A Bulky Chelating Diamidoaluminum Monohydride − Synthesis, Structure and Reactions with Me_3SnF and Heavy Group 16 Elements

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday

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The bulky chelating diamidoaluminum monohydride $[ArN(CH_2)_3NAr]AlH(NMe_3)$ (Ar = 2,6-$i$$Pr_2C_6H_3$; **1**) was prepared in excellent yield from the reaction of the diamine $ArNH(CH_2)_3HNAr$ with a small excess of $AlH_3{\cdot}NMe_3$ in toluene. Subsequent fluorination of **1** with Me_3SnF resulted in the formation of the aluminum monofluoride $[ArN(CH_2)_3NAr]AlF(NMe_3)$ (**2**). Reaction of **1** with elemental E (E = S, Se and Te) proceeded in toluene with heating to yield the aluminum chalcogenides $\{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2$ [E = S (**3**), Se (**4**), and Te (**5**)]. The structures of complexes **1**, **2** and **4** have been determined by X-ray diffraction analyses. Compounds **1** and **2** are well-separated monomers with a central aluminum atom in a tetrahedral environment. The diamide ligand $[ArN(CH_2)_3NAr]^{2-}$ chelates the Al atom to form a distorted six-membered AlN_2C_3 ring which features a boat conformation for **1** and a flattened chair conformation for **2**. Compound **4**, however, is a dimer with a central Al_2Se_2 core bearing an ideal four-membered planar ring and two six-membered AlN_2C_3 rings, both displaying a boat conformation. The latter two rings are arranged perpendicularly to the Al_2Se_2 core in a *trans* configuration. The IR spectra and ^1H NMR spectroscopic data of compounds **3**–**5** suggest that the migration of the hydrogen from selenium to one of the nitrogens at the diamide ligand is involved in the course of the reaction.

Introduction

Studies of aluminum hydrides have received considerable attention due to their scientific importance and numerous applications.[1] In recent years, much work has been devoted to aluminum hydrides of low aggregation, especially the monomeric forms. The synthesis of monomeric aluminum hydrides helps us to understand the reaction chemistry of surface-bound AlH_n groups formed during thin-film growth from organoaluminum sources.[2] Moreover, aluminum hydrides of low aggregation can be very effective precursors for preparing aluminum chalcogenides.[3] However, reactions involving aluminum hydrides of low aggregation with chalcogen or organochalcogenides have been reported to a lesser extent. Raston et al.[4] have investigated the reaction of the trimethylamine adduct of alane $Me_3N{\cdot}AlH_3$ with chalcogen or organochalcogenides. Power et al.[5] have reported one example of the reaction of an aluminum dihydride with an organochalcogenide and our group has discussed the reaction of a series of aluminum dihydrides with chalcogen,[3,6] where the isolation and structural characterization of some novel compounds {such as $LAl(SeH)_2$, $LAl(SeH)Se(SeH)AlL$,[3] $LAl(SH)_2$ [6a] [L = N(Ar)C(Me)-CHC(Me)N(Ar), Ar = 2,6-$i$$Pr_2C_6H_3$); $(RAlE)_2$ (R = 2,4,6-$t$$Bu_3C_6H_2$, E = S;[5] R = $N(SiMe_3)C(Ph)C(SiMe_3)_2$,[6b] 2,6-$(Et_2NCH_2)_2C_6H_3$, 2-$Et_2NCH_2$-6-$MeC_6H_3$;[6c] E = Se, Te], *trans*-$[\{Me_3N(H)Al(\mu\text{-}E)\}_2]$ (E = Se, Te),[4b] *trans*-$[\{Me_3N(PhTe)Al(\mu\text{-}Se)\}_2]$;[4c] $[(\eta^1\text{-}3,5\text{-}t\text{Bu}_2\text{pz}(\mu\text{-Al})H]_2E$ (E = S, Se, Te);[6d] $Me_3NAl(ER)_3$ (E = Se, R = Et, Ph, CH_2Ph; E = Te, R = Ph)[4a] and $Al_4Se_5(H)_2(NMe_3)_4$ [4c]} showed a rich chemistry. Although further reaction of the dimeric chalcogenidoalane, *trans*-$[\{Me_3N(H)Al(\mu\text{-}E)\}_2]$ (E = Se, Te) with chalcogen or organochalcogenides has been investigated,[4b] studies of the reaction of bulky, monomeric aluminum monohydrides with chalcogens, which might generate the corresponding monomeric Al-EH moieties, have not been reported so far. Therefore we became interested in finding a sufficiently bulky ligand to synthesize an intramolecularly stabilized aluminum monohydride, and further studies on its reactivity with the fluorinating agent Me_3SnF and heavy group 16 elements.

The divalent bulky chelating diamide ligand $[ArN(CH_2)_3NAr]^{2-}$ (Ar = 2,6-$i$$Pr_2C_6H_3$) is increasingly being used as a ligand[7] due to its special steric and electronic properties that help to control effectively the geometry at the metal center. Known complexes containing this ligand include main group metal (Li, K, Al) and transition metal (Ti, Zr, Y, Lu) derivatives.[7−11] The only reported alumi-

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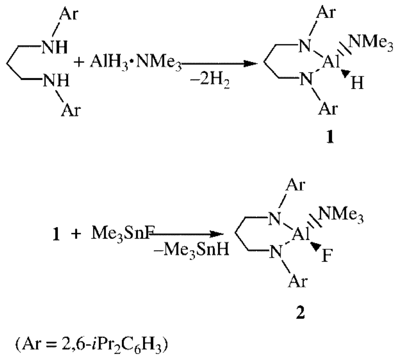
num complexes are a series of compounds containing alkyl and aryl groups $[ArN(CH_2)_3NAr]AlR$ (R = Me, *i*Bu, C_6F_5).[11] Herein we report on the synthesis and characterization of the bulky chelating diamidoaluminum monohydride $[ArN(CH_2)_3NAr]AlH(NMe_3)$ (Ar = 2,6-*i*$Pr_2C_6H_3$; **1**). The metathesis of **1** with Me_3SnF to give the monofluoride $[ArN(CH_2)_3NAr]AlF(NMe_3)$ (**2**) and the reaction with heavy group 16 elements to afford the dimeric aluminum chalcogenides $\{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2$ [E = S (**3**), Se (**4**), and Te (**5**)] are also described.

Results and Discussion

Syntheses and Characterization of $[ArN(CH_2)_3NAr]AlH(NMe_3)$ (1) and $[ArN(CH_2)_3NAr]AlF(NMe_3)$ (Ar = 2,6-*i*$Pr_2C_6H_3$) (2)

The synthesis of aluminum hydrides has been reported in a number of publications.[12] The use of $AlH_3{\cdot}NMe_3$ as a precursor to react with *N*-substituted diamine, diimine and analogues containing N-H groups or $E(SiMe_3)_2$ (E = P, As) with elimination of H_2 or $HSiMe_3$ has been shown to be a facile route to aluminum hydrides of low aggregation.[3,13] Reaction of the diamine $[ArNH(CH_2)_3HNAr]$ with a small excess of $AlH_3{\cdot}NMe_3$ in toluene under heating (80 °C) affords the intramolecularly stabilized diamidoaluminum monohydride $[ArN(CH_2)_3NAr]AlH(NMe_3)$ (**1**) in excellent yield. Subsequent fluorination of **1** with Me_3SnF either at room temperature or at high temperature (80 °C) results in the formation of the aluminum monofluoride $[ArN(CH_2)_3NAr]AlF(NMe_3)$ (**2**; Scheme 1).



Scheme 1

Complexes **1** and **2** were characterized by NMR, MS (EI) and IR spectroscopy, and elemental analyses. The presence of the hydride in **1** is evident from the IR spectrum. The broad IR band at 1799 cm^{-1} can be assigned to the Al−H stretching absorption.[14] In the IR spectrum of **2**, this absorption disappears, indicating that compound **1** is completely fluorinated. The ^{19}F NMR spectrum of **2** exhibits one singlet resonance ($\delta = -175.4$ ppm), which is similar to the terminal Al−F resonance in a closely related series of compounds $\{ArN[Si(R)Me_2]AlF_2{\cdot}THF$: Ar = 2,6-*i*$Pr_2C_6H_3$, R = Me, $\delta = -178.1$; R = *i*Pr, $\delta = -177.0$ ppm; R = *t*Bu, $\delta = -175.1$ ppm; Ar = 2,6-$Me_2C_6H_3$, R = *t*Bu, $\delta = -175.0$ ppm; R = 2,4,6-$Me_3C_6H_2$, $\delta = -175.9$ ppm$\}$.[15] In the ^1H NMR spectra of **1** and **2** the presence of complex resonances for the backbone protons of the diamide ligand [two isopropyl methine (C*H*Me$_2$), four isopropyl methyl (CH*Me$_2$*), two methene (N*CH$_2$*) and two methene (NCH$_2$*CH$_2$*) resonances] is consistent with a pseudotetrahedral geometry and C_s symmetry at aluminium. Similar resonances are observed in compounds $[M\{ArN(CH_2)_3NAr\}(\eta\text{-}C_5H_5)Cl]$ (M = Zr, Y; Ar = 2,6-*i*$Pr_2C_6H_3$).[7,9] The resonance for the Al−H proton is not seen, which is typical for amidoaluminum hydride species.[13b] Substitution of Al−H in **1** by Al−F has a stronger effect on the chemical shift of the NMe_3 group (**1**: $\delta = 1.66$ ppm; **2**: $\delta = 1.75$ ppm), while a smaller effect is observed for the backbone protons of the ligand. The MS (EI) spectrum shows the molecular ion of $[M^+ - NMe_3]$ for **1**, and $[M^+]$ and $[M^+ - NMe_3]$ for **2** and the single-crystal X-ray structural determinations of **1** and **2** confirm the composition of $[ArN(CH_2)_3NAr]AlR(NMe_3)$ (R = H, **1**; F, **2**), where the former contains half a molecule of *n*-hexane per molecule of complex **1** in the asymmetric unit.

Compounds **1** and **2** are well-separated monomers both of which contain a central aluminum atom in a distorted tetrahedral environment (Figures 1 and 2). Selected bond lengths and angles are listed in Table 1. The terminal Al−H bond length (1.52 Å) is closer to those in compounds (2,4,6-*t*$Bu_3C_6H_2)_2AlH$[16] [1.53(4) Å] and $[HAl(NMe_2)_3]^-$[17] [1.52(2) Å], but shorter than those in AlH(Cl)-[*t*BuNCH$_2$CH$_2$N(*t*Bu)H][13a] (1.60 Å), $Al_2(\mu\text{-}NEt_2)_2$-$[N(iPr)_2]_2H_2$ [18] (1.67 Å) and (2,4,6-*t*$Bu_3C_6H_2$)Al(H)Cl·THF[19] [1.73(5) Å]. The terminal Al−F separation [1.678(1) Å] is in the range of 1.657−1.681 Å

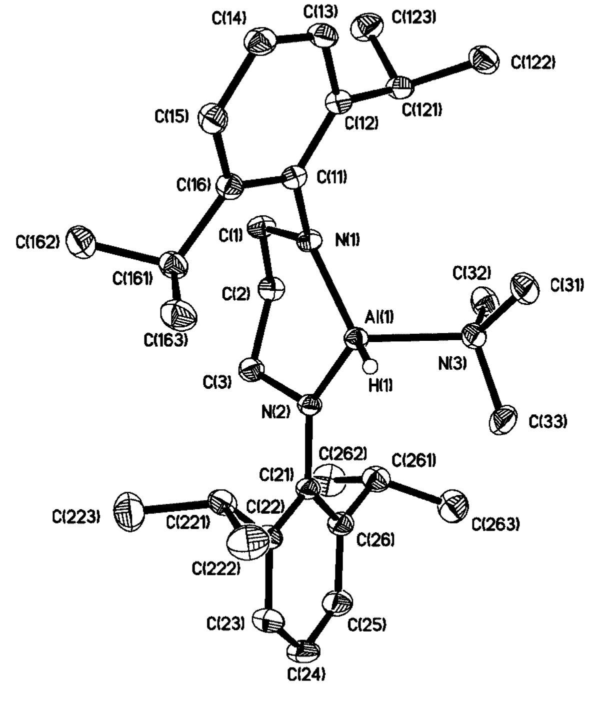


Figure 1. Molecular structure of **1** with the thermal ellipsoids at 30% probability level; H atoms are omitted for clarity except for the Al−H hydrogen atom

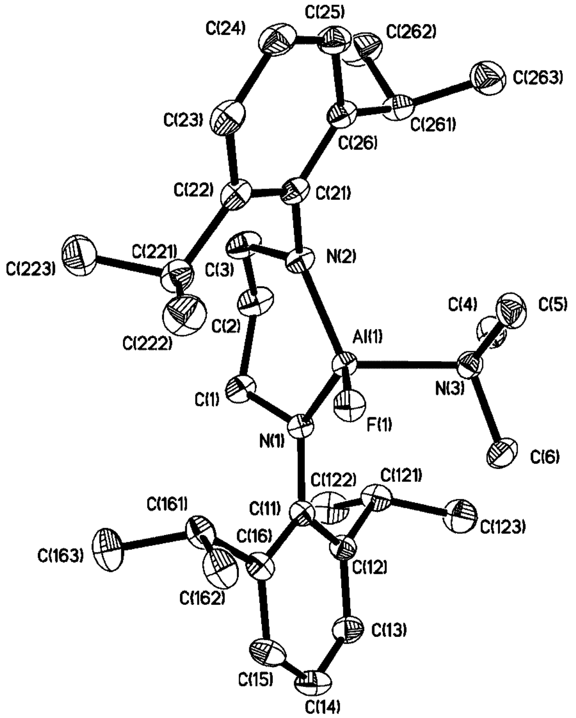


Figure 2. Molecular structure of **2** with the thermal ellipsoids at 30% probability level; H atoms are omitted for clarity

Table 1. Selected bond lengths [Å] and bond angles [°] for compounds **1**·1/2 *n*-hexane, **2** and **4**·2 toluene

Compound **1**·1/2 *n*-hexane			
Al(1)−N(1)	1.820(1)	Al(1)−N(3)	2.024(2)
Al(1)−N(2)	1.828(1)	Al(1)−H(1)	1.52
N(1)−Al(1)−N(2)	106.52(6)	H(1)−Al(1)−N(1)	116.1
N(1)−Al(1)−N(3)	111.31(7)	H(1)−Al(1)−N(2)	120.2
N(2)−Al(1)−N(3)	105.74(7)	H(1)−Al(1)−N(3)	96.0
Compound **2**			
Al(1)−F(1)	1.678(1)	Al(1)−N(2)	1.804(2)
Al(1)−N(1)	1.810(2)	Al(1)−N(3)	2.000(2)
N(1)−Al(1)−N(2)	107.45(7)	F(1)−Al(1)−N(1)	119.12(6)
N(1)−Al(1)−N(3)	108.55(8)	F(1)−Al(1)−N(2)	115.24(6)
N(2)−Al(1)−N(3)	112.69(8)	F(1)−Al(1)−N(3)	93.00(6)
Compound **4**·2 toluene			
Al(1)−Se(1)	2.339(1)	Al(1)−N(1)	1.932(11)
Al(1)−Se(1A)	2.381(1)	Al(1)−N(2)	1.916(11)
Al(1)−Al(1A)	2.988(2)	Se(1)−Al(1)−Se(1A)	101.44(5)
Al(1)−Se(1)−Al(1A)	78.56(5)	N(1)−Al(1)−N(2)	98.13(14)
N(1)−Al(1)−Se(1)	119.2(4)	N(2)−Al(1)−Se(1A)	109.7(4)
N(2)−Al(1)−Se(1)	118.6(4)	N(1)−Al(1)−Se(1A)	109.7(4)
Al(1)−N(1)−C(1)	119.6(8)	Al(1)−N(2)−C(3)	121.1(9)
Al(1)−N(1)−C(16)	126.4(8)	Al(1)−N(2)−C(4)	130.1(7)
C(1)−N(1)−C(16)	113.2(9)	C(3)−N(2)−C(4)	108.0(9)

observed in $[(Me_3Si)_3CAlF_2]_3$ [20] and somewhat longer than those in $[\{(2,6\text{-}i\mathrm{Pr}_2C_6H_3)N(SiMe_3)AlF_2\}_3]$[15] (1.634−1.642 Å) and AlF_3 [21] (1.63 Å), as determined by electron diffraction. The diamide ligand chelates the Al atom to form an AlN_2C_3 six-membered non-planar ring, in which Al(1) and C(2) occupy the head positions with distances to the quasi-plane N(1)−N(2)−C(3)−C(1) (mean deviation Δ = 0.0716 Å) of 0.1034 and 0.6852 Å in **1** and the plane N(1)−N(2)−C(3)−C(1) (Δ = 0.0316 Å) of −0.0109 and 0.6730 Å in **2**. It is obvious that the former displays a boat conformation and the latter a flattened chair conformation, and this can be explained in terms of the strain imposed by the Ar group. The F atom has a stronger electron-attracting tendency than the H atom, which generates different charge distributions at the central Al atom of **1** and **2**. This gives rise to the small difference in the $Al-N_{diamide}$ bond length between **1** and **2** (average 1.824, **1**; 1.807 Å, **2**), as well as the $Al\text{-}N_{NMe_3}$ bond length [2.024(2), **1**; 2.000(2) Å, **2**] and the N(1)−Al(1)−N(2) chelating angle [106.52(6)°, **1**; 107.45(7)°, **2**]. The $Al-N_{diamide}$ distances in **1** and **2** can be compared with the terminal Al−N(amide) distances in $CH_2(CH_2CMe_2)_2NAlH_2\cdot NMe_3$ [13h] [1.838(2) Å], $AlH(Cl)[t\mathrm{Bu}NCH_2CH_2N(t\mathrm{Bu})H]$[13a] [1.80(1) Å] and $\{Al(\mu\text{-}H)[N(CMe_2CH_2)_2CH_2]_2\}_2$ [22] [1.836(3) Å], and are longer than the $Al-N_{diamide}$ bond lengths in the three-coordinate aluminum compound $[ArN(CH_2)_3NAr]AlMe$[11] [1.760(3), 1.766(3) Å]. The $Al-N_{NMe_3}$ distances in **1** and **2** are as expected.[13h,23,24]

Syntheses of $\{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2$ [E = S (3), Se (4) and Te (5)] and X-ray Structural Analysis of Compound 4

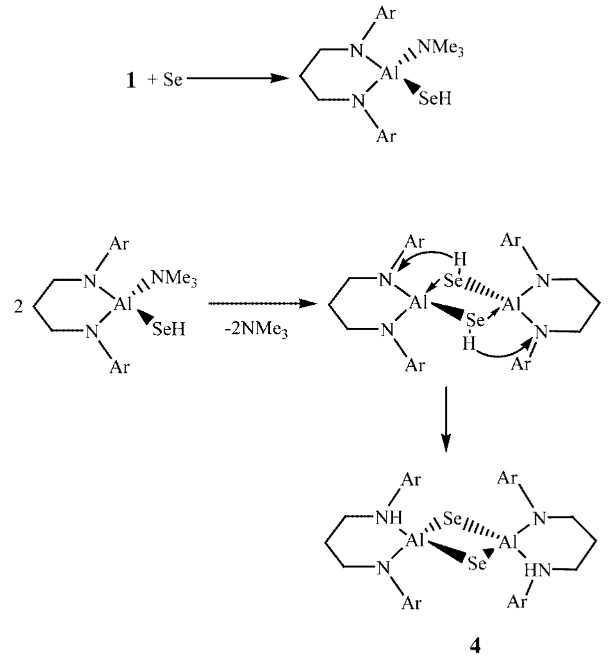
The successful fluorination of **1** using Me_3SnF is indicative of its reactivity despite the steric hindrance of the bulky ligand. Treatment of **1** with equivalent amounts of sulfur, selenium or tellurium proceeded in toluene at elevated temperature to afford the solvated aluminum sulfide **3** as light yellow crystals, the selenide **4** as yellow crystals and the telluride **5** as green-yellow crystals. The former two compounds were obtained in good yield and the latter in moderate yield [Equation (1)].

$$2[ArN(CH_2)_3NAr]AlH(NMe_3) + 2E \rightarrow \{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2 + 2NMe_3 \qquad (1)$$

E = S (**3**), 80 °C, 12 h
= Se (**4**), reflux, 12 h
= Te (**5**), reflux, 120 h

Compounds **3**−**5** are air and moisture sensitive and soluble in hot toluene and benzene, while poorly soluble in THF, $CHCl_3$ and *n*-hexane. They were characterized by IR and NMR spectroscopy and MS (EI) spectrometry, as well as by elemental analyses. The MS (EI) spectra of **3**−**5** show the dimeric molecular ion with the correct isotope pattern and their ^1H NMR spectra show the very similar characters of the ligand, including the resonances of solvent toluene protons. The doublets in the range of δ = 1.10−1.25 ppm, one septet centered at ca. δ = 3.38 ppm and a multiplet at δ = 7.02−7.10 ppm correspond to the protons of the 2,6-$i\mathrm{Pr}_2C_6H_3$ group. One broad singlet at ca. δ = 1.36 ppm can be assigned to the NH resonance,[13a,13c] with a satisfactory integral intensity indicating two protons, and two areas of unresolved multiplet resonances centered at ca. δ = 1.78 and 3.00 ppm arising from the six non-equivalent methylene protons, with the latter probably coming from the overlapping proton resonances of the two amido NCH_2 and two amine HNCH_2 groups. The IR spectra exhibit the NH absorption in the $\nu_{N\text{-}H}$ region[13a,13b] (**3**: 3190; **4**: 3187; **5**: 3185 cm^{-1}). All these data indicate that compounds **3**, **4** and **5** have the same structure corresponding to the formula $\{[ArNH(CH_2)_3NAr]Al(\mu\text{-}E)\}_2$.

The reaction of aluminum dihydride with selenium has been reported by our group,[3,6b,6c] where the formation of a dimeric compound might proceed through an Al−SeH intermediate. In a similar way the reaction of the aluminum monohydride **1** with selenium might involve the formation of intermediate $[ArN(CH_2)_3NAr]Al(SeH)(NMe_3)$, which dimerizes to produce $\{[ArN(CH_2)_3NAr]Al(\mu\text{-}SeH)\}_2$ with elimination of gaseous NMe_3. However, with reference to the related Al-SeH compounds $LAl(SeH)_2$ and LAl(SeH)Se(SeH)AlL [L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-$i$$Pr_2C_6H_3$],[25] no absorptions in the range of 2000−2500 cm^{-1} in the IR spectrum are observed to indicate the formation of an Al-SeH moiety. This suggests that the dimer $\{[ArN(CH_2)_3NAr]Al(\mu\text{-}SeH)\}_2$ is not stable under heating and the hydrogen atom attached to the selenium atom migrates quickly to one of the nitrogen atoms of the diamide ligand to afford stable compound **4**. The most likely mecha-



(Ar = 2,6-$i$$Pr_2C_6H_3$)

Scheme 2

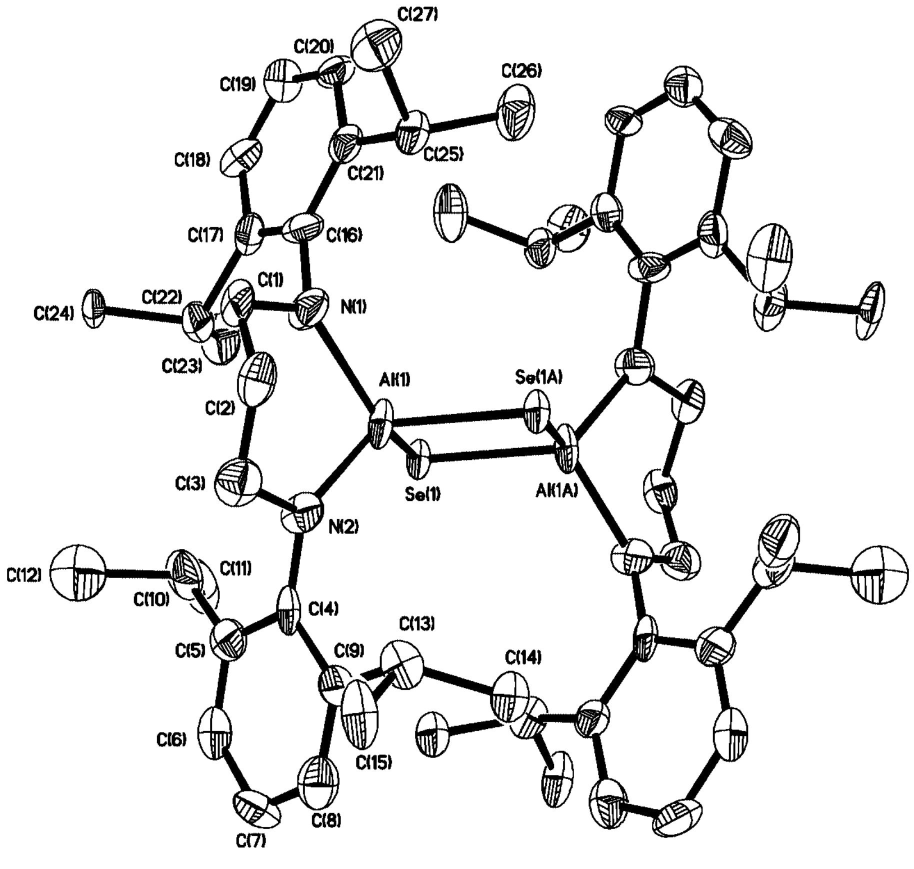


Figure 3. Molecular structure of **4** with the thermal ellipsoids at 30% probability level; H atoms are omitted for clarity

nism is given in Scheme 2. The formation of compounds **3** and **5** is probably similar to that of **4**.

A suitable single crystal of compound **4** was measured by X-ray diffraction. The structure analysis of compound **4** shows a dimeric species containing two molecules of toluene. Unfortunately, the quality of the crystal structure did not allow the location of the hydrogen atoms on the nitrogen atoms. Nevertheless, the presence of NH groups was established by IR and ^{1}H NMR spectroscopy. The molecular structure is shown in Figure 3, and selected bond lengths and angles are listed in Table 1. The Al(1)−N(1) [1.932(11) Å] and Al(1)−N(2) [1.916(11) Å] bond lengths are midway between the Al−N$_{amine}$ and Al−N$_{amido}$ bond lengths observed in AlH(Cl)[*t*BuNCH$_2$CH$_2$N(*t*Bu)H][13a] [Al−N(1) (amine): 2.00(1) Å; Al−N(2) (amido): 1.80(1) Å], and are longer than those Al−N distances found in Al[*t*BuNCH$_2$CH$_2$N(*t*Bu)][*t*BuNCH$_2$CH$_2$NH(*t*Bu)],[13b] where the NH hydrogen atom is disordered over all four nitrogen centers [1.850(5), 1.870(5) Å], and much longer than Al−N$_{amido}$ distances in **1** [1.820(1), 1.828(1) Å] and **2** [1.804(2), 1.810(2) Å]. However, compared to AlH(Cl)[*t*BuNCH$_2$CH$_2$N(*t*Bu)H],[13a] where a remarkable difference (0.20 Å) between Al−N(1) (amine) and Al−N(2) (amido) distances was observed, the very slight difference (0.016 Å) between Al(1)−N(1) and Al(1)−N(2) in **4** may imply the disorder of the two hydrogen atoms over the sides of all four nitrogen centers. Moreover, the similar coordination environments and approximately planar coordination geometries at N(1) and N(2) [at N(1), Al(1)−N(1)−C(1) 119.6(8)°, Al(1)−N(1)−C(16) 126.4(8)°, C(1)−N(1)−C(16) 113.2(9)°; at N(2), Al(1)−N(2)−C(3) 121.1(9)°, Al(1)−N(2)−C(4) 130.1(7)°, C(3)−N(2)−C(4) 108.0(9)°, (C−N−Al, C) = 359.2°] do not allow us to distinguish between the amine nitrogen and the amido nitrogen centers. In summary, it is assumed that the almost equal possibility of the hydrogen migration from the selenium atom to any nitrogen atom at the diamide ligand is included in the course of the reaction.

The Al$_2$Se$_2$ core exhibits an ideal planar ring (least-square deviation Δ of 0.0005) with an Al(1)−Se(1) distance of 2.339(1) Å, an Al(1)−Se(1A) distance of 2.381(1) Å and an Al(1)−Se(1)−Al(1A) bond angle of 78.56(5)°, which are as expected for Al$_2$Se$_2$ core compounds,[4a,4b,6b,6c] while the Al(1)−Se(1) and Al(1)−Se(1A) distances differ by ca. 0.042 Å probably due to the steric effects of the backbone ligand on the Al$_2$Se$_2$ ring. The ligand chelates the Al atom to fuse two six-membered AlN$_2$C$_3$ rings, which are arranged in *trans* positions on each side of the Al$_2$Se$_2$ core. The two AlN$_2$C$_3$ rings both display a boat conformation with Al(1) and Al(1A) at the bow and C(2) and C(2A) at the stern, respectively, and are arranged almost perpendicularly to the Al$_2$Se$_2$ ring (the dihedral angle between the ring (Al$_2$Se$_2$) and the N(1)−N(2)−C(3)−C(1) plane (Δ = 0.0238 Å) being 90.5°).

In summary we have shown that the [ArNCH$_2$-CH$_2$NAr]$^{2-}$ ligand forms a stable chelate with the aluminium hydride. The hydride functionally can be replaced by a fluorine atom or substituted by a chalcogen (S, Se, Te) under migration of the hydrogen to an adjacent nitrogen of the chelating ring. The latter reaction does not yield an aluminium chalcogen double bond system but rather a four-membered ring of composition Al$_2$E$_2$ (E = S, Se, Te).

Experimental Section

General: All operations were carried out under purified nitrogen atmosphere using Schlenk techniques. Solvents were purified and dried by distillation over sodium under nitrogen prior to use. Elemental sulfur, selenium and tellurium were purchased from Aldrich and used as received. ArNH(CH$_2$)$_3$HNAr (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[7] AlH$_3$·NMe$_3$ [26]and Me$_3$SnF[27] were prepared according to the literature.

^{1}H (200.13 MHz), ^{19}F (188.29 MHz) and ^{77}Se NMR (500 MHz) spectra were recorded on a Bruker AM 200 or a Bruker AM 250 spectrometer and the chemical shifts were externally referenced to SiMe$_4$ for ^{1}H nuclei, C$_6$F$_6$ for ^{19}F and Me$_2$Se for ^{77}Se. (In this paper the chemical shift for ^{19}F NMR spectroscopy was adjusted to the scale where CFCl$_3$ is used as external reference). The IR spectra were measured on a Bio-Rad Digilab FTS-7 spectrometer. EI (70 eV) mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes and were not corrected.

[ArN(CH$_2$)$_3$NAr]AlH(NMe$_3$) (1): A solution of ArNH(CH$_2$)$_3$-HNAr (4.03 g, 10.24 mmol) (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) in toluene (20 mL) was added to a solution of AlH$_3$·NMe$_3$ (1.18 g, 13.24 mmol) in toluene (30 mL). While stirring, gas evolution was observed. The mixture was slowly heated to 80 °C and stirred for 5 h. All volatiles were removed in vacuo and the residue was extracted with *n*-hexane. After filtration through Celite, the extract was evaporated to dryness to afford [ArN(CH$_2$)$_3$NAr]AlH(NMe$_3$) as a white solid (4.41 g, 90%). X-ray quality crystals were grown from *n*-hexane. M.p. 196−197 °C. ^{1}H NMR (200.13 MHz, C$_6$D$_6$): δ = 1.22, 1.37, 1.47, 1.66 (d, 24 H, CH*Me$_2$*), 1.66 (s, 9 H, N*Me$_3$*), 2.10, 3.00 (m, 2 H, NCH$_2$*CH$_2$*), 3.25−3.45 (m, 4 H, N*CH$_2$*), 3.63, 4.25 (sept, 4 H, *CH*Me$_2$), 7.10−7.16 (m, 6 H, Ar) ppm. MS (EI): *m*/*z* = 420 [M$^+$ − NMe$_3$]. IR (KBr, Nujol mull): $\nu_{Al\text{-}H}$ = 1799 cm^{-1}(br. sh.). C$_{33}$H$_{57}$AlN$_3$ (522.02) (**1**·1/2 *n*-hexane): calcd. C 75.93, H 11.00, N 8.05; found C 75.44, H 10.64, N 8.26.

[ArN(CH$_2$)$_3$NAr]AlF(NMe$_3$) (2). Method 1: A suspension of **1** (1.44 g, 3 mmol) and Me$_3$SnF (0.55 g, 3 mmol) in toluene (30 mL) was heated to 80 °C and stirred for 12 h. After filtration, the filtrate was concentrated to ca. 10 mL in vacuo and kept at 4 °C for 48 h to afford colorless block-shaped crystals of **2** (1.20 g, 80%). M.p. 220−222 °C. ^{1}H NMR (200.13 MHz, C$_6$D$_6$): δ = 1.22, 1.35, 1.47, 1.71 (d, 24 H, CH*Me$_2$*), 1.75 (s, 9 H, N*Me$_3$*), 2.00, 3.00 (m, 2 H, NCH$_2$*CH$_2$*), 3.27, 3.40 (m, 4 H, N*CH$_2$*), 3.64, 4.29 (sept, 4 H, *CH*Me$_2$), 7.10−7.32 (m, 6 H, Ar) ppm. ^{19}F NMR (188.29 MHz, C$_6$D$_6$): δ = −12.4 (adjusted value, −175.4) ppm. MS (EI): *m*/*z* = 497 [M$^+$], 438 [M$^+$ − NMe$_3$]. C$_{30}$H$_{49}$AlFN$_3$ (497.72): calcd. C 72.40, H 9.92, N 8.44; found C 72.31, H 9.71, N 8.28.

Method 2: A suspension of **1** (1.44 g, 3 mmol) and Me$_3$SnF (0.55 g, 3 mmol) in toluene (30 mL) was stirred for 4 days at room temperature until Me$_3$SnF was almost consumed. After filtration, the filtrate was concentrated to ca. 10 mL in vacuo and kept at 4 °C for a week to afford colorless crystals. All spectroscopic data confirmed the same compound as that obtained from method 1.

Table 2. Summary of crystallographic data for compounds **1**·1/2 *n*-hexane, **2** and **4**·2 toluene

	1·1/2 *n*-hexane	**2**	**4**·2 toluene
Empirical formula	$C_{33}H_{57}AlN_3$	$C_{30}H_{49}AlFN_3$	$C_{68}H_{96}Al_2N_4Se_2$
Molecular weight	522.80	497.70	1181.37
Temperature [K]	203(2)	200(2)	133(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2$
a (Å)	12.285(3)	13.323(6)	19.104(4)
b (Å)	20.125(4)	12.480(2)	17.561(4)
c (Å)	14.274(3)	17.979(5)	12.286(3)
β [°]	110.47(3)	92.57(5)	129.10(3)
Volume [Å^3]	3306.2(12)	2986.5(16)	3198.5(11)
Z	4	4	2
Density (calcd.) [Mg·m^{-3}]	1.050	1.107	1.227
Absorption coefficient [mm^{-1}]	0.085	0.096	1.225
F(000)	1156	1088	1252
θ range [°]	3.52−25.00	3.61−25.04	1.80−24.81
Index ranges	$-14 \le h \le 14$	$-15 \le h \le 15$	$-22 \le h \le 22$
	$-23 \le k \le 23$	$-10 \le k \le 14$	$-20 \le k \le 20$
	$-16 \le l \le 16$	$-16 \le l \le 21$	$-14 \le l \le 13$
Reflections collected	11566	5643	18430
Independent reflections	5786 (R_{int} = 0.0346)	5249 (R_{int} = 0.1332)	5488 (R_{int} = 0.0718)
Data/restraints/parameters	5786/0/350	5249/0/327	5488/1/312
Goodness-of-fit on F^2	1.004	1.069	0.996
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0418	R_1 = 0.0486	R_1 = 0.0433
	wR_2 = 0.0994	wR_2 = 0.1282	wR_2 = 0.1112
R indices (all data)	R_1 = 0.0586	R_1 = 0.0532	R_1 = 0.0529
	wR_2 = 0.1101	wR_2 = 0.1340	wR_2 = 0.1164
Largest different peak and hole (e·Å^{-3})	0.200, −0.228	0.519, −0.300	0.694, −0.514

{[ArNH(CH$_2$)$_3$NAr]Al(μ-S)}$_2$ (3): A suspension of **1** (1.48 g, 3 mmol) and elemental S (0.096 g, 3 mmol) in toluene (30 mL) was heated to 80 °C and stirred for 12 h. After filtration, the orange-red filtrate was concentrated to ca. 10 mL and kept at 4 °C for 48 h to afford light yellow crystals of **3**·toluene (1.00 g, 67%). M.p. 278−279 °C (> 250 °C, decomp.). ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.17, 1.22 (d, 48 H, CH*Me$_2$*), 1.36 (s, 2 H, N*H*), 1.78 (m, 4 H, NCH$_2$*CH$_2$*), 2.1 (s, 3 H, *Me*Ph), 3.00 (t, 8 H, N*CH$_2$*), 3.38 (sept, 8 H, *CH*Me$_2$), 6.96−7.04 (m, 5 H, Me*Ph*), 7.02−7.10 (m, 12 H, Ar) ppm. MS (EI): *m*/*z* = 904 [M$^+$]. IR (KBr Nujol mull): $\tilde{\nu}_{N-H}$ = 3190 cm^{-1}. $C_{61}H_{90}Al_2N_4S_2$ (996.8) (**3**·toluene): calcd. C 73.50, H 9.10, N 5.62; found C 73.25, H 8.90, N 5.07.

{[ArNH(CH$_2$)$_3$NAr]Al(μ-Se)}$_2$ (4): A suspension of **1** (1.44 g, 3 mmol) and elemental Se powder (0.24 g, 3 mmol) in toluene (30 mL) was refluxed for 12 h until almost all the selenium was consumed. In the course of hot filtration, yellowish crystals grew from the orange filtrate, and these were collected by filtration. (0.10 g). The mother liquor was concentrated to ca. 10 mL and kept at 4 °C for 24 h to afford another crop of yellowish crystals of **4**·2 toluene (1.00 g). Total yield: 1.10 g (62%). M.p. 291 °C (> 259 °C, decomp.). ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.17, 1.22 (d, 48 H, CH*Me$_2$*), 1.36 (s, 2 H, N*H*), 1.78 (m, 4 H, NCH$_2$*CH$_2$*), 2.1 (s, 6 H, *Me*Ph), 3.00 (t, 8 H, N*CH$_2$*), 3.38 (sept, 8 H, *CH*Me$_2$), 6.94−7.04 (m, 10 H, Me*Ph*), 7.02−7.10 (m, 12 H, Ar) ppm. ^{77}Se NMR (500 MHz, C_6D_6, $CDCl_3$, or C_7D_8): no resonances were observed. MS (EI): *m*/*z* = 998 [M$^+$]. IR (KBr Nujol mull): $\tilde{\nu}_{N-H}$ = 3187 cm^{-1}. $C_{68}H_{98}Al_2N_4Se_2$ (1182.9) (**4**·2 toluene): calcd. C 69.04, H 8.35, N 4.74; found C 68.79, H 8.22, N 4.63.

{[ArNH(CH$_2$)$_3$NAr]Al(μ-Te)}$_2$ (5): A suspension of **1** (1.44 g, 3 mmol) and elemental Te powder (0.39 g, 3 mmol) in toluene (40 mL) was refluxed for 5 days and a small amount of unreacted Te powder still remained. After filtration, the green-yellow filtrate was concentrated to ca. 10 mL and *n*-hexane (5 mL) was added. The solution was kept at 4 °C for 24 h to afford green-yellow crystals of **5**·toluene (0.85 g, 48%). M.p. 320 °C (decomp.). ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.17, 1.22 (d, 48 H, -CH*Me$_2$*), 1.35 (s, 2 H, N*H*), 1.75 (m, 4 H, NCH$_2$*CH$_2$*), 2.1 (s, 3 H, *Me*Ph), 3.00 (t, 8 H, N*CH$_2$*), 3.37 (sept, 8 H, *CH*Me$_2$), 6.94−7.04 (m, 5 H, Me*Ph*), 7.02−7.10 (m, 12 H, *Ar*) ppm. MS (EI): *m*/*z* = 1096 [M$^+$]. IR (KBr Nujol mull): $\tilde{\nu}_{N-H}$ = 3185 cm^{-1}. $C_{61}H_{90}Al_2N_4Te_2$ (1188.1) (**5**·toluene): calcd. C 61.67, H 7.63, N 4.71; found C 61.72, H 7.61, N 4.76.

X-ray Structural Determinations and Refinements for 1, 2 and 4: The crystallographic data for compounds **1** and **2** were collected on a Stoe−Siemens−Huber four-circle diffractometer coupled to a Siemens CCD area-detector and for **4** on a Stoe IPDS II-array detector system. In both cases graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used. All structures were solved by direct methods (SHELXS-96)[28] and refined against F^2 using SHELXL-97.[29] In **1** and **2**, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms, except for the Al−H hydrogen atom in **1**, which was located by difference Fourier synthesis and refined isotropically. In **4** the non-hydrogen atoms in the dimeric structure were refined anisotropically while those in the two solvent molecules were refined isotropically. Treatment of hydrogen atoms was the same as those in **1** and **2**, except for the two NH hydrogen atoms, which could not be located. A summary of cell parameters, data collections, and structure solutions is given in Table 2.

CCDC-207050 (**1**), -207051 (**2**), and -207052 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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