Main-Group Metal Complexes

Preparation of Monomeric $[LAl(NH_2)_2]$—A Main-Group Metal Diamide Containing Two Terminal NH_2 Groups**

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Dedicated to Professor Dietmar Seyferth on the occasion of his 75th birthday

Aluminum amides supported by organic ligands are important molecular precursors for the preparation of aluminum nitrides, such as Al–N based semiconductors and Al–N ceramics.[1] Amides with the general formula $[R_2Al(NH_2)]$, in which R corresponds to an organic substituent, are rare. The presence of a reactive NH_2 group, which can be involved in further substitution reactions, may lead to mixed-metal imides that have the Al–N(H)–M skeleton (M = metal atom). However the known amides show a strong tendency to oligomerize and form unstable trimers $[\{R_2Al(\mu\text{-}NH_2)\}_3]$ (R = Me, *t*Bu)[2a,b] or dimers $[\{R_2Al(\mu\text{-}NH_2)\}_2]$ (R = Me_3Si)[2b–d] because of the Lewis acidity of the aluminum center and the presence of the electron lone pair at the nitrogen atom of the NH_2 group. The steric bulk of the substituents is the major factor that determines the degree of association. The most recent example of such an aluminum amide $[\{[(Me_3Si)_2Al(\mu\text{-}NH_2)_2]_3\}Al]$ was published in 1988 by Janik et al., in which the central aluminum cation is octahedrally coordinated to three $[(Me_3Si)_2Al(\mu\text{-}NH_2)_2]^-$ ions.[2c] The only known aluminum amide that contains a terminal NH_2 group $[AlCl_3(NH_2i\text{Pr})][\{Al(NH_3)(NH_2)[Al(NHi\text{Pr})(Ni\text{Pr})Cl]_2\}_2]$ was prepared in low yield in 1997 by Chang et al. by using $AlCl_3$, *i*PrNHLi, and an excess of *i*$PrNH_2$.[3] However, the mechanism of the formation of the product remains unclear. The adducts of composition $R_3Al{\cdot}NH_3$ are thermodynamically unstable and thus decompose at elevated temperatures to the corresponding amides under elimination of alkanes.[2a,4] So far there are no reports known on the preparation of aluminum amides by treating KNH_2 or $NaNH_2$ with the corresponding aluminum halides. Previous experi-

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ments indicate that such reactions result mostly in the decomposition of the starting material to yield insoluble white powders under elimination of the free ligand.[5]

Recently, we showed that an N-heterocyclic carbene can be used as an HCl acceptor for the preparation of a Ge^{II} hydroxide derivative when water is used as a source of OH ions.[6] Consequently we tried the same procedure for the preparation of aluminum amides and hydroxides by adding NH_3 and H_2O, respectively, to the corresponding aluminum chloride derivative. It should be mentioned that previous attempts to prepare compounds with terminal Al–OH and Al–NH_2 groups in the presence of NMe_3, NEt_3, or pyridine as an HCl acceptor were not successful.[5] The addition of dry ammonia to a toluene solution of $[LAlCl_2]$ (**1**; (L = $HC[C(Me)N(Ar)]_2$, Ar = 2,6-*i*$Pr_2C_6H_3$)[7] and two equivalents of 1,3-di-*tert*-butylimidazol-2-ylidene (**2**)[8] over a period of 10 min at −20 °C resulted in the formation of a slurry of insoluble 1,3-di-*tert*-butylimidazolium chloride. Subsequent filtration followed by extraction of the remaining solid with toluene gave an oily residue after removal of the volatiles in vacuo. Treatment of the residue with cold pentane afforded $[LAl(NH_2)_2]$ (**3**) as a white powder in 70% yield. Furthermore, when water is used instead of ammonia and benzene as a solvent a white microcrystalline powder of $[LAl(OH)_2]$ (**4**) can be obtained within 10 min in a yield of 65%. Previously **4** was prepared in an NH_3(l)/toluene two-phase system,[9] after 7 h in a yield of 48%. This new method clearly demonstrates the advantages for the preparation of aluminum amides and hydroxides. Scheme 1 summarizes the reactions for preparing **3** and **4**.

So far we have not given an answer to the question: Why does the addition of the N-heterocyclic carbene lead to the desired product? Clearly, because of the high reactivity of **3** and **4** towards protons it appears that the amine is not suitable as a HCl acceptor. On the one hand, there is always an equilibrium between the protonated amine and the free base and thus the protons cause side reactions. On the other hand, in the presence of the N-heterocyclic carbene there is no such an equilibrium of free protons due to the favored covalent C–H bond formation.[10] Moreover, the resulting imidazolium chloride is very sparingly soluble in hydrocarbon solvents such as hexane, toluene, or THF, which allows an easy separation of the product from the reaction mixture by filtration. In addition the imidazolium chloride can be easily recycled to the free carbene by using a strong base such as KO*t*Bu or NaH.[8]

Surprisingly, compound **3** is monomeric in the solid state and what is even more striking, the NH_2 groups are not involved in any kind of hydrogen bonding as shown by X-ray structural analysis and IR spectroscopy. Moreover, **3** is thermally stable and can be maintained at 70 °C for 2 h without any significant decomposition, which is also reflected by its high melting point (166 °C). Based on the assumption that **3** is exposed to air, the rate of decomposition is significantly slower than that of **4** (see below). Furthermore we carried out some additional investigations on **4** to learn more about its stability. Compound **4** is unstable and decomposes upon heating to temperatures exceeding 70 °C or rapidly after contact with air as indicated by temperature dependent ^{1}H NMR studies (Figure 1).

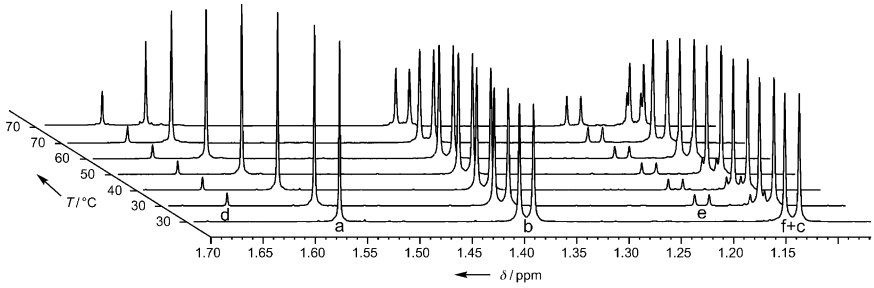
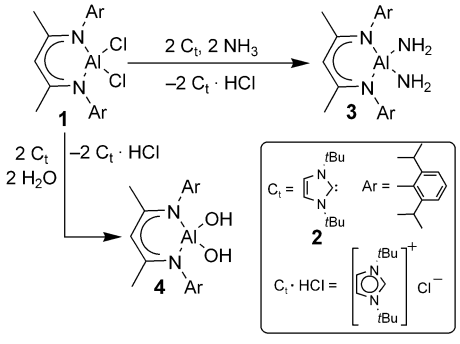


Figure 1. ^{1}H NMR spectroscopic kinetic study of the thermal decomposition of **4** to the free ligand (LH). Resonances between $\delta = 1.5$ and 1.7 ppm are assigned to the α-methyl groups (a **4**; d LH), and the doublets belong to the diastereotopic methyl groups of the *i*Pr moieties (b + c **4**; e + f LH). The only soluble organic product of this decomposition is the free ligand, which was identified by comparison with an original sample. The spectrum taken at 30 °C represents pure **4** in a sealed tube, whereas, the following spectrum was taken after three days. Further spectra show thermally initiated decomposition of **4**, which is slow below 60 °C, but accelerates significantly at 70 °C. Finally the last spectrum was recorded after 15 min maintained at 70 °C and confirms the thermal lability of **4**. Similar degradation of **4** was observed after its exposure to air in both the solid and solution state.



Scheme 1. Syntheses of **3** and **4**.

The ^{1}H NMR spectrum of **3** shows the typical pattern for the ligand (L) and a broad singlet at −0.55 ppm assigned to the NH_2 moieties with ^{15}N satellites ($^1J_{NH} = 64$ Hz). The NH_2 groups resonate in the ^{15}N NMR at −378 ppm, whereas the remaining two nitrogen atoms have a resonance at −205 ppm. The IR spectrum shows two weak sharp absorptions for ν_{asym} at 3468 and ν_{sym} at 3396 cm^{-1}, which also confirm the absence of hydrogen bonds in the crystal lattice. Finally because of the high thermal stability of **3**, the EIMS spectrum shows the molecular ion at *m*/*z* 476 (16%) while the most intense peak at *m*/*z* 444 (100%) was assigned to the $[M^+ - 2NH_2]$ fragment.

Single crystals of **3** suitable for X-ray structural analysis were obtained by slow crystallization of its saturated pentane solution at −32 °C. Compound **3** crystallizes in the monoclinic space group *P*2(1)/*c*.[11] Figure 2 shows the molecular structure and numbering Scheme of **3**.

The AlN_4 core has a deformed tetrahedral geometry with the smallest and biggest N-Al-N angle of 95.7° and 117.2°,

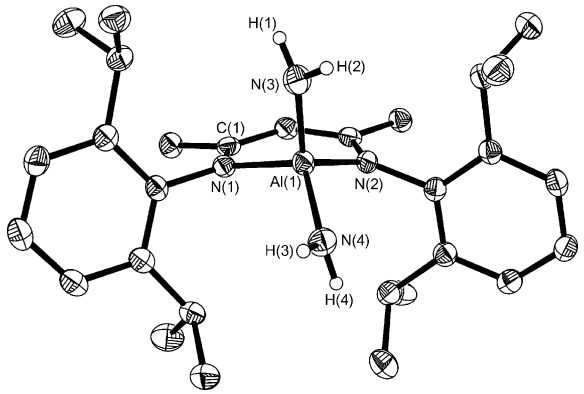


Figure 2. Thermal ellipsoids plot of **3** showing the atoms at the 50% probability level. H atoms, except N*H*, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 1.921(2), Al(1)-N(2) 1.903(2), Al(1)-N(3) 1.790(2), Al(1)-N(4) 1.788(2), N(3)-H(1) 0.88(2), N(3)-H(2) 0.85(2), N(4)-H(3) 0.87(2), N(4)-H(4) 0.86(2); N(1)-Al(1)-N(2) 95.7(1), N(1)-Al(1)-N(3) 107.2(1), N(1)-Al(1)-N(4) 117.2(1), N(3)-Al(1)-N(4) 112.2(1), H(1)-N(3)-H(2) 106(2), H(3)-N(4)-H(4) 109(2), H(1)-N(3)-Al(1) 122(1), H(2)-N(3)-Al(1) 127(1), H(3)-N(4)-Al(1) 123(1), H(4)-N(4)-Al(1) 125 (1).

respectively. The N(1)-Al-N(2) angle (95.7°) within the six-membered ring is in the normal range, whereas the large N(3)-Al-N(4) angle of 112.2° (compare with 86.9–106.1° in the dimeric and trimeric cyclic species)[2,3] might be due to the monomeric nature of **3** and thus missing the ring strain characteristics of the cyclic congeners. There are also significant differences of the Al–N bond lengths within the molecule. The Al–N(1) and Al–N(2) bond lengths (1.921, 1.903 Å) are in the normal range, while the Al–N(3) and Al–N(4) bond lengths (1.790, 1.788 Å) represent the shortest bonds for NH_2 groups with Al so far known (compare with 1.873–2.034 Å).[2,3] A similar shortening of the Al–$(NH_2)_{terminal}$ bond length was observed in $[AlCl_3(NH_2iPr)][\{Al(NH_3)(NH_2)[Al(NHiPr)(NiPr)Cl]_2\}_2]$ and was assigned to the ionic resonance effects of the Al–N bond.[3,12] The hydrogen atoms of the NH_2 groups were localized in the difference electron-density map and the N–H bond lengths (0.85, 0.86, 0.87, and 0.88 Å) are in the range of known compounds (0.75–1.10 Å).[2,3] The nitrogen atoms of the NH_2 groups have almost planar environments (the sum of the surrounding angles 356°—N(3) and 357°—N(4)), which indicates a lowering of the inversion barrier at the nitrogen center due to the electropositive aluminum atom.[13] A similar phenomenon was observed for $[Cp^*_2TiNH_2]$ and $[\{[DippN(SiMe_3)]Ge(NH_2)NH\}_3]$ ($Cp^* = C_5Me_5$, Dipp = diisopropylphenyl).[14,15]

In summary, we have presented a novel method for preparing aluminum amides and hydroxides from the corresponding chlorides. The main by-product—1,3-di-*tert*-butylimidazolium chloride—can be easily separated from the product by filtration and recycled to the free base. $[LAl(NH_2)_2]$ is to the best of our knowledge the first monomeric main-group metal diamide that contains two terminal NH_2 groups. Further research will be focused on the preparation of the heavier Group 13 analogues.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glovebox techniques.

Synthesis of **3**: Dry gaseous NH_3 was added in excess to a solution of (2.410 g, 4.675 mmol) $[LAlCl_2]$ and 1.686 g (9.349 mmol) of 1,3-di-*tert*-butylimidazol-2-ylidene in toluene (60 mL) cooled to −20 °C. Immediately after the addition of NH_3, a precipitate of 1,3-di-*tert*-butylimidazolium chloride was formed. After 10 min the gas stream of NH_3 was disconnected, the cooling bath was removed, and the suspension was stirred for additional 10 min. The excess ammonia was released through a mineral oil bubbler attached to the flask. The precipitate was removed by filtration, washed twice with toluene (10 mL), and all the volatiles were removed in vacuo. The oily residue was treated twice with cold pentane (5 mL) and after filtration and drying in vacuo, **3** was obtained as a white microcrystalline powder. Yield 1.67 g (75%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = -0.52$ (bs, ^1J(N,H) = 64 Hz, 4H, NH_2), 1.17 (d, ^3J(H,H) = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.37 (d, ^3J(H,H) = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.58 (s, 6H, CH_3), 3.47 (sept, ^3J(H,H) = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 4.88 (s, 1H, γ-CH), 7.05–7.20 ppm (m, 6H, *m*-, *p*- Ar-H); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C, TMS): $\delta = 23.4$, 24.8 (CH(*C*H$_3$)$_2$), 25.4 (*C*H(CH$_3$)$_2$), 28.5 (*C*H$_3$), 96.5 (γ-*C*H), 124.3, 127.0, 141.2, 144.5 (*i*-, *o*-, *m*-, *p*- *Ar*), 169.2 ppm (*C*=N); ^{15}N NMR (50.7 MHz, C_6D_6, 25 °C, $MeNO_2$): $\delta = -378$ (*N*H$_2$); −205 ppm (C=*N*); ^{27}Al NMR (78.2 MHz, C_6D_6, 25 °C, $[Al(OH_2)_6]^{3+}$): $\delta = 102$ ppm ($\nu_{1/2} = 4031$ Hz); IR (KBr pellet): $\tilde{\nu} =$ 3468 vw, 3396 vw (NH) cm^{-1}; EI-MS (70 eV): *m*/*z* (%): 476 (16) [*M*$^+$], 459 (20) [*M*$^+$−NH$_3$], 444 (100) [*M*$^+$−2NH$_2$]; elemental analysis (%) calcd for $C_{29}H_{45}AlN_4$ (476.7): C 73.1, H 9.5; found: C 72.9, H 9.4.

Synthesis of **4**: H_2O (180 μL, 9.989 mmol) was added quickly to a solution of $[LAlCl_2]$ (2.560 g, 4.966 mmol) and 1,3-di-*tert*-butylimidazol-2-ylidene (1.790 g, 9.932 mmol) in benzene (60 mL) cooled to 10 °C. Immediately after the addition of water, a slurry of the 1,3-di-*tert*-butylimidazolium chloride was formed. The suspension was vigorously stirred for an additional 10 min and filtered. The precipitate was washed twice with benzene (5 mL) and all the volatiles were removed in vacuo. The solid residue was treated twice with cold pentane (5 mL) and after filtration and drying in vacuo, **4** was obtained as a white powder. Yield 1.55 g (65%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C, TMS): $\delta = 0.22$ (s, 2H, OH), 1.16 (d, ^3J(H,H) = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.42 (d, ^3J(H,H) = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.58 (s, 6H, CH_3), 3.47 (sept, ^3J(H,H) = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 4.92 (s, 1H, γ-CH), 7.14–7.16 ppm (m, 6H, *m*-, *p*- Ar-H); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C, TMS): $\delta = 23.1$, 24.8 (CH(*C*H$_3$)$_2$), 25.2 (*C*H(CH$_3$)$_2$), 28.3 (*C*H$_3$), 96.5 (γ-*C*H), 124.5, 127.4, 139.9, 144.8 (*i*-, *o*-, *m*-, *p*- *Ar*), 170.3 ppm (*C*=N); IR (KBr pellet): $\tilde{\nu} = 3458$ wbr (OH) cm^{-1}. EI-MS (70 eV): *m*/*z* (%): 478 (38) [*M*$^+$], 460 (10) [*M*$^+$−H$_2$O], 445 (100) [*M*$^+$−H$_2$O−CH$_3$]; elemental analysis (%) calcd for $C_{29}H_{43}AlN_2O_2$ (480.7): C 72.5, H 9.4; found: C 72.4, H 9.5.

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[11] Crystal data for **3**: $C_{29}H_{45}AlN_4$, $Mr = 476.67$, monoclinic, space group $P2(1)/c$, $a = 16.995(2)$, $b = 13.057(2)$, $c = 13.565(2)$ Å, $\beta = 109.26(2)°$, $V = 2841.7(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.114$ Mg m^{-3}, $F(000) = 1040$, $\lambda = 1.54178$ Å, $T = 100(2)$ K, $\mu(Cu_{K\alpha}) = 0.781$ mm^{-1}. Data for the structure were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. Intensity measurements were performed on a rapidly cooled crystal (dimensions $0.30 \times 0.10 \times 0.10$ mm^3) in the range $8.7 \le 2\theta \le 116.2°$. Of the 17547 measured reflections, 3915 were independent. The structure was solved by direct methods (SHELXS-97)[16] and refined with all data by full-matrix least-squares on F^2. The hydrogen atoms of C–H bonds were placed in idealized positions, whereas the hydrogen atoms from the NH_2 moieties were localized from the difference electron-density map and refined isotropically. The final refinements converged at $R1 = 0.0390$ for $I > 2\sigma(I)$, $wR2 = 0.1033$ for all data. The final difference Fourier synthesis gave a min/max residual electron density $-0.281/+0.227$ e Å^{-3}. CCDC-226258 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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