrazolato ligands and examining its reactivity with various reagents including group 16 elements and acetylenes,
 - c) Investigations on the structures of aluminoxanes,
 - d) Examination of cycloaddition reactions of aluminum-pyrazolato complexes with $\text{HC}\equiv\text{CSiMe}_3$,
 - e) Preparation of aluminum cage compounds with Al-C-N blocks.

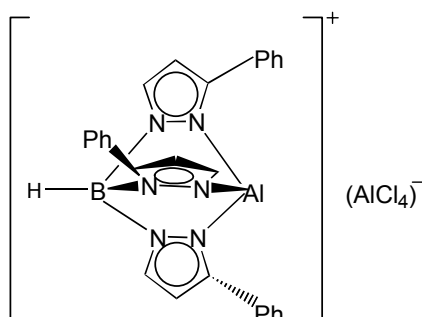
2. Results and Discussion

2.1. Aluminum alkyl and halide compounds with the 3,5-di-*tert*-butylpyrazolato ligands³⁹

Several pyrazolato aluminum compounds and one pyrazolato aluminum-magnesium ate complex have been reported to date (Schemes 8 and 9),⁴⁰ the related 3,5-di-*tert*-butylpyrazolato aluminum derivatives, however, have not yet been investigated and structurally characterized. Since aluminum alkyls and halides are potentially useful reagents in organic synthesis^{2,14} or possible precursors in chemical vapor deposition (CVD) technology, aluminum complexes with 3,5-di-*tert*-butylpyrazolato ligands were therefore investigated.



Scheme 8. The aluminum-magnesium ate complex with pyrazolato ligands.

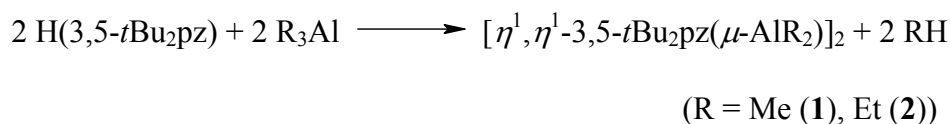


Scheme 9. One example of a pyrazolyborato aluminum compound.

2.1.1. Preparation of complexes $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlR}_2)]_2$ (R = Me, **1; R = Et, **2**)**

Alkyl derivatives of aluminum with pyrazolato ligands were previously prepared by reacting benzene solutions of the appropriate aluminum compound with a stoichiometric amount of pyrazole at room temperature.^{40a}

In a modified synthesis compounds **1** and **2** were prepared at ambient temperature by the reaction of Me₃Al or Et₃Al and 3,5-di-*tert*-butylpyrazole H(3,5-*t*Bu₂pz)⁴¹ in *n*-hexane to give in good yields compounds $[(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlR}_2)]_2$ (R = Me, **1**; R = Et, **2**), (Scheme 10).

**Scheme 10.** Synthesis of compounds **1** and **2**.

In both cases alkane elimination occurred at room temperature. Compounds **1** and **2** were purified by crystallization from *n*-hexane at -26 °C, **1** can also be purified by sublimation in vacuo. The ¹H-NMR (C₆D₆) spectrum of compound **1** shows three sharp singlets (δ -0.55, 1.37, and 6.23 ppm in a ratio of 12:36:2), indicating the resonances of Al-CH₃, *t*Bu and C-H protons, respectively. The mass spectrum (EI) shows the peak of highest mass *m/z* at 457 (M⁺ - Me), indicating a dimeric composition of **1**. The ¹H-NMR (C₆D₆) spectrum of compound **2** reveals besides the resonances of *t*Bu (δ 1.40, s, 36 H) and CH protons (δ 6.30, s, 2 H) the signals at δ 0.15 (t, CH₂, 8 H) as well as at 0.95 ppm (m, CH₃, 12 H), clearly demonstrating four Al-Et groups in this compound. The mass spectrometry (EI) also confirmed the formation of **2** (M⁺ - Et (*m/z*) = 499 %).

2.1.2. Molecular structure of complex 1

Crystals suitable for X-ray diffraction studies were obtained from *n*-hexane at $-26\text{ }^{\circ}\text{C}$. Compound **1** crystallizes in the orthorhombic crystal system, space group *Pbcn*. The X-ray diffraction analysis of **1** shows a dimeric molecule with a six-membered Al_2N_4 -ring and four terminal methyl groups (Figure 1), comparable to that observed in the pyrazolato derivative $[(\eta^1, \eta^1\text{-pz})(\mu\text{-AlMe}_2)]_2$.^{40f} Two 3,5-di-*tert*-butylpyrazolato groups serve as bridges between the two aluminum atoms and the six-membered Al_2N_4 -ring consists of four nitrogen atoms from two 3,5-di-*tert*-butylpyrazolato groups and two aluminum atoms. Surprisingly, the Al_2N_4 -ring features a distorted conformation in sharp contrast to the related compound $[(\eta^1, \eta^1\text{-pz})(\mu\text{-AlMe}_2)]_2$ consisting of a boat conformation. This structural difference might be due to the bulky *tert*-butyl groups. Both the Al-N and Al-C bond lengths (e. g. Al(1)-N(1), 1.9638(13) Å and Al(1)-C(6), 1.962(2) Å) as well as the N-Al-N angle (e. g. N(1)-Al(1)-N(2), 99.77(6) $^{\circ}$) are in the expected range and are comparable to the related bond lengths and angles in $[(\eta^1, \eta^1\text{-pz})(\mu\text{-AlMe}_2)]_2$ (Al(1)-N(1), 1.923(1) Å, Al(1)-C(8), 1.939 Å, N(1)-Al(1)-N(3), 99.3 $^{\circ}$).^{40f} The C(5)-Al(1)-C(6) angle (121.80(9) $^{\circ}$) is somewhat larger than the corresponding one in $[(\eta^1, \eta^1\text{-pz})(\mu\text{-AlMe}_2)]_2$ (C(8)-Al(1)-C(10), 118.8(1) $^{\circ}$).

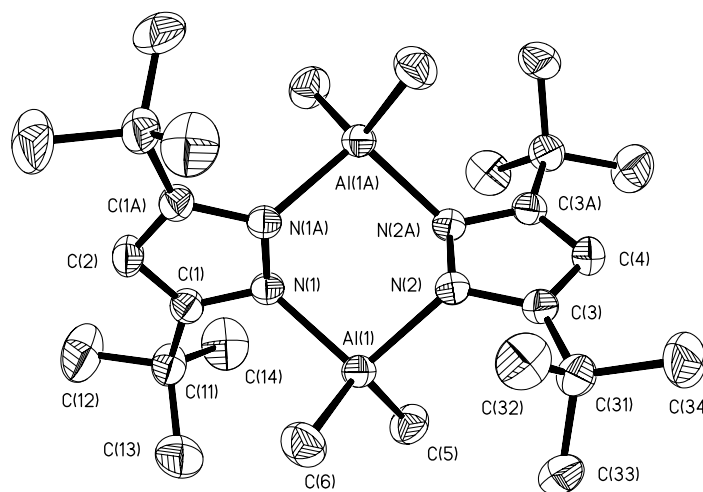
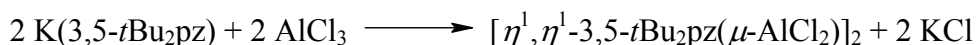


Figure 1. Perspective view of the complex $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlMe}_2)]_2$ (**1**), showing the numbering scheme and the thermal ellipsoids at the 50 % probability level. Selected bond lengths [\AA] and angles [$^\circ$]: Al(1)-N(1) 1.9638(13), Al(1)-C(6) 1.962(2); C(5)-Al(1)-C(6) 121.80(9), C(5)-Al(1)-N(1) 114.67(7), C(5)-Al(1)-N(2) 102.09(7), C(6)-Al(1)-N(1) 102.17(7), C(6)-Al(1)-N(2) 114.56(7), N(1)-Al(1)-N(2) 99.77(6).

2.1.3. Preparation of mixed methyl aluminum halides $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlR}_1\text{R}_2)]_2$ ($\text{R}_1 = \text{R}_2 = \text{Cl}$ (3**); $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{Cl}$ (**4**); $\text{R}_1 = 3/2 \text{ Me}$, $\text{R}_2 = 1/2 \text{ Cl}$ (**5**); $\text{R}_1 = \text{R}_2 = \text{I}$ (**6**), and a homoleptic complex $[(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_3\text{Al}]$ (**7**)**

The addition of an equivalent amount of aluminum trichloride to $\text{K}(3,5\text{-}t\text{Bu}_2\text{pz})^{23a}$ in toluene at room temperature gave $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlCl}_2)]_2$ (**3**) (Scheme 11).

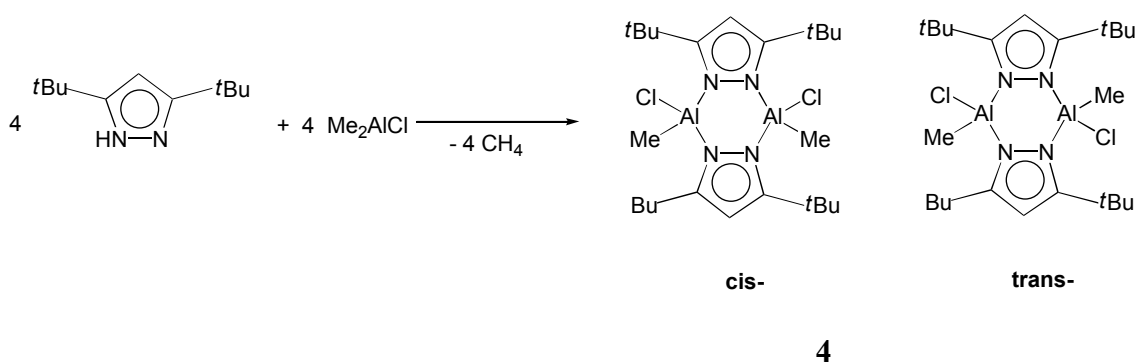


3

Scheme 11. Synthesis of compound **3**.

Generally, compound **3** can be easily synthesized and purified. Nevertheless, it is advisable to grind the starting materials K(3,5-*t*Bu₂pz) and AlCl₃ into fine powders, otherwise the by-product **7** (*vide infra*) will form together with the expected product **3**. Actually it seems impossible to separate these two compounds by common methods including sublimation or recrystallization due to their similar properties. It is also advisable to add cold solvent (toluene, 0 °C) before starting the reaction since the elimination of KCl is exothermic. In order to promote the virtually quantitative yield of compound **3**, an excess of AlCl₃ (about 33 %) should be employed. The ¹H-NMR (C₆D₆) spectrum of **3** shows two sharp singlets (δ 1.43 and 6.33 ppm in a ratio of 36:2), indicating the resonances of *t*Bu and CH protons, respectively. The resonance of the *t*Bu protons is slightly downfield shifted in the ¹H-NMR spectrum in comparison with that of compound **1** (δ 1.37), due to the higher electron density of Cl atoms than of Me groups. The mass spectrometry (EI) reveals the molecular ion at *m/z* 554 (M⁺, 100 %), implying compound **3** to be dimeric.

The reaction of Me₂AlCl and H(3,5-*t*Bu₂pz) (1:1) in *n*-hexane at room temperature yielded the compound [(η^1, η^1 -3,5-*t*Bu₂pz)(μ -AlMeCl)]₂ (**4**) as a mixture of isomers (Scheme 12), confirmed by ¹H- as well as ¹³C-NMR (in a ratio of 1:1). The isomer mixture (**4a** + **4b**) could be readily purified by crystallization in *n*-hexane at low temperature for at least two times to give cubic crystals in medium yield. However, it is impossible to further separate the two isomers by recrystallization or sublimation.

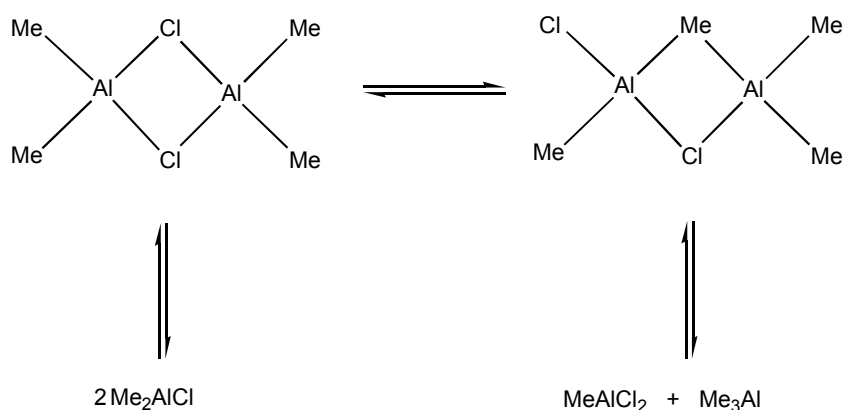


Scheme 12. Synthesis of compound **4** (**cis-** (**4a**) and **trans-** (**4b**)).

Mass spectrometry of the product shows a peak of highest mass at 497 ($M^+ - \text{Me}$, 100 %), and the elemental analysis is in agreement with the formulation of **4** as well. The melting point of **4** (113 °C) is much lower in comparison to those of **1** (173 °C) and **3** (175 °C) due to the presence of two isomers. The ratio of C-H, Me and *t*Bu protons in the $^1\text{H-NMR}$ spectrum corresponds to the composition of **4** (2:6:36), and the signals of the three different protons (CH_3 , *t*Bu and CH) reveal two sets of resonances (δ -0.41, 1.340, and 6.278 ppm; -0.43, 1.397 and 6.279 ppm, respectively), clearly exhibiting the existence of two isomers in solution. It seems to be difficult to determine the exact conformations of these isomers although explanations for such features have been suggested nearly three decades ago.^{40a}

The reaction of Me_2AlCl with $\text{K}(3,5\text{-}t\text{Bu}_2\text{pz})$ in toluene at room temperature gave a mixture in a molar ratio of 1:1 of $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlMe}_2)]_2$ (**1**) and $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-AlMe}_2)(\mu\text{-AlMeCl})]$ (**5**), respectively. The formation of **5** was unforeseen, it can be only obtained by sublimation in high vacuum affording a white solid together with **1**. Attempts to separate these two compounds were not successful. In addition to the resonances of **1**, the $^1\text{H-NMR}$ spectrum of **5** shows three resonances for Al-Me

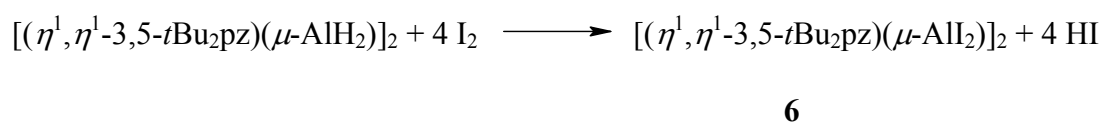
protons (δ -0.57, -0.54 and -0.42 ppm, ratio 1:1:1) which are tentatively assigned to the methyl protons of AlMe_2 and AlMeCl groups, respectively. However, the resonances of *t*Bu protons yield only one sharp singal (200.130 MHz) at 1.38 ppm. The mass spectrometry reveals a peak of highest mass ($(M^+ - 15) m/z = 477$ (100%) for **5** and 457 (100%) for **1**), indicating the formation of **5** along with **1** as well. The explanation for such a phenomenon is that compound **5** is formed probably due to the equilibrium of Me_2AlCl in solution (Scheme 13)⁵ from which alkyaluminum halides dissociate into monomers.



Scheme 13. Probable equilibrium of Me_2AlCl in solution.

Organoaluminumiodide compounds, important precursors for preparing low-valent aluminum compounds, are usually prepared by oxidation of the related organomethylaluminum compounds with iodine in toluene.^{42a-b} In order to increase the rate of cleavage of the Al-C bonds, unfavorable reaction conditions such as long reaction times under reflux are often employed. In the present case **6** was formed in refluxing toluene for 24 hours from the reaction of **1** and 4 equivalents of I_2 in good

yield. Alternatively, the reaction of the organoaluminum dihydride $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**, Section 2.2) and I_2 at room temperature in toluene proceeds smoothly yielding **6** with elimination of HI in high yield (Scheme 14). Apparently, this approach is a new way to prepare organoaluminumiodide compounds and has not yet been reported in the literature, whereas some reports were published where the reactions of aminoalanes and HgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) led to N-substituted aluminum halide compounds.^{42c} The mechanism of the formation of **6** is presently unknown but probably through the oxidation process between hydride and I_2 molecule thereby leads to the elimination of HI.



Scheme 14. Synthesis of compound **6**.

Compound **6** is well soluble in toluene but sparingly soluble in *n*-hexane and was purified by crystallization from toluene at low temperature. Compound **6** is stable in the solid state for several months in inert gas atmosphere in the dark. $^1\text{H-NMR}$, mass spectrometry, and elemental analysis data are consistent with the formulation of **6**. The mass spectrum (EI) shows the peak of highest intensity at 793 ($(\text{M}^+ - \text{I})$, 100 %) and one peak at 905 ($(\text{M}^+ - \text{Me})$, 3 %). The $^1\text{H-NMR}$ (C_6D_6) reveals two resonances (δ 1.51 and 6.42 ppm), assignable to resonances of *t*Bu and C-H protons, respectively. The $^{27}\text{Al-NMR}$ (C_6D_6) spectrum exhibits only one sharp signal at δ 62.3 ppm, indicating coordination number four at the Al-atoms.^{42c}

Interestingly, in a manner analogous to the preparation of **3**, the reaction of K(3,5-*t*Bu₂pz) with AlCl₃ in a ratio of 3:1 in toluene gave the homoleptic compound [(η^2 -3,5-*t*Bu₂pz)₃Al] (**7**) in good yield, well soluble in hexane and thermally quite stable. Sometimes **7** will crystallize together with compound **3**. Therefore a modified synthetic approach for **7** was elaborated by treatment of the compound [(η^1, η^1 -3,5-*t*Bu₂pz)(μ -AlH₂)₂] (**8**, *vide infra*) with 4 equivalents of H(3,5-*t*Bu₂pz).⁴¹ This method directly led to the pure product (**7**) in nearly quantitative yield at room temperature in toluene with elimination of hydrogen.

The data of mass spectrum and elemental analysis are in agreement with the formulation of **7** (M⁺ (*m/z*) = 564, 100 %). The ¹H-NMR shows only one set of resonances (δ 1.35 ppm for the protons of the *t*Bu group and 6.13 ppm for the CH proton), indicating a symmetric molecule. The ²⁷Al-NMR signal is too broad to be observed. Compound **7** is the first example of a homoleptic compound with pyrazolato ligands and therefore it might be employed as a precursor in developing aluminum nitride films (AlN), although several transition metal complexes with this ligand have already been employed to prepare such as TiN films.^{21b}

2.1.4. Molecular structures of complexes **3** and **7**

Single crystals suitable for X-ray diffraction studies were obtained from *n*-hexane at -26 °C. Figure 2 shows a perspective view of compound **3** along with the atom-labeling scheme. **3** crystallizes in the orthorhombic crystal system, space group *Pbcn*. The similar cell parameters of [(η^1, η^1 -3,5-*t*Bu₂pz)(μ -AlCl₂)₂] (**3**) and [(η^1, η^1 -3,5-*t*Bu₂pz)(μ -AlMe₂)₂] (**1**) indicate structural similarities between these two compounds (Figures 1 and 2). Both compounds contain a six-membered ring with pyrazolato groups as

bridging ligands. As in compound **1**, the six-membered ring in compound **3** adopts a distorted conformation due to steric effects. The Al(1)-N(1) bond length (1.904(2) Å) is slightly shorter than that in compound **1** (Al(1)-N(1), 1.9638(13) Å) due to the higher electron withdrawing properties of the chlorine atoms. In **3**, the N(1A)-Al(1)-N(1) angle (104.86(12)°) is somewhat larger than that of compound **1** (N(1)-Al(1)-N(2), 99.77(6)°).

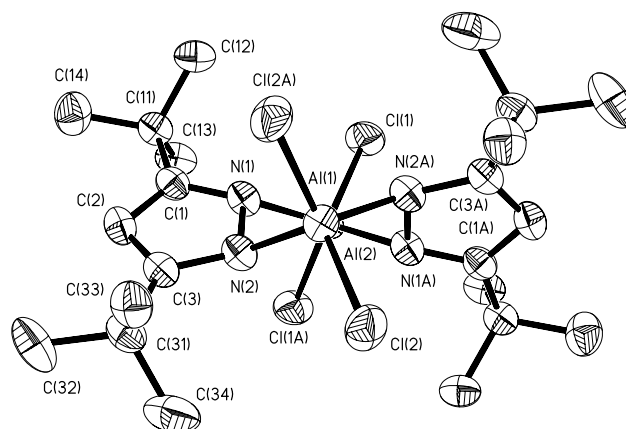


Figure 2. Perspective view of the complex $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlCl}_2)]_2$ **3**, showing the numbering scheme and the thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.904(2), Al(2)-N(2) 1.903(2), Al(1)-Cl(1) 2.1181(9); Cl(1)-Al(1)-N(1) 114.36(6), Cl(1)-Al(1)-Cl(1A) 112.22(6), Cl(2A)-Al(2)-N(2A) 112.52(6), N(1)-Al(1)-N(1A) 104.86(12), N(2)-Al(2)-N(2A) 105.02(12).

Compound **7** has a monomeric structure with three chelating pyrazolato ligands resulting in a formally six-coordinated aluminum atom. Both N-atoms of each pyrazolato ligand coordinate to the Al-atom in a η^2 -mode, constituting the first example of a aluminum η^2 -pyrazolato complex.

The Al-N distances (1.916(3) Å) in **7** are comparable with those found in the four coordinated $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlCl}_2)]_2$ (**3**, 1.904(2) Å) but are significantly shorter than those in **1** (Al(1)-N(1), 1.9638(13) Å).

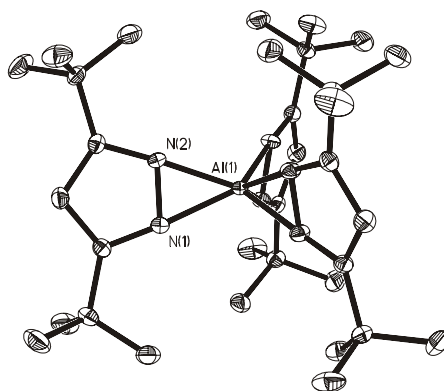


Figure 3. Perspective view of the complex $[(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_3\text{Al}]$ (**7**), showing the numbering scheme and the thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.916(3), Al(1)-N(2), 1.916(3); N(1)-Al(1)-N(2) 107.82(9), N(1)-Al(1)-N(2) 43.02(10).

2.2. Preparation of the aluminum hydride complex $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**)⁴³

Recently, aluminum hydrides with bulky substituents attracted interest due to their suitability as starting materials for several other aluminum compounds either unavailable or difficult to prepare by other routes.^{44,45} In the case of group 13 element hydride compounds the pyrazabole $[\text{pz}(\mu\text{-BH}_2)]_2$ ^{40g} is commercially available and the pyrazolato gallane $[\text{pz}(\mu\text{-GaH}_2)]_2$ ^{40a,h} was prepared nearly three decades ago, an aluminum hydride with an ancillary pyrazolato ligand was yet unknown. Most likely, the pyrazolato alane $[\text{pz}(\mu\text{-AlH}_2)]_2$ is rather poorly soluble in organic solvents.

Accordingly, it was assumed that the use of bulky pyrazolato ligands might overcome this problem, furthermore, such compounds were expected as ideal precursors for the preparation of other aluminum complexes.

The aluminum dihydride dimer $[(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**) was successfully synthesized by the reaction of $\text{AlH}_3\cdot\text{NMe}_3$ ⁴⁶ with $\text{H}(3,5\text{-}t\text{Bu}_2\text{pz})$ ⁴¹ (Scheme 15) in nearly quantitative yield (91 %), after the reaction excess $\text{H}_3\text{Al}\cdot\text{NMe}_3$ was removed in vacuo for at least 6 hours to afford the pure product. **8** could also be purified by recrystallization from toluene at $-26\text{ }^\circ\text{C}$ in fair yield (76 %). Compound **8** can be conveniently prepared in larger scales (over 50 mmol) in the laboratory and is thermally quite stable, but very sensitive to oxygen and water. No decomposition occurred when **8** was stored in a glove-box for at least two months at ambient temperature or refluxed for 4 days in toluene. However, a metallic aluminum film formed on the wall of the flask within several days if the excess of $\text{H}_3\text{Al}\cdot\text{NMe}_3$ was not completely removed. Actually, **8** does not dissolve readily in toluene at ambient temperature and consequently warm toluene (*ca.* $50\text{ }^\circ\text{C}$) was often employed to increase its solubility before **8** was reacted with other reagents in solution at room temperature.

Compound **8** was fully characterized by ^1H -NMR, elemental analysis, and MS(EI). In the ^1H -NMR spectrum it exhibits a broad Al-H signal at $\delta 5.3$ ppm ($W_{1/2} = 144$ Hz) and in addition, typical asymmetric and symmetric absorptions for $\nu_{\text{Al-H}}$ at 1869 and 1920 cm^{-1} in the IR spectrum indicate terminal Al-H bonds in the solid state.⁴⁷ However, the ^{27}Al -NMR signal is too broad to be observed. High quality crystals of **8** were readily obtained by recrystallization from the crude product in toluene at ambient temperature; X-ray studies revealed **8** as a dimer.





8

Scheme 15. Synthesis of compound **8**

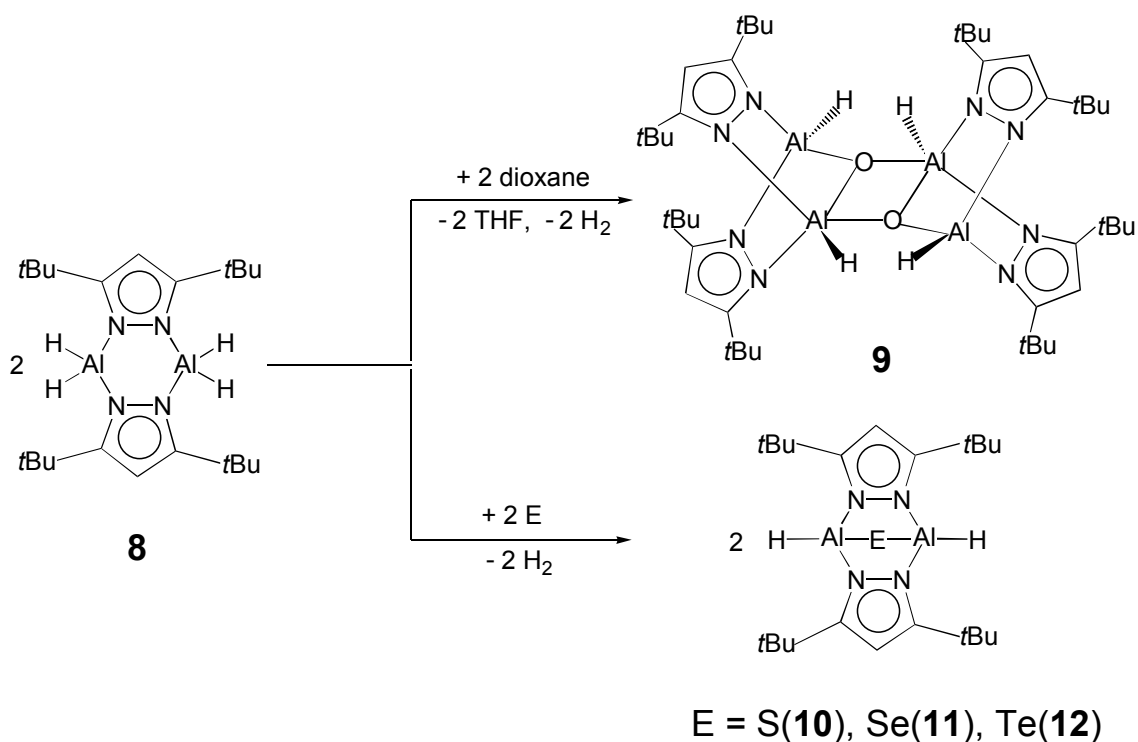
2.3. Aluminum group 16 compounds

2.3.1. Preparation of an aluminoxane hydride $[(\eta^1, \eta^1\text{-}t\text{Bu}_2\text{pz})_4(\mu_3\text{-O})_2(\mu\text{-AlH})_4]$ (9**) and the aluminum chalcogenide hydrides $[\{\eta^1, \eta^1\text{-3,5-}t\text{Bupz}(\mu\text{-AlH})\}_2\text{E}]$ (E = S (**10**); Se (**11**); Te (**12**))⁴⁸**

Recently several aluminoxanes ($t\text{BuAlO}$)_n (n = 6 - 9) as well as aluminum hydroxides or oxide hydroxides were prepared by the reactions of R₃Al (R = *t*Bu, Me, Mes, Ph) with water or anhydrous lithium hydroxide.^{31,49,50b} In contrast, it has been shown that aluminum hydride compounds can be used as precursors for the synthesis of organoaluminum chalcogenides with the formula (RAIE)_n (R = organic group; E = O, S, Se, Te) by reactions with species such as (Me₂SiO)₃,⁵¹ S(SiMe₃)₂,⁵² Se, or Te.^{53,54}

Herein described are the syntheses of compounds $[\{\eta^1, \eta^1\text{-3,5-}t\text{Bu}_2\text{pz}(\mu\text{-AlH})\}_2\text{E}]_n$ (E = O (**9**) (n = 2), S (**10**), Se (**11**), Te (**12**) (n = 1)).

When a solution of compound **8** in dry dioxane was stirred at room temperature for several days complex **9** was formed in low yield (Scheme 16).



Scheme 16. Syntheses of compounds **9** - **12**.

The $^1\text{H-NMR}$ spectrum of **9** shows only one set of signals (δ 1.32 and 5.80 ppm), implying dynamic behavior in solution. GC-MS(EI) investigations of the reaction solution of **9** indicate the formation of THF. Therefore, we assume that the formation of **9** proceeds via a nucleophilic attack at the aluminum center of **8** by one of the oxygen atoms of dioxane and ensuing insertion into one Al-H bond leading to the degradation of dioxane and forming an Al-O bond of an intermediate which in turn dimerizes under loss of H_2 yielding **9**.^{50a} However, other oxygen transfer reagents such as $n\text{Bu}_2\text{SnO}$ led only to small amounts of **9**, in addition, several unidentified by-products were formed.

Treatment of **8** in toluene with the congeners of oxygen afforded three chalcogenide compounds of the type $[\{\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz}(\mu\text{-AlH})\}_2\text{E}]$ ($\text{E} = \text{S}$ (**10**), Se (**11**), Te (**12**))

(Scheme 16). It is important, especially for the preparation of **10**, to use strictly equivalent amounts of the reactants and the mixed solvent system THF/toluene (1:9), otherwise an insoluble polymeric material is formed. This might explain why reactions of aluminum hydrides with sulfur have not yet been reported. All compounds, especially **11** and **12**, are very sensitive towards moisture. Small amounts of air immediately led to decomposition of **10** and **11**. An attempt to substitute all the H-atoms at the Al-atoms of **8** with two equivalents of Se resulted in the homoleptic compound $[(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_3\text{Al}]$ (**7**).³⁹

Compound **9** represents the first example of a structurally characterized aluminoxane hydride with coordination number five at two of the Al-atoms. **10** is the first compound prepared by the reaction involving an aluminum hydride and elemental sulfur. The higher aggregation of **9** compared to **10** - **12** is probably due to the increased nucleophilicity of oxygen compared to the heavier congeners. The formation of **10** - **12** probably proceeds via Al-E-H intermediates. These species then react with one of the H-atoms of another Al center, and subsequently form the Al-E-Al bridge and H₂ (Scheme 8). This assumption is supported by the recent results on fully characterized Al-SeH compounds.^{54b}

2.3.2. X-ray analyses of compounds **9** - **12**

The X-ray crystal structure analysis of **9** confirms the dimeric arrangement with four Al-atoms (Figure 4) as also indicated for the gas phase by the MS(EI) spectrum with the molecular ion at $m/z = 860$. The Al₂O₂ core of the molecule consists of a quite regular parallelogram and, interestingly, all the Al- and O-atoms are coplanar, the sum of angles at the O-atoms is 359.98(22)°. Each oxygen atom is connected to three Al-H groups to

form a μ_3 -O bridge. The Al-atoms located outside the parallelogram connect μ, η^1, η^1 -pyrazolato ligands to form two six-membered Al_2N_4 rings in a boat conformation. As already mentioned, the most striking feature of **9** is the coordination number five at the Al-atoms in the Al_2O_2 core that differs from other characterized aluminoxanes in which the Al-atoms usually show coordination numbers of both three and four.^{31,49-51} Only one structurally characterized aluminoxane hydroxide that contains five coordinated Al-atoms has been published.^{49c} Reports of compounds with coordination numbers five,^{55a,b} six,^{55c} and even seven^{55d} at Al are known, but these systems involve multi-chelating ligands such as a tetradentate Schiff-base, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ and crown ether. In compound **9** significantly longer bond lengths and smaller angles are observed at the five coordinated Al(1)- compared to the four coordinated Al(2)-atom (Figure 4). The bond lengths of Al(1)-O(1A) (1.786(2) Å) and Al(2)-O(1) (1.7260(14) Å) are shorter than the sum of covalent radii.⁵⁶

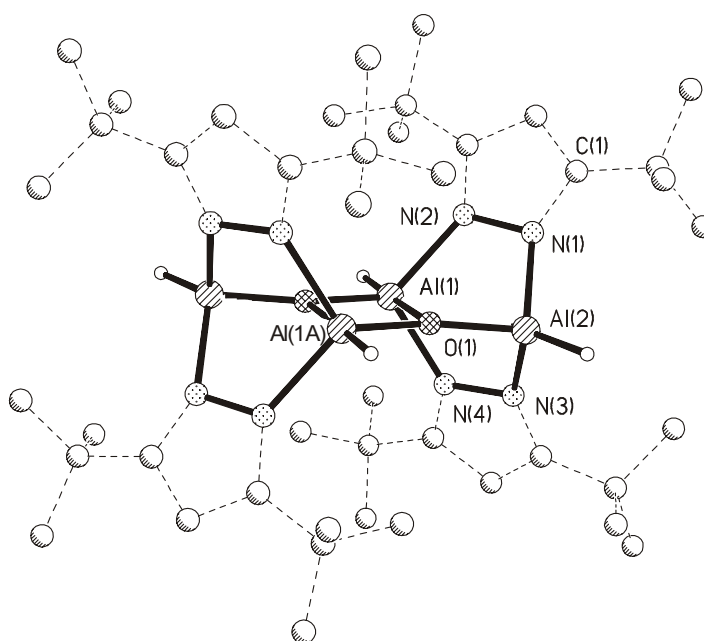


Figure 4. Molecular structure of **9**. Selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.922(2), Al(1)-O(1A) 1.786(2) Al(2)-O(1) 1.7260(14); Al(1)-O(1)-Al(1A)

99.83(7), Al(1)-O(1)-Al(2) 105.07(7), Al(1A)-O(1)-Al(2) 155.08(8), O(1)-Al(1)-O(1A), 80.17(7).

X-ray crystallographic studies reveal compounds **10** - **12** to be isostructural. They are represented by the illustration of **10** in Figure 5. They contain boat-shaped six-membered Al₂N₄ rings. A chalcogen atom forms a bridge between the two Al-atoms, and one Al-H bond remains at each Al center. Two pyrazolato ligands are located on the same side of the molecule due to the constraint imposed by the chalcogen atom. The average Al-E bond lengths (**10**: Al-S 2.1099(7) Å, **11**: Al-Se 2.3511(10) Å, **12**: Al-Te 2.5692(11) Å) are slightly shorter than those in (Mes*AlS)₂ (2.2095(11) Å) (Mes* = 2,4,6-Me₃-C₆H₂-),^{52b} [Me₃N·Al(SeEt)₃] (2.357(8) Å),⁵³ and [Me₃N·Al(TePh)₃] (2.585(2) Å).⁵³ The angles Al-E-Al (**10**: 79.58(2)° and **11**: 75.78(3)°) are close to those in (Mes*AlS)₂ (78.09(3)°)^{52b} and [N(SiMe₃)C(Ph)C(SiMe₃)₂Al(μ-Se)]₂ (77.58(3)°),^{54a} whereas the Al-Te-Al angle (**12** 69.41(3)°) is significantly smaller than that in [N(SiMe₃)C(Ph)C(SiMe₃)₂Al(μ-Te)]₂ (76.88(4)°).^{54a} The Al-E-Al unit (E = O (Al(1)-O(1)-Al(2)), S, Se and Te) become more acute going from the lighter to the heavier congeners.

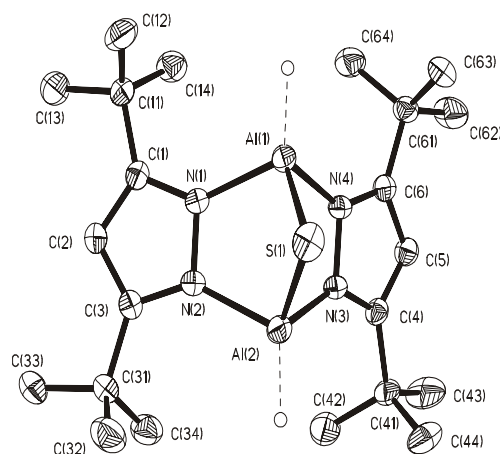
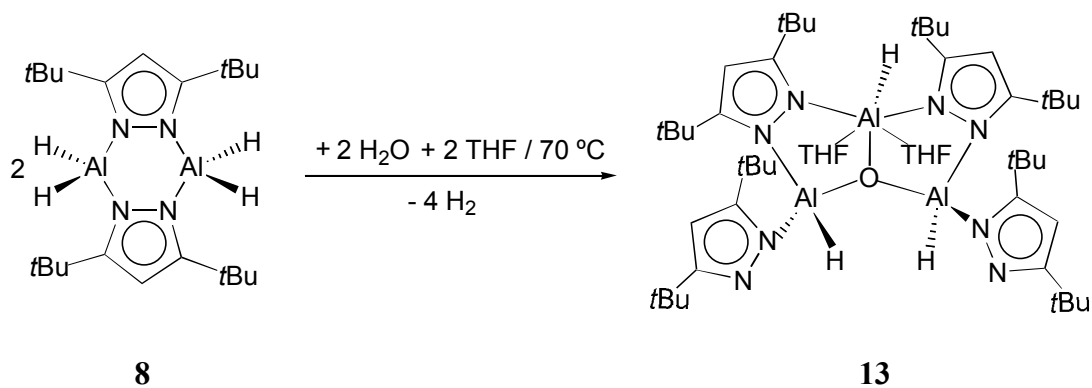


Figure 5. Molecular structure of **10**. The structures of **11** and **12** are analogous with Se(1) (**11**) and Te(1) (**12**) in place of S(1). Selected bond lengths [\AA] and angles [$^\circ$]: **10**: Al(1)-N(1) 1.9469(12), Al(1)-S(1) 2.2080(6), Al(2)-S(1) 2.2117(7); Al(1)-S(1)-Al(2) 79.58(2), N(1)-Al(1)-N(4) 99.09(5), N(1)-Al(1)-S(1) 100.90(4), N(4)-Al(1)-S(1) 99.29(4). **11**: Al(1)-N(1) 1.932(2), Al(1)-Se(1) 2.3449(10), Al(2)-Se(1) 2.3574(11); Al(1)-Se(1)-Al(2) 75.78(3). **12**: Al(1)-N(1) 1.944(3), Al(1)-Te(1) 2.5763(11), Al(2)-Te(1) 2.5621(12); Al(1)-Te(1)-Al(2) 69.41(3).

2.4. Preparation and structure of an aluminoxane hydride bearing terminal pyrazolato ligands $[(\mu, \eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu_3\text{-O})(\mu\text{-AlH})_3] \cdot 2\text{THF}$ (**13**)⁴³

As discussed above (Section 1.3.), the unknown structure of methyl aluminoxane (MAO) is an interesting subject to clarify its cocatalyst role. Various synthetic routes have been employed.^{28,30} However, reactions of organoaluminum hydrides with water to synthesize organoaluminoxanes or organoaluminoxane hydrides have not been reported.

To a stirred solution of compound **8** in dry THF at 70 °C one equivalent of water in THF was added slowly to yield an aluminoxane hydride $[(\mu, \eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu_3\text{-O})(\mu\text{-AlH})_3]\cdot 2\text{THF}$ (**13**) (Scheme 17).



Scheme 17. Synthesis of compound **13**.

The X-ray single crystal structural analysis of **13** reveals an arrangement involving three aluminum atoms and four ligands (Figure 6), its composition is also supported by the MS(EI) spectrum ($(M^+ - H)$, $m/z = 815$). The presence of remaining Al-H bonds in compound **13** was confirmed by $^1\text{H-NMR}$ spectroscopy (δ 4.2 (ppm) in $\text{THF-}d_8$) and by the IR spectrum ($\tilde{\nu}_{\text{Al-H}}$ 1872 and 1896 cm^{-1}).⁴⁷ The three Al atoms of the Al_3O core form a regular triangle (Al(1)-O(1) 1.774(3) Å, Al(2)-O(1) 1.861(6) Å). The Al atoms use two μ, η^1, η^1 -pyrazolato ligands to generate two envelope-shaped five-membered $\text{Al}_2\text{N}_2\text{O}$ rings. An interesting feature is that the oxygen atoms of two THF molecules bind to the Al(2) atom to generate a coordination number of six. Surprisingly in **13** two of the pyrazolato ligands, which have been found to form stable complexes with aluminum in an η^1, η^1 - and very recently, an η^2 -mode,^{39,40} are terminally coordinated to two of the aluminum centers. This coordination pattern is rather uncommon for

pyrazolato complexes.²⁴ Only few transition metal complexes (M = Ir, Ta, Ni, Cr) with terminal η^1 -pyrazolato ligands have been reported recently in the literature.⁵⁷ In **13**, the coordination number of six of the Al(2) atom differs sharply from other characterized aluminoxanes, in which coordination numbers of three, four,^{31,49a,51} and five⁴⁸ have been found. The Al-O bond lengths of the Al₃O core range from 1.774(3) Å (Al(1)-O(1)) to 1.861(6) Å (Al(2)-O(1)) (Figure 6), being shorter than the sum of the respective covalent radii.⁵⁶

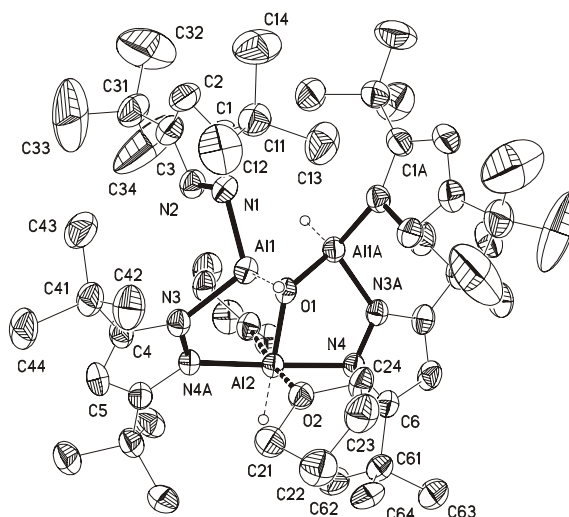


Figure 6. Perspective view and atom-labeling scheme of compound **13**, showing the numbering scheme and the thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.860(5), Al(1)-N(3) 1.930(5), Al(2)-N(4) 2.050(4), Al(1)-O(1) 1.774(2), Al(2)-O(1) 1.861(6) Al(2)-O(2) 2.023(4); Al(1)-N(1)-C(1) 142.9(4), Al(1)-N(3)-C(4) 137.2(4), Al(1)-O(1)-Al(2) 115.56(16), N(1)-Al(1)-O(1) 110.7(2), N(2)-N(1)-Al(1) 106.78(3), N(3)-Al(1)-O(1) 96.3(2), N(4)-Al(2)-O(1) 89.12(14), O(1)-Al(2)-O(2) 85.96(13).

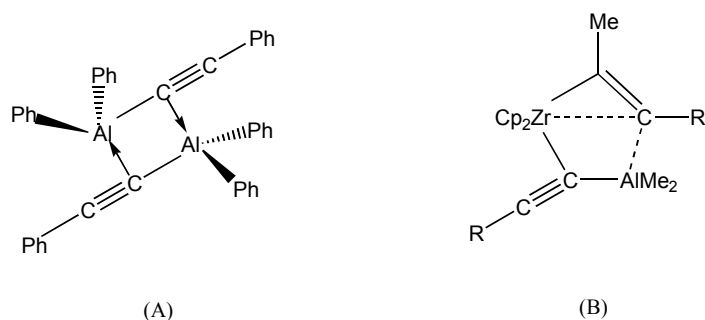
The ^1H NMR spectrum of **13** in THF- d_8 shows each type of the pyrazolato ligands producing independent sets of signals (δ 1.24, 5.88 and 1.34, 1.5 br, $W_{1/2} = 33$ Hz, 6.07 ppm at 25°C), implying no rapid exchange on the NMR time scale at this temperature. Furthermore, the two different chemical shifts of the protons of the *t*Bu groups of the η^1 -pyrazolato ligands (δ 1.34, 1.5 ppm) and one broad signal indicate that exchange between the Al(1)-N(1) and Al(1)-N(2) is hindered. These features are in sharp contrast to transition metal complexes with terminal pyrazolato ligands (e. g. pyrazolato Ta-complex $[\text{Ta}(3,5\text{-R}_2\text{pz})_n(\text{N}(\text{CH}_3)_{5-n})]$, R = CH₃, n = 5; R = *t*Bu, n = 2), where such features were not observed even at -80 °C.^{57b} The reaction leading to **13** showed that only small amounts of a white unidentifiable insoluble solid as well as H₂ were formed at +70 °C. The yield of **13** decreased along with the formation of more insoluble by-products when the hydrolysis was conducted at room temperature or -78 °C. The mechanism of this process is yet unknown, but probably involves an initial intermediate containing Al-OH species.

The structure of **13** illustrates for the first time that the pyrazolato ligand is also able to bind terminally to aluminum(III) centers besides the known η^1, η^1 - or η^2 - modes. Although some arguments in favor of this terminal arrangement have been proposed, this feature is probably caused by steric or electronic factors in the structures.^{57b} It is difficult to predict which factor plays a central role in determining the overall structure yet. However, as in the case of compound **13**, it seems that the terminal arrangement is likely due to the sterically demanding *t*Bu groups of the ligands rather than to electronic factors.

2.5. Terminal aluminum acetylide complexes

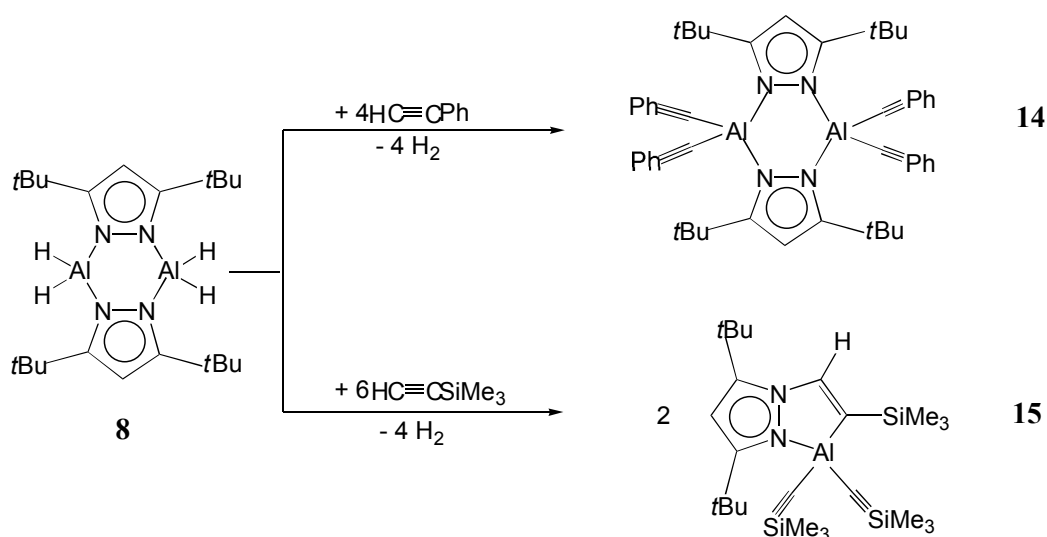
2.5.1. Preparation of complexes $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2\{\mu\text{-Al}\}(\text{C}\equiv\text{CPh})_2]_2$ (14**) and $[\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C}(\text{SiMe}_3)\}\text{Al}(\text{C}\equiv\text{CSiMe}_3)_2]$ (**15**)**⁵⁸

Aluminum compounds containing acetylide groups are known since 1960.⁵⁹ All aluminum acetylides published to date feature dimeric structures with a bridging acetylide ligand between two aluminum centers⁶⁰ or between one aluminum atom and one early transition metal atom (Scheme 18).⁶¹ Since the addition of aluminum acetylides to unsaturated hydrocarbons is of interest in organic synthesis,⁶² it is surprising that up to now only a few structurally characterized aluminum acetylides have been reported.^{60,61}



Scheme 18. Aluminum acetylides featuring a dimeric structure with a bridging acetylide ligand between two aluminum centers (A) or between one aluminum atom and one early transition metal atom (B).

The terminal acetylide compound $[(\eta^1, \eta^1\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})(\text{C}\equiv\text{CPh})_2]_2$ (**14**) was prepared from **8** and an excess of HC≡CPh. Reaction of **8** with an excess of HC≡CSiMe₃ afforded compound (**15**) (Scheme 19).



Scheme 19. Synthesis of **14** and **15**.

2.5.2. X-ray crystal structure analyses of **14** and **15**

The X-ray crystal structure of **14** shows a dimeric species with some interesting features (Figure 7). Again, the six-membered Al_2N_4 ring adopts a twisted conformation, in contrast to other bridged bis-pyrazolato compounds.^{24,40} Another interesting feature is the marked deviation of one $\text{Al}-\text{C}\equiv\text{C}$ moiety at each Al atom from linearity ($\text{Al}(1)-\text{C}(11)-\text{C}(12)$, $160.2(3)^\circ$ vs $\text{Al}(1)-\text{C}(21)-\text{C}(22)$, $178.3(3)^\circ$, the $\text{C}(11)-\text{C}(12)$ and $\text{C}(21)-\text{C}(22)$ bond lengths are $1.211(4)$ and $1.218(4)$ Å, respectively). Whereas some examples of small $\text{M}-\text{C}\equiv\text{C}$ angles in transition metal complexes have been reported,⁶³ only two examples in main group chemistry have been published to date (160.5° with Bi ^{64a} and 166.4° with Ge ^{64b}).

The X-ray crystallographic analysis of **15** reveals a mononuclear aluminum compound with an aluminum atom coordinated by a chelating $[3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3)]$ unit and two $\text{C}\equiv\text{CSiMe}_3$ groups (Figure 8).

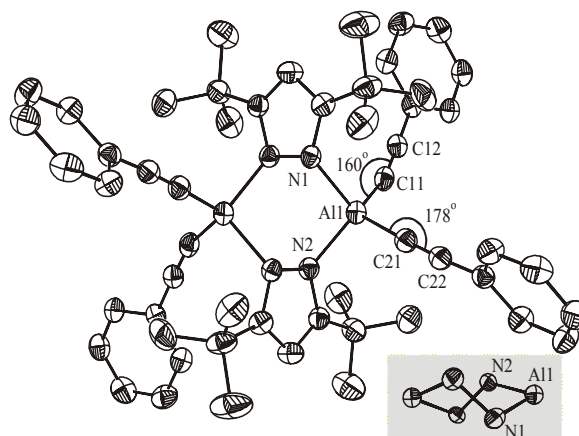


Figure 7. Molecular structure of **14**. Selected bond lengths [\AA] and angles [$^\circ$]: Al(1)-C(11) 1.929, Al(1)-C(21) 1.913(3), C(11)-C(12) 1.211(4), C(21)-C(22) 1.218(4); C(12)-C(11)-Al(1) 160.2(3), C(22)-C(21)-Al(1) 178.3(3), C(11)-Al(1)-C(21) 116.99(12), N(1)-Al(1)-N(2) 102.88(10). Bottom right: the distorted core of **14**.

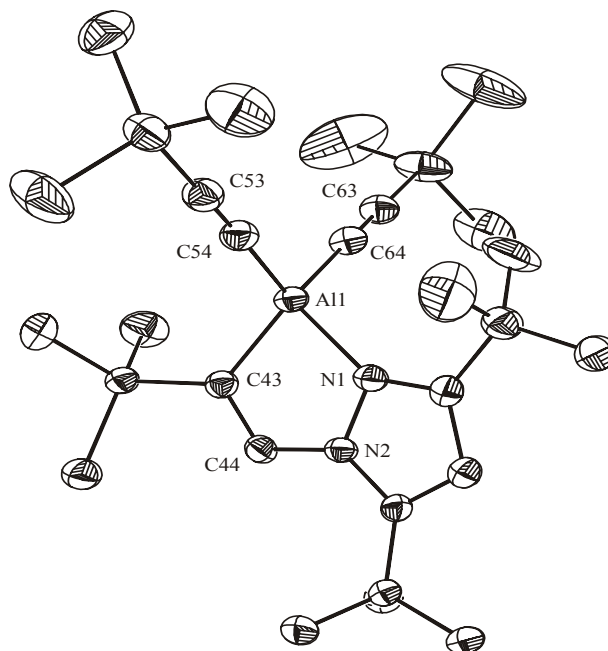


Figure 8. Molecular structure of **15**. Selected bond lengths [Å] and angles [°]: Al(1)-C(43) 2.015(3), Al(1)-N(1) 1.977(2), Al(1)-C(54) 1.957 (3), C(43)-C(44) 1.337(4), C(53)-C(54) 1.223(4); C(54)-Al(1)-C(64) 113.42(12), N(1)-Al(1)-C(43) 87.31(10), C(53)-C(54)-Al(1) 178.2(2).

The chelating unit of **15** consists of a pyrazolato ligand that has formally added to a C≡C triple bond thereby forming a five-membered metaheterocycle. The two fused five-membered rings, AlN₂C₂ and pyrazolate, are close to coplanarity. The C=C bond length of the inserted acetylene moiety is significantly elongated (C(43)-C(44), 1.337(4) Å vs C(63)-C(64), 1.219(4) Å) indicating double bond character. The geometry of the aluminum atom is distorted tetrahedral (N(1)-Al(1)-C(43) 87.31(10)° and C(54)-Al(1)-C(64) 113.42(12)°) due to the strain imposed by the chelate ring. The angles of the Al-C≡C bonds (178.2(2)° and 175.5(2)°) are close to linearity.

The formation of the chelating unit in **15** is unusual and therefore, its use for other metal ions as a new ligand can be anticipated.

2.5.3 Ab-initio calculation for 14

In order to understand the geometry of **14**, ab initio calculations were carried out.⁶⁵ An idealized molecule of symmetry D_{2h}^{65a} was computed and the forces leading to the deviation from linearity were subsequently analyzed.^{65b} Four instability coordinates of the reference backbone^{65c} with A_u, B_{1u}, B_{2g} and B_{3g} symmetries have been identified.^{65d} These correspond to vibrations with computed imaginary frequencies and are manifestations of a pseudo Jahn-Teller effect.^{65b} The experimentally found geometry may be described as a superposition of 93.2 % A_u and 6.8 % B_{1u}, the contributions of

B_{2g} and B_{3g} are negligible. The distortion of the A_u type is in good agreement with the results of the X-ray structure determination.

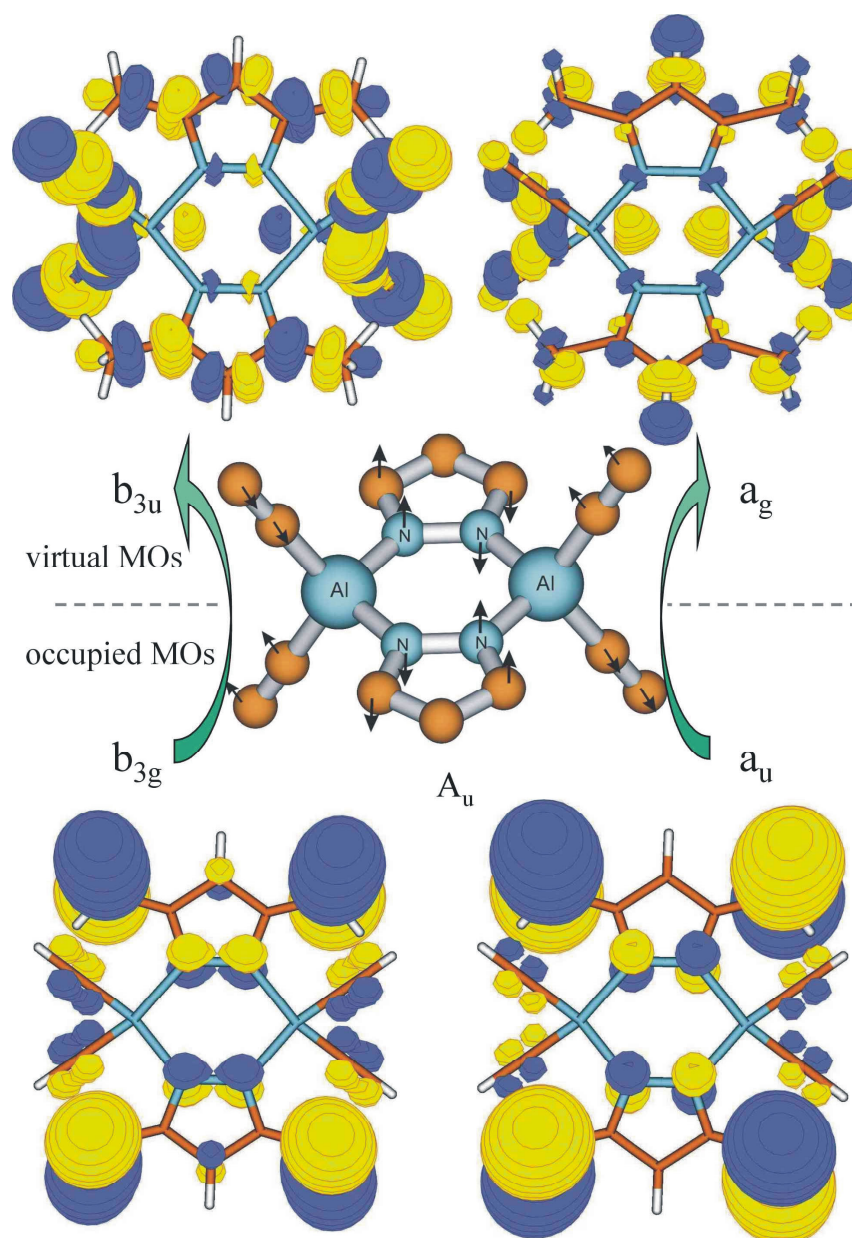


Figure 9. Two pairs of the transformed orbitals are shown, which are vibronically coupled *via* the normal coordinate of the A_u distortion. The notion of transformed orbitals refers to the states whose coupling leads to transition densities that concentrate

the electron density flow associated with the distortion in a maximal way.^{65f} The represented excitations, $a_u \rightarrow a_g$ and $b_{3g} \rightarrow b_{3u}$ are matching 25 % of the vibronic curvature.

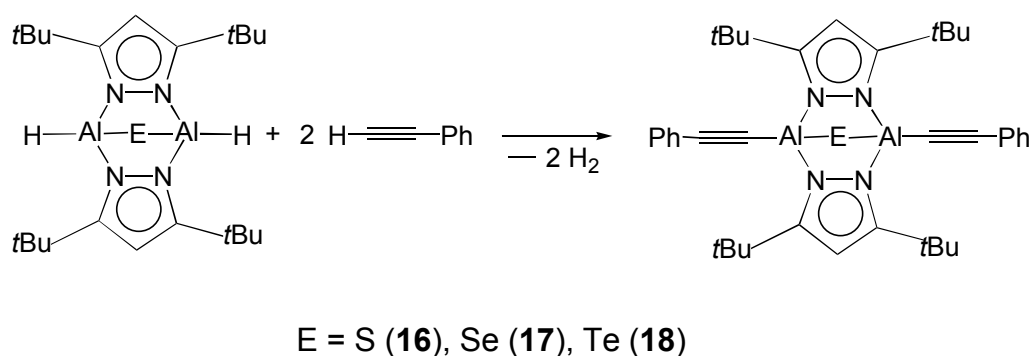
The analysis of the different contributions included in the vibronic curvature of the A_u nuclear coordinate $K_v(A_u)$, gives an insight in the intimate stereochemical mechanism.^{65e} The driving force seems to be the strong reluctance of Al atoms for π -bonding leading to a higher σ character. This effect can be viewed in Figure 9, where two possible $\pi \rightarrow \sigma^*$ electron promotions are shown. The depicted unoccupied states of the σ type contain aluminum AOs, while the π significant states are located on the ligands. The vibronic energy gain accompanying such excitations^{65f} determines the above discussed distortion. Therefore, the observed bending and deviation from linearity in **14** seems to be symbiotically, caused by inner features of the pyrazolato ligands rather than by the electronic structure of the acetylide ligands themselves.

2.6. Chalcogenide aluminum complexes with terminal acetylide groups³⁹

2.6.1. Preparation of $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bupz})_2(\mu\text{-E})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (E = S (**16**); Se (**17**); Te (**18**))

The preparation of the first structurally characterized aluminum complexes with terminal acetylide groups⁵⁸ as well as the reaction of aluminum hydride with the congeners of oxygen affording the related aluminum chalcogenide hydrides⁴⁸ have been described in previous sections. However, attempts to substitute the remaining hydrogen atoms at both aluminum atoms of the chalcogenide hydrides in **10** - **12** by E (E = S, Se, Te) were not successful. It was of interest whether the remaining hydrogen atoms on each aluminum atom in these chalcogenide compounds are still replaceable since aluminum compounds with fused functional transfer-groups, namely with both chalcogenide and acetylide, have not been reported to date and might be unique reagents in organic synthesis.^{26,62} Therefore, aluminum chalcogenide complexes with terminal acetylide groups $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bupz})_2(\mu\text{-E})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (E = S, Se, Te) have been investigated.

An excess of phenylacetylene reacted with $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-E})(\mu\text{-AlH})_2]$ (E = S, Se, Te)⁴⁸ in toluene to give the compounds $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bupz})_2(\mu\text{-E})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (**16** - **18**) in good yields (Scheme 20).



Scheme 20. Syntheses of **16** – **18**.

Compounds **16** and **17** were purified by washing the solid residues with cold pentane while compound **18** could only be obtained by crystallization from toluene at room temperature. These three compounds, especially **18**, are extremely sensitive to moisture; exposure to air immediately led to decomposition of **18** (becoming black).

Compounds **16** - **18** have been characterized by ^1H -, ^{13}C -NMR and EI mass spectroscopy as well as by elemental analysis. The ^1H -NMR spectra of **16** - **18** show only one set of signals for the *t*Bu, CH and phenyl protons each (e.g. **16**: δ 1.58 (*t*Bu), 5.97 (CH) and 7.32 - 7.50 (Ph) ppm), clearly evidencing symmetric environments of these three compounds. The similarities of the ^1H -NMR spectra of **16** - **18** indicate isostructural configurations. However, in order to gain insight into the bonding situation, X-ray diffraction analyses had to be carried out.

2.6.2. X-ray structure analyses of **16** and **17**

Suitable single crystals for X-ray diffraction of compounds **16** and **17** were obtained by crystallization from toluene at room temperature. The crystal structures, the crystallographic data and selected bond lengths as well as angles of compounds **16** and

17 are shown in Figures 10 and 11. Indeed, compounds **16** and **17** are isostructural and crystallize in the monoclinic system, space group $P2_1/c$. Both compounds adopt boat-shaped six-membered ring geometries due to the strain imposed by the chalcogenide bridges (S for **16**, Se for **17**) between the two Al-atoms. The interesting features are that the two phenyl groups on both sides of the molecule are perpendicular and the phenylacetylide groups arrange terminally. The Al-C-C angle of $174.3(3)^\circ$ shows a nearly linear arrangement of the acetylide ligands. The Al-C bond lengths (Al(1)-C(7), $1.911(3)$ Å in **16** and $1.905(4)$ Å in **17**) are comparable to those in $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})(\text{C}\equiv\text{CPh})_2]_2$ (**14** Al(1)-C(11) 1.929 Å and Al(1)-C(21) $1.913(3)$ Å).⁵⁸ The Al-E bond lengths (**16** Al(1)-S(1) $2.1977(11)$ Å; **17** Al(1)-Se(1) $2.3293(11)$ Å) are slightly shorter than those in $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-E})(\mu\text{-AlH})_2]$ (**10**, Al(1)-S(1) $2.2080(4)$ Å; **11**, Al(1)-Se(1) $2.3449(10)$ Å).⁴⁸ The Al-E-Al angles (Al(1)-S(1)-Al(2), $79.46(4)^\circ$ in **16** and Al(1)-Se(1)-Al(2), $75.28(4)^\circ$ in **17**) are close to those in the $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-E})(\mu\text{-AlH})_2]$ compounds (**10** Al(1)-S(1)-Al(2) $79.58(2)^\circ$, **11** Al(1)-Se(1)-Al(2) $75.78(3)^\circ$).

Although the structure of compound **18** was not determined it can be concluded to be isostructural to **16** and **17** due to the similarities of their physical data.

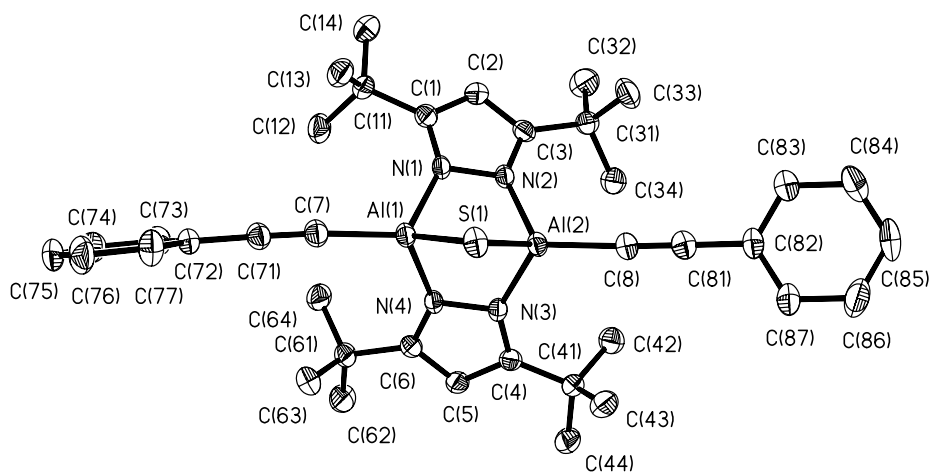


Figure 10. Perspective view of the complex $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bupz})_2(\mu\text{-S})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (**16**), showing the numbering scheme and the thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Al(1)-S(1) 2.1977(11), Al(1)-C(7) 1.911(3), Al(1)-N(1) 1.938(2), Al(1)-N(4) 1.963(2), C(7)-C(71) 1.204(4), C(8)-C(81) 1.206(4); Al(1)-S(1)-Al(2) 79.46(4), C(7)-Al(1)-N(1) 118.15(11), C(7)-Al(1)-N(4) 115.49(11), N(1)-Al(1)-N(4) 98.65(10), C(7)-Al(1)-S(1) 119.80, N(1)-Al(1)-S(1) 100.18(7), N(4)-Al(1)-S(1) 101.01(7).

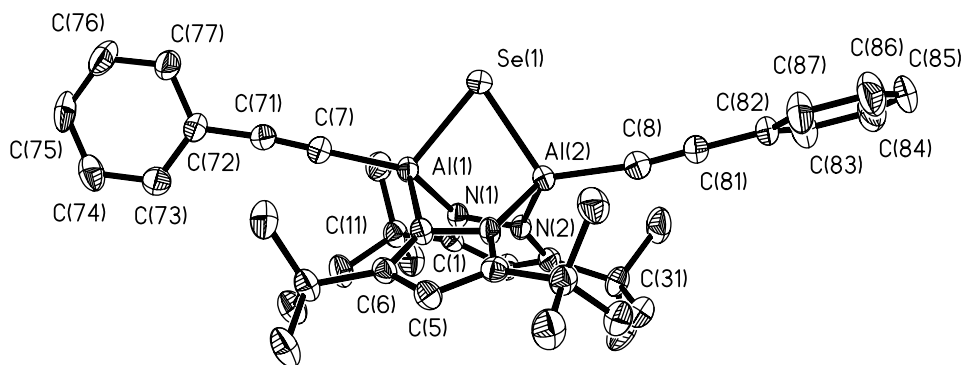


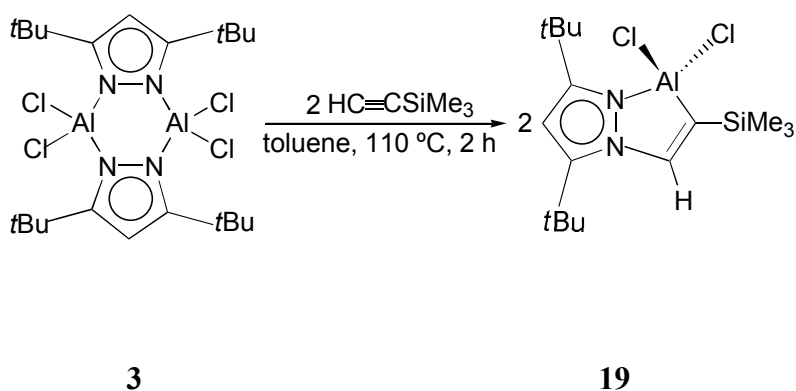
Figure 11. Perspective view of the complex $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-Se})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (**17**), showing the numbering scheme and the thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Se(1)-Al(1) 2.3293(11), Al(1)-C(7) 1.905(4), Al(1)-N(1) 1.938(3), Al(1)-N(4) 1.958(3), C(7)-C(71) 1.209(5), C(8)-C(81) 1.204(5). Al(1)-Se(1)-Al(2) 75.28(4), C(7)-Al(1)-N(1) 118.2(2), C(7)-Al(1)-N(4) 115.44(14), N(1)-Al(1)-N(4) 98.38(13), C(7)-Al(1)-Se(1) 118.84(12), N(1)-Al(1)-Se(1) 100.81(9), N(4)-Al(1)-Se(1) 101.81(9).

2.7. An unusual monomeric alkenyl-substituted pyrazolato aluminum system

2.7.1. Preparation of complexes $[(3,5\text{-}t\text{Bu}_2\text{-N-CH=C}(\text{SiMe}_3)\text{-pz})\text{AlR}^1\text{R}^2]$ ($\text{R}^1 = \text{R}^2 = \text{Cl}$ (**19**); $\text{R}^1 = 3,5\text{-}t\text{Bu}_2\text{pz}$, $\text{R}^2 = \text{Cl}$ (**20**); $\text{R}^1 = \text{R}^2 = 3,5\text{-}t\text{Bu}_2\text{pz}$ (**21**))

As mentioned above, in the course of our investigations on the reactivity of the pyrazolato aluminum dihydride $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**) towards acetylene reagents, a formal insertion of trimethylsilylacetylene into an aluminum nitrogen bond was observed resulting in a bulky chelating alkenyl-substituted pyrazolato ligand, $[3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C}(\text{SiMe}_3)]\text{Al}(\text{C}\equiv\text{CSiMe}_3)_2$ (**15**). This reaction may be viewed as a [2 + 3]-cycloaddition with the aluminum pyrazolato species functioning as the dipolar component. This type of reaction may be of general significance in the preparation of heterocyclic compounds, and has attracted interest in aluminum catalyzed enantioselective conversions.⁶⁷ It was of interest whether such cycloadditions are generally extendable for broader applications. In this section the preparation of $[(3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C}(\text{SiMe}_3))\text{AlCl}_2]$ (**19**) from $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlCl}_2)]_2$ (**3**) and $\text{HC}\equiv\text{CSiMe}_3$ and its reactivity towards $\text{K}(3,5\text{-}t\text{Bu}_2\text{pz})$ forming η^1 - and η^2 -coordinated aluminum pyrazolato species are described.

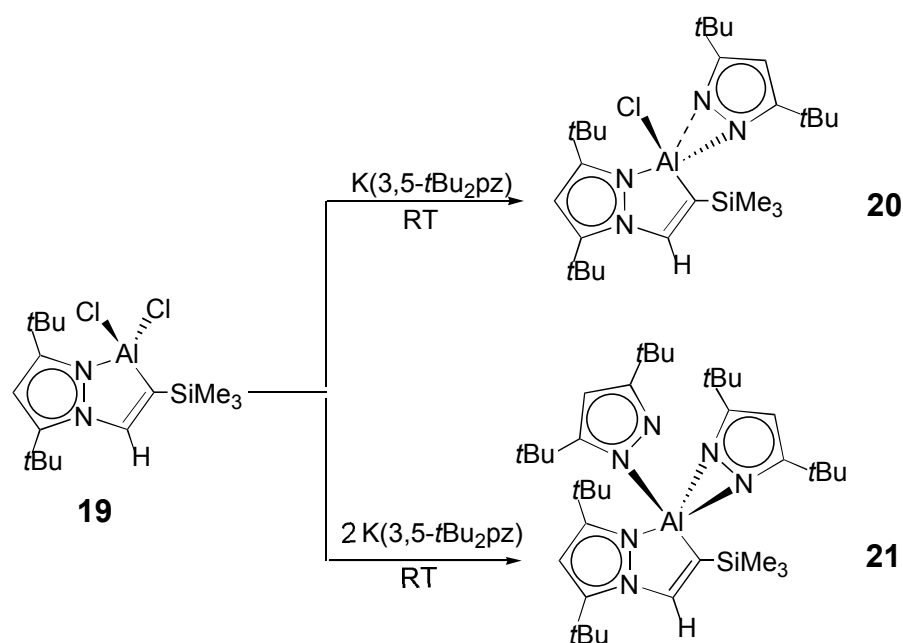
Treatment of **3** with a slight excess of $\text{HC}\equiv\text{CSiMe}_3$ in refluxing toluene for 2 h gave smoothly the product **19** in virtually quantitative yield (Scheme 21).⁶⁸ Drying commercially available $\text{HC}\equiv\text{CSiMe}_3$ over molecular sieves for at least two days prior to use is crucial otherwise hydrolysis of the product occurs. For the synthesis in larger scales (over 20 mmol) it is advisable to monitor the reaction by $^1\text{H-NMR}$ spectroscopy. If **3** is not completely consumed, the reaction has to be continued with addition of more $\text{HC}\equiv\text{CSiMe}_3$ since separation of the product from the starting material is not possible.



Scheme 21. Synthesis of compound **19**.

The $^1\text{H-NMR}$ spectrum of **19** shows two resonances for the *t*Bu protons (δ 0.84 and 1.35 ppm, C_6D_6), evidencing the asymmetric environment of the 3,5-*t*Bu₂pz ring. The proton resonances of the inserted $\text{HC}\equiv\text{CSi}(\text{CH}_3)_3$ molecule (δ 7.48 ppm for H-C= and 0.35 ppm for Si(CH₃)₃) show significant downfield shifts in comparison to the free trimethylsilylacetylene (δ 2.06 and 0.094 ppm). The resonance in the $^{27}\text{Al-NMR}$ spectrum is too broad to be observed.

The formation of **19** may be rationalized by dissociation of **3** prior to the reaction with trimethylsilylacetylene. The different nucleophilicities of the carbon atoms and the N_2Al dipole are probably responsible for the regioselectivity of the cycloaddition forming exclusively isomer **19**.



Scheme 22. Synthesis of **20** and **21**.

The synthesis of η^2 -coordinated pyrazolato aluminum species was one of initial goals of this thesis. The high yield and high solubility in most common organic solvents of **19** triggered the use as an excellent starting material. Therefore reactions of **19** with one and two equivalents of $K(3,5-tBu_2pz)$ were investigated (Scheme 22).

The conversion of **19** with one equivalent of $K(3,5-tBu_2pz)$ in toluene afforded complex $[\{3,5-N-tBu_2pz-N'-CH=C(SiMe_3)\}AlCl(3,5-tBu_2pz)]$ (**20**) (Scheme 22), which was readily purified by crystallization from *n*-hexane.

At room temperature the $^1\text{H-NMR}$ spectrum shows only one resonance of protons at δ 1.40 ppm (C_6D_6) for the *t*Bu group in the *t*Bu₂pz ligand. The resonances for the alkenyl-substituted pyrazolato ligand appear at δ 1.03 and 1.21 ppm for the protons of the *t*Bu groups and at δ 0.25 ppm for the $\text{Si}(\text{CH}_3)_3$ protons.

The addition of two equivalents of $\text{K}(3,5\text{-}t\text{Bu}_2\text{pz})$ to **19** in toluene gave compound $[\{3,5\text{-}N\text{-}t\text{Bu}_2\text{pz-N}'\text{-CH=C}(\text{SiMe}_3)\}\text{Al}(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})]$ (**21**) (Scheme 22). Compound **21** was purified by crystallization from *n*-hexane.

Analogous to **20**, at room temperature the $^1\text{H-NMR}$ spectrum of **21** displays aside to the resonances for the chelating moiety at δ 1.10 and 1.12 ppm (C_6D_6), only one sharp resonance for the protons of the *t*Bu groups of the two exocyclic *t*Bu₂pz ligands at δ 1.37 ppm (C_6D_6), implying a dynamic process in solution. Variable temperature $^1\text{H-NMR}$ spectroscopy does not verify this process in toluene-*d*₈, since the exchange is still fast on the NMR time scale even at 183 K.

2.7.2. X-ray structural analyses of 19 - 21

The X-ray crystal structure analysis reveals the mononuclear aluminum complex **19** with the metal atom coordinated by a $[3,5\text{-}N\text{-}t\text{Bu}_2\text{pz-N}'\text{-CH=C}(\text{SiMe}_3)]$ chelate and two Cl atoms (Figure 12).

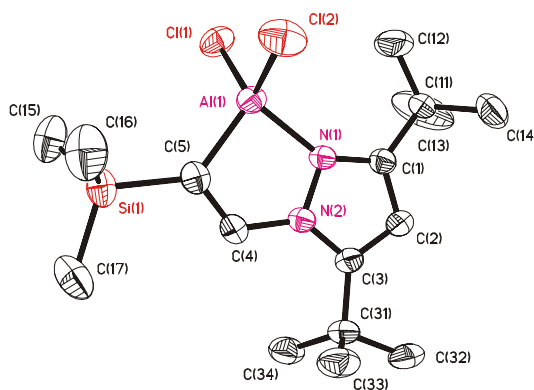


Figure 12. Perspective view and atom-labeling scheme of compound **19**, showing the thermal ellipsoids at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Al(1)-C(5) 1.954(2), Al(1)-Cl(1) 2.1347(10), Al(1)-N(1) 1.960(2), C(1)-C(2) 1.3940(3), C(4)-C(5) 1.323(3), C(4)-N(2) 1.439(3), C(5)-Si(1) 1.861(2), N(1)-N(2) 1.385(2); Al(1)-C(5)-C(4) 107.72(16), Al(1)-N(1)-N(2) 107.60(13), C(4)-C(5)-Si(1) 121.09(18), C(5)-Al(1)-Cl(1) 116.07(7), C(5)-Al(1)-N(1) 88.03(9), C(5)-C(4)-N(2) 120.5(2), Cl(1)-Al(1)-Cl(2) 109.87(4), Si(1)-C(5)-Al(1) 131.18(13).

The geometry of the aluminum atom is distorted tetrahedral (N(1)-Al(1)-C(5) 88.03(9)° and C(11)-Al(1)-C(12) 109.87(4)°) due to the strain imposed by the chelating ring. The two fused five-membered AlN₂C₂ and pyrazolato rings are approximately coplanar. The C=C bond length of the inserted trimethylsilylacetylene molecule is significantly increased (C(4)-C(5), 1.323(4) Å) but slightly shorter than those of the C=C double bonds of the σ -complex of AlCl₃ with tetramethylcyclobutadiene (**a**) (1.387(3) Å)⁶⁹ and the 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene (**b**) (1.367(3) Å),⁷⁰ respectively. The Al(1)-C(5) bond length (1.954(2) Å) is slightly shorter than those in the former (Al-C 1.979(5) Å)⁶⁹ and the latter (Al-C 1.990 (av) Å).⁷⁰

The X-ray diffraction analysis of **20** reveals a monomeric molecule coordinated by one chelating [3,5-N-*t*Bu₂pz-N'-CH=C(SiMe₃)] moiety, one *t*Bu₂pz ligand and one Cl atom (Figure 13).

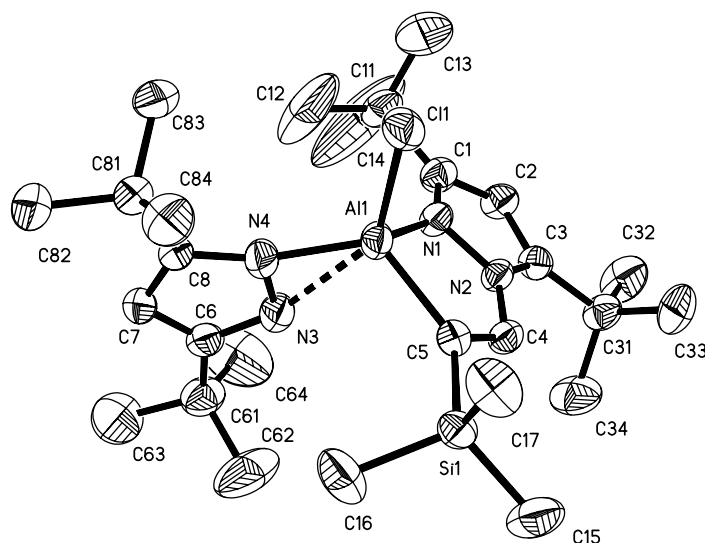


Figure 13. Perspective view and atom-labeling scheme of compound **20**, showing the thermal ellipsoids at the 50 % probability level. Selected bond lengths [\AA] and angles [$^\circ$]: Al(1)-N(1) 1.956(2), Al(1)-N(3) 2.312(3), Al(1)-N(4) 1.838(2), Al(1)-C(5) 1.961(3), Al(1)-Cl(1) 2.1531(11), N(1)-N(2) 1.376(3), C(4)-C(5) 1.320(4); C(5)-Al(1)-Cl(1) 113.27(9), C(6)-N(3)-Al(1) 159.6(2), C(8)-N(4)-Al(1) 159.4(2), Cl(1)-Al(1)-N(1) 105.87(8), Cl(1)-Al(1)-N(4) 110.11(9), N(1)-Al(1)-C(5) 87.99(10), N(4)-Al(1)-C(5) 119.52(11), N(1)-Al(1)-N(4) 117.91(11), N(3)-Al(1)-N(4) 36.75(10).

In order to understand the bonding properties of **21**, an X-ray single crystal diffraction analysis was carried out. Crystallographic data, selected bond lengths and angles are listed in Figure 14. Compound **21** crystallizes as a monomer with a five coordinated aluminum atom surrounded by one chelating [3,5-*t*Bu₂pz-N'-CH=C(SiMe₃)] moiety, a η^1 -, and a η^2 - *t*Bu₂pz ligand (Figure 14). The Al-N bond distances, Al(1)-N(3) 1.999(3), Al(1)-N(4) 1.899(2), Al(1)-N(5) 1.889(2) and Al(1)-N(6) 2.655(2) \AA , clearly exhibit η^1 - as well as η^2 -coordination of the two pyrazolato ligands, respectively. The bond

lengths of the η^2 -coordinated ligand are slightly shorter than those in $[(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_3\text{Al}]$,³⁹ presumably due to the lower coordination number at aluminum.

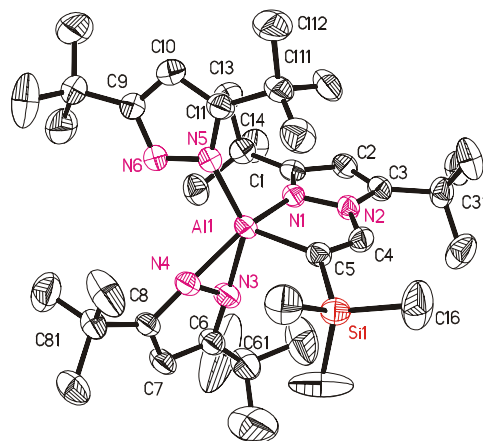


Figure 14. Perspective view and atom-labeling scheme of compound **21**, showing the thermal ellipsoids at the 50 % probability level. Selected bond lengths [\AA] and angles [$^\circ$]: Al(1)-C(5) 1.970(3), Al(1)-N(1) 1.999(2), Al(1)-N(2) 2.751(3), Al(1)-N(3) 1.999(3), Al(1)-N(4) 1.899(2), Al(1)-N(5) 1.889(2), Al(1)-N(6) 2.655(2), C(4)-C(5) 1.331(4); Al(1)-N(3)-C(6) 172.8(2), Al(1)-N(4)-C(8) 176.7(2), C(5)-Al(1)-N(1) 86.59(11), N(4)-Al(1)-N(5) 105.84(11), N(4)-Al(1)-C(5) 112.69(12), N(4)-Al(1)-N(3) 41.62(10), N(5)-Al(1)-C(5) 118.38(12), N(5)-Al(1)-N(3) 140.38(11).

However, attempts to prepare analogous complexes using other substituted acetylenes $\text{HC}\equiv\text{CR}$ (R = alkyl, aryl) were not successful. The Al-Cl bonds in **19** seem to be readily cleaved by a metathesis reaction. Compound **20** contains a rare example of an unsymmetrically η^2 -coordinated and compound **21** involves a true η^2 -coordinated

pyrazolato ligand. Complex **19** is of particular interest as a precursor for the synthesis of a series of related aluminum complexes due to its convenient high yield synthesis.

2.7.3. The dynamic behavior of compound **20**

To investigate the behavior of compound **20** in solution variable temperature $^1\text{H-NMR}$ spectra in toluene- d_8 have been recorded (Figure 15). At 273 K the spectrum shows three resonances in a ratio of 1:1:2 for the protons of the *t*Bu groups, indicating a fast rotation of the *t*Bu₂pz ligand. At 193 K the (C/D) resonances coalesce and below that temperature the exchange is slow evidenced by two new shoulders (δ 1.73 and 1.37 ppm).

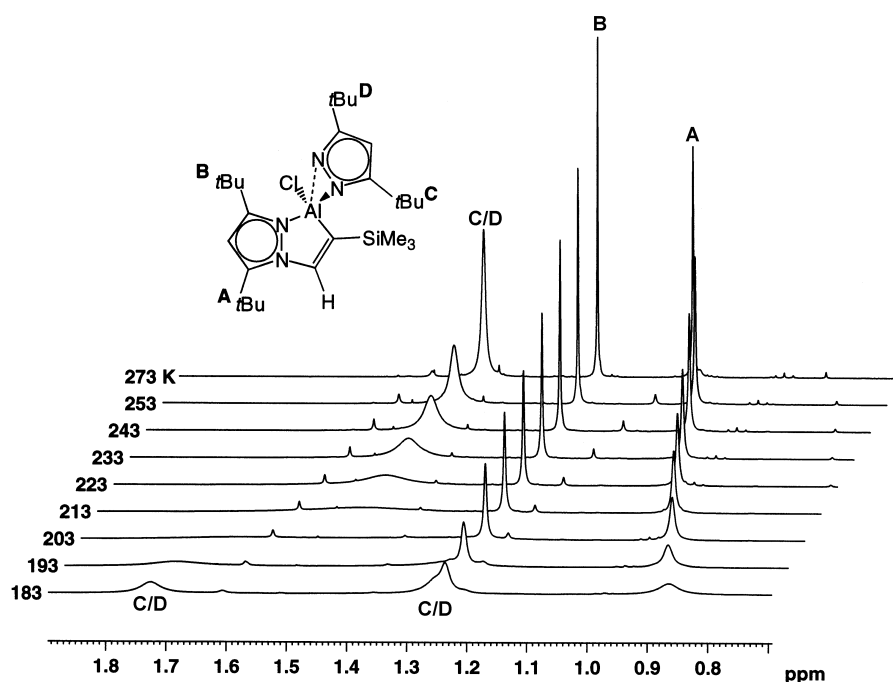


Figure 15. Variable temperature $^1\text{H-NMR}$ spectra of compound **20**.

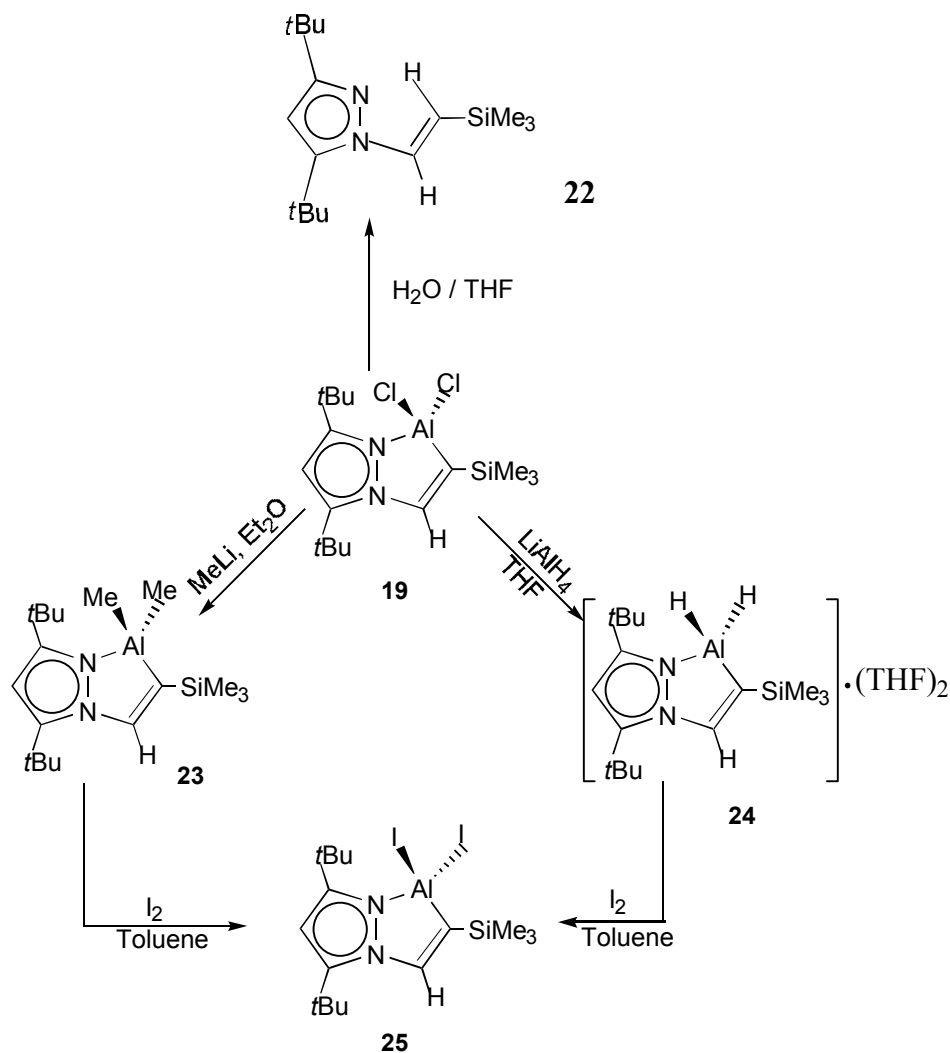
2.8. A new monomeric alkenyl-substituted pyrazolato ligand and its aluminum derivatives

As described in section 2.7. in the course of our investigations of the reaction of **3** and acetylenes an unusual compound **19** was formed and it has been shown that the Al-Cl bonds in **19** are readily cleaved and can be substituted by other basic groups. Apparently the chelating ligand [3,5-N-*t*Bu₂pz-N'-CH=C(SiMe₃)] in compound **19** is bulkier than 3,5-di-*tert*-butylpyrazole. Due to our interest as potential precursors of sterically demanding aluminum halides, alkyls as well as hydrides, reactions using **19** as the starting material have been examined.

2.8.1. Preparation of the complexes [(3,5-N-*t*Bu₂pz-N'-CH=C(SiMe₃)H] (**22**); [(3,5-N-*t*Bu₂pz-N'-CH=C(SiMe₃)-pz)AlR₂] (R = Me (**23**); R = H (**24**); R = I (**25**))

The reaction of [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N'-CH=C(SiMe}_3\text{)-pz}\}\text{AlCl}_2$] (**19**) with two equivalents of water in THF led to the formation of the free ligand [3,5-N-*t*Bu₂pz-N'-CH=C(SiMe₃)] (**22**) (Scheme 23), which could be purified by sublimation at 90 °C in high vacuo (0.01 mbar). **22** is soluble in both aliphatic and aromatic solvents at ambient temperature. The mass spectrum (EI) ($M^+ = 278$, 20 %; $(M^+ - 15) = 263$, 100 %) and the elemental analysis are in accordance with a monomeric formula for **22**. The ¹H-NMR spectrum (C₆D₆) shows two doublets at δ 6.77 ppm and 7.48 ppm with ²J = 16.3 Hz, indicating two hydrogen atoms of the TMS(H_a)C=H_b- group. No proton resonance was observed in the range of 10 - 12 ppm (cf. $\delta_{\text{N-H}}$ of pyrazoles ranging from 10 to 12 in C₆D₆), implying the H_a atom of the TMS(H_a)C= group is in a terminal position. However, no lithium salt of **22** was obtained in attempts to deprotonate **22** with *t*BuLi at

-78 °C and at ambient temperature. Why compound **22** could not be deprotonated is yet unclear; obviously, the H_a atom is not acidic enough.



Scheme 23. Syntheses of **22** - **25**.

A solution of **19** and two equivalents of LiMe in Et₂O was stirred at -78 °C for 3 h and then at ambient temperature for 15 h to give compound [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3\text{)}\}\text{AlMe}_3$] (**23**) in fair yield (*ca.* 70 %). Compound **23** is extremely soluble in *n*-hexane and was purified in two steps. First, the resulting residue was sublimed at

0.01 mbar at 100 °C and then recrystallized from *n*-hexane at -26 °C to afford colorless crystals. The mass spectrometry (EI) indicates a monomeric species **23** (M^+ (m/z) = 334, 10 %; (M^+ -15) = 319, 100 %). The $^1\text{H-NMR}$ spectrum shows besides the set of resonances of the chelating moiety only one resonance for the protons of the Al-Me groups at δ -0.15 ppm, clearly indicating the formation of **23**.

Treatment of **19** with 2.1 equivalents of LiAlH_4 in THF at -30 °C yielded [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3\text{)}\}\text{AlH}_2$] (**24**) as a white solid, only slightly soluble in common organic solvents except THF. Compound **24** is extremely sensitive to light, oxygen, and water. The mass spectrum (EI) suggests that **24** is monomeric (m/z = 306, M^+ , 100 %). The formation of the monomeric species **24** is probably due to the sterically demanding chelating ligand [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3\text{)}\}$]. The $^1\text{H-NMR}$ ($\text{THF-}d_8$) reveals besides of the set of resonances of the chelating moiety, a broad Al-H signal (δ 3.1 ppm, $W_{1/2}$ = 85 Hz) and signals for two coordinating THF molecules. The two signals of the protons of the non-equivalent *t*Bu groups are close to each other (δ 1.490 and 1.495 ppm). The IR spectrum exhibits two strong bands in the range of Al-H stretching frequencies (1780 and 1812 cm^{-1}) implying terminal Al-H bonds in the solid state.⁴⁷

The reaction of **23** with two equivalents of I_2 in toluene afforded compound [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3\text{)}\}\text{AlI}_2$] (**25**) after refluxing for 24 h (Scheme 23). It is well soluble in toluene but only slightly soluble in hexane and can be readily purified by crystallization from toluene at -26 °C to give small pale crystals. The mass spectrum is in good agreement with the formulation of **25** (m/z = 558, M^+ , 4 %; 553, (M^+ - Me), 15 %; 431, (M^+ - I), 100 %) as a monomer. The $^1\text{H-NMR}$ shows one set of resonances for the chelating moiety [$3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3\text{)}$] (δ 0.42, 0.82, 1.43, 5.81 and 7.36 ppm, C_6D_6) indicating the formation of **25**. Alternatively, **25** has also been prepared by

the reaction of **24** and two equivalents of I_2 under mild conditions (rt). It seems that the reaction of I_2 with **24** is more favorable than that with **23**. This is probably due to the higher dissociation energy of the Al-C bond than that of the Al-H bond. It is crucial that the coordinating THF molecules in precursor **24** are removed in high vacuum at 50 °C prior to the reaction of **24** and I_2 , otherwise the product is difficult to separate from the oily residue.

2.8.2. X-ray structural analysis of **23**

Crystallographic data, selected bond lengths and angles of **23** are listed in figure 16. Compound **23** crystallizes in the monoclinic crystal system, space group $C2/c$. The similar cell parameters of [$\{3,5\text{-}i\text{Bu}_2\text{pz-N}^{\prime}\text{-CH=C(SiMe}_3\text{)}\}\text{AlMe}_2$] (**23**) and [$\{3,5\text{-}i\text{Bu}_2\text{pz-N}^{\prime}\text{-CH=C(SiMe}_3\text{)}\}\text{AlCl}_2$] (**19**) indicate a structural relation between these two compounds (Figures 12 and 16). Like in compound **19**, the geometry at the aluminum atom is tetrahedrally distorted (N(1)-Al(1)-C(5) $84.90(9)^\circ$ and C(21)-Al(1)-C(22) $115.24(11)^\circ$) due to the strain imposed by the chelate ring.

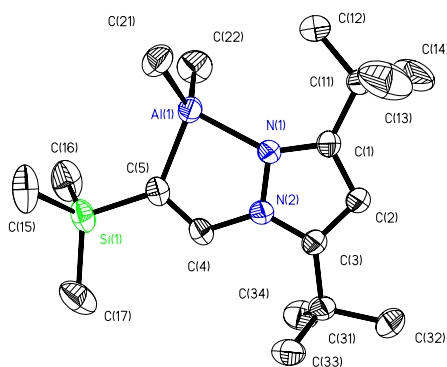


Figure 16. Perspective view and atom-labeling scheme of compound **23**, showing the thermal ellipsoids at the 50 % probability level. Al(1)-C(21) 1.971(2), Al(1)-C(22)

1.971(3), Al(1)-C(5) 1.993(3), Al(1)-N(1) 2.016(3), C(4)-C(5) 1.328(3); C(5)-Al(1)-N(1) 84.90(9), C(21)-Al(1)-C(22) 115.24(11).

2.9. A polyhedral aluminum compound with an $\text{Al}_4\text{C}_4\text{N}_4$ framework and a binuclear aluminum complex with an Al-N-C-Al bridge⁷⁴

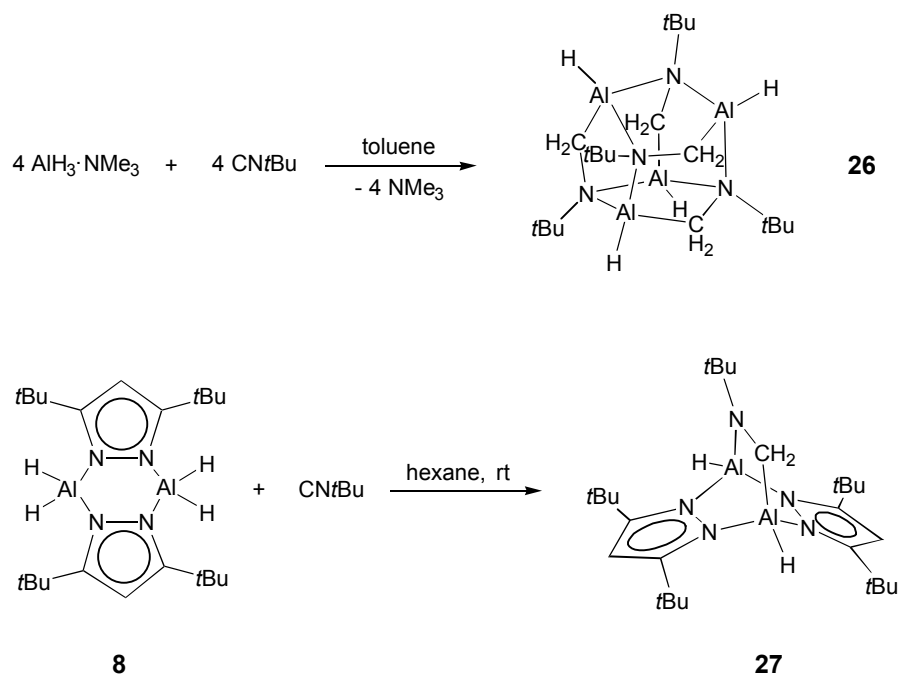
Recently, oligomeric and polyhedral compounds of aluminum involving Al-N and Al-C cores have gained considerable interest following the preparation of a few three-coordinated iminoalanes⁷⁵ and determination of the structures of carbaalanes.³⁸ Although the formation of iminoalanes and carbaalanes seems to be almost understood,^{38,75-79} cage species containing an $\text{Al}_m\text{C}_n\text{N}_o$ framework ($m, n, o > 2$) are still unknown.⁸⁰ It was assumed that such cage species should exhibit some interesting features. Herein the structure of an aluminum carbon nitrogen cage $[(\text{HAl})(\text{CH}_2\text{N}t\text{Bu})]_4$ (**26**) and the synthesis of a binuclear species with bulky pyrazolato ligands $[(\eta^1, \eta^1-t\text{Bu}_2\text{pz})_2(\mu\text{-CH}_2\text{N}t\text{Bu})(\mu\text{-AlH})_2]$ (**27**) are described.

2.9.1. Preparation of $[(\text{AlH})_4(\text{CH}_2\text{N}t\text{Bu})_4]$ (**26**) and $[(3,5-t\text{Bu}_2\text{pz})_2(\text{CH}_2\text{N}t\text{Bu})(\text{AlH})_2]$ (**27**)

Treatment of $\text{H}_3\text{Al}\cdot\text{NMe}_3$ with one equivalent of $\text{CN}t\text{Bu}$ in refluxing toluene gave **26** in 75 % yield (Scheme 24). Compound **26** is well soluble in toluene and readily crystallizes.

Reaction of the dimeric aluminum dihydride $[(\eta^1, \eta^1-t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**)⁴³ and $\text{CN}t\text{Bu}$ at room temperature led to the formation of **27** in 91 % yield (Scheme 24). However, further reaction of **27** with excess $\text{CN}t\text{Bu}$ at room temperature was not observed. The $^1\text{H-NMR}$ spectrum of **27** displays three different sharp resonances for the

protons of the *t*Bu groups (δ 1.39, 1.46, and 1.52 ppm, ratio 2:1:2) indicating the different chemical environments of the *t*Bu groups.



Scheme 24. Syntheses of compounds **26** and **27**.

2.9.2. X-ray single crystal structure analysis of compounds **26** and **27**

The X-ray diffraction analysis of **26** reveals a remarkable $\text{Al}_4\text{C}_4\text{N}_4$ cage configuration in which the C-atoms may be formally viewed as inserted methylene groups into four Al-N bonds of an Al_4N_4 cube (Figure 17). The core of **26** consists of six faces formed by two boat-shaped six-membered $\text{Al}_2\text{C}_2\text{N}_2$ rings and four puckered five-membered Al_2CN_2 rings.^{31,81} The two six-membered heterocycles are opposite to each other and the four five-membered rings are arranged between the two. Each atom of the core shares two different types of ring systems and the geometries at both Al- and N-atoms

are slightly distorted tetrahedral. The Al-C bond lengths (1.979(2) to 1.992(2) Å) are at the lower limit of known carbaalanes (Al-C 1.948(3)-2.212(2) Å)³⁸ whereas the Al-N bond lengths (1.966(2) to 1.978(2) Å) are slightly longer than those in iminoalanes with 12-membered Al₆N₆ core structures (e. g. Al-N 1.898(3) - 1.955(3) Å in (HAlNiPr)₆).^{76e} The molecular symmetry is close to *S*₄ whereas no further elements of symmetry exist in **26**. No critical intramolecular contacts were observed since the closest Al...Al distance (e. g. Al(1)···Al(2)) is longer than 3.073 Å.

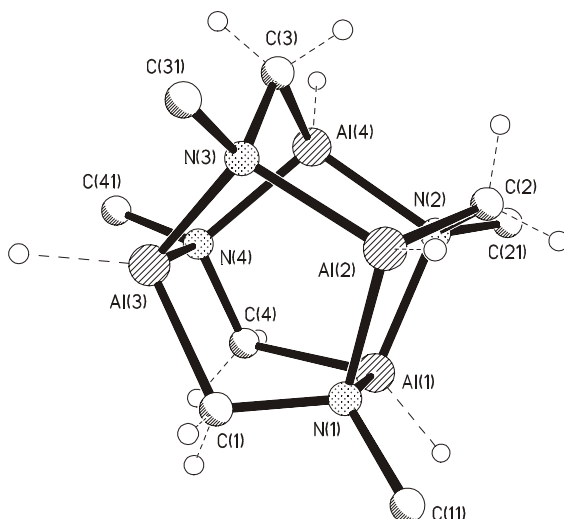


Figure 17. Molecular structure of **26**. Selected bond lengths [Å] and angles [°]. The *t*Bu groups are represented by the ipso C atoms: Al(1)-N(1) 1.968(2), Al(1)-N(2) 1.9693(19), Al(1)-C(4) 1.992(2), Al(2)-N(1) 1.9727(19), Al(2)-N(3) 1.978(2), Al(2)-C(2) 1.987(2), N(1)-C(1) 1.529(3), N(2)-C(2) 1.525(3); N(1)-Al(1)-N(2) 104.44(8), N(1)-Al(1)-C(4) 107.09(9), N(2)-Al(1)-C(4) 98.60(9), C(1)-N(1)-Al(1) 105.42(13), C(1)-N(1)-Al(2) 106.33(13), Al(1)-N(1)-Al(2) 102.49(8), N(1)-C(1)-Al(3) 109.95(14), N(2)-C(2)-Al(2) 110.07(14).

The crystallographic analysis of **27** exhibits a structure with a Al_2N_4 heterocycle bridged by a -C-N- unit (Figure 18). To our surprise the Al(1)-N(5) bond length (1.778(2) Å) is significantly shorter than those in comparable four coordinated iminoalanes ranging from 1.898(3) to 1.955(3) Å,^{76e} and even shorter than in three-coordinated Al-N compounds (from 1.804 to 1.824 Å)⁷⁵ whereas the other Al-N bond lengths of **27** fall in the expected range (1.9265(19) - 1.9698(18) Å). The Al(2)-C(5) distance of 1.966(2) Å is at the lower limit of those found in the carbaalanes (Al-C 1.948(3) - 2.212(2) Å).³⁸

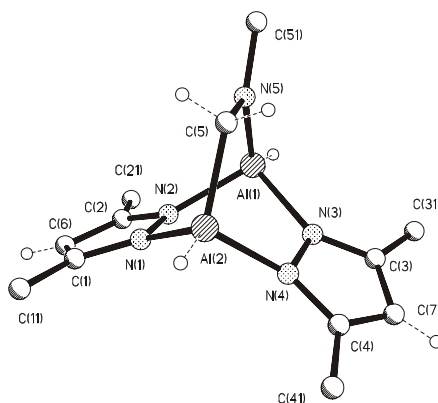


Figure 18. Molecular structure of **27**. C(11, 21, 31, 41, 51) represent the ipso C-atoms of the *t*Bu groups. Selected bond lengths [Å] and angles [°]: Al(1)-N(5) 1.778(2), Al(1)-N(2) 1.9698(18), Al(2)-N(4) 1.9335(18); N(2)-Al(1)-N(3) 99.38(8), N(1)-Al(2)-N(4) 99.87(8), Al(2)-C(5)-N(5) 118.43(15), Al(1)-N(5)-C(5) 110.59(14), N(1)-Al(2)-C(5) 102.54(9), N(2)-Al(1)-N(5) 106.73(9).

2.9.3. The dynamic behavior of compound **26**

The data of mass spectroscopy and elemental analysis are in agreement with the formula of **26**. The ²⁷Al-NMR spectrum shows only one resonance at 148.5 ppm indicating Al-atoms of coordination number four.⁸² However, the ¹H-NMR (C_6D_6 , rt)

spectrum displays a quite broad resonance (δ 1.4 ppm, $W_{1/2} = 60$ Hz, 36 H) and two sets of doublets (δ 1.61 and 1.85 ppm, $^2J = 12.65$ Hz, 8 H, ratio 1:1). The resonances of the ^{13}C -NMR spectrum are too broad to be distinguished. Broad resonances in the ^1H - and ^{13}C -NMR spectra suggest dynamic processes in **26** in solution at room temperature.⁸³ This feature is manifested by variable temperature ^1H -NMR spectra in toluene- d_8 (Figure 19(B)). At 60 °C the spectrum shows only one sharp resonance at δ 1.37 ppm indicating fast rotation of the *t*Bu groups. This signal (*t*Bu_{a/b}) coalesces at about 10 °C, and below this temperature the exchange is slow demonstrated by the two new shoulders (δ 1.33 (*t*Bu_a) and 1.50 ppm (*t*Bu_b)), ratio 2:1 (-20 °C)). Surprisingly, the proton resonance of the *t*Bu_a group further splits into two singlets below -40 °C (the ratio is close to 1:1). In any case the integration of the resonances ($\text{H}_a:\text{H}_b:t\text{Bu}_b:t\text{Bu}_a$) strictly has a ratio of 1:1:3:6. Such dynamic behavior is unprecedented and it is currently not clear whether the three sharp resonances (3:3:3) of the *t*Bu_{a/b} groups below -40 °C really correspond to the three frozen non-equivalent methyl groups or indicate a dissociation of the molecules in solution. However, the two sets of coupled resonances are tentatively assigned to the two unequal hydrogen atoms (H_a and H_b) of the core of **26** due to steric effects. The IR spectrum shows two strong bands in the range of Al-H stretching frequencies (1831 and 1858 cm^{-1}) implying terminal Al-H bonds in the solid state.⁴⁷

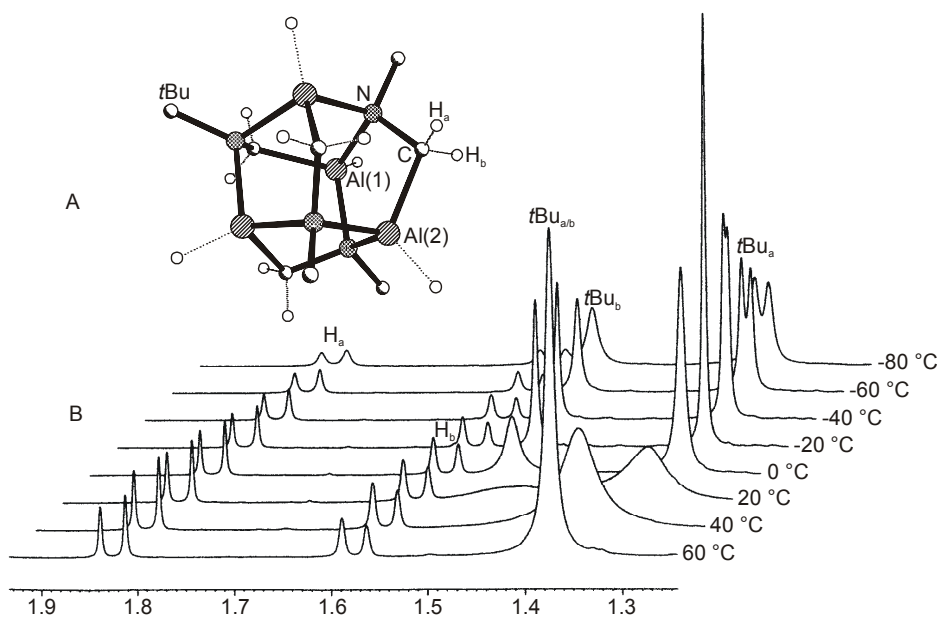


Figure 19. Variable temperature ^1H -NMR spectra of **26** in toluene- d_8 .

2.9.4. Ab initio calculation for **26**

Further insight into the molecular structure of **26** is gained by an ab-initio calculation⁸⁴ of the model compound $[(\mu_3\text{-AlH})(\mu_3\text{-CH}_2\text{NMe})]_4$ (**26a**)⁸⁵ with the molecular symmetry S_4 .

A suggestive image of the bonding situation is offered by the representation of Laplacian of the electronic density.⁸⁶ The negative zones (dark areas in Figure 20) exhibit the tendencies of charge accumulation, as are the terminal hydrides and the σ skeleton of the embedded CH_2NMe fragments. The positive Laplacian show the depletion of the electron density around the nitrogen atoms.

The Al-N and Al-C contacts reveal accumulated charge on N and C with lone pairs of the non-metals directed toward the metal atom. The Laplacian analysis shows that the CH_2NMe fragments can be regarded as μ_3 -coordinating ligands. The (3,-1) bond critical

points are placed closer to the electropositive partner, clearly seen for the Al-C and Al-N bonds. Moreover, the analysis reveals the (3,+1) critical points (cycle) on all the faces of the cluster and a (3,+3) critical point in the center of gravity. This is specific for a closed cage. The small ellipticities of the Hessian eigenvalues of the Al-C, Al-N, and C-N (3,-1) critical points show the σ nature of the bonds.

The coordination-type of the bonding is seen by the natural bond orbital (NBO) analysis.⁸⁷ This shows that in both types of Al-N bonds the content of nitrogen AOs is ~92 % corresponding to a ligand field regime. The Al-C bonds contain 85 % non-metal character. The composition of the NBOs of the Al-N bonds shows sp^3 -like hybrids in the bonding with s character ranging from 22 to 25 % (the content of d-orbitals is low, ~1.5 %). The Al-C bond show 32.8 % s and 67.2 % p participation for the carbon AOs. However, the apparent sp^2 character of carbon does not correspond to the π bonding. The lower content of p in the natural hybrids of the C atom reveals only a higher C-N bond character (79.3 %).

The dynamic NMR experiment detected changes of the resonances related to the *t*Bu protons with temperature. This phenomenon can be assigned to the promotion of rotational disorder around the C-N bond of the terminal fragments. The differentiation of protons takes probably place by through-space dipolar interactions of the corresponding *t*Bu and CH₂ groups.

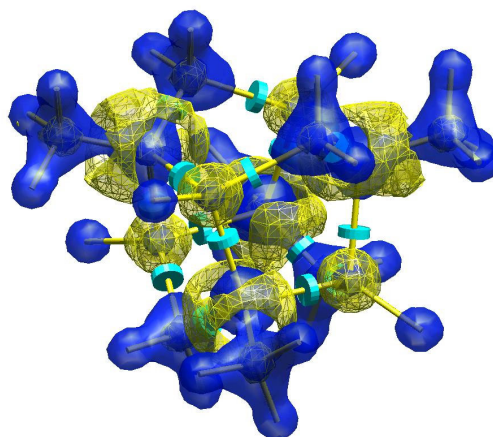


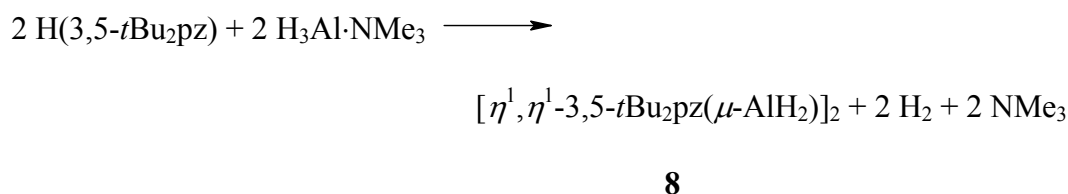
Figure 20. The iso-surfaces (taken at the 0.175 value) for the Laplacian of electron density in $[(\mu_3\text{-AlH})(\mu_3\text{-CH}_2\text{NMe})_4]$ (**26a**) study case. The dark areas correspond to negative Laplacian (density accumulation). The small spheres represent the (3,-1) critical bonds of the cluster core.

Briefly, this section described the preparation of a polyhedral aluminum compound **26** and a dinuclear aluminum species **27** by hydroalumination of $\text{CN}t\text{Bu}$. The $\text{Al}_4\text{C}_4\text{N}_4$ core of **26** is unique and thus can be considered as a fused carba-aminoalane. The exact mechanism for the formation of **26** and **27** is yet unknown, but probably an initial donor-acceptor intermediate is involved, where the isocyanide carbon coordinates to aluminum followed by hydrogen migration from aluminum to carbon to yield the CH_2 moiety.⁸⁰

3. Summary

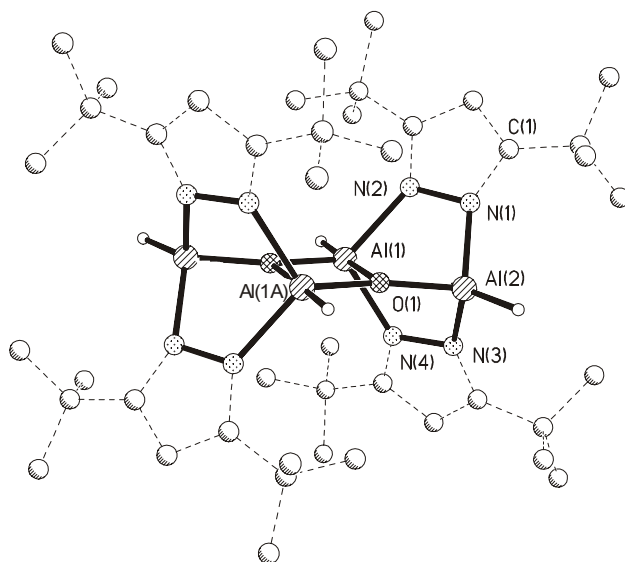
A series of aluminum complexes have been prepared by the use of the bulky 3,5-*t*Bu₂pz ligand. Some of the major achievements of this doctoral work are summarized as follows:

1. The first example of an aluminum dihydride dimer $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-AlH}_2)]_2$ (**8**) involving the pyrazolato ligand was synthesized by the reaction of H(3,5-*t*Bu₂pz) and H₃Al·NMe₃ in toluene. Its convenient high yield preparation makes it a versatile starting material in reactions with various reagents. Compound **8** was fully characterized by ¹H-NMR, elemental analysis and MS(EI).

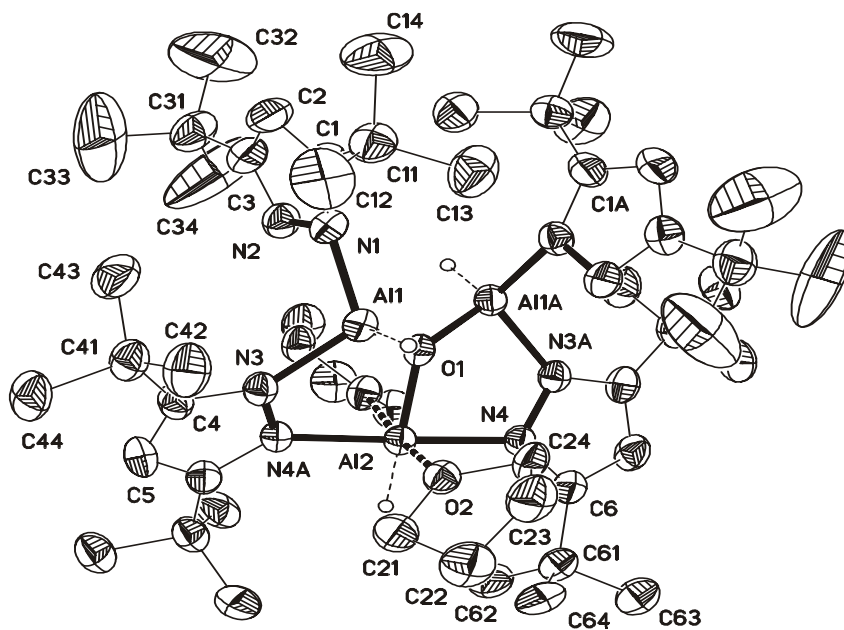


2. Two aluminoxanes (**9** and **13**) were prepared from **8** as starting material. **9** was synthesized by the oxygen transfer reagent dioxane and represents the first example of a structurally characterized aluminoxane hydride with the coordination number five at two of the Al-atoms. The formation of **9** probably proceeds via nucleophilic attack at the aluminum center of **8** by one of the oxygen atoms of dioxane and then insertion into an Al-H bond leading to the degradation of dioxane and forming the Al-O bond in **9**. The aluminoxane hydride $[(\mu, \eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu_3\text{-O})(\mu\text{-AlH}_3)]\cdot 2\text{THF}$ (**13**) was formed when the aluminum dihydride $[(\mu, \eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**) was reacted with 1 equivalent of water. For the first time an aluminoxane was prepared by hydrolysis of the aluminumhydride. The core of compound **13** consists of two tetra and one hexa coordinated Al atoms with short Al-O bonds. The two central

N_2Al_2O ring systems share a common Al-O edge with a hexa coordinated Al atom and two of the pyrazolato ligands bind in η^1 - and μ, η^1, η^1 - arrangements.

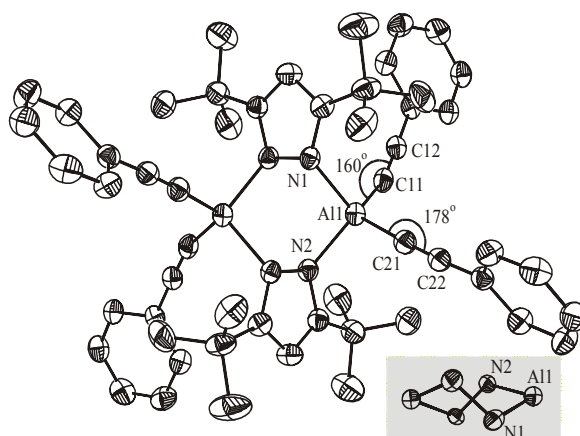


9

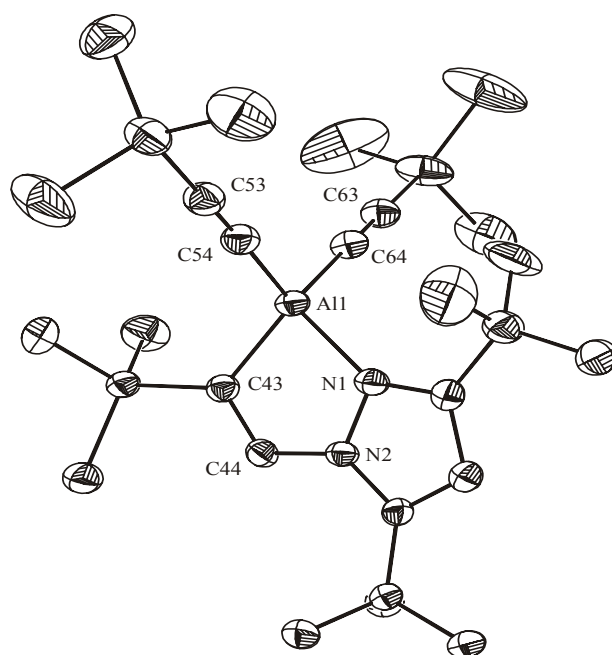


13

3. Two terminal aluminumacetylide complexes (**14** and **15**) were prepared by the reactions of **8** and $\text{HC}\equiv\text{CPh}$ or $\text{HC}\equiv\text{CSiMe}_3$. Several interesting features have been found in these two compounds comprising the first examples with aluminum atom coordinated by terminal acetylide ligands. Most surprisingly, the six-membered Al_2N_4 ring in **14** adopts a twisted conformation, in sharp contrast to other bridged bispyrazolate compounds. Another interesting feature of **14** is the considerable deviation of the two $\text{Al-C}\equiv\text{C}$ backbones from linearity ($\text{Al}(1)\text{-C}(11)\text{-C}(12)$, $160.2(3)^\circ$ vs $\text{Al}(1)\text{-C}(21)\text{-C}(22)$, $178.3(3)^\circ$; the $\text{C}(11)\text{-C}(12)$ and $\text{C}(21)\text{-C}(22)$ bond lengths are $1.211(4)$ and $1.218(4)$ Å, respectively).

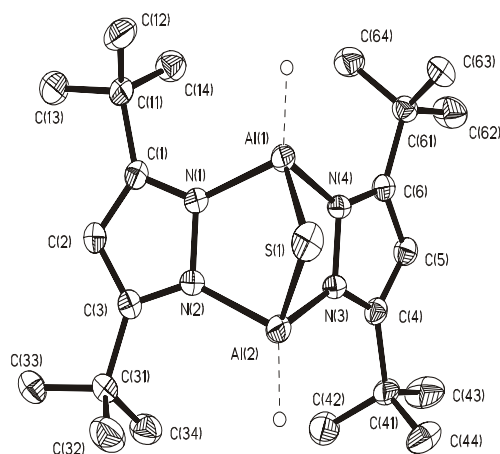
**14**

The formation of **15** is unusual and the structure reveals a mononuclear aluminum compound with an aluminum atom coordinated by the $[3,5\text{-N-}t\text{Bu}_2\text{pz-N}^{\prime}\text{-CH=C(SiMe}_3)]$ chelating unit and two $\text{C}\equiv\text{CSiMe}_3$ groups. The chelating unit consists of a pyrazolate ligand and has added formally to a $\text{C}\equiv\text{C}$ triple bond thereby forming a five-membered metalheterocycle. The formation of **15** is probably via a $[2 + 3]$ cycloaddition and its use as a new ligand for other metal ions can be envisaged.



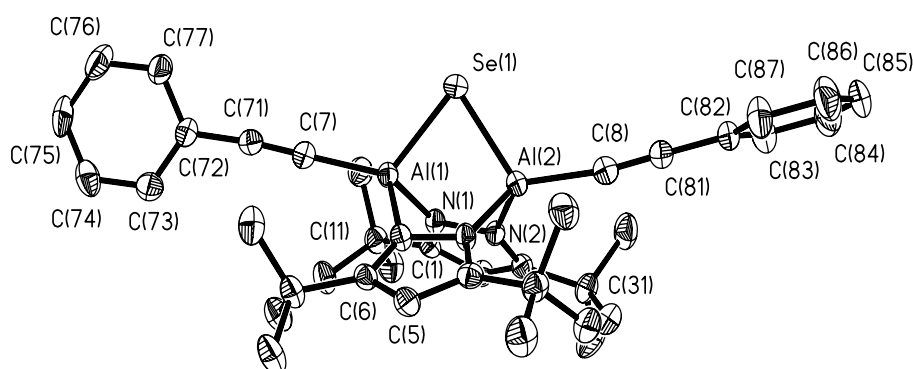
15

4. Three novel aluminum chalcogenide hydride complexes [$\{\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz}(\mu\text{-AlH})_2\text{E}\}$] (E = S (**10**), Se (**11**), Te (**12**)) have been synthesized by the reaction of **8** and elemental chalcogen in toluene in good yield. It is important, especially for the preparation of **10**, to use strictly equivalent amounts of the reactants and the mixed solvent system (THF/toluene (1:9)), otherwise insoluble polymeric materials are formed. Compound **10** is the first example of a reaction involving an aluminum dihydride and elemental sulfur.



10

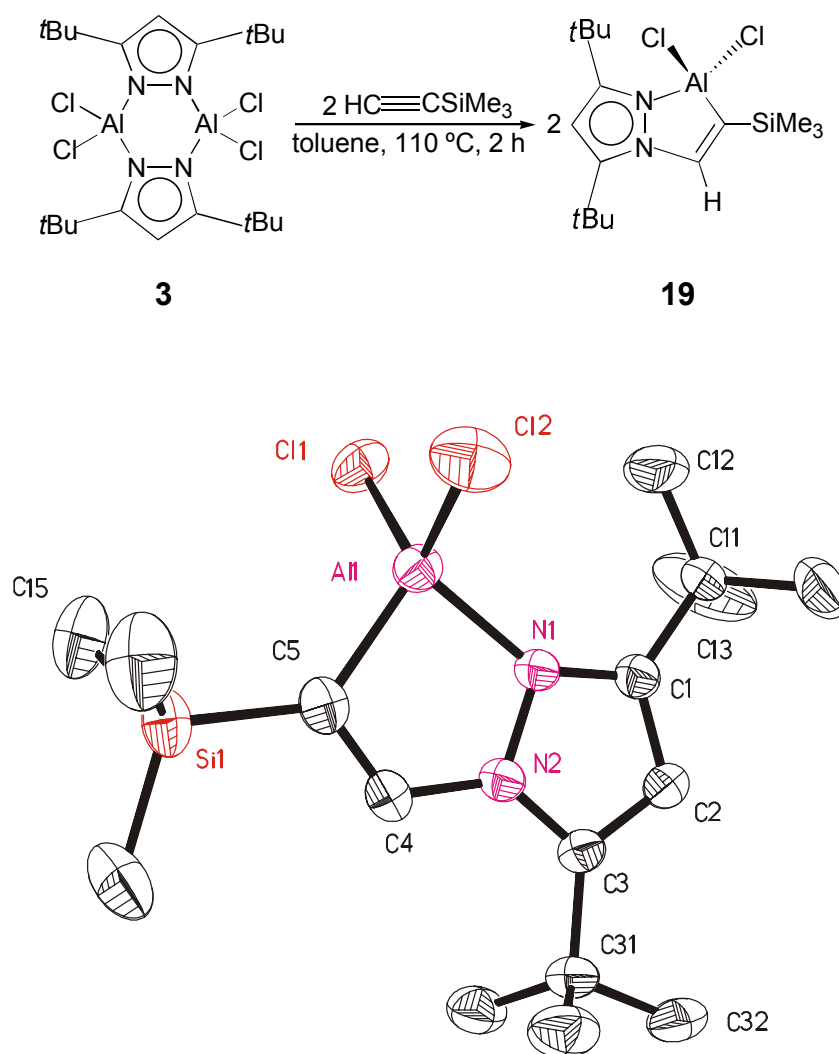
5. Three fused aluminum acetylide chalcogenide complexes $[\text{Al}_2(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-E})(\text{C}\equiv\text{CPh})_2]$ (E = S (**16**); Se (**17**); Te (**18**)) were prepared via the reactions of $[\{\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz}(\mu\text{-AlH})\}_2\text{E}]$ (E = S (**10**), Se (**11**), Te (**12**)) and $\text{HC}\equiv\text{CPh}$. The structures of compounds **16** and **17** are isostructural consisting of a boat-shaped six-membered ring geometry due to the strain of the chalcogenide bridge (S for **16**, Se for **17**) between the two Al-atoms. The interesting features are the two phenyl groups on both sides of the molecule occupying a vertical position to each other and the phenylacetylene groups arranging terminally comparable to compound $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-Al})(\text{C}\equiv\text{CPh})_2]_2$ (**14**).



17

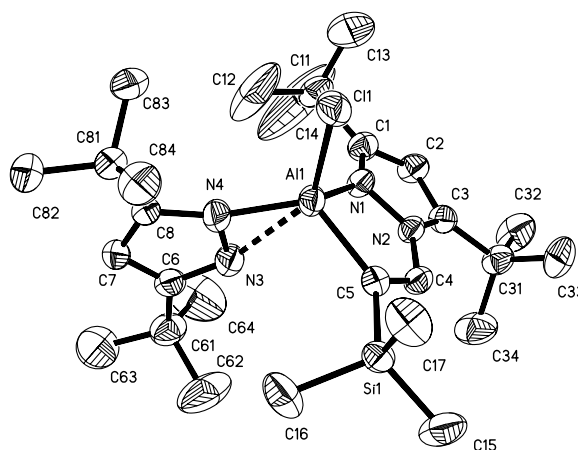
6. The facile formation of the unusual monomeric alkenyl-substituted pyrazolato aluminum dichloride $[(3,5\text{-}N\text{-}t\text{Bu}_2\text{pz}\text{-}N'\text{-CH=C}(\text{SiMe}_3)\text{AlCl}_2]$ (**19**) was achieved in high yield by reacting the dimeric pyrazolato aluminum dichloride $[(\mu, \eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz}(\mu\text{-AlCl}_2)]_2$ (**3**) with two equivalents of trimethylsilylacetylene. This reaction may be viewed as a $[2 + 3]$ -cycloaddition with the aluminum pyrazolato species functioning as the dipolar component. This type of reaction may be of general significance in the preparation of heterocyclic compounds and has attracted interest in

aluminum catalyzed enantioselective reactions. The formation of **19** may be assumed as that compound **3** dissociates prior to the reaction with the trimethylsilylacetylene. It seems likely that in the dissociated species the three coordinate aluminum is the more reactive site.

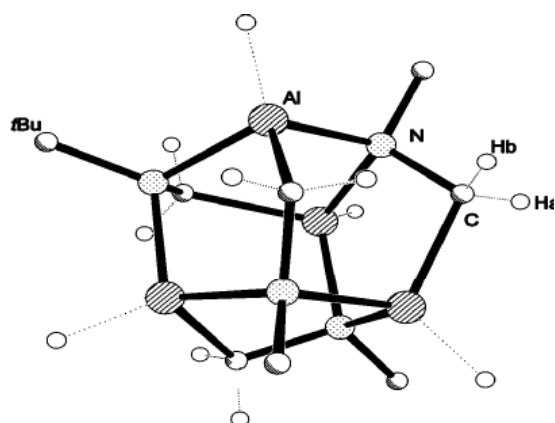
**19**

The addition of one and two equivalents of $\text{K}[3,5\text{-}t\text{Bu}_2\text{pz}]$ to **19**, respectively, resulted in the formation of two novel complexes $[\{3,5\text{-}N\text{-}t\text{Bu}_2\text{pz-N}^{\prime}\text{-}$

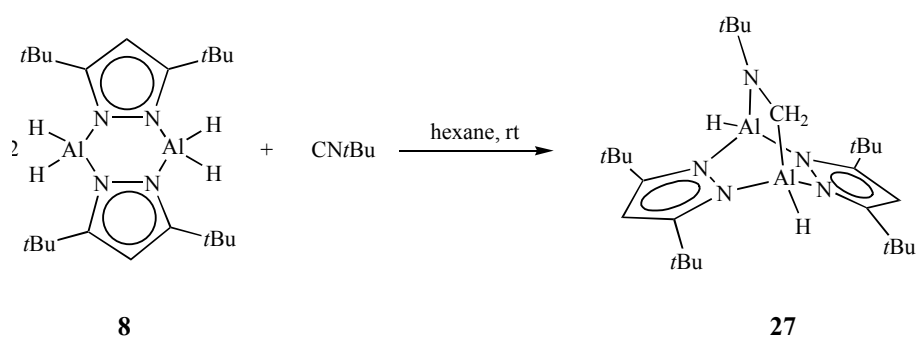
$\text{CH}=\text{C}(\text{SiMe}_3)\{\text{AlCl}(3,5\text{-}t\text{Bu}_2\text{pz})\}$ (**20**) and $[\{3,5\text{-}N\text{-}t\text{Bu}_2\text{pz}\text{-}N'\text{-}\text{CH}=\text{C}(\text{SiMe}_3)\}\text{Al}(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})]$ (**21**), for which crystallographic data are presented. The coordination of the pyrazolato ligand in **21** represents a rare example of the ‘slipped’ η^2 -coordination.

**21**

7. A polyhedral aluminum compound **26** and a dinuclear aluminum species **27** have been generated by hydroalumination of $\text{CN}t\text{Bu}$ with $\text{H}_3\text{Al}\cdot\text{NMe}_3$ or with compound **8**, respectively. A significant difference in the arrangement of the atoms within the cage skeleton of **26** was found in comparison with other known hexagonal prismatic arrays of aluminum compounds involving a twelve-membered core. The $\text{Al}_4\text{C}_4\text{N}_4$ core of **26** is unique and thus it could be considered as a fused carba-aminoalane. The exact mechanism for the formation of **26** and **27** is unknown, but probably an initial donor-acceptor intermediate is involved, where the isocyanide carbon coordinates to aluminum followed by hydrogen migration from aluminum to carbon to yield the CH_2 moiety.



26



4. Experimental Section

4. 1. General procedures

All manipulations, unless otherwise specified, were performed on a high-vacuum line or in a glove box under a purified N₂ atmosphere using Schlenk techniques with rigorous exclusion of moisture and air. All glassware was oven-dried at 150 °C for a minimum period of 12 h, assembled hot and cooled under high vacuum with intermittent flushing with nitrogen or argon. The samples for spectral measurements were prepared inside a MBraun MB 150-GI glove-box where the O₂ and H₂O levels were normally maintained below 1 ppm. Solvents were distilled from Na/benzophenone ketyl prior to use.

4. 2. Physical Measurements

The *melting points* of the compounds synthesized were measured in sealed capillaries on a Büchi B 540 instrument.

¹H, ¹³C and ²⁹Si NMR spectra (benzene-*d*₆, THF-*d*₈, toluene-*d*₈ and CDCl₃) were recorded on Bruker Avance 500, MSL-400, AM-250, and Avance 200 instruments. The chemical shifts are reported in ppm with reference to external standards, namely SiMe₄ for ¹H, ¹³C, and ²⁹Si nuclei, and AlCl₃ for ²⁷Al nuclei. All heteroatom NMR spectra were measured in the ¹H decoupled mode. Downfield shifts from the reference are quoted positive and upfield shifts are reported as negative values. The signal types are assigned as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The solvents for NMR measurements were dried over K or CaH₂ and trap-to-trap distilled before use. The NMR data of unsymmetrical and complex compounds are assigned in

accordance with the atom labeling schemes of the X-ray structure determinations in the theoretical part.

Mass spectra were obtained on Finnigan MAT 8230 or Varian MAT CH5 instruments by EI technique.

Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer as nujol mulls between KBr. Intensities were abbreviated as follows: vs (very strong), s (strong), m (medium), w (weak).

Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

X-ray structure determinations: Suitable crystals were mounted on glass fibers in a rapidly cooled perfluoropolyether. Intensity data for **1**, **3**, **9**, **11**, **12**, **13**, **16**, **17**, **19**, **20**, **21**, **23**, **26** and **27** were collected on a Siemens/Stoe AED2 four circle diffractometer performing $2\theta/\omega$ scans. Diffraction data for **7**, **10**, **14** and **15** were collected on a Siemens/Stoe Huber four circle diffractometer coupled to a Siemens CCD area-detector with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), performing φ - and ω -scans. Data reduction and space group determination routines were satisfied using the Siemens SHELXTL family of programs.⁸⁸ The structures were solved using direct methods employing SHELXS-96/97 programs. The structure refinements were carried out by full-matrix least-squares methods against F^2 using SHELXS-96/97.⁸⁸ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The crystal data for the compounds mentioned along with structure factors and refinements parameters are tabulated in Section 6.

Ab initio calculations for compounds **14** and **26** were carried out with the GAMESS package in the RHF limit, on the STO-3G basis.^{65d}

Starting Materials

Chemicals were purchased from Aldrich and used as received. $\text{H}_3\text{Al}\cdot\text{NMe}_3$,⁴⁶ 3,5-di-*tert*-butylpyrazole⁴¹ and 3,5-di-*tert*-butylpyrazolato potassium^{23a} were prepared as described in the literature.

4. 4 Synthesis of aluminum complexes with the 3,5-di-*tert*-butylpyrazolato ligand

4. 4. 1 Synthesis of $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlMe}_2)]_2$ (**1**)

The diluted Me_3Al (1.43 M in *n*-hexane 1.5 mL, 2.1 mmol) was added slowly via syringe to a stirred solution of $\text{H}(3,5\text{-}t\text{Bu}_2\text{pz})$ (0.36 g, 2.0 mmol) in *n*-hexane (40 mL) under evolution of CH_4 at room temperature. After the mixture was stirred for 4 h, the solvent was reduced in volume (to about 10 mL) and **1** crystallized at $-26\text{ }^\circ\text{C}$ (0.40 g, 85 %). Alternatively, after removal of the solvent the residue was sublimed at $120\text{ }^\circ\text{C}$ under reduced pressure (0.01 mbar) (0.43 g, 91 %).

Melting point: $173\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ -0.55 (s, 12 H, Al- CH_3), 1.37 (s, 36 H, C(CH_3)₃), 6.23 (s, 2 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ -6.62 (br, Al-C), 30.94 (CH_3), 32.70 (CMe_3), 107.3 (CH), 171.93 (C-*t*Bu) ppm.

MS(EI) m/z (%): 457 ($(\text{M}^+ - \text{Me})$, 100).

Elemental analysis for C₂₆H₅₀Al₂N₄ (472.67):

	C	H	N
Calcd	66.07	10.66	11.85;
Found	65.8	10.4	11.6 %

4. 4. 2 Synthesis of [(η^1, η^1 -3,5-*t*Bu₂pz)(μ -AlEt₂)]₂ (**2**)

The method of preparation was analogous to **1**. After the reaction of AlEt₃ (2.0 mmol) and H(3,5-*t*Bu₂pz) (0.36 g, 2.0 mmol), compound **2** was isolated by crystallization from *n*-hexane at -26 °C (0.41 g, 78 %).

Melting point: 127 °C.

¹H-NMR (200.130 MHz, C₆D₆): δ 0.15 (t, 8 H, CH₂), 0.95 (m, 12 H, CH₃), 1.40 (s, 36 H, C(CH₃)₃), 6.30 (s, 2 H, CH) ppm.

¹³C-NMR (125.758 MHz, C₆D₆): δ 3.85 (Al-CH₂-), 8.77 (Al-CH₂-CH₃), 30.99 (CH₃), 32.87 (CMe₃), 108.02 (CH), 172.06 (C-*t*Bu) ppm.

MS(EI) *m/z* (%): 499 ((M⁺ - Et), 100).

Elemental analysis for C₃₀H₅₈Al₂N₄ (528.78):

	C	H	N
Calcd	68.14	11.06	10.60;
Found	68.0	11.1	10.4 %

4. 4. 3 Synthesis of [(η^1, η^1 -3,5-*t*Bu₂pz)(μ -AlCl₂)]₂ (**3**)

A suspension of AlCl₃ (0.27 g, 2.0 mmol) and K(3,5-*t*Bu₂pz) (0.44 g, 2.0 mmol) in toluene (40 mL) was stirred for 15 h at room temperature. The solvent was removed under reduced pressure (0.01 mbar) and the resulting residue was extracted with *n*-

hexane. Compound **3** crystallized from *n*-hexane at -26°C (0.35 g, 63 %). Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from *n*-hexane.

Melting point: 175°C .

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 1.43 (s, 36 H, CH_3), 6.33 (s, 2 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ 30.65 (CH_3), 33.34 (CMe_3), 110.81 (CH), 176.99 ($\text{C-}t\text{Bu}$) ppm.

MS(EI) m/z (%): 554 (M^+ , 100), 539 ($(\text{M}^+ - \text{Me})$, 50).

Elemental analysis for $\text{C}_{22}\text{H}_{38}\text{Al}_2\text{Cl}_4\text{N}_4$ (554.34):

	C	H	Cl	N
Calcd	47.67	6.91	25.58	10.11;
Found	47.8	7.0	26.2	10.0 %

4.4.4 Synthesis of $[(\eta^1, \eta^1\text{-3,5-}t\text{Bu}_2\text{pz})(\mu\text{-AlClMe})_2]$ (**4**), isomers **4a**, **4b**

To a solution of $\text{H}(3,5\text{-}t\text{Bu}_2\text{pz})$ (0.36 g, 2.0 mmol) in *n*-hexane (40 mL), the diluted Me_2AlCl (1.0 M in *n*-hexane, 2.0 mL, 2.0 mmol) was added slowly via syringe at room temperature. The solution was stirred for 15 h and the solvent volume was reduced (to 10 mL). **4** crystallized at -26°C (0.32 g, 62.5 %).

Melting point: 113°C .

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ -0.502, -0.485, (2 s, 6 H, Al-CH_3); 1.343, 1.346 (2 s, 36 H, CH_3); 6.226, 6.227 (2 s, 2 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ -6.9 (very br, Al-C); 30.799, 30.806, (CH_3); 33.032, 33.034, (CMe_3); 109.004, 109.045 (CH); 174.611, 174.664 ($\text{C-}t\text{Bu}$) ppm.

MS(EI): m/z (%) 497 ($(\text{M}^+ - \text{Me})$, 100).

Elemental analysis for $C_{24}H_{44}Al_2Cl_2N_4$ (513.50):

	C	H	Cl	N
Calcd	56.14	8.64	13.81	10.91;
Found	56.2	8.5	13.9	10.8 %

4. 4. 5 Synthesis of $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-Al})_2\text{Me}_3\text{Cl}]$ (**5**)

To a suspension of $K(3,5\text{-}t\text{Bu}_2\text{pz})$ (0.44 g, 2.0 mmol) in toluene (40 mL) the diluted Me_2AlCl (1.0 M in *n*-hexane, 2.0 mL, 2.0 mmol) was added slowly via syringe and then stirred for 15 h at room temperature. The solvent was removed, the residue first sublimed at 50 °C (0.01 mbar) to eliminate a small amount of uncharacterizable substances the remaining residue was finally sublimed at 120 °C under reduced pressure (0.01 mbar) to afford a mixture of **1** and **5** in an approximate 44/56 ratio (total yield 0.34 g, 71 %).

Melting point: 181 °C.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ -0.57, -0.54 (2s, 6 H, $\text{Al}(\text{CH}_3)_2$), -0.41 (s, 3 H, $\text{Al}(\text{Cl})\text{CH}_3$), 1.38 (s, 36 H, CH_3), 6.25 (s, 2 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ 6.62 (br, Al-CH_3), 30.87 (CH_3), 32.86 (CMe_3), 108.05 (CH), 173.29 ($\text{C-}t\text{Bu}$) ppm.

$\text{MS}(\text{EI})$: m/z (%), 477 ($(\text{M}^+ - \text{Me})$, 100).

Elemental analysis for (44 % **1** C₂₆H₅₀Al₂N₄ (472.67) + 56 % **5** C₂₅H₄₇Al₂ClN₄ (493.09)):

	C	H	N
Calcd	63.10	10.07	11.58;
Found	62.9	10.1	11.7 %

4. 4. 6 Synthesis of $[(\eta^1, \eta^1\text{-3,5-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**6**)

Method 1: A solution of I₂ (1.02 g, 4.0 mmol) in toluene (30 mL) was added slowly to a solution of **1** (0.47 g, 1.0 mmol) in toluene (15 mL). The mixture was stirred for 15 h and then refluxed for additional 24 h. After filtration the solvent volume was reduced (to *ca.* 10 mL) and **6** crystallized at -26 °C as colorless crystals (0.65 g, 71 %).

Method 2: A solution of I₂ (1.02 g, 4.0 mmol) in toluene (30 mL) was added slowly to a solution of $[(\eta^1, \eta^1\text{-3,5-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**) (0.42 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 3 h at room temperature. The solvent was removed and the resulting brown residue extracted with *n*-hexane (3 x 10 mL) and **6** crystallized at -26 °C to afford colorless crystals (0.77 g, 84 %).

Melting point: 256 - 257 °C.

¹H-NMR (200.130 MHz, C₆D₆): δ 1.51 (s, 36 H, CH₃), 6.42 (s, 2 H, CH) ppm.

¹³C-NMR (125.758 MHz, C₆D₆): δ 31.46 (CH₃), 33.81 (CMe₃), 114.27 (CH), 179.03 (C-*t*Bu) ppm.

²⁷Al-NMR (65.170 MHz, C₆D₆): δ 62.3 ppm.

MS(EI) *m/z* (%): 905 ((M⁺ - Me), 3), 793 ((M⁺ - I), 100).

Elemental analysis for $C_{22}H_{38}Al_2I_4N_4$ (920.15):

	C	H	N
Calcd	28.72	4.16	6.09;
Found	29.2	4.3	6.1 %

4. 4. 7 Synthesis of $[(\eta^2\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_3\text{Al}]$ (**7**)

$[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})(\mu\text{-AlH}_2)]_2$ (**8**) (0.42 g, 1.0 mmol) and $\text{H}(3,5\text{-}t\text{Bu}_2\text{pz})$ (0.72 g, 4.0 mmol) were dissolved in toluene (50 mL) and the solution was stirred at room temperature for 15 h until elimination of H_2 ceased. The solvent was removed under reduced pressure (0.01 mbar). The residue was extracted with *n*-hexane (4 x 10 mL) and **7** crystallized at $-26\text{ }^\circ\text{C}$ (1.05 g, 93 %).

Melting point: $200\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 1.35 (s, 18 H, CH_3), 6.13 (s, 1 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.130 MHz, C_6D_6): δ 30.94 (CH_3), 32.19 (CMe_3), 101.11 (CH), 162.25 ($\text{C-}t\text{Bu}$) ppm.

MS(EI): m/z (%), 564 (M^+ , 100), 549 ($(\text{M}^+ - \text{Me})$, 20).

Elemental analysis for $C_{33}H_{57}AlN_6$ (564.83):

	C	H	N
Calcd	70.17	10.17	14.88;
Found	70.8	10.3	14.9 %

4. 4. 8 Synthesis of $[(\eta^1, \eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz})_2(\mu\text{-AlH}_2)]_2$ (**8**)

To a stirred solution of $\text{H}(t\text{Bu}_2\text{pz})$ (0.36 g, 2.0 mmol) in toluene (50 mL) $\text{AlH}_3 \cdot \text{NMe}_3$ (4.0 mL of a 0.80 M solution in C_6H_6 , 3.2 mmol) was added slowly at 50 °C with evolution of H_2 . The mixture was stirred for 3 h at 50 °C and for 15 h at room temperature. The solvent was removed and the crude product dried under reduced pressure for at least 6 h to afford **8** as a white powder (0.38 g, 91 %). Alternatively, the crude product was recrystallized from toluene at -26 °C (0.31 g, 76 %).

Melting point: 194 - 196 °C.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 1.44 (s, 36 H, CH_3), 5.4 (very br, s, $W_{1/2} = 144$ Hz, 4 H, Al-H), 6.14, (s, 2 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ 30.75 (CH_3), 32.79 (CMe_3), 104.11 (CH), 167.26 ($\text{C-}t\text{Bu}$) ppm.

MS(EI) m/z (%): 415 ($(\text{M}^+ - \text{H})$, 100).

IR (KBr, nujol mull): $\tilde{\nu}_{\text{Al-H}} = 1871$ (m), 1921 (m) cm^{-1} .

Elemental analysis for $\text{C}_{22}\text{H}_{42}\text{Al}_2\text{N}_4$ (416.56):

	C	H	Al	N
Calcd	63.43	10.17	12.95	13.45;
Found	63.1	10.1	12.8	13.4 %

4. 4. 9. Synthesis of $[(\eta^1, \eta^1\text{-}t\text{Bu}_2\text{pz})_4(\mu_3\text{-O})_2(\mu\text{-AlH})_4]$ (**9**)

A solution of **8** (0.83 g, 2.0 mmol) in dry dioxane (50 mL) was stirred for 5 d at room temperature. The solution was filtered through celite. The filtrate was reduced in volume to about 10 mL and compound **9** was isolated as colorless crystals at room

temperature (3 - 4 weeks, yield: 15 - 25 %). Single crystals suitable for X-ray diffraction analysis were obtained from dioxane at room temperature.

Melting point: 240 - 243 °C (dec.).

$^1\text{H-NMR}$ (200.130 MHz, CDCl_3): δ 1.32 (s, 72 H, CH_3), 4.8 (very br, s, $W_{1/2} = 80$ Hz, 4 H, Al- H), 5.80 (s, 4 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, CDCl_3): δ 31.19 (CH_3), 32.29 (CMe_3), 101.09 (CH), 163.31 ($\text{C-}t\text{Bu}$) ppm.

MS(EI): m/z (%), 860 (M^+ , 100).

An elemental analysis for $\text{C}_{56}\text{H}_{104}\text{Al}_4\text{N}_8\text{O}_8$ incl. dioxane (1125.39) was not available.

4. 4. 10 Synthesis of $[(\eta^1\text{-3,5-}t\text{Bupz})_2(\mu\text{-S})(\mu\text{-AlH})_2]$ (**10**)

To equivalent amounts of **8** (0.83 g, 2.0 mmol) and sulfur (0.064 g, 2.0 mmol, dried before use) toluene and THF (50 mL, 9:1) were added and the suspension was stirred at 50 °C for 15 h. The resulting solution was filtered through celite and the filtrate was concentrated to about 10 mL. THF (2 mL) was added to the filtrate to isolate **10** at room temperature as colorless crystals (0.52 g, 58 %).

Melting point: > 230 °C (dec.).

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 1.33 (s, 36 H, CH_3), 5.6 (very br, 2 H, Al- H), 5.97 (s, 2 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ 31.17 (CH_3), 32.40 (CMe_3), 102.25 (CH), 165.30 ($\text{C-}t\text{Bu}$) ppm.

MS(EI): m/z (%) 446 (M^+ , 98), 445 ($(\text{M}^+ - \text{H})$, 100).

Elemental analysis for C₂₂H₄₀Al₂N₄S (446.60):

	C	H	N
Calcd	59.17	9.03	12.54;
Found	59.3	9.1	12.5 %

4. 4. 11 Synthesis of [(η^1, η^1 -3,5-*t*Bu₂pz)₂(μ -Se)(μ -AlH)₂] (**11**)

To equivalent amounts of **8** (0.83 g, 2.0 mmol) and grey Se (0.16 g, 2.0 mmol, used as received), toluene (50 mL) was added and the suspension was refluxed for 2 - 3 h until the grey selenium had disappeared. The resulting solution was filtered through celite and concentrated to about 10 mL to afford colorless crystals of **11** at 4 °C (0.61 g, 62 %).

Melting point: 272 °C.

¹H-NMR (200.130 MHz, C₆D₆): δ 1.33 (s, 36 H, CH₃), 5.7 (very br, s, 2 H, Al-H), 5.98 (s, 2 H, CH) ppm.

¹³C-NMR (125.758 MHz, C₆D₆): δ 31.08 (CH₃), 32.45 (CMe₃), 102.57 (CH), 165.25 (C-*t*Bu) ppm.

MS(EI): *m/z* (%), 494 (M⁺, 80), 491 ((M⁺ - 3 H), 100).

Elemental analysis for C₂₂H₄₀Al₂N₄Se (493.50):

	C	H	Al	N	Se
Calcd	53.54	8.17	10.93	11.35	16.00;
Found	54.0	8.1	10.5	11.4	16.5 %

4. 4. 12 Synthesis of $[(\eta^1, \eta^1\text{-3,5-}t\text{Bu}_2\text{pz})_2(\mu\text{-Te})(\mu\text{-AlH})_2]$ (**12**)

To equivalent amounts of **8** (0.83 g, 2.0 mmol) and Te (0.26 g, 2.0 mmol, used as a black powder as received), toluene (50 mL) was added and the suspension was refluxed for 4 d until most of the Te had disappeared. The solution was filtered through celite and concentrated to about 10 mL to give **12** as colorless crystals at 4 °C (0.58 g, 54 %).

Melting point: 250 - 251 °C.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 1.35 (s, 36 H, CH_3), 5.7 (very br, s, 2 H, Al-H), 5.98 (s, 2 H, CH) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ 30.94 (CH_3), 32.58 (CMe_3), 103.24 (CH), 165.05 (C- $t\text{Bu}$) ppm.

MS(EI): m/z (%), 542 (M^+ , 100).

Elemental analysis for $\text{C}_{22}\text{H}_{40}\text{Al}_2\text{N}_4\text{Te}$ incl. 0.85 toluene (542.14 + 0.85 toluene):

	C	H	N
Caclcd	52.88	7.38	8.83;
Found	54.2	7.6	8.8 %

4. 4. 13 $[(\mu, \eta^1, \eta^1\text{-3,5-}t\text{Bu}_2\text{pz})_2(\eta^1\text{-3,5-}t\text{Bu}_2\text{pz})_2(\mu_3\text{-O})(\mu\text{-AlH})_3] \cdot 2\text{THF}$ (**13**)

Method 1: To a stirred solution of **8** (2.08 g, 5.0 mmol) in dioxane (50 mL), water (0.036 mL, 2.0 mmol) in dioxane (100 mL) was added slowly (over 5 h) at 70 °C with evolution of H_2 . The solution was filtered through celite. The filtrate was reduced in volume (to 15 mL) and **13** crystallized at room temperature as colorless crystals (0.84 g, 41 %).

Method 2: The procedure was in an analogous manner as method 1 except that THF was used as a solvent and **9** crystallized at -26 °C (1.30 g incl. 2 THF, 54 %). Single crystals suitable for X-ray diffraction analysis were obtained from THF at -26 °C.

Melting point: 188°C.

¹H-NMR (200.130 MHz, THF-*d*₈): δ (η^1, η^1 -3,5-*t*Bu₂pz): 1.24 (s, 36 H, C(6)-C(CH₃)₃), 5.88 (s, 2 H, C(5)H); δ (η^1 -3,5-*t*Bu₂pz): 1.34 (s, 18 H, C(1)-(CH₃)₃), 1.5 (br, s, $W_{1/2}$ = 33 Hz, 18 H, C(3)-(CH₃)₃), 4.5 (very br, s, $W_{1/2}$ = 90 Hz, 3 H, Al-H), 6.09 (s, 2 H, C(2)H) ppm.

¹³C-NMR (125.758 MHz, THF-*d*₈): δ (η^1, η^1 -3,5-*t*Bu₂pz): 31.53 (C(62)), 32.63 (C(61)), 99.42 (C(5)), 162.67 (C(6)); δ (η^1 -3,5-*t*Bu₂pz): 31.1 (br, C(32)), 31.2 (br, C(31)), 31.46 (C(12)), 33.01 (C(11)), 103.64 (C(2)H), 164.38 (C(1, 3)) ppm.

MS(EI) *m/z* (%): 815 ((M⁺ - H), 100), 759 ((M⁺ - *t*Bu), 35).

IR (KBr, nujol mull): $\tilde{\nu}_{\text{Al-H}} = 1874$ (m), 1895 (m), 1941 (m) cm⁻¹.

Elemental analysis for C₄₄H₇₉Al₃N₈O (817.10):

	C	H	N
Calcd	64.71	9.68	13.71;
Found	65.0	9.6	12.3 %

4. 4. 14 Synthesis of $[(\eta^1\text{-3,5-}t\text{Bu}_2\text{pz})_2\{\mu\text{-Al}(\text{C}\equiv\text{CPh})_2\}_2]$ (**14**)

Excess HC≡CPh (1.8 mL, 16 mmol) was added to a solution of **8** (0.83 g, 2.0 mmol) in toluene (50 mL). The mixture was stirred for 5 h at 50 °C and then for 2 h at room temperature. After removal of the volatiles the residue was washed with cold pentane (3 × 7 mL) to yield **14** (0.96 g, 59 %). Single crystals suitable for X-ray diffraction analysis were obtained from toluene/hexane (5:1) at -26 °C.

Melting point: 212 °C.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 1.72 (s, 18 H, CH_3), 6.44 (s, 1 H, CH), 6.91 - 7.40 (m, 10 H, Ph-H) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ 31.46 (CH_3), 33.38 (CMe_3), 102.9 (br, s, Al-C), 108.31 (C-Ph), 108.42 (CH), 125.35, 127.78, 128.31, 132.04 (Ph-C), 174.54 ($\text{C-}t\text{Bu}$).

MS(EI) : m/z (%), 816 (M^+ , 100) ppm.

$\text{IR (KBr, nujol mull)}$: $\tilde{\nu} = 691$ (s), 756 (s), 1596 (s), 2129 (m), 2143 (m) cm^{-1} .

Elemental analysis for $\text{C}_{54}\text{H}_{58}\text{Al}_2\text{N}_4$ (817.04):

	C	H	N
Calcd	79.38	7.16	6.86;
Found	79.2	7.4	6.8 %

4. 4. 15 Synthesis of [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}^{\prime}\text{-CH=C(SiMe}_3\text{)}\}\text{Al(C}\equiv\text{CSiMe}_3\text{)}_2$] (**15**)

Excess $\text{HC}\equiv\text{CSiMe}_3$ (2.0 mL, 14 mmol) was added to a solution of **8** (0.83 g, 2.0 mmol) in toluene (50 mL). The mixture was stirred under reflux for 1.5 h and then for 2 h at room temperature. Volatiles were removed and **15** was isolated in hexane as white crystals at -26 °C (1.0 g, 51 %). Single crystals suitable for X-ray diffraction analysis were obtained from THF at -26 °C.

Melting point: 133 °C.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 0.13 (s, 18 H, $\equiv\text{CSi(CH}_3\text{)}_3$), 0.44 (s, 9 H, $\text{Si(CH}_3\text{)}_3$), 0.81 (s, 9 H, $\text{C3-C(CH}_3\text{)}_3$), 1.56 (s, 9 H, $\text{C1-C(CH}_3\text{)}_3$), 5.79 (s, 1 H, C2-H), 7.42 (s, 1 H, C44-H) ppm.

^{13}C -NMR (125.758 MHz, C_6D_6): δ -0.08 (Si1-C), 0.29 (Si2(3)-C), 29.52 (C11,12,13), 30.79 (C31,32,33), 31.34 (C30), 32.91 (C10), 103.80 (C44), 116.35 (Si2-C \equiv), 125.40 (br, Al-C \equiv), 141.80 (br, Al-C=), 134.62 (C2), 152.00 (C1), 163.08 (C3) ppm.

^{29}Si -NMR (99.362 MHz, C_6D_6): δ -21.5 (Si (2, 3)), -5.7 (Si (1)) ppm.

IR (KBr, nujol mull): 618 (s), 857 (s), 955 (s), 1079 (vs), 1941 (s), 2075 (m), 3041 (m) cm^{-1} .

MS(EI): m/z (%) 498 (M^+ , 20), 441 ($(\text{M}^+ - t\text{Bu})$, 100).

Elemental analysis for $\text{C}_{26}\text{H}_{47}\text{AlN}_2\text{Si}_3$ (498.91):

	C	H	N
Calcd	62.59	9.50	5.61;
Found	63.3	9.5	5.8 %

4. 4. 16 Synthesis of $[(\eta^1, \eta^1\text{-3,5-}t\text{Bupz})_2(\mu\text{-S})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (**16**)

An excess of phenylacetylene (0.67 mL, 6.0 mmol) was added slowly to a solution of $[(\eta^1, \eta^1\text{-3,5-}t\text{Bupz})_2(\mu\text{-S})(\mu\text{-AlH})_2]$ (**10**) (0.89 g, 2.0 mmol) in toluene (40 mL) via syringe and stirred overnight at 50 °C. The solution was allowed to cool to room temperature and the volatiles removed under reduced pressure (0.01 mbar). The residue was washed with cold pentane (2 x 8 mL) to give the white solid of **16** (0.83 g, 64 %). Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from toluene at room temperature.

Melting point: 149 - 151 °C.

^1H -NMR (200.130 MHz, CDCl_3): δ 1.58 (s, 36 H, CH_3), 5.97 (s, 2 H, CH), 7.32 - 7.50 (m, 10 H, Ph- H) ppm.

^{13}C -NMR (125.758 MHz, CDCl_3): δ 31.47 (CH_3), 32.40 (CMe_3), 102.93 (CH), 109.20 (br, Al-C), 112.00 (s, CPh), 123.99, 128.40, 131.58, 131.80 (Ph-C), 165.58 (C-*t*Bu) ppm.

MS(EI) m/z (%): 646 (M^+ , 100).

IR (KBr, nujol mull): 408(vs), 614(vs), 761(vs), 527(vs), 819(vs), 1028(vs), 1049(vs), 1217(vs), 1251(vs), 1320(s), 1365 (vs), 1465(vs) 1488(vs), 1519(vs), 1595(m), 2140(vs) cm^{-1} .

Elemental analysis for $\text{C}_{38}\text{H}_{48}\text{Al}_2\text{N}_4\text{S}$ (646.84):

	C	H	N
Calcd	70.56	7.48	8.66;
Found	69.9	7.5	8.6 %

4. 4. 17 Synthesis of $[(\eta^1, \eta^1\text{-3,5-}i\text{Bupz})_2(\mu\text{-Se})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (**17**)

An excess of phenylacetylene (0.67 mL, 6.0 mmol) was slowly added to a solution of $[(\eta^1, \eta^1\text{-3,5-}i\text{Bu}_2\text{pz})_2(\mu\text{-Se})(\mu\text{-AlH})_2]$ (**11**) (1.39 g, 2.0 mmol) in toluene (40 mL) via syringe and stirred at 60 °C for 2 h. Volatiles were removed under reduced pressure (0.01 mbar) and the resulting residue washed with cold pentane (2 x 8 mL) to afford a white solid **17** (0.85 g, 61 %). Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from toluene at room temperature.

Melting point: 172 °C.

^1H -NMR (200.130 MHz, CDCl_3): δ 1.58 (s, 36 H, CH_3), 5.98 (s, 2 H, CH), 7.30 - 7.50 (m, 10 H, Aryl-H) ppm.

^{13}C -NMR (125.758 MHz, CDCl_3): δ 31.47 (CH_3), 32.46 (CMe_3), 101.50 (br, Al-C), 103.25 (CH), 112.41 (C-Ph), 124.01, 128.27, 128.38, 131.52 (*Ph*-C), 165.57 (C-*t*Bu) ppm.

MS(EI) m/z (%): 694 (M^+ , 30), 613 ($\text{M}^+ - \text{H}_2\text{Se}$, 100).

IR (KBr, nujol mull): 497(m), 610(m), 814(m), 1207(m), 1261(m), 1518(m), 2137(s) cm^{-1} .

Elemental analysis for $\text{C}_{38}\text{H}_{48}\text{Al}_2\text{N}_4\text{Se}$ (693.74):

	C	H	N
Calcd	65.79	6.97	8.08;
Found	66.3	6.7	8.1 %

4. 4. 18 Synthesis of $[(\eta^1, \eta^1\text{-3,5-}i\text{Bupz})_2(\mu\text{-Te})(\mu\text{-Al-C}\equiv\text{CPh})_2]$ (**18**)

An excess of phenylacetylene (0.35 mL, 3.0 mmol) was added slowly to a solution of $[(\eta^1, \eta^1\text{-3,5-}i\text{Bu}_2\text{pz})_2(\mu\text{-Te})(\mu\text{-AlH})_2]$ (**12**) (0.54 g, 1.0 mmol) in toluene (50 mL) via syringe and stirred overnight at room temperature. Volatiles were removed under reduced pressure (0.01 mbar). Finally, the residue was washed with cold pentane (2 x 8 mL) and **18** recrystallized from toluene at room temperature to give a crystalline solid (0.43 g, 57.8 %).

Melting point: 216 °C (dec.).

^1H -NMR (200.130 MHz, CDCl_3): δ 1.59 (s, 36 H, CH_3), 6.00 (s, 2 H, CH), 7.30 - 7.50 (m, 10 H, Ph-*H*) ppm.

^{13}C -NMR (125.758 MHz, CDCl_3): δ 31.49 (CH_3), 32.59 (CMe_3), 102.8 (br, Al-C), 103.92 (CH), 113.00 (C-Ph), 124.11, 128.19, 128.32, 131.40 (*Ph*-C), 165.43 (C-*t*Bu) ppm.

MS (EI) m/z (%): 744 (M^+ , 100).

IR (KBr, nujol mull): 429(s), 492(s), 609(s), 759(s), 818(vs), 1027(vs), 1065(s), 1215(s), 1365(s), 1487(s), 1517(vs), 2135(vs) cm^{-1} .

Elemental analysis for $\text{C}_{38}\text{H}_{48}\text{Al}_2\text{N}_4\text{Te}$ (742.38):

	C	H	N
Calcd	61.48	6.52	7.55;
Found	62.3	6.5	7.9 %

4. 4. 19 Synthesis of [$\{3,5\text{-}i\text{Bu}_2\text{pz-N}^2\text{-CH=C(SiMe}_3\}\text{AlCl}_2$] (**19**)

Method 1: To a solution of **3** (5.54 g, 10.0 mmol) in toluene (50 mL) $\text{HC}\equiv\text{CSiMe}_3$ (3.2 mL, 22.5 mmol) was added slowly via syringe at room temperature. The solution was refluxed for 2 h and then volatiles removed in vacuo. The resulting residue was washed with cold *n*-pentane ($-20\text{ }^\circ\text{C}$, 2 x 5 mL) to give **19** as a white powder (7.18 g, 96 %).

Method 2: To a suspension of CuCl (0.40 g, 4.0 mmol) in toluene (20 mL), a solution of **15** (1.0 g, 2.0 mmol) in THF (30 mL) was added slowly at room temperature. The suspension was stirred for 15 h at $50\text{ }^\circ\text{C}$ in the dark. The yellow solution was filtered through celite and the solvent was removed in vacuo. The resulting residue was washed with cold pentane to afford **19** as a white powder (0.32 g, 41 %). Single crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at $4\text{ }^\circ\text{C}$.

Melting point: $196\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 0.35 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.84 (s, 9 H, $\text{C}(3)\text{-C}(\text{CH}_3)_3$), 1.35 (s, 9 H, $\text{C}(1)\text{-C}(\text{CH}_3)_3$), 5.78 (s, 1 H, $\text{C}(2)\text{H}$), 7.48 (s, 1 H, $=\text{C}(4)\text{H}$) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ -0.4 (Si-C), 29.5 (C12), 30.6 (C32), 31.4 (C31), 33.1 (C11), 104.8 (C4), 135.8 (C2), 138.1 (br, Al-C(5)=), 153.1 (C1), 164.5 (C3) ppm.

^{29}Si -NMR (99.362 MHz, C_6D_6): δ -6.4 ppm.

MS(EI) m/z (%): 374 (M^+ , 15), 359 ($(\text{M}^+ - \text{Me})$, 100).

Elemental analysis for $\text{C}_{16}\text{H}_{29}\text{AlCl}_2\text{N}_2\text{Si}$ (375.38):

	C	H	N
Calcd	51.19	7.79	7.46;
Found	50.7	7.6	7.3 %

4. 4. 20 Synthesis of [$\{3,5\text{-}i\text{Bu}_2\text{pz-N}^{\ominus}\text{-CH=C}(\text{SiMe}_3)\}\text{AlCl}(\eta^2\text{-}3,5\text{-}i\text{Bu}_2\text{pz})$] (**20**)

After the suspension of **19** (0.75 g, 2.0 mmol) and $\text{K}(3,5\text{-}i\text{Bu}_2\text{pz})$ (0.44 g, 2.0 mmol) in toluene (40 mL) was stirred for 15 h the solvent was removed. The resulting residue was extracted with *n*-hexane (3 x 10 mL). The solvent was reduced in volume to 10 mL and **20** crystallized at room temperature (0.96 g, 93 %). Single crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at room temperature.

Melting point: 189 - 190 °C.

^1H -NMR (200.130 MHz, C_6D_6): δ 0.25 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 0.84 (s, 9 H, $\text{C}(3)\text{-C}(\text{CH}_3)_3$), 1.04 (s, 9 H, $\text{C}(1)\text{-C}(\text{CH}_3)_3$), 1.39 (s, 18 H, $\text{C}(6,8)\text{-C}(\text{CH}_3)_3$); 5.85 (s, 1 H, $\text{C}(2)\text{H}$), 6.10 (s, 1 H, $\text{C}(7)\text{H}$), 7.62 (s, 1 H, $\text{C}(4)\text{H}$) ppm.

^{13}C -NMR (125.758 MHz, C_6D_6): δ -0.48 (Si-C), 29.68 ($\text{C}(12)$), 30.08 ($\text{C}(62,82)$), 31.07 ($\text{C}(32,33,34)$), 31.42 ($\text{C}(31)$), 32.23 ($\text{C}(61,81)$), 32.70 ($\text{C}(11)$), 100.65 ($\text{C}(7)$), 103.49 ($\text{C}(4)$), 134.06 ($\text{C}(2)$), 140.51 (br, Al-C=), 151.43 ($\text{C}(1)$), 161.50 ($\text{C}(6)$), 162.19 ($\text{C}(3)$) ppm.

^{29}Si -NMR (99.362 MHz, C_6D_6): δ -6.3 ppm.

MS(EI) m/z (%): 518 (M^+ , 100), 503 ($(\text{M}^+ - \text{Me})$, 35);

Elemental analysis for $\text{C}_{27}\text{H}_{48}\text{AlClN}_4\text{Si}$ (519.22):

	C	H	N
Calcd	62.46	9.32	10.79;
Found	62.0	9.4	10.6 %

4. 4. 21 Synthesis of $[\{3,5\text{-}i\text{Bu}_2\text{pz-N}^{\prime}\text{-CH=C(SiMe}_3)\}\text{Al}(\eta^1\text{-}3,5\text{-}i\text{Bu}_2\text{pz})(\eta^2\text{-}3,5\text{-}i\text{Bu}_2\text{pz})]$ (**21**)

In a procedure similar to the synthesis of **20**, **19** (0.75 g, 2.0 mmol) and two equivalents of K(3,5-*t*Bu₂pz) (0.88 g, 4.0 mmol) were reacted in toluene (40 mL) and then **21** crystallized from ca. 15 mL *n*-hexane at 4 °C to give colorless crystals (1.10 g, 83 %). Single crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at room temperature.

Melting point: 187 °C.

¹H-NMR (200.130 MHz, C₆D₆): δ 0.15 (s, 9 H, Si(CH₃)₃), 1.10 (s, 9 H, C(3)-C(CH₃)₃), 1.12 (s, 9 H, C(1)-C(CH₃)₃), 1.37 (s, 36 H, C(6,8,9,11)-C(CH₃)₃), 5.88 (s, 1 H, C(2)H), 6.17 (s, 2 H, C(7,10)H), 7.74 (s, 1 H, =C(4)H) ppm.

¹³C-NMR (125.758 MHz, C₆D₆): δ 0.06 (Si-C), 29.73 (C(12)), 30.31 (C(62, 82, 92, 112)), 32.26 (C(61, 81, 91, 111)), 31.32 (C(32)), 31.33 (C(31)), 32.64 (C(11)), 100.31 (C(7)), 103.57 (C(4)), 135.40 (C(2)), 142.00 (br, Al-C=), 150.21 (C(1)), 161.18 (C(6, 8, 9)), 161.92 (C(3)) ppm.

²⁹Si-NMR (99.362 MHz, C₆D₆): δ -4.9 ppm.

MS(EI) *m/z* (%): 662 (M⁺, 35), 483 ((M⁺ - *t*Bu₂pz), 100);

Elemental analysis for C₃₈H₆₇AlN₆Si (663.05):

C	H	N
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Calcd	68.84	10.18	12.67;
Found	68.5	10.2	12.1 %

4. 4. 22 Synthesis of [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3\}\text{H}$] (**22**)

0.036 mL water (2.0 mmol) in THF (10 mL) were added slowly to a solution of compound **15** (1.0 g, 2.0 mmol) or **19**, 0.75 g, 2.0 mmol) in THF (30 mL) at room temperature. After stirring for 15 h at room temperature, the solvent was removed in vacuo. The resulting residue was sublimed at 90 °C in high vacuum (0.01 mbar) to afford the colorless solid **22** (0.39 g, 70 %).

Melting point: 173 °C.

$^1\text{H-NMR}$ (200.130 MHz, C_6D_6): δ 0.12 (s, 9 H, $\text{Si}(\text{CH}_3)_3$), 1.17 (s, 9 H, $\text{C}(3)\text{-C}(\text{CH}_3)_3$), 1.44 (s, 9 H, $\text{C}(1)\text{-C}(\text{CH}_3)_3$); 6.01 (s, 1 H, $\text{C}(2)\text{H}$), 6.77 (d, $^2J_{\text{HH}} = 16.3$ Hz, 1 H, $\text{C}(5)\text{H}$), 7.48 (d, $^2J_{\text{HH}} = 16.3$ Hz 1 H, $=\text{C}(4)\text{H}$) ppm.

$^{13}\text{C-NMR}$ (125.758 MHz, C_6D_6): δ -1.28 ($\text{Si-C}(16)$), 30.02 ($\text{C}(12, 13, 14)$), 30.32 ($\text{C}(11)$), 30.88 ($\text{C}(32, 33, 34)$), 33.08 ($\text{C}(31)$), 101.19 ($\text{C}(4)$), 111.16 ($\text{C}(5)$), 135.71 ($\text{C}(2)$), 150.78 ($\text{C}(1)$), 161.39 ($\text{C}(3)$) ppm.

MS(EI) m/z (%): 278 (M^+ , 20), 263 ($(\text{M}^+ - \text{Me})$, 100).

Elemental analysis for $\text{C}_{16}\text{H}_{30}\text{N}_2\text{Si}$ (278.51):

	C	H	N
Calcd	69.00	10.86	10.06;
Found	70.4	11.0	10.3 %

4. 4. 23 Synthesis of [$\{3,5\text{-N-}t\text{Bu}_2\text{pz-N}'\text{-CH=C(SiMe}_3\}\text{AlMe}_2$] (**23**)

To the suspension of **19** (0.74 g, 2.0 mmol) in Et₂O (40 mL), LiMe (4 mL, 4 mmol) in Et₂O (20 mL) was added slowly at -78 °C. The solution was allowed to warm to room temperature and then stirred for 15 h. The solvent was removed and the resulting residue sublimed at 100 °C in high vacuum (0.01 mbar) to give a white powder mainly consisting of **23**. Pure **23** was obtained by recrystallization from hexane at -26 °C (0.46 g, 70 %). Crystals suitable for X-ray diffraction analysis were obtained from *n*-hexane at 4 °C.

Melting point: 157 °C.

¹H-NMR (200.130 MHz, C₆D₆): δ -0.15 (s, 6 H, Al-CH₃), 0.37 (s, 9 H, Si(CH₃)₃), 1.00 (s, 9 H, C(3)-C(CH₃)₃), 1.28 (s, 9 H, C(1)-C(CH₃)₃); 5.86 (s, 1 H, C(2)H), 7.63 (s, 1 H, =C(4)H) ppm.

¹³C-NMR (125.758 MHz, C₆D₆): δ -7.13 (br, s, Al-C(5)=), -0.93 (Al-CH₃), -0.013 (Si-C(16)), 29.71 (C(12, 13, 14)), 30.57 (C(11)), 31.42 (C(32, 33, 34)), 32.58 (C(31)), 103.17 (C(4)), 132.65 (C(2)), 150.67 (C(1)), 161.90 (C(3)) ppm.

MS(EI) *m/z* (%): 334 (M⁺, 10), 319 ((M⁺ - Me), 100).

Elemental analysis for C₁₈H₃₅AlN₂Si (334.55):

	C	H	N
Calcd	64.62	10.54	8.37;
Found	64.3	10.1	8.2 %

4. 4. 24 Synthesis of [**3,5-N-*t*Bu₂pz-N'-CH=C(SiMe₃)AlH₂**] (**24**)

To a suspension of LiAlH₄ (0.16 g, 4.2 mmol) in THF (30 mL) a solution of **19** (0.74 g, 2.0 mmol) in THF (20 mL) was added slowly at -30 °C. The suspension was stirred for additional 15 h at room temperature and then filtered through celite. The solution was concentrated to *ca.* 8 mL and **24** crystallized as a white crystalline solid at -26 °C (0.35 g, 57 %).

Melting point: 134 °C.

¹H-NMR (200.130 MHz, THF-*d*₈): δ 0.14 (s, 9 H, Si-(CH₃)₃), 3.90 (br, s, 2 H, Al-H), 1.490 (s, 9 H, C(3)-C(CH₃)₃), 1.495 (s, 9 H, C(1)-C(CH₃)₃); 6.21 (s, 1 H, C(2)H), 7.60 (s, 1 H, =C(4)H) ppm.

¹³C-NMR (125.758 MHz, THF-*d*₈): δ -0.014 (Si-C(16)), 29.86 (C(12, 13, 14)), 30.24 (C(11)), 32.40 (C(32, 33, 34)), 32.78 (C(31)), 104.18 (C(4)), 135.10 (C(2)), 143.63 (br, Al-C=), 151.96 (C(1)), 162.25 (C(3)) ppm.

²⁹Si-NMR (99.362 MHz, THF-*d*₈): δ -6.2 ppm.

MS(EI) *m/z* (%): 306 (M⁺, 100), 291 ((M⁺ - Me), 70).

IR (KBr, Nujol mull): $\tilde{\nu}_{\text{Al-H}} = 1812$ (ms), 1780 (ms) cm⁻¹.

Elemental analysis for C₁₆H₃₁AlN₂Si (306.50):

	C	H	N
Calcd	62.70	10.19	9.14;
Found	61.8	9.9	9.0 %

4. 4. 25 Synthesis of [{3,5-*t*Bu₂pz-N'-CH=C(SiMe₃)}AlI₂] (25)

Method 1: To a solution of **23** (0.66 g, 2.0 mmol) in toluene (20 mL) I₂ (1.00 g, 4.0 mmol) in toluene (40 mL) was added slowly at room temperature. The solution was stirred for 15 h at room temperature and then refluxed for 12 h. The solution was filtered through celite and then concentrated to *ca.* 10 mL to give small colorless crystals at -26 °C (0.82 g, 73 %).

Method 2: To a suspension of **24** (0.61 g, 2.0 mmol) in toluene (20 mL) I₂ (1.00 g, 4.0 mmol) in toluene (40 mL) was added slowly and then stirred for 12 h at room temperature until the brown color disappeared. The solution was filtered through celite and the filtrate was concentrated to about 10 mL. **24** crystallized as a pale solid at -26 °C from the solution (0.49 g, 43 %).

Melting point: 192 °C.

¹H-NMR (200.130 MHz, C₆D₆): δ 0.42 (s, 9 H, Si(CH₃)₃), 0.82 (s, 9 H, C(3)-C(CH₃)₃), 1.43 (s, 9 H, C(1)-C(CH₃)₃), 5.81 (s, 1 H, C(2)H), 7.36 (s, 1 H, =C(4)H) ppm.

¹³C-NMR (125.758 MHz, C₆D₆): δ 0.09 (Si-C(16)), 29.44 (C(12, 13, 14)), 31.39 (C(11)), 31.44 (C(32, 33, 34)), 33.32 (C(31)), 104.97 (C(4)), ~128 (br, Al-C=, overlapped by C₆D₆ signals), 134.69 (C(2)), 153.49 (C(1)), 165.27 (C(3)) ppm.

²⁹Si-NMR (99.362 MHz, C₆D₆): δ -6.4 ppm.

MS(EI) *m/z* (%): 558 (M⁺, 4), 543 ((M⁺ - Me), 15), 431 ((M⁺ - I), 100).

Elemental analysis for C₁₆H₂₉AlI₂N₂Si (558.29):

	C	H	N
Calcd	34.42	5.24	5.02;
Found	33.8	5.1	5.2 %

4. 4. 26 Synthesis of [(AlH)₄(CH₂N*t*Bu)₄] (26)

To the solution of H₃Al·NMe₃ (15.0 mL, 0.8 M solution in toluene, 12.0 mmol) in toluene (30 mL) CN*t*Bu (1.4 mL, 12.4 mmol) was added via syringe at room temperature. The solution was refluxed for 0.5 h and the solvent of the red solution was removed under reduced pressure. The resulting residue was dried for 3 h in vacuum and then dissolved in warm toluene (10 mL) to afford colorless crystals of **26** at -26 °C within 2 h (1.02 g, 75 %). Single crystals suitable for X-ray diffraction analysis were obtained from toluene at room temperature.

Melting point: 261 °C.

¹H-NMR (500.130 MHz, C₆D₆): δ 1.4 (br, s, *W*_{1/2} = 60 Hz, 36 H, CH₃), 1.61 (d, ²*J*(H_aH_b) = 12.65 Hz, 4 H, Al-CH_b), 1.85 (d, ²*J*(H_bH_a) = 12.65 Hz, 4 H, Al-CH_a), 4.3 (very br, s, *W*_{1/2} = 550 Hz, 4 H, Al-*H*) ppm.

¹³C-NMR (125.130 MHz, [D₈]toluene, 90 °C): δ 27.6 (CH₃), 33.0 (br, Al-C), 57.5 (N-C(CH₃)₃) ppm.

²⁷Al-NMR (65.170 MHz, C₆D₆): δ 148.5 ppm.

IR (KBr, nujol mull): $\tilde{\nu}_{\text{Al-H}} = 1831$ (vs), 1858 (vs) cm⁻¹.

MS(EI) *m/z* (%): 451 ((M⁺ - H), 1), 395 ((M⁺ - *t*Bu), 100).

Elemental analysis for C₂₀H₄₈Al₄N₄ (452.55):

	C	H	N
Calcd	53.08	10.69	12.38;
Found	52.9	10.5	11.9 %

4. 4. 27 Synthesis of [(3,5-*t*Bu₂pz)₂(CH₂N*t*Bu)(AlH)₂] (27)

To a suspension of **8** (0.83 g, 2.0 mmol) in hexane (50 mL) CN*t*Bu (0.24 mL, 2.1 mmol) was added via syringe at room temperature. After stirring for 3 h the solvent of the clear solution was removed under reduced pressure to afford the colorless solid **27** (0.91 g, 91 %). Single crystals suitable for X-ray diffraction analysis were obtained from Et₂O at -26 °C.

Melting point: 176 °C.

¹H-NMR (200.130 MHz, C₆D₆): δ 1.39 (s, 18 H, C(11,41)-CH₃), 1.46 (s, 9 H, C(51)-CH₃), 1.52 (s, 18 H, C(21,31)-CH₃), 6.08 (s, 2 H, C(6,7)H), 2.30 (s, 2 H, NC-H) ppm.

¹³C-NMR (125.758 MHz, C₆D₆): δ 28.5 (br, Al-C(5)), 30.5 (C(51)C), 31.1 (C(2,3)C-CH₃), 31.0 (C(1,4)C-CH₃), 32.6 (C(2,3)C), 32.3 (C(1,4)C), 53.2 (C(51)), 102.0 (C(6,7)), 163.8 (C(1,4)), 165.2 (C(2,3)) ppm.

IR (KBr, nujol mull): $\tilde{\nu}_{\text{Al-H}} = 1887$ (ms), 1918 (ms) cm⁻¹.

MS(EI) *m/z* (%): 498 ((M⁺ - H), 10), 442 ((M⁺ - *t*Bu), 100).

Elemental analysis for $C_{27}H_{51}Al_2N_5$ (499.69):

	C	H	N
Calcd	64.90	10.29	14.02;
Found	63.9	10.2	13.5 %

5. Handling and Disposal of Wastes and Residual 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 wastes, respectively.
3. The heavy metal residues were dissolved in nitric acid and were stored in containers for heavy metal waste after neutralization.
4. Drying agents (KOH, CaCl₂, CaH₂) were hydrolyzed and disposed as basic wastes.
5. Metallic sodium used for drying solvents was collected and recycled.⁸⁹ 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 was disposed into the container for basic wastes.
7. The acid bath used for cleaning glassware was neutralized with Na₂CO₃ and the resulting NaCl solution was 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. Summary of Crystal Data for Compound 1

Empirical formula	C ₂₆ H ₅₀ Al ₂ N ₄
Formula weight	472.66
Temperature	203(2) K
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	$a = 9.3230(10) \text{ \AA}$ $b = 20.403(3) \text{ \AA}$ $c = 16.186(3) \text{ \AA}$
Volume, <i>Z</i>	3078.9(8) Å ³ , 4
Density (calculated)	1.020 Mg/m ³
Absorption coefficient	0.113 mm ⁻¹
<i>F</i> (000)	1040
Crystal size	0.6 x 0.6 x 0.5 mm ³
Range for data collection (θ)	3.71 - 25.04°
Limiting indices	-10 ≤ <i>h</i> ≤ 11, -24 ≤ <i>k</i> ≤ 24, -19 ≤ <i>l</i> ≤ 19
Reflections collected	5656
Independent reflections	2718 [<i>R</i> (int) = 0.0184]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2714 / 0 / 154
Goodness-of-fit on <i>F</i> ²	1.053
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0384, <i>wR</i> ₂ = 0.1027
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0469, <i>wR</i> ₂ = 0.1130
Largest difference peak and hole	0.211 and -0.192 e·Å ⁻³

Table 2. Summary of Crystal Data for Compound 3

Empirical formula	C ₂₂ H ₃₈ Al ₂ Cl ₄ N ₄
Formula weight	554.32
Temperature	203(2) K
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	$a = 13.171(3) \text{ \AA}$ $b = 17.706(4) \text{ \AA}$ $c = 12.870(2) \text{ \AA}$
Volume, <i>Z</i>	3001.3(11) Å ³ , 4
Density (calculated)	1.227 Mg/m ³
Absorption coefficient	0.470 mm ⁻¹
<i>F</i> (000)	1168
Crystal size	0.9 x 0.6 x 0.3 mm ³
Range for data collection (θ)	3.52 - 25.05°
Limiting indices	-15 ≤ <i>h</i> ≤ 15, -21 ≤ <i>k</i> ≤ 10, -15 ≤ <i>l</i> ≤ 15
Reflections collected	4438
Independent reflections	2655 [<i>R</i> (int) = 0.0564]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2651 / 0 / 152
Goodness-of-fit on <i>F</i> ²	1.052
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0427, w <i>R</i> ₂ = 0.1061
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0559, w <i>R</i> ₂ = 0.1242
Largest difference peak and hole	0.319 and -0.343 e·Å ⁻³

Table 3. Summary of Crystal Data for Compound 7

Empirical formula	C ₃₃ H ₅₇ AlN ₆
Formula weight	564.83
Temperature	133(2) K
Crystal system	Hexagonal
Space group	$P\bar{3}$
Unit cell dimensions	$a = 14.508(2) \text{ \AA}$ $b = 14.508(2) \text{ \AA}$ $c = 10.437(2) \text{ \AA}$
Volume, Z	1902.5(5) \AA^3 , 2
Density (calculated)	0.986 Mg/m ³
Absorption coefficient	0.080 mm ⁻¹
$F(000)$	620
Range for data collection (θ)	2.81 - 27.53°
Limiting indices	-18 ≤ h ≤ 9 0 ≤ k ≤ 18 0 ≤ l ≤ 13
Reflections collected	2917
Refinement method	Full-matrix least-squares on F^2
Independent reflections	2917 ($R(\text{int}) = 0.0000$)
Data / restraints / parameters	2917 / 0 / 129
Goodness-of-fit on F^2	1.287
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0717$ $wR_2 = 0.2244$
R indices (all data)	$R_1 = 0.0736$ $wR_2 = 0.2258$
Largest difference peak and hole	2.787 and -0.336 e· \AA^{-3}

Table 4. Summary of Crystal Data for Compound **9**

Empirical formula	C ₅₆ H ₁₀₄ Al ₄ N ₈ O ₈ incl. Dioxane
Formula weight	1125.39
Temperature	203(2)
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.202(5) \text{ \AA}$, $\alpha = 112.39(3)^\circ$ $b = 13.128(6) \text{ \AA}$, $\beta = 101.90(2)^\circ$ $c = 13.612(5) \text{ \AA}$, $\gamma = 96.936(13)^\circ$
Volume, Z	1608.7(12), 1
Density (calculated)	1.162
Absorption coefficient	0.127
$F(000)$	612
Crystal size	1.0 x 0.3 x 0.3 mm ³
Range for data collection (θ)	3.60 - 25.04°
Limiting indices	-21 ≤ h ≤ 12 -15 ≤ k ≤ 15 -16 ≤ l ≤ 16
Reflections collected	9401
Independent reflections	5673 ($R(\text{int}) = 0.0289$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5663 / 1 / 363
Goodness-of-fit on F^2	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0404$ $wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.0543$ $wR_2 = 0.1113$
Largest difference peak and hole	0.307 and -0.253 e ⁻ Å ⁻³

Table 5. Summary of Crystal Data for Compound **10**

Empirical formula	C ₂₂ H ₄₀ Al ₂ N ₄ S
Formula weight	446.60
Temperature	203(2) K
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 14.407(2) Å <i>b</i> = 11.0570(14) Å, <i>β</i> = 98.54(2) ° <i>c</i> = 16.506(3) Å
Volume, <i>Z</i>	2600.1(8) Å ³ , 4
Density (calculated)	1.141 Mg/m ³
Absorption coefficient	0.207 mm ⁻¹
<i>F</i> (000)	968
Crystal size	0.7 x 0.6 x 0.4 mm ³
Range for data collection (<i>θ</i>)	3.51 - 25.03°
Limiting indices	-17 ≤ <i>h</i> ≤ 17 -13 ≤ <i>k</i> ≤ 13 -19 ≤ <i>l</i> ≤ 19
Reflections collected	9761
Independent reflections	4581 (<i>R</i> (int) = 0.0258)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4576 / 1 / 283
Goodness-of-fit on <i>F</i> ²	1.047
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0301 <i>wR</i> ₂ = 0.0825
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0325 <i>wR</i> ₂ = 0.0870
Largest difference peak hole	0.263 and -0.183 e·Å ⁻³

Table 6. Summary of Crystal Data for Compound **11**

Empirical formula	C ₂₂ H ₄₀ Al ₂ N ₄ Se
Formula weight	493.39
Temperature	133(2) K
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 14.385(3) Å <i>b</i> = 11.035(2) Å, <i>β</i> = 98.90(3)° <i>c</i> = 16.522(3) Å
Volume, <i>Z</i>	2591.1(9) Å ³ , 6
Density (calculated)	1.265 Mg/m ³
Absorption coefficient	1.532 mm ⁻¹
<i>F</i> (000)	1040
Crystal size	0.5 x 0.5 x 0.5 mm ³
Range for data collection (<i>θ</i>)	2.23 - 26.37°
Limiting indices	-17 ≤ <i>h</i> ≤ 17 0 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 20
Reflections collected	5301
Independent reflections	5301 (<i>R</i> (int) = 0.0000)
Data / restraints / parameters	5301 / 0 / 282
Goodness-of-fit on <i>F</i> ²	1.125
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0415 <i>wR</i> ₂ = 0.1402
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0539 <i>wR</i> ₂ = 0.1474
Largest difference peak and hole	0.551 and -0.944 e·Å ⁻³

Table 7. Summary of Crystal Data for Compound **12**

Empirical formula	C ₂₉ H ₄₈ Al ₂ N ₄ Te incl. Toluene
Formula weight	634.27
Temperature	203(2) K
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 12.288(2) Å <i>b</i> = 15.592(3) Å, <i>β</i> = 106.295(14)° <i>c</i> = 18.031(3) Å
Volume, <i>Z</i>	3316.1(9) Å ³ , 4
Density (calculated)	1.270 Mg/m ³
Absorption coefficient	0.972 mm ⁻¹
<i>F</i> (000)	1312
Crystal size	0.4 x 0.4 x 0.3 mm ³
Range for data collected(<i>θ</i>)	3.51-25.02°
Limiting indices	-14 ≤ <i>h</i> ≤ 14 -17 ≤ <i>k</i> ≤ 18 -21 ≤ <i>l</i> ≤ 21
Reflections collected	7932
Independent reflections	5847 (<i>R</i> (int) = 0.0880)
Data / restraints / parameters	5834 / 0 / 346
Goodness-of-fit on <i>F</i> ²	1.062
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0389 <i>wR</i> ₂ = 0.0859
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0521 <i>wR</i> ₂ = 0.0991
Largest difference peak and hole	1.006 and -0.694 e·Å ⁻³

Table 8. Summary of Crystal Data for Compound **13**

Empirical formula	$C_{68}H_{127}Al_3N_8O_7$
Formula weight	1249.72
Temperature	200(2) K
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 15.312(10) \text{ \AA}$ $b = 26.90(4) \text{ \AA}, \beta = 109.53(2)^\circ$ $c = 19.7796 \text{ \AA}$
Volume, Z	$7680(12) \text{ \AA}^3, 4$
Density (calculated)	1.081 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
$F(000)$	2744
Crystal size	$1.0 \times 0.3 \times 0.3 \text{ mm}^3$
Range for data collection (θ)	$3.61 - 22.58^\circ$
Limiting indices	$-16 \leq h \leq 16 \quad -10 \leq k \leq 28 \quad -21 \leq l \leq 21$
Reflections collected	5817
Independent reflections	5035 ($R(\text{int}) = 0.0729$)
Data / restraints / parameters	5035 / 410 / 401
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0850 \quad wR_2 = 0.2057$
R indices (all data)	$R_1 = 0.1469 \quad wR_2 = 0.2575$
Largest difference peak and hole	0.450 and $-0.291 \text{ e} \cdot \text{\AA}^{-3}$

Table 9. Summary of Crystal Data for Compound 14

Empirical formula	C ₅₄ H ₅₈ Al ₂ N ₄
Formula weight	817.00
Temperature	133(2) K
Crystal system	monoclinic
Space group	<i>C2/c</i>
Unit cell dimensions	$a = 22.079(4) \text{ \AA}$ $b = 9.541(2) \text{ \AA}, \beta = 96.60(3)^\circ$ $c = 23.734(5) \text{ \AA}$
Volume, <i>Z</i>	4966.20(17) \AA^3 , 4
Density (calculated)	1.093 Mg/m ³
Absorption coefficient	0.096 mm ⁻¹
<i>F</i> (000)	1744
Crystal size	0.6 x 0.4 x 0.2 mm ³
Range for data collection (θ)	2.33 - 21.73°
Limiting indices	-21 ≤ <i>h</i> ≤ 21 -18 ≤ <i>k</i> ≤ 18 -22 ≤ <i>l</i> ≤ 22
Reflections collected	3145
Independent reflections	2924 (<i>R</i> (int) = 0.0553)
Data / restraints / parameters	2309 / 277 / 546
Goodness-of-fit on <i>F</i> ²	1.073
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0487 <i>wR</i> ₂ = 0.1059
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0674 <i>wR</i> ₂ = 0.1125
Largest difference peak and hole	0.253 and -0.238 e· \AA^{-3}

Table 10. Summary of Crystal Data for Compound **15**

Empirical formula	$C_{26}H_{47}AlN_2Si_3 \cdot C_4H_8O$
Formula weight	571.01
Temperature	133(2) K
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 12.261(3) \text{ \AA}$ $b = 16.424(3) \text{ \AA}, \beta = 103.02(3)^\circ$ $c = 20.151(4) \text{ \AA}$
Volume, Z	$3954(1) \text{ \AA}^3, 4$
Density (calculated)	0.959 Mg/m^3
Absorption coefficient	0.163 mm^{-1}
$F(000)$	1248
Crystal size(mm)	$0.5 \times 0.5 \times 0.15 \text{ mm}^3$
Range for data collection (θ)	$2.17 - 24.73^\circ$
Limiting indices	$-14 \leq h \leq 13 \quad 0 \leq k \leq 19 \quad 0 \leq l \leq 23$
Reflections collected	6909
Independent reflections	6650 ($R(\text{int}) = 0.0000$)
Data / restraints / parameters	6650 / 616 / 449
Goodness-of-fit on F^2	1.109
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0529 \quad wR_2 = 0.1244$
R indices (all data)	$R_1 = 0.0728 \quad wR_2 = 0.1351$
Largest difference peak and hole	0.312 and $-0.326 \text{ e} \cdot \text{\AA}^{-3}$

Table 11. Summary of Crystal Data for Compound **16**

Empirical formula	C ₅₂ H ₆₄ Al ₂ N ₄ S incl. Toluene
Formula weight	831.09
Temperature	203(2) K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 18.260(3) Å <i>b</i> = 15.835(7) Å, <i>β</i> = 115.590(12)° <i>c</i> = 18.652(4) Å
Volume, <i>Z</i>	4864(2) Å ³ , 4
Density (calculated)	1.135 Mg/m ³
Absorption coefficient	0.140 mm ⁻¹
<i>F</i> (000)	1784
Crystal size	0.5 x 0.4 x 0.3 mm ³
Range for data collection (<i>θ</i>)	3.53 - 25.03°
Limiting indices	-21 ≤ <i>h</i> ≤ 21 -12 ≤ <i>k</i> ≤ 18 -19 ≤ <i>l</i> ≤ 22
Reflections collected	9561
Independent reflections	8530 (<i>R</i> (int) = 0.0528)
Data / restraints / parameters	8491 / 0 / 546
Goodness-of-fit on <i>F</i> ²	1.075
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0563 <i>wR</i> ₂ = 0.1148
<i>R</i> indices	<i>R</i> ₁ = 0.0791 <i>wR</i> ₂ = 0.1415
Largest difference peak and hole	0.800 and -0.816 e·Å ⁻³

Table 12. Summary of Crystal Data for Compound **17**

Empirical formula	C ₅₂ H ₆₄ Al ₂ N ₄ Se incl.toluene
Formula weight	877.99
Temperature	203(2) K
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 18.291(3) Å <i>b</i> = 5.891(6) Å, <i>β</i> = 115.261(11)° <i>c</i> = 18.594(3) Å
Volume, <i>Z</i>	4888(2) Å ³ , 4
Density (calculated)	1.193 Mg/m ³
Absorption coefficient	0.842 mm ⁻¹
<i>F</i> (000)	1856
Crystal size	0.7 x 0.2 x 0.2 mm ³
Range for data collection (<i>θ</i>)	3.53 - 25.05°
Limiting indices	-21 ≤ <i>h</i> ≤ 21 -18 ≤ <i>k</i> ≤ 18 -22 ≤ <i>l</i> ≤ 22
Reflections collected	12675
Independent reflections	8620 (<i>R</i> (int) = 0.0553)
Data / restraints / parameters	8583 / 15 / 546
Goodness-of-fit on <i>F</i> ²	1.089
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0511 <i>wR</i> ₂ = 0.0992
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0813 <i>wR</i> ₂ = 0.1221
Largest difference peak and hole	0.824 and -0.750 e·Å ⁻³

Table 13. Summary of Crystal Data for Compound **19**

Empirical formula	C ₁₆ H ₂₉ AlCl ₂ N ₂ Si
Formula weight	375.38
Temperature	200(2) K
Crystal system	Monoclinic
Space group	<i>C2/c</i>
Unit cell dimensions	$a = 29.678(7) \text{ \AA}$ $b = 9.381(3) \text{ \AA}, \beta = 121.564(8)^\circ$ $c = 18.093(5) \text{ \AA}$
Volume, <i>Z</i>	4292(2) \AA^3 , 8
Density (calculated)	1.162 Mg/m ³
Absorption coefficient	0.398 mm ⁻¹
<i>F</i> (000)	1600
Crystal size	1.0 x 0.9 x 0.6 mm ³
Range for data collection (θ)	3.75 - 25.06°.
Limiting indices	-35 ≤ <i>h</i> ≤ 35, -11 ≤ <i>k</i> ≤ 11, -21 ≤ <i>l</i> ≤ 21
Reflections collected	8080
Independent reflections	3785 [<i>R</i> (int) = 0.0807]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3785 / 0 / 208
Goodness-of-fit on <i>F</i> ²	1.033
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0524, <i>wR</i> ₂ = 0.1359
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0574, <i>wR</i> ₂ = 0.1427
Largest difference peak and hole	0.403 and -0.542 e· \AA^{-3}

Table 14. Summary of Crystal Data for Compound **20**

Empirical formula	C ₂₇ H ₄₈ AlClN ₄ Si
Formula weight	519.21
Temperature	203(2) K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 10.2032(12) Å <i>b</i> = 21.065(6) Å, <i>β</i> = 105.961(12)° <i>c</i> = 15.849(3) Å
Volume, <i>Z</i>	3275.2(11) Å ³ , 4
Density (calculated)	1.053 Mg/m ³
Absorption coefficient	0.200 mm ⁻¹
<i>F</i> (000)	1128
Crystal size	0.7 x 0.5 x 0.3 mm ³
Range for data collection (<i>θ</i>)	3.57 - 25.03°.
Limiting indices	-12 ≤ <i>h</i> ≤ 12, -6 ≤ <i>k</i> ≤ 25, -18 ≤ <i>l</i> ≤ 18
Reflections collected	7790
Independent reflections	5764 [<i>R</i> (int) = 0.0643]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5764 / 0 / 322
Goodness-of-fit on <i>F</i> ²	1.035
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0593, <i>wR</i> ₂ = 0.1458
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0728, <i>wR</i> ₂ = 0.1573
Largest difference peak and hole	0.772 and -0.324 e·Å ⁻³

Table 15. Summary of Crystal Data for Compound **21**

Empirical formula	C ₃₈ H ₆₇ AlN ₆ Si
Formula weight	663.05
Temperature	200(2) K
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 19.888(5) Å <i>b</i> = 11.5236(18) Å, <i>β</i> = 98.828(19)° <i>c</i> = 18.789(3) Å
Volume, <i>Z</i>	4255.1(14) Å ³ , 4
Density (calculated)	1.035 Mg/m ³
Absorption coefficient	0.107 mm ⁻¹
<i>F</i> (000)	1456
Crystal size	0.9 x 0.4 x 0.3 mm ³
Range for data collection (<i>θ</i>)	3.52 - 25.03°.
Limiting indices	-5 ≤ <i>h</i> ≤ 23, -13 ≤ <i>k</i> ≤ 2, -22 ≤ <i>l</i> ≤ 22
Reflections collected	7510
Independent reflections	7496 [<i>R</i> (int) = 0.1458]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7496 / 0 / 437
Goodness-of-fit on <i>F</i> ²	1.050
Final <i>R</i> indices [<i>I</i> > 2 <i>σ</i> (<i>I</i>)]	<i>R</i> ₁ = 0.0642, <i>wR</i> ₂ = 0.1440
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0989, <i>wR</i> ₂ = 0.1708
Largest difference peak and hole	0.480 and -0.358 e·Å ⁻³

Table 16. Summary of Crystal Data for Compound **23**

Empirical formula	$C_{18}H_{35}AlN_2Si$
Formula weight	334.55
Temperature	200(2) K
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 29.890(24) \text{ \AA}$ $b = 9.478(10) \text{ \AA}, \beta = 122.44(3)^\circ$ $c = 18.256(20) \text{ \AA}$
Volume, Z	$4364.7(75) \text{ \AA}^3, 8$
Density (calculated)	1.018 Mg/m^3
Absorption coefficient	0.148 mm^{-1}
$F(000)$	1472
Crystal size	$1.0 \times 1.0 \times 0.2 \text{ mm}^3$
Range for data collection (θ)	$3.77 - 25.02^\circ$
Limiting indices	$-35 \leq h \leq 35, -11 \leq k \leq 11, -21 \leq l \leq 21$
Reflections collected	7698
Independent reflections	3849 [$R(\text{int}) = 0.0251$]
Data / restraints / parameters	3845 / 0 / 210
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0457, wR_2 = 0.1241$
R indices (all data)	$R_1 = 0.0515, wR_2 = 0.1327$
Largest difference peak and hole	0.532 and $-0.376 \text{ e} \cdot \text{\AA}^{-3}$

Table 17. Summary of Crystal Data for Compound **26**

Empirical formula	C ₂₀ H ₄₈ Al ₄ N ₄
Formula weight	452.54
Temperature	203(2) K
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 11.5689(13) Å <i>b</i> = 13.405(2) Å, <i>β</i> = 91.280(12)° <i>c</i> = 17.021(3) Å
Volume, <i>Z</i>	2639.0(6) Å ³ , 4
Density (calculated)	1.139 Mg/m ³
Absorption coefficient	0.190 mm ⁻¹
<i>F</i> (000)	992
Crystal size	0.8 x 0.6 x 0.4 mm ³
Range for data collection (<i>θ</i>)	3.51 - 23.99°.
Limiting indices	-13 ≤ <i>h</i> ≤ 13, -6 ≤ <i>k</i> ≤ 16, -11 ≤ <i>l</i> ≤ 19
Reflections collected	4202
Independent reflections	4133 [<i>R</i> (int) = 0.0558]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4133 / 6 / 281
Goodness-of-fit on <i>F</i> ²	1.049
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0406, w <i>R</i> ₂ = 0.1011
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0494, w <i>R</i> ₂ = 0.1084
Largest difference peak and hole	0.445 and -0.245 e·Å ⁻³

Table 18. Summary of Crystal Data for Compound **27**

Empirical formula	C ₂₉ H ₅₆ Al ₂ N ₅ O _{0.5} incl.0.5 Et ₂ O
Formula weight	536.75
Temperature	200(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.436(3) \text{ \AA}$, $\alpha = 78.954(18)^\circ$ $b = 12.007(3) \text{ \AA}$, $\beta = 99.003(11)^\circ$ $c = 15.275(4) \text{ \AA}$, $\gamma = 66.679(12)^\circ$
Volume, Z	1711.0(8) \AA^3 , 2
Density (calculated)	1.042 Mg/m ³
Absorption coefficient	0.110 mm ⁻¹
$F(000)$	590
Crystal size	0.5 x 0.5 x 0.5 mm ³
Theta range for data collection	3.51 - 25.11°.
Limiting indices	-12 ≤ h ≤ 12, -13 ≤ k ≤ 14, -13 ≤ l ≤ 18
Reflections collected	7007
Independent reflections	6051 [$R(\text{int}) = 0.0567$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6051 / 5 / 375
Goodness-of-fit on F^2	1.010
Final R indices [$I > \sigma 2(I)$]	$R_1 = 0.0486$, $wR_2 = 0.1117$
R indices (all data)	$R_1 = 0.0676$, $wR_2 = 0.1254$
Largest difference peak and hole	0.261 and -0.202 e· \AA^{-3}

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