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Reactions between Base-Stabilized AlH_3 and Diisopropylphenylamine: Syntheses and X-ray Structures of Amino- and Iminoalanes

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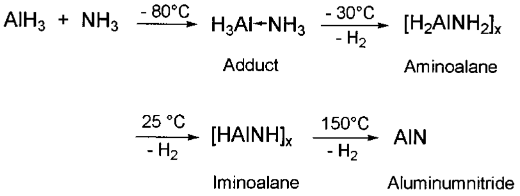
Reactions between amine-stabilized H_3Al (amine = NMe_3, NMe_2Et) and $DippNH_2$ (Dipp = 2,6-(i-Pr)$_2C_6H_3$) were studied at different reaction temperatures and in different molar ratios. Lewis base stabilized heterocyclic iminoalanes [base·HAlNDipp]$_2$ (base = NMe_3 (**1**), NMe_2Et (**7**)), monomeric aminoalanes $Me_3N\cdot(H_{3-x})Al(N(H)Dipp)_x$ (x = 2 (**2**), 3 (**4**)) and base-free, heterocyclic aminoalanes [Dipp(H)NAl(H)-μ-N(H)Dipp]$_2$ (**3**), respectively, were obtained in high yields. The NMe_3 group of **2** can be thermally removed, yielding a mixture of **3** and **4**, while that of **4** can be replaced by 4-(dimethylamino)pyridine (dmap), giving dmap·Al(N(H)Dipp)$_3$ (**5**). In addition, Li(OEt_2)Al[N(H)Dipp]$_4$ (**6**) and the amine-stabilized heterocycle DippN(H)Al(H)N(Dipp)AlH(NMe_2Et)N(H)Dipp (**8**) were synthesized. The new compounds **1**−**8** were fully characterized by IR, mass, and multinuclear NMR spectroscopy (^1H, ^{13}C); **2**−**4**, **6**, and **8** were also characterized by single-crystal X-ray structure analyses.

Introduction

Since the first synthesis of $H_3Al\cdot NMe_3$ by Stecher and Wiberg in 1942,[1] tertiary amine−alane adducts of the type $H_3Al\cdot NR_3$ have been studied in detail for more than half a century due to their fascinating structural chemistry[2] and their versatility in organic and inorganic syntheses.[3] More recently, their potential to serve as molecular precursors (*single-source precursors*) for the synthesis of a variety of solid-state materials was demonstrated, restimulating fundamental research on this class of compounds.[4] Several alanes such as $H_3Al\cdot NMe_3$, $H_3Al\cdot NMe_2Et$, $H_3Al\cdot NEt_3$, $H_3Al\cdot(NMe_3)_2$, $H_3Al\cdot$TMEDA, and $Me_2AlH\cdot NMe_2Et$ were shown to be promising candidates for the deposition of Al films and of various III−V material films by MOCVD technology (*metalloorganic chemical vapor deposition*).[5] However, the utility of amine−alane adducts in materials science also was initially studied by Wiberg et al. They investigated in detail the equimolar reaction of AlH_3 and NH_3, demonstrating the complete range of amine−alane chemistry. First, the simple Lewis acid−base adduct $H_3Al\cdot NH_3$ is formed, which is only stable at low temperature (−80 °C). Raising the temperature subsequently leads to H_2 elimination reactions, resulting in the stepwise formation first of the aminoalane [H_2AlNH_2]$_x$ and, at higher temperatures, of the iminoalane [HAlNH]$_x$. At 150 °C, the reaction finally gives aluminum nitride, AlN.[6] The reaction of AlH_3 with an excess of NH_3 results in the formation of $Al(NH_2)_3$,[7] which also can be thermally converted into AlN (Scheme 1).

Scheme 1. Initial Studies by Wiberg et al. on the Reaction of AlH_3 and NH_3



Unfortunately, the solid-state structures of the oligomeric amino- and iminoalane as well as of $Al(NH_2)_3$ remained unknown, due to their unsatisfactory crystallizing properties and their tendency to undergo consecutive H_2 or NH_3 elimination reactions. Therefore, reactions of base-stabilized AlH_3 with secondary amines R_2NH were studied in detail in order to obtain structural information on as-prepared oligomeric aminoalanes. The reaction temperature, the stoichiometry of the reactants, and the steric demand of the substituents bound to N were found to play key roles in what degree of oligomerization was attained. Monomeric aminoalanes of the type base·Al(H)$_2NR_2$[8] and $Al(NR_2)_3$[9]), as well as

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(1) (a) Stecher, O.; Wiberg, E. *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 2003. (b) Wiberg, E.; Amberger, E. *Hydrides of the Elements of Main Groups I −IV*; Elsevier: Amsterdam, 1971.

(2) (a) Jones, C.; Koutsantonis, G. A.; Raston, C. L. *Polyhedron* **1993**, *12*, 1829. (b) Gardiner, M. G.; Raston, C. L. *Coord. Chem. Rev.* **1997**, *166*, 1. (c) Downs, A. J. *Coord. Chem. Rev.* **1999**, *189*, 59. (d) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, *101*, 3305.

(3) Hudlicky, M. In *Reductions in Organic Chemistry*, 2nd ed.; American Chemical Society: Washington, DC, 1996.

(4) For a recent review see, for example: Jegier, J. A.; Gladfelter, W. L. *Coord. Chem. Rev.* **2000**, *206*−*207*, 631.

(5) (a) Gladfelter, W. L.; Boyd, D. C.; Jensen, K. F. *Chem. Mater.* **1989**, *1*, 339. (b) Wee, A. T. S.; Murell, A. J.; Singh, N. K.; O'Hare, D.; Ford, J. S. *J. Chem. Soc., Chem. Commun.* **1990**, 11. (c) Baum, T. H.; Larson, C. E.; Jackson, R. L. *Appl. Phys. Lett.* **1989**, *55*, 1264.

(6) Wiberg, E.; May, A. *Z. Naturforsch., B* **1955**, *10*, 229.

(7) Wiberg, E.; May, A. *Z. Naturforsch., B* **1955**, *10*, 231.

(8) (a) Atwood, J. L.; Kousantonis, G. A.; Lee, F.-C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 91. (b) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4652. (c) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100. (d) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 1349.

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oligomeric aminoalanes such as $[H_2AlNR_2]_x$,[10] $[HAl(NR_2)_2]_x$,[11] and $[Al(NR_2)_3]_2$,[12] were obtained, mainly in the form of four- and six-membered heterocycles.[13] In contrast, equimolar reactions of $H_3Al·NR_3$ with primary amines RNH_2 preferentially yielded iminoalanes $[HAlNR]_x$ or mixed imino- and aminoalanes rather than aminoalanes $[H_2AlN(H)R]_x$, depending on their instability toward further H_2 elimination reactions. Several Al−N cages ($x = 4$, 6−8) were structurally characterized,[14] clearly showing the influence of the steric demand of the substituents on the degree of oligomerization. In contrast, monomeric compounds have been synthesized to a far lesser extent. Monomeric iminoalanes of the type HAlNR are completely unknown,[15] while aminoalanes of the type $H_2AlN(H)R$ are only known in the form of intramolecular stabilized heterocycles.[8b,d] In addition, the monomeric bis- and tris(amino)alanes $HAl[N(H)R]_2$ and $Al[N(H)R]_3$ also have not been structurally characterized, to date.[16] Several attempts to prepare them have been made, but reactions of $AlCl_3$ with LiNHR (R = Dipp, *t*Bu) yielded monomeric Li aluminates of the type $LiAl[N(H)R]_4$,[17] and reactions of $LiAlH_4$ with $DippNH_2$ gave heterocyclic compounds.[18]

We became interested in monomeric compounds of the types mentioned above not only because of their underexplored structural chemistry but also due to the fact that monomeric compounds usually show higher volatilities compared to heterocyclic or cage compounds. This, of course, is of fundamental importance for potential applications of such compounds in CVD processes. In addition, carbon contamination of the resulting material generally can be reduced by use of H-substituted precursors, as was shown in different studies.

The most common pathway for the preparation of monomeric aminoalanes makes use of very bulky substituents such as Mes* and Dipp (Mes* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$, Dipp = 2,6-(i-Pr)$_2$C$_6$H$_3$), leading to the formation of kinetically stabilized moieties.[19] More recently, we have shown that monomeric group 13/15 compounds also can be electronically stabilized. The heterocycles $[R_2MER'_2]_x$ (M = Al, Ga; E = P, As, Sb, Bi), which may be described as head-to-tail adducts, generally can be converted into their monomeric form by addition of a Lewis base, which coordinates to the group 13 metal.[20] Combining these two general pathways, we became interested in the reaction of amine-stabilized AlH_3 with $DippNH_2$, which contains the bulky Dipp group, in order to synthesize monomeric amine-stabilized amino- and iminoalanes containing both Al−H and N−H functionalities.

We report here reactions of $AlH_3·NMe_3$ and $AlH_3·NMe_2Et$ with $DippNH_2$, leading to several new amino- and iminoalanes, which were obtained either as heterocycles or Lewis base stabilized monomers. The products were investigated in detail by elemental analyses, IR, mass, and multinuclear NMR spectroscopy (^{1}H, ^{13}C); five compounds were also characterized by single-crystal X-ray diffraction.

Results and Discussion

Depending on the molar ratio of $H_3Al·NMe_3$ and $DippNH_2$ and the reaction temperature, the hydridic H atoms of AlH_3 can be substituted by one, two, or three amino groups (Scheme 2).

The equimolar reaction between $H_3Al·NMe_3$ and $DippNH_2$ probably yielded first $Me_3N·H_2AlN(H)Dipp$,[21] which, however, could not be isolated due to its lability toward a second H_2-elimination reaction, subsequently yielding the base-stabilized iminoalane $[Me_3N·HAlNDipp]_2$ (**1**). The ^{1}H and ^{13}C NMR spectra of **1** show two sets of resonances due to the nonequivalent *i*-Pr groups

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[9] (a) Brothers, P. J.; Wehmschulte, R. J.; Olmstead, M. M.; Ruhlandt-Senge, K.; Parkin, S. R.; Power, P. P. *Organometallics* **1994**, *13*, 2792. (b) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. A* **1969**, 2279.

[10] (a) Downs, A. J.; Duckworth, D.; Machell, J. C.; Pulham, C. R. *Polyhedron* **1992**, *11*, 1295. (b) Dumichen, U.; Gelbrich, V.; Sieler, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 262. (c) Kuhn, N.; Fuchs, S.; Steimann, M. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1387. (d) Hair, G. S.; Battle, S. L.; Decken, A.; Cowley, A. H.; Jones, R. A. *Inorg. Chem.* **2000**, *39*, 27. (e) Klein, C.; Nöth, H.; Tacke, M.; Thomann, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 886. (f) Bensiek, S.; Bangel, M.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *Organometallics* **2000**, *19*, 1292. (g) Atwood, J. L.; Lawrence, S. M.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 73.

[11] (a) Ouzounis, K.; Riffel, H.; Hess, H.; Kohler, U.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1983**, *504*, 67. (b) Chang, C.-C.; Li, M.-D.; Chiang, M. Y.; Peng, S.-M.; Wang, Y.; Lee, G.-H. *Inorg. Chem.* **1997**, *36*, 1955. (c) Janik, J. F.; Wells, R. L.; Rheingold, A. L.; Guzei, I. A. *Polyhedron* **1998**, *17*, 4101.

[12] Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257.

[13] For a recent review see for example: Chang, C.-C.; Ameerunisha, M. S. *Coord. Chem. Rev.* **1999**, *189*, 199.

[14] (a) Veith, M. *Chem. Rev.* **1990**, *90*, 3. (b) Perego, G.; del Piero, G.; Cesari, M.; Zazzetta, A.; Dozzi, G. *J. Organomet. Chem.* **1975**, *87*, 53. (c) del Piero, G.; Cesari, M.; Dozzi, G.; Mazzei, A. *J. Organomet. Chem.* **1977**, *129*, 281. (d) Cesari, M.; Perego, G.; del Piero, G.; Cucinella, S.; Cernia, E. *J. Organomet. Chem.* **1974**, *78*, 203. (e) del Piero, G.; Perego, G.; Cucinella, S.; Cesari, M.; Mazzei, A. *J. Organomet. Chem.* **1977**, *136*, 13. (f) Perego, G.; Dozzi, G. *J. Organomet. Chem.* **1981**, *205*, 21. (g) Perego, G.; Cesari, M.; del Piero, G.; Balducci, A.; Cernia, E. *J. Organomet. Chem.* **1975**, *87*, 33. (h) del Piero, G.; Cucinella, S.; Cesari, M. *J. Organomet. Chem.* **1979**, *173*, 263. (i) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 637.

[15] The only monomeric iminoalane was recently synthesized by reaction of a low-valent alane and a sterically encumbered azide: Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2172.

[16] Al[N(H)Mes*]$_3$ (Silverman, J. S.; Carmalt, C. J.; Cowley, A. H.; Culp, R. D.; Jones, R. A.; McBurnett, B. G. *Inorg. Chem.* **1999**, *38*, 296) and Al[N(H)t-Bu]$_3$ (Brask, J. K.; Chivers, T.; Yap, G. P. A. *Chem. Commun.* **1998**, 2543) have been synthesized, but no structural details are given in the original contribution. However, the severely disordered structure of Al[N(H)t-Bu]$_3$ cocrystallized with Li[Al(Nt-Bu)(NHt-Bu)$_2$]$_2$·(t-BuLi) was recently reported, showing Al[N(H)t-Bu]$_3$ to form a dimer in the solid state (Brask, J. K.; Chivers, T.; Schatte, G.; Yap, G. P. A. *Organometallics* **2000**, *19*, 5683).

[17] (a) Silverman, J. S.; Carmalt, C. J.; Neumeyer, D. A.; Cowley, A. H.; McBurnett, B. G.; Decken, A. *Polyhedron* **1998**, *17*, 977. (b) Beswick, M. A.; Choi, N.; Harmer, C. N.; McPartlin, M.; Mosquera, M. E. G.; Raithby, P. R.; Tombul, M.; Wright, D. S. *Chem. Commun.* **1998**, 1383.

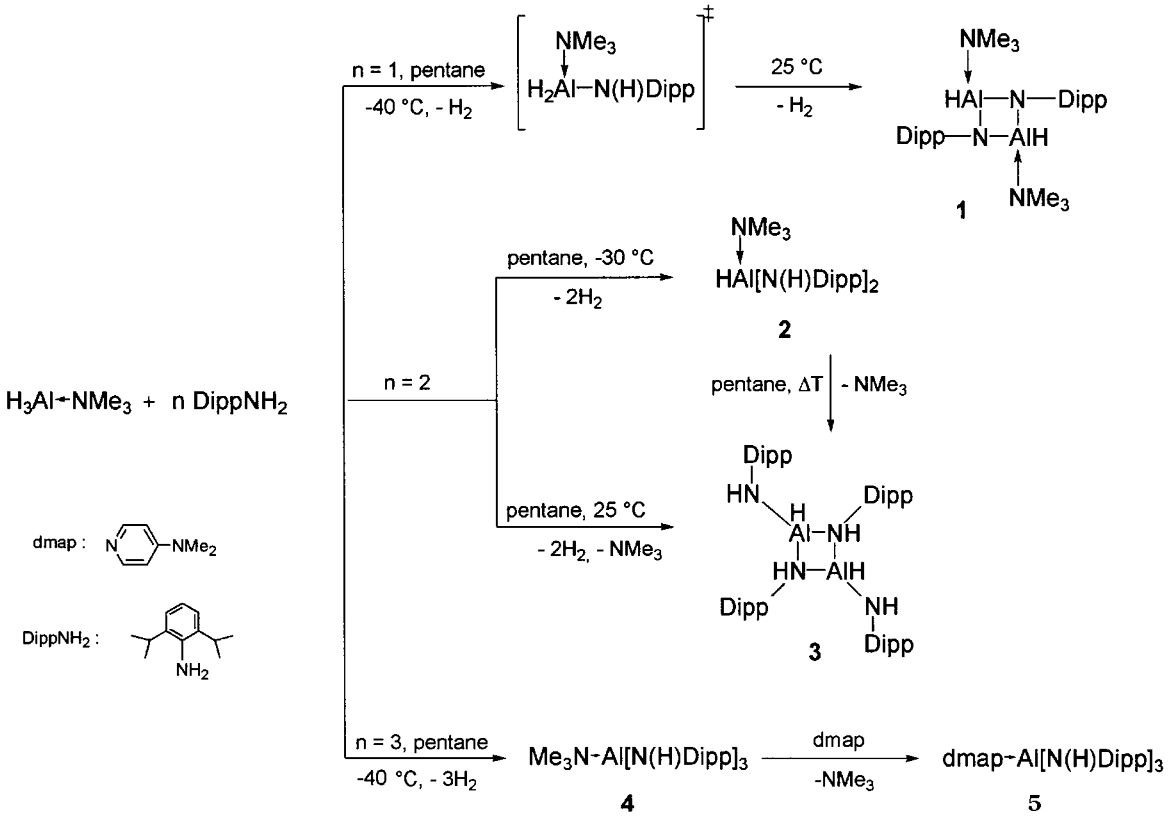
[18] Montero, M. L.; Wessel, H.; Roesky, H. W.; Teichert, M.; Uson, I. *Angew. Chem., Int. Ed.* **1997**, *36*, 629.

[19] (a) Waggoner, K. M.; Ruhlandt-Senge, K.; Wehmschulte, R. J.; He, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2557. (b) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791. (c) Li, X.-W.; Su, J.; Robinson, G. H. *Chem. Commun.* **1998**, 1281. (d) Rutherford, D.; Atwood, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 11535. For a recent review, see for example: Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

[20] (a) Schulz, S.; Nieger, M. *Organometallics* **2000**, *19*, 2640. (b) Kuczkowski, A.; Thomas, F.; Schulz, S.; Nieger, M. *Organometallics* **2000**, *19*, 5758. (c) Thomas, F.; Schulz, S.; Nieger, M. *Eur. J. Inorg. Chem.* **2001**, 161.

[21] It should be noted that for the synthesis of all compounds described in this contribution it is crucial to maintain the correct stoichiometry between the reactants. This can be a problem due to the tendency of $H_3Al·NMe_3$ to decompose at elevated temperatures, giving polymeric $(AlH_3)_x$. If such an impure $H_3Al·NMe_3$ sample is used, higher substituted compounds are formed due to an excess of $DippNH_2$. To avoid their formation, all reactions can be performed using a slight excess (<10%) of $H_3Al·NMe_3$.

Scheme 2. Reaction of $H_3Al{\cdot}NMe_3$ and $DippNH_2$ in Different Molar Ratios



of the Dipp ligands. The IR spectrum of **1** displays a strong Al–H absorption band at 1799 cm^{-1}, while no N–H absorption band is detected. The EI mass spectrum does not show a molecular ion peak, but peaks with low intensity due to $[M^+/2]$ and $[M^+/2 - NMe_3]$ are observed. In addition, a fragment peak (*m*/*z* 812) indicates the presence of the heterocubane $[HAlNDipp]_4$, whose formation starting from **1** after loss of the NMe_3 group followed by dimerization of the thus-formed base-free iminoalane $[HAlNDipp]_2$ seems reasonable.

Reaction of $H_3Al{\cdot}NMe_3$ and 2 equiv of $DippNH_2$ was accompanied by H_2 elimination, resulting in the formation of the Lewis base stabilized bis(amino)alane $NMe_3{\cdot}Al(H)[N(H)Dipp]_2$ (**2**). Its IR spectrum shows strong N–H (3408, 3363 cm^{-1}) and Al–H (1832 cm^{-1}) absorption bands. The ^1H NMR spectrum of **2** also displays resonances due to N–H and Al–H groups. In addition, resonances due to the Dipp protons and the NMe_3 group in a 2:1 molar ratio were detected, indicating the stability of the Lewis base stabilized bis(amino)alane **2** in solution at ambient temperature. In contrast, its EI mass spectrum does not show the molecular ion peak due to consecutive reactions of **2** in the gas phase. In an attempt to initiate the dissociation of NMe_3, a solution of **2** was heated in pentane at reflux for about 2 h. Evaporation of all volatiles in vacuo gave a colorless solid, whose ^1H NMR spectrum proved the complete conversion of **2** into equal amounts of the base-free heterocycle $[Dipp(H)NAl(H)\text{-}\mu\text{-}N(H)Dipp]_2$ (**3**) and the base-stabilized tris(amino)alane $Me_3N{\cdot}Al[N(H)Dipp]_3$ (**4**). Pure **3** was obtained after recrystallization from hexane at 0 °C. In contrast, heating **2** to 100 °C in the absence of solvent for 1 h did not give **3**. According to ^1H NMR studies, **2** was quantitatively converted to the iminoalane **1** and the tris(amino)alane **4**. An additional Me_3N-free Al–N compound was formed in low yield, while no resonances due to **3** were observed. The unknown Me_3N-free compound might be the iminoalane $[HAlNDipp]_4$, whose formation in the gas phase was shown in the mass spectra of **1** and **2**. However, further studies aimed at the isolation and identification of this particular compound are needed. Since the synthesis of **3** by heating **2** in pentane solution was accompanied by the formation of **4**, we were interested in a more straightforward, byproduct-free synthesis and, therefore, investigated the 2:1 molar reaction between $DippNH_2$ and $H_3Al{\cdot}NMe_3$ in more detail. Pure **3** was obtained in high yield when the reaction was performed at 25 °C in pentane, followed by storage of the resulting solution at 0 °C. Obviously, the higher reaction temperature favors the dissociation of (weakly bound) NMe_3, which agrees with what was observed when **2** was heated in refluxing pentane. The ^1H NMR spectrum of **3** obtained at ambient temperature shows resonances due to N–H and Al–H groups. Broad resonances of the bridging NHDipp groups point to exchange reactions between the nonequivalent Me groups, which could be resolved at lower temperature. At −30 °C *two* doublets at 0.76 and 1.48 ppm and *two* septets were observed, which coalesce at about 0 °C. Further heating to 60 °C led to *one* well-resolved doublet and *one* septet. At this temperature, the exchange reactions between the *i*-Pr protons are fast on the NMR time scale. Comparable findings were observed in temperature-dependent ^{13}C NMR spectra. Figure 1 displays the ^1H NMR spectra obtained between −30 and 60 °C.

Reaction of 3 equiv of $DippNH_2$ and $H_3Al{\cdot}NMe_3$ yielded the Me_3N-stabilized tris(amino)alane $Me_3N{\cdot}Al[N(H)Dipp]_3$ (**4**), which was obtained as a colorless crystalline solid after crystallization at −10 °C. Its IR

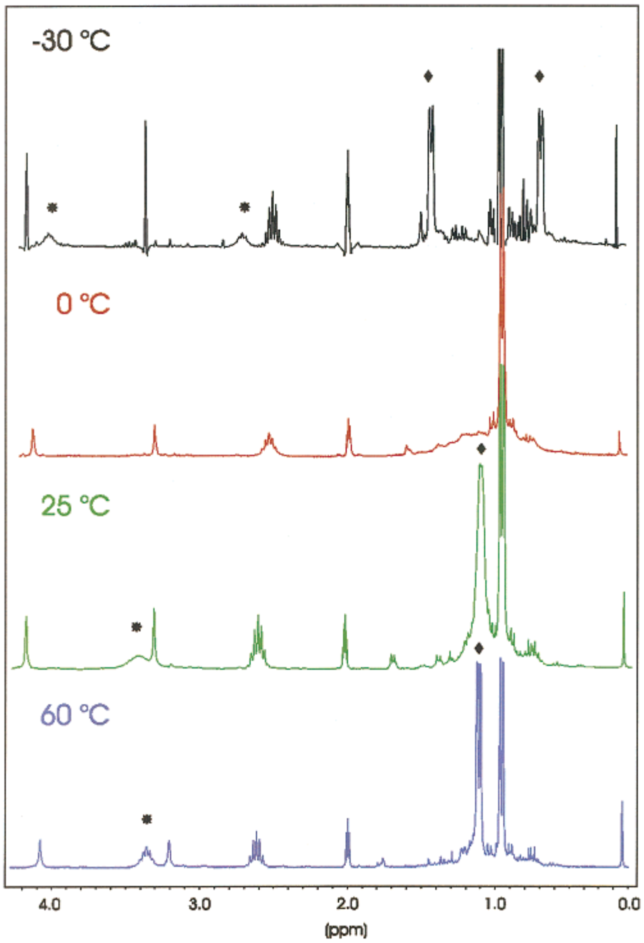


Figure 1. Temperature-dependent ^{1}H NMR spectra of **3** recorded between −30 and 60 °C in toluene-d_8.

spectrum does not show Al−H but strong N−H absorption bands. The ^{1}H NMR spectrum of **4** also shows only resonances due to DippNH and NMe_3 protons in the expected 3:1 stoichiometry. Its EI mass spectrum does not show the molecular ion but peaks due to the fragments AlN(H)Dipp and $Al(NHDipp)_2$. Peaks with higher molecular masses (m/z 580 $[Al_2(NHDipp)_3]$, 758 $[Al_2(NHDipp)_4]$, 781 $[Al_3(NDipp)_4]$) demonstrate the lability of **4** toward loss of NMe_3, followed by consecutive gas-phase oligomerization reactions. The lability of the NMe_3 group was also demonstrated in the reaction of **4** with 4-(dimethylamino)pyridine (dmap). This particular Lewis base, whose capacity to stabilize monomeric group 13/15 compounds has been demonstrated previously,[20] displaces the NMe_3 ligand, giving dmap-coordinated dmap·Al[N(H)Dipp]$_3$ (**5**) in quantitative yield. Its ^{1}H NMR spectrum shows typical resonances due to the dmap group, while the resonance of NMe_3 disappeared. The IR spectrum of **5** is very similar to that of **4**, also showing strong N−H absorption bands.

To examine the solid-state structures of the new imino- and aminoalanes, considerable efforts were undertaken to grow single crystals of the compounds. Several data sets of colorless crystals of **1** were recorded but could not be refined, due to severe disorder problems. Therefore, no information with respect to bond lengths and angles can be given. However, the collected data sets unambiguously confirmed the connectivity of **1**, containing a planar four-membered ring with both Al centers coordinated by one NMe_3 group. This result is interesting, in view of the fact that the degree of oligomerization of iminoalanes $[RAlNR']_x$ generally depends on the steric bulk of the substituents: (small) four-membered rings are usually formed with sterically bulky ligands bound to both the Al and the N centers, while use of smaller ligands generally results in the formation of more highly associated cyclic (six-membered rings) or cage compounds ($x \geq 4$). In **1**, only the N centers are substituted by a bulky Dipp group, while the Al centers each only carry a H atom. Clearly, the coordination of NMe_3 stabilizes the four-membered heterocycle. The formation of **1** proves the principle of electronic stabilization to be very powerful for the synthesis of lower associated iminoalanes. In addition, due to the use of one reactive ligand (H) and a coordinatively bound Lewis base, which might be eliminated under specific conditions, electronically stabilized iminoalanes such as **1** promise to show a much higher reactivity and potential for further synthetic studies compared to kinetically stabilized iminoalanes containing very bulky substituents.

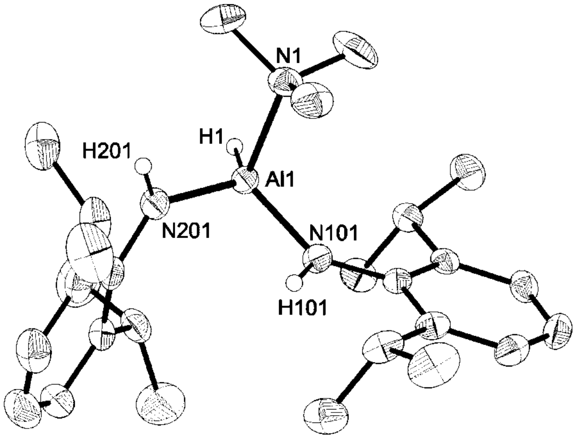


Figure 2. Molecular structure and atom-numbering scheme of compound **2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N and Al, have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−N101 = 1.827(2), Al1−N201 = 1.833(2), Al1−N1 = 2.019(2), Al1−H1 = 1.501(12), N101−H101 = 0.847(14), N201−H201 = 0.855(14); N101−Al1−N201 = 105.7(1), N101−Al1−N1 = 104.6(1), N201−Al1−N1 = 101.7(1).

Colorless crystals of **2** suitable for an X-ray structure analysis were obtained from hexane at 0 °C. Figure 2 shows its solid-state structure. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ (No. 2). The central skeleton of **2** is built by two N(H)Dipp groups and one H atom bound to the Al center. Coordination of the Lewis base NMe_3 allows Al to reach the stable coordination number 4. The Al−N σ-bonds are significantly shorter (1.827(2), 1.833(2) Å) compared to the Al−N dative bond (2.019(2) Å). However, they fall within typical ranges for dative Al−N bonds and for Al−N σ-bonds between 3-fold-coordinated N and 4-fold-coordinated Al centers. Intermolecularly stabilized [N-methyl-N',N''-bis(trimethylsilyl)diethylenetriamino]alane, $[(Me_3SiNCH_2CH_2)_2NMe]AlH$, also shows significantly different Al−N bond distances (1.832, 2.014 Å).[22]

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[22] Emig, N.; Nguyen, H.; Krautscheid, H.; Reau, R.; Cazaux, J.-B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599.

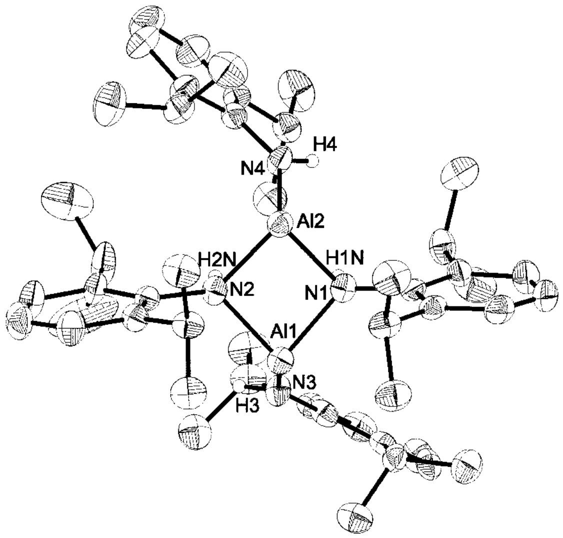

Figure 3. Molecular structure and atom-numbering scheme of compound **3**. Thermal ellipsoids are drawn at the 50% probability level. *i*-Pr-groups and H atoms, except those attached to ring N and Al, have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−N1 = 1.970(3), Al1−N2 = 1.972(3), Al1−N3 = 1.809(3), Al1−H1Al = 1.446(16), Al2−N4 = 1.801(3), Al2−N1 = 1.956(3), Al2−N2 = 1.979(3), Al2−H2Al = 1.447(16), N1−H1N = 0.906(16), N2−H2N = 0.859(16), N3−H3 = 0.885(17), N4−H4 = 0.882(17); N3−Al1−N1 = 106.2(2), N3−Al1−N2 = 106.7(2), N1−Al1−N2 = 84.3(2), N4−Al2−N1 = 104.4(2), N4−Al2−N2 = 107.5(2), N1−Al2−N2 = 84.5(2), C11−N1−Al2 = 126.3(2), C11−N1−Al1 = 128.3(2), Al2−N1−Al1 = 93.8(2), C21−N2−Al1 = 125.6(2), C21−N2−Al2 = 129.0(2), Al1−N2−Al2 = 93.0(2).

To the best of our knowledge, **2** is the first monomeric bis(amino)alane stabilized by an external Lewis base. **2** contains vicinal Al−H and N−H functionalities, a structural motif that was found only in oligomeric Li aluminates,[18,23] heterocycles,[24] or cages[14b,f] and in Lewis acid−base adducts such as 2,2,6,6-tetramethylpiperidine−alane[25] and (2,6-*t*-Bu-4-Me-$C_6H_2O)_2AlH\cdot NH_2$*t*-Bu, thus far.[26]

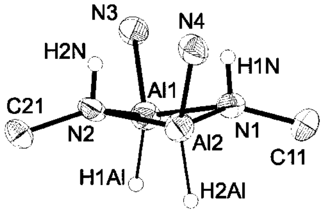

Figure 4. Reduced ORTEP plot of **3** showing the nonplanar Al_2N_2 ring and the all-cis orientation of the substituents. Only the *ipso*-C atoms of the Dipp ligands are shown for clarity.

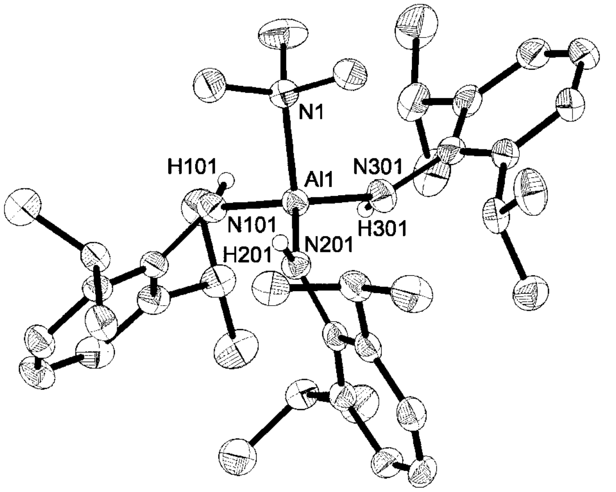

Figure 5. Molecular structure and atom-numbering scheme of compound **4**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N, have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−N201 = 1.823(2), Al1−N101 = 1.839(2), Al1−N301 = 1.840(2), Al1−N1 = 2.038(2), N101−H101 = 0.899(16), N201−H201 = 0.853(17), N301−H301 = 0.888(17); N201−Al1−N101 = 119.1(2), N201−Al1−N301 = 120.4(2), N101−Al1−N301 = 104.5(1), N201−Al1−N1 = 102.2(1), N101−Al1−N1 = 103.2(1), N301−Al1−N1 = 105.1(2).

Colorless crystals of **3** of X-ray quality were obtained from hexane at −20 °C (Figures 3 and 4). Compound **3** crystallizes in the monoclinic space group *C*2/*c* (No. 15). Its central unit is the nonplanar four-membered Al_2N_2 ring containing a bridging N(H)Dipp moiety. A second N(H)Dipp group and an H atom are terminally bound to each Al atom. The terminal substituents and the bridging N-Dipp groups are arranged in a cisoid orientation. The formation of a planar, centrosymmetric Al_2N_2 ring with the ligands adopting all-trans positions likely would lead to increased repulsive interactions between the very bulky Dipp groups. The Al−N distances differ significantly, according to the different coordination numbers (CN) between terminal (CN 3) and bridging N centers (CN 4). The Al−N distance within the ring (1.969(3) Å) is elongated by about 0.16 Å compared to that of the terminal N(H)Dipp group (1.805(3) Å). The same findings were observed in $[Me_2N\text{-}Al(H)\text{-}\mu\text{-}NMe_2]_2$,[11a] to the best of our knowledge the only bis(amino)alane containing identically substituted amino groups in terminal (1.805 Å) and bridging positions (1.965 Å), and in the mixed aminoalane [*i*-$Pr_2NAl(H)\text{-}\mu\text{-}NEt_2]_2$.[11b] The endocyclic N−Al−N angles (84.4°) found in **3** are smaller than the endocyclic Al−N−Al angles (93.4°), as is typical for Al_2N_2 rings.

Colorless crystals of **4** were obtained from hexane at 0 °C. The solid-state structure of **4**, which crystallizes in the monoclinic space group *P*2$_1$/*c* (No. 14), is shown in Figure 5. Compound **4** is the first structurally characterized monomeric tris(amino)alane. The Al−N σ-bonds are about 0.2 Å shorter than the dative Al−N bond. The average Al−N σ-bond distances of **2** and **4** are almost identical, despite the greater steric demand of three N(H)Dipp groups in **4** compared to the two N(H)Dipp groups in **2**. The N−Al−N bond angles between the N(H)Dipp ligands are significantly larger compared to those between the N(H)Dipp and NMe_3 substituents, clearly showing the higher steric demand of the σ-bound N(H)Dipp groups compared to that of the coordinatively bound NMe_3 group. The unexpectedly

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(23) Al-Juaid, S. S.; Eaborn, C.; Gorrell, I. B.; Hawkes, S. A.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1998**, 2411.

(24) (a) Atwood, J. L.; Lawrence, S. M.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 73. (b) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4652. (c) Gardiner, M. G.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 1349.

(25) (a) Atwood, J. L; Koutsantonis, G. A.; Lee, F.-C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1994**, 91. (b) Krossing, I.; Nöth, H.; Schwenk-Kircher, H.; Seifert, T.; Tacke, C. *Eur. J. Inorg. Chem.* **1998**, 1925.

(26) Healy, M. D.; Mason, M. R.; Gravelle, P. W.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 441.

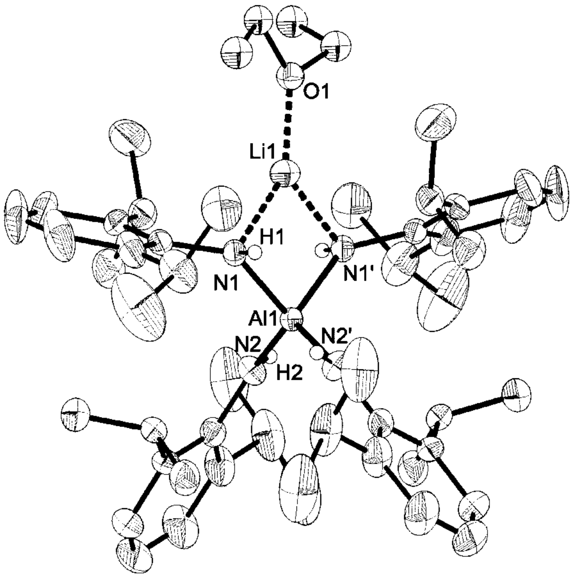


Figure 6. Molecular structure and atom-numbering scheme of compound **6**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N, have been omitted for clarity. Only one orientation of the disordered Et_2O molecule is shown. Selected bond lengths (Å) and angles (deg): Al1−N2 = 1.827(2), Al1−N1 = 1.912(2), N1−Li1 = 2.036(3), N1−H1 = 0.889(15), N2−H2 = 0.861(14), O1−Li1 = 1.847(8); N2′-Al1−N2 = 119.8(2), N2′−Al1−N1 = 119.3(1), N2−Al1−N1 = 100.7(1), N1−Al1−N1′ = 95.4(1), Al1−N1−Li1 = 88.3(2).

large variation of about 15° indicates substantial repulsive interactions between the very bulky substituents.

In a single case, the reaction of $H_3Al{\cdot}NMe_3$ with 3 equiv of $DippNH_2$ led to a mixture of **4** and, in low yield, the second product **6**, which was isolated by recrystallization from toluene. Figure 6 shows the solid-state structure of **6**. Compound **6** crystallizes in the monoclinic space group *C*2/*c* (No. 15). It contains an anionic Al center bound to four N(H)Dipp groups and a Li cation, which is 3-fold-coordinated by one Et_2O molecule and two N(H)Dipp groups. Obviously, **6** is formed from a $H_3Al{\cdot}NMe_3$ sample which was partially contamined with $LiAlH_4{\cdot}OEt_2$. This is reasonable, since the synthesis of $H_3Al{\cdot}NMe_3$ starts from a solution of $LiAlH_4$ in Et_2O. **6** is isostructural with the corresponding THF complex[17b] and shows almost the same structural parameters. The Al−N bond distances clearly show the different coordination numbers of the N atoms. Those distances to the 4-fold-coordinated N are about 0.09 Å elongated compared to those to the 3-fold-coordinated NHDipp group. The bond angles vary between 95.4(1) and 119.8(2)°, with the smallest angle being between the 4-fold-coordinated N centers.

In an attempt to overcome the crystallographic disorder problems observed for the iminoalane **1**, we reacted $DippNH_2$ with $H_3Al{\cdot}NMe_2Et$. The equimolar reaction yielded the iminoalane $[NMe_2Et{\cdot}Al(H)NDipp]_2$ (**7**). Its ^1H NMR spectrum shows resonances due to Al−H and NMe_2Et groups and two doublets due to the nonequivalent *i*-Pr groups. The IR spectrum also proves the presence of Al−H groups (1802 cm^{-1}), while N−H absorption bands were not detected. However, several attempts to obtain single crystals of **7** suitable for an X-ray crystal structure analysis were unsuccessful.

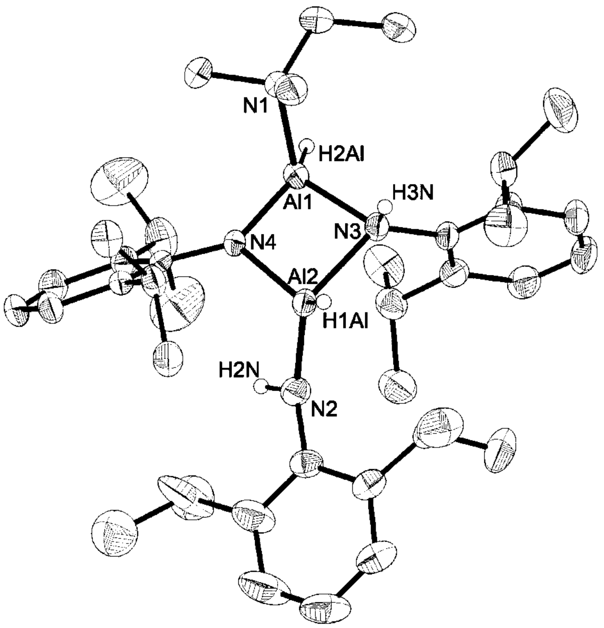


Figure 7. Molecular structure and atom-numbering scheme of compound **8**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N, have been omitted for clarity. Only one orientation of the disordered *i*-Pr group (terminal NHDipp substituent) is shown. Selected bond lengths (Å) and angles (deg): Al1−N1 = 2.010(3), Al1−N3 = 1.925(3), Al1−N4 = 1.804(2), Al1−H2Al = 1.43(3), Al2−N2 = 1.812(3), Al2−N3 = 2.026(3), Al2−N4 = 1.854(2), Al2−H1Al = 1.53(3), N2−H2N = 0.90(4), N3−H3N = 0.86(3), N4−C29 = 1.406(4), N3−C17 = 1.449(4); N4−Al1−N3 = 90.4(2), N4−Al1−N1 = 106.9(2), N3−Al1−N1 = 109.7(2), N2−Al2−N4 = 107.5(2), N2−Al2−N3 = 123.8(2), N4−Al2−N3 = 85.9(2), C17−N3−Al1 = 125.3(2), C17−N3−Al2 = 129.6(2), Al1−N3−Al2 = 87.2(2), C29−N4−Al1 = 138.8(2), C29−N4−Al2 = 124.2(2), Al1−N4−Al2 = 96.4(2).

We also reacted $H_3Al{\cdot}NMe_2Et$ with 0.5 and 1.5 equiv of $DippNH_2$ in pentane in order to obtain Al-rich or N-rich aminoalanes. While the reaction of $H_3Al{\cdot}NMe_2Et$ with 0.5 equiv of $DippNH_2$ yielded **7** as the only isolable product, the reaction with 1.5 equiv of $DippNH_2$ gave the unsymmetrically substituted aminoalane **8**. The IR spectrum of **8** shows strong absorption bands due to N−H and Al−H groups, while the ^1H NMR spectrum obtained at ambient temperature displays a very complex peak pattern due to the presence of several chemically nonequivalent *i*-Pr groups. To obtain further structural information on the solid-state structure of **8**, single crystals, which were obtained from pentane at 0 °C, were investigated by X-ray diffraction (Figures 7 and 8). Compound **8** crystallizes in the monoclinic space group $P2_1/n$ (No. 14). Its central structural unit contains a planar four-membered Al_2N_2 ring with both the Al and N centers in different chemical environments. Its backbone is built by a DippN unit, to which two Al(H)N(H)-Dipp units are covalently bound. One Al center is intermolecularly stabilized by a NMe_2Et base, while the second Al atom is intramolecularly stabilized by coordination of the N(H)Dipp group bound to the first Al center. The synthesis of **8** can be rationalized according to a reaction sequence as described in Scheme 4.

8 shows two long Al−N dative bonds (2.010(3), 2.026(3) Å), while the Al−N σ-bonds toward the 3-fold coordinated N centers are significantly shorter (1.804(2),

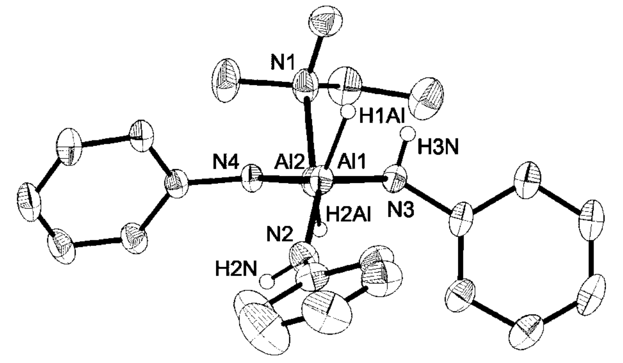
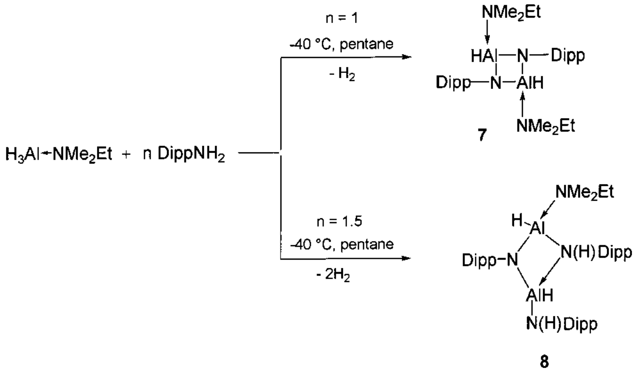
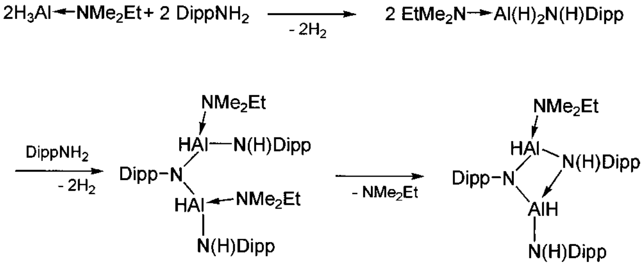


Figure 8. Reduced ORTEP plot of **8** showing the planar Al_2N_2 ring. The *i*-Pr groups of the Dipp ligands are omitted for clarity.

Scheme 3. Reaction of $H_3Al{\cdot}NMe_2Et$ and $DippNH_2$ in Different Molar Ratios



Scheme 4. Proposed Reaction Course for the Synthesis of 8



1.812(3), 1.854(2) Å). The sum of the bond angles of N4 (359.3°) clearly proves the absence of any H atom. Al−H and N−H distances are comparable to those found in other compounds described herein. However, in particular the Al−H distances show a relatively large variation.

Conclusions. Reactions of the amine-stabilized alanes $H_3Al{\cdot}NMe_3$ and $H_3Al{\cdot}NMe_2Et$ and the primary amine $DippNH_2$ were investigated in detail. Depending on the reaction temperature and stoichiometry, base-stabilized dimeric iminoalanes and monomeric aminoalanes as well as heterocyclic aminoalanes were obtained. In $Me_3N{\cdot}Al[N(H)Dipp]_3$, the NMe_3 group is only weakly bound and can be thermally removed or replaced by 4-(dimethylamino)pyridine (dmap). The as-prepared compounds demonstrate the principle of electronic stabilization to be very useful for the preparation of low associated amino- and iminoalanes containing Al−H and N−H functionalities. Investigations concerning the potential of such compounds for consecutive reactions and for potential applications as single-source precursors in MOCVD processes are currently under investigation.

Experimental Section

General Considerations. All manipulations were performed in a glovebox under an N_2 atmosphere or with standard Schlenk techniques. Solvents were dried over sodium/potassium and degassed prior to use. $DippNH_2$ was purchased from Aldrich, dried over KOH and distilled and stored under Ar. $H_3Al{\cdot}NMe_3$ and $H_3Al{\cdot}NMe_2Et$[27] were prepared according to literature methods. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal C_6D_5H (^1H, δ 7.154; ^{13}C, δ 128.0), while temperature-dependent NMR spectra were measured in toluene-d_8 (^1H, δ 2.03 (q), 6.98 (m), 7.00 (br), 7.09 (m); ^{13}C, δ 20.4 (sept), 125.2 (t), 128.0 (t), 128.9 (t), 137.5 (s) ppm). Mass spectra (EI) were recorded on a VG Masslab 12-250 spectrometer. Infrared spectra were recorded in Nujol between KBr plates with a Nicolet Magna 550 and are reported in wavenumbers. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn. Please note that amino- and iminoalanes generally tend to give low percentage numbers for C and N due to the formation of aluminum carbide and/or nitride. Yields are given for the pure products and are based on the amount of $AlH_3{\cdot}NR_3$ used.

$[Me_3N{\cdot}Al(H)NDipp]_2$ (1). A 0.18 g (2 mmol) portion of $AlH_3{\cdot}NMe_3$ was dissolved in 20 mL of pentane, cooled to −40 °C, and combined with 0.35 g (2 mmol) of $DippNH_2$. Slow warming to ambient temperature within 2 h occurred with gas evolution. The resulting colorless solution was stored at −20 °C, to give colorless crystals.

Yield: 0.42 g (81%). Mp: >270 °C. Anal. Found (calcd) for $C_{30}H_{54}N_4Al_2$ (524.7): H, 10.28 (10.37); C, 68.24 (68.67); N, 10.31 (10.68). ^1H NMR (C_6D_6, 300 MHz): δ 1.34 (d, $^3J_{HH} = 7.0$ Hz, 12H, $CH(CH_3)_2$), 1.48 (d, $^3J_{HH} = 6.6$ Hz, 12H, $CH(CH_3)_2$), 1.79 (s, 18H, $N(CH_3)_3$), 4.44 (sept, $^3J_{HH} = 6.8$ Hz, 4H, $CH(CH_3)_2$), 6.96−7.22 (6H, H_{ring}). ^{13}C NMR (C_6D_6, 74 MHz): δ 25.4 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 27.4 ($CH(CH_3)_2$), 45.8 (NMe_3), 117.7 (C_{ring}), 123.8 (C_{ring}), 141.6 (C_{ring}), 150.2 ($N-C_{ring}$). IR (Nujol): $\tilde{\nu}$ 1799 (Al−H), 1587, 1103, 997, 698 cm^{-1}. EI-MS (20 eV, 100 °C): *m/z* 59 (60) (NMe_3^+), 162 (10) ($Dipp^+$), 177 (100) ($DippNH_2^+$), 203 (1) ($HAlNDipp^+$), 262 (5) ($Me_3N{\cdot}HAlNDipp^+$), 769 (1) ($(HAlNDipp)_4^+$ − *i*-Pr), 812 (2) ($(HAlNDipp)_4^+$).

$Me_3N{\cdot}Al(H)[N(H)Dipp]_2$ (2). A 0.71 g (4 mmol) portion of $DippNH_2$ was added at −30 °C to a solution of 0.18 g (2 mmol) of $AlH_3{\cdot}NMe_3$ in 20 mL of hexane. Warming to ambient temperature within 3 h resulted in gas evolution. The colorless solution was stored at −10 °C to give colorless crystals.

Yield: 0. 76 g (87%). Mp: 112 °C. Anal. Found (calcd) for $C_{27}H_{46}N_3Al$ (439.7): H, 10.43 (10.55); C, 73.28 (73.75); N, 9.32 (9.56). ^1H NMR (C_6D_6, 300 MHz): δ 1.33 (d, $^3J_{HH} = 6.8$ Hz, 24H, $CH(CH_3)_2$), 1.78 (s, 9H, $N(CH_3)_3$), 2.85 (s, 2H, NH), 3.54 (sept, $^3J_{HH} = 6.8$ Hz, 4H, $CH(CH_3)_2$), 4.2 (s (br), Al−H), 6.94−7.17 (6H, H_{ring}). ^{13}C NMR (C_6D_6, 74 MHz): δ 23.6 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 46.7 (NMe_3), 118.6 (C_{ring}), 123.5 (C_{ring}), 136.8 (C_{ring}), 146.1 ($N-C_{ring}$). IR (Nujol): $\tilde{\nu}$ 3406, 3363 (NH), 1832 (AlH), 1591, 1429, 1338, 1107, 991, 891, 758 cm^{-1}. EI-MS (25 eV, 150 °C): *m/z* 59 (20) (NMe_3^+), 162 (10) ($Dipp^+$), 177 (100) ($DippNH^+$), 203 (5) ($AlN(H)Dipp^+$).

$[Dipp(H)NAl(H)$-μ-$N(H)Dipp]_2$ (3). A 0.18 g (2 mmol) portion of $AlH_3{\cdot}NMe_3$ was dissolved in 20 mL of pentane and combined with 0.71 g (4 mmol) of $DippNH_2$. Strong gas evolution resulted. The resulting colorless solution was stirred for 30 min. After storage at 0 °C for 12 h, colorless crystals of **3** were obtained.

Yield: 0.59 g (78%). Mp: 115 °C dec. Anal. Found (calcd) for $C_{48}H_{74}Al_2N_4$ (761.1): H, 9.59 (9.80); C, 75.53 (75.75); N,

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[27] Kovar, R. A.; Callaway, J. O. *Inorg. Synth.* **1977**, *17*, 36.

7.29 (7.36). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.09 (d, $^3J_{HH} = 6.6$ Hz, 24H, $CH(CH_3)_2$ (term.)), 1.21 (s (br), 24 H, $CH(CH_3)_2$ (μ-NHDipp)), 2.71 (sept, $^3J_{HH} = 6.6$ Hz, 4H, $CH(CH_3)_2$ (term.)), 3.37 (s, 2H, NH), 3.44 (sept (br), 4H, $CH(CH_3)_2$ (μ-NHDipp)), 4.21 (s, 2H, NH), 4.8 (s (br) AlH), 6.77−7.03 (12H, H_{ring}). ^{13}C NMR (C_6D_6, 74 MHz): δ 23.0 ($CH(CH_3)_2$ (term.)), 25.0 (br, $CH(CH_3)_2$ (μ-NHDipp)), 29.7 ($CH(CH_3)_2$ (μ-NHDipp)), 30.7 ($CH(CH_3)_2$ (term.)), 118.4, 123.4, 124.3, 125.2, 134.3, 136.8 (C_{ring}), 139.0, 144.8 (N−C_{ring}). IR (Nujol): $\tilde{\nu}$ 3389, 3244 (NH), 1937, 1916 (AlH), 1591, 1341, 1168, 930, 870, 740, 691 cm^{-1}. EI-MS (70 eV, 350 °C): *m/z* 73 (20) (NMe_2Et^+), 162 (10) (Dipp), 177 (100) ($DippNH_2^+$), 234 (30) ($Dipp(H)N(AlH)_2^+$), 721 (6) ($M^+ - i$-Pr), 762 (10) (M^+), 805 (6) ($Al_2(NHDipp)_6^+ - 3\ i$-Pr − Dipp), 981 (2) ($Al_2(NHDipp)_6^+ - 3\ i$-Pr), 1024 (2) ($Al_2(NHDipp)_6^+ - 2\ i$-Pr).

Temperature-Dependent NMR Spectra. The most important parts of the ^{1}H NMR spectra are displayed in Figure 1.

243 K: ^{1}H NMR (toluene-d_8, 300 MHz) δ 0.76 (d, $^3J_{HH} = 5.0$ Hz, 12H, $CH(CH_3)_2$ (μ-NHDipp)), 1.02 (d, $^3J_{HH} = 6.4$ Hz, 24H, $CH(CH_3)_2$ (term.)), 1.48 (d, $^3J_{HH} = 5.0$ Hz, 12H, $CH(CH_3)_2$ (μ-NHDipp)), 2.52 (sept, $^3J_{HH} = 6.4$ Hz, 4H, $CH(CH_3)_2$ (term.)), 2.72 (sept (br), 2H, $CH(CH_3)_2$ (μ-NHDipp)), 3.36 (s, 2H, NH), 4.00 (sept (br), 2H, $CH(CH_3)_2$ (μ-NHDipp)), 4.14 (s, 2H, NH), 4.76 (s (br) AlH), 6.72−6.95 (12H, H_{ring}); ^{13}C NMR (toluene-d_8, 74 MHz) δ 22.6 ($CH(CH_3)_2$ (term.)), 23.4 ($CH(CH_3)_2$ (μ-NHDipp)), 26.0 ($CH(CH_3)_2$ (μ-NHDipp)), 29.4 ($CH(CH_3)_2$ (μ-NHDipp)), 29.8 ($CH(CH_3)_2$ (μ-NHDipp)), 30.8 ($CH(CH_3)_2$ (term.)), 117.9, 123.2, 124.1, 126.1, 133.4, 136.5 (C_{ring}), 137.7, 139.5, 144.8 (N−C_{ring}).

273 K: ^{1}H NMR (toluene-d_8, 300 MHz) δ 0.8−1.3 ($CH(CH_3)_2$ (μ-NHDipp, very br)), 1.01 (d, $^3J_{HH} = 6.4$ Hz, 24H, $CH(CH_3)_2$ (term.)), 2.56 (sept, $^3J_{HH} = 6.4$ Hz, 4H, $CH(CH_3)_2$ (term.)), 3.31 (s, 2H, NH), 4.12 (s, 2H, NH), 4.7 (s (br) AlH), 6.70−6.92 (12H, H_{ring}); ^{13}C NMR (toluene-d_8, 74 MHz) δ 22.8 ($CH(CH_3)_2$ (term.)), 24−26 ($CH(CH_3)_2$ (μ-NHDipp, very br)), 29.7 ($CH(CH_3)_2$ (μ-NHDipp, br)), 30.8 ($CH(CH_3)_2$ (term.)), 118.1, 123.3, 124.2, 133.7, 136.7 (C_{ring}), 137.4, 144.8 (N−C_{ring}).

333 K: ^{1}H NMR (toluene-d_8, 300 MHz) δ 1.00 (d, $^3J_{HH} = 6.7$ Hz, 24H, $CH(CH_3)_2$ (term.)), 1.15 (d, $^3J_{HH} = 6.6$ Hz, 24H, $CH(CH_3)_2$ (μ-NHDipp)), 2.65 (sept, $^3J_{HH} = 6.6$ Hz, 4H, $CH(CH_3)_2$ (term.)), 3.23 (s, 2H, NH), 3.39 (sept, $^3J_{HH} = 6.6$ Hz, 4H, $CH(CH_3)_2$ (μ-NHDipp)), 4.10 (s, 2H, NH), 4.5 (s (very br) AlH), 6.62−6.94 (12H, H_{ring}); ^{13}C NMR (toluene-d_8, 74 MHz) δ 23.2 ($CH(CH_3)_2$ (term.)), 25.1 ($CH(CH_3)_2$ (μ-NHDipp)), 29.8 ($CH(CH_3)_2$ (μ-NHDipp)), 30.8 ($CH(CH_3)_2$ (term.)), 118.6, 123.4, 124.4, 125.3, 134.7, 137.0 (C_{ring}), 139.4, 144.9 (N−C_{ring}).

$Me_3N{\cdot}Al[N(H)Dipp]_3$ (4). A 0.18 g (2 mmol) portion of $AlH_3{\cdot}NMe_3$ was dissolved in 20 mL of hexane, cooled to −40 °C, and combined with 1.06 g (6 mmol) of $DippNH_2$. Warming to ambient temperature within 1 h was accompanied by strong gas evolution. The resulting colorless solution was stored at −10 °C to give colorless crystals.

Yield: 1.12 g (91%). Mp: 178 °C. Anal. Found (calcd) for $C_{39}H_{63}N_4Al$ (614.9): H, 10. 31 (10.33); C, 76.09 (76.18); N, 9.02 (9.11). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.21 (d, $^3J_{HH} = 6.7$ Hz, 36H, $CH(CH_3)_2$), 1.92 (s, 9H, $N(CH_3)_3$), 2.78 (s, 3H, NH), 3.45 (sept, $^3J_{HH} = 6.7$ Hz, 6H, $CH(CH_3)_2$), 6.93−7.11 (9H, H_{ring}). ^{13}C NMR (C_6D_6, 74 MHz): δ 23.9 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 48.1 (NMe_3), 119.6 (C_{ring}), 123.5 (C_{ring}), 138.3 (C_{ring}), 145.7 (N−C_{ring}). IR (Nujol): $\tilde{\nu}$ 3404, 3354, 3321 (NH), 1591, 1432, 1327, 1200, 1105, 987, 889, 863, 750 cm^{-1}. EI-MS (20 eV, 250 °C): *m/z* 59 (30) (NMe_3^+), 162 (100) ($Dipp^+$), 177 (70) ($DippNH_2^+$), 204 (1) ($AlN(H)Dipp^+$), 378 (3) ($Al(NHDipp)_2^+$), 580 (4) ($Al_2(NHDipp)_3^+$), 758 (2) ($Al_2(NHDipp)_4^+$), 781 (5) ($Al_3(NDipp)_4^+$).

dmap·Al[N(H)Dipp]$_3$ (5). A 0.12 g (0.2 mmol) portion of **4** and 0.02 g (0.2 mmol) of 4-(dimethylamino)pyridine were dissolved in 25 mL of hexane and stirred at ambient temperature for 5 h. The solvent was removed in vacuo, and **5** was obtained as a colorless, crystalline solid.

Yield: 0.12 g (93%). Mp: 220 °C dec. Anal. Found for $C_{43}H_{64}N_5Al$ (678.0): H, 9.38 (9.52); C, 75. 98 (76.18); N, 10.16 (10.33). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.28 (d, $^3J_{HH} = 6.7$ Hz, 36H, $CH(CH_3)_2$), 1.74 (s, 9H, $N(CH_3)_3$), 3.26 (s, 3H, NH), 3.49 (sept, $^3J_{HH} = 6.7$ Hz, 6H, $CH(CH_3)_2$), 5.64 (d, $^3J_{HH} = 6.7$ Hz, 2H, dmap), 6.94−7.19 (9H, H_{ring}), 8.37 (d, $^3J_{HH} = 6.7$ Hz, 2H, dmap). ^{13}C NMR (C_6D_6, 74 MHz): δ 23.9 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 38.0 (NMe_2), 106.2 ($C3_{dmap}$), 118.6 (C_{Dipp}), 123.3 (C_{Dipp}), 137.9 (C_{Dipp}), 147.0 (N− C_{Dipp}), 147.5 ($C2_{dmap}$). IR (Nujol): $\tilde{\nu}$ 3389, 3348 (NH), 1628, 1586, 1550, 1342, 862, 797, 738 cm^{-1}. EI-MS (70 eV, 300 °C): *m/z* 121 (10) ($dmap^+$), 162 (20) ($Dipp^+$), 176 (100) ($DippNH^+$), 203 (30) ($AlN(H)Dipp^+$), 379 (5) ($Al(NHDipp)_2^+$), 555 (1) (M^+ − dmap), 678 (1) (M^+).

Li(OEt$_2$)AlN(H)Dipp$_4$ (6). Anal. Found (calcd) for $C_{52}H_{82}AlLiN_4O$ (813.1): H, 9.99 (10.17); C, 76.21 (76.81); N, 6.58 (6.89). ^{1}H NMR (C_6D_6, 300 MHz): δ 0.63 (t, $^3J_{HH} = 6.7$ Hz, 6H, $(CH_3CH_2)_2O$), 1.20 (d, $^3J_{HH} = 6.8$ Hz, 36H, $CH(CH_3)_2$), 1.92 (s, 9H, $N(CH_3)_3$), 2.85 (q, $^3J_{HH} = 6.7$ Hz, 6H, $(CH_3CH_2)_2O$), 3.26 (s, 4H, NH), 3.40 (sept, $^3J_{HH} = 6.8$ Hz, 6H, $CH(CH_3)_2$), 6.80−7.13 (12H, H_{ring}). ^{13}C NMR (C_6D_6, 74 MHz): δ 24.4 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 123.7 (C_{ring}), 125.6 (C_{ring}), 136.1 (C_{ring}), 137.8 (N−C_{ring}).

[Me$_2$EtN·Al(H)NDipp]$_2$ (7). A 0.21 g (2 mmol) portion of $AlH_3{\cdot}NMe_2Et$ was dissolved in 15 mL of pentane, cooled to −40 °C, and combined with 0.35 g (2 mmol) of $DippNH_2$. Slow warming to ambient temperature within 2 h occurred with gas evolution. The resulting colorless solution was stored at −10 °C to give colorless crystals.

Yield: 0.46 g (83%). Mp: 110 °C dec. Anal. Found (calcd) for $C_{32}H_{58}N_4Al_2$ (552.8): H, 10.52 (10.58); C, 69.48 (69.53); N, 1.09 (10.14). ^{1}H NMR (C_6D_6, 300 MHz): δ 0.36 (t, $^3J_{HH} = 7.3$ Hz, 6H, NCH_2CH_3), 1.35 (d, $^3J_{HH} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 1.50 (d, $^3J_{HH} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 1.91 (s, 12H, $N(CH_3)_3$), 2.23 (q, $^3J_{HH} = 7.3$ Hz, 4H, NCH_2CH_3), 4.46 (sept, $^3J_{HH} = 6.8$ Hz, 4H, $CH(CH_3)_2$), 6.92−7.22 (6H, H_{ring}). ^{13}C NMR (C_6D_6, 74 MHz): δ 7.8 (NCH_2CH_3), 25.6 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 27.4 ($CH(CH_3)_2$), 42.0 (NMe_2), 7.8 (NCH_2CH_3), 117.9 (C_{ring}), 123.9 (C_{ring}), 141.9 (C_{ring}), 150.4 (N−C_{ring}). IR (Nujol): $\tilde{\nu}$ 1895, 1802 (AlH), 1259, 908, 8629, 795, 699 cm^{-1}. EI-MS (70 eV, 250 °C): *m/z* 59 (40) (NMe_3^+), 162 (100) ($Dipp^+$), 176 (60) ($DippNH_2^+$), 204 (5) ($AlN(H)Dipp^+$).

DippN(H)Al(H)N(Dipp)AlH(NMe$_2$Et)N(H)Dipp (8). A 0.21 g (2 mmol) portion of $AlH_3{\cdot}NMe_2Et$ was dissolved in 15 mL of pentane, cooled to −40 °C, and combined with 0.53 g (3 mmol) of $DippNH_2$. Slow warming to ambient temperature within 3 h was accompanied by gas evolution. After the colorless solution was stirred for 2 h and stored at −20 °C for 10 h, colorless crystals were obtained.

Yield: 0.52 g (79%). Crystal turns brown above 90 °C without melting and decomposes at 171 °C. Anal. Found (calcd) for $C_{40}H_{66}Al_2N_4$ (656.9): H, 10.01 (10.13); C, 72.96 (73.14); N, 8.38 (8.53). ^{1}H NMR (C_6D_6, 300 MHz): δ 0.27 (t, $^3J_{HH} = 7.2$ Hz, 3H, NCH_2CH_3), 0.89 (d, $^3J_{HH} = 6.6$ Hz, 6H, $CH(CH_3)_2$), 1.16 (d, $^3J_{HH} = 6.6$ Hz, 6H, $CH(CH_3)_2$), 1.30 (d, $^3J_{HH} = 7.0$ Hz, 12H, $CH(CH_3)_2$), 1.46 (m, 6H, $CH(CH_3)_2$), 1.62 (d, $^3J_{HH} = 6.9$ Hz, 6H, $CH(CH_3)_2$), 1.70 (s, 3H, NCH_3), 1.79 (s, 3H, NCH_3), 2.16 (q, $^3J_{HH} = 7.2$ Hz, 4H, NCH_2CH_3), 2.90 (sept, $^3J_{HH} = 6.8$ Hz, 2H, $CH(CH_3)_2$), 2.98 (sept, $^3J_{HH} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.14 (s, 1H, NH), 4.06 (s, 1H, NH), 4.06 (sept, $^3J_{HH} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 4.29 (sept, $^3J_{HH} = 6.8$ Hz, 2H, $CH(CH_3)_2$), 4.8 (s (br), AlH), 6.80−7.28 (9H, H_{ring}). IR (Nujol): $\tilde{\nu}$ 3376, 3298, 2956 (NH), 1869, 1808 (AlH), 1589, 1247, 1169, 922, 829, 702 cm^{-1}. MS (70 eV, 300 °C): *m/z* 43 (15) (i-Pr$^+$), 73 (10) (NMe_2Et^+), 162 (100) ($Dipp^+$), 177 (40) ($DippNH_2^+$), 202 (25) ($AlNDipp^+$), 378 (10) ($DippNAlNHDipp^+$), 581 (10) ($M^+ - NMe_2Et - H_2$).

X-ray Structure Solution and Refinement. Crystallographic data of **2**−**4**, **6**, and **8** are summarized in Table 1. Figures 2−8 show ORTEP diagrams of the solid-state structures of **2**−**4**, **6**, and **8**. Data were collected on a Nonius Kappa-CCD diffractometer. The structures were solved by Patterson methods (SHELXS-97)[28] and refined by full-matrix least

Table 1. Crystallographic Details for 2−4, 6, and 8

	2	**3**	**4**	**6**	**8**
empirical formula	$C_{27}H_{46}AlN_3$	$C_{48}H_{74}Al_2N_4$	$C_{39}H_{63}AlN_4$·(hexane)	$C_{52}H_{82}AlLiN_4O$[d]	$C_{40}H_{66}Al_2N_4$[e]
mol mass	439.7	761.1	701.1	813.1	656.9
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No.14)
a (Å)	8.4309(1)	22.1181(24)	13.6724(2)	22.7354(5)	11.1631(2)
b (Å)	9.8406(2)	13.3759(12)	23.8819(4)	11.5512(2)	25.2828(4)
c (Å)	17.2348(3)	32.2007(35)	13.5283(2)	22.0804(5)	15.1317(3)
α (deg)	90.714(1)	90	90	90	90
β (deg)	97.038(1)	103.829(5)	93.298(1)	120.148(1)	103.684(1)
γ (deg)	105.249(1)	90	90	90	90
V (Å^3)	1367.66(4)	9250.4(16)	4409.98(12)	5014.38(18)	4149.46(13)
Z	2	8	4	4	4
T (K)	123(2)	123(2)	123(2)	123(2)	123(2)
radiation (λ (Å))	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ (mm^{-1})	0.092	0.098	0.079	0.079	0.100
D_{calcd} (g cm^{-3})	1.068	1.093	1.056	1.077	1.052
$2\theta_{max}$ (deg)	50	50	50	50	50
cryst dimens (mm)	0.60 × 0.50 × 0.15	0.20 × 0.10 × 0.10	0.25 × 0.20 × 0.10	0.40 × 0.35 × 0.30	0.50 × 0.40 × 0.30
no. of rflns	24 422	21 606	33 640	19 114	41 846
no. of unique rflns	4799	7403	7660	4379	7274
R_{merg}	0.0313	0.1160	0.0444	0.0397	0.0458
no. of params refined/restraints	289/3	505/6	460/106	286/80	424/224
R1[a]	0.0405	0.0639	0.0581	0.0490	0.0574
wR2[b]	0.1113	0.1089	0.1728	0.1338	0.1552
goodness of fit[c]	1.038	0.879	1.071	1.071	1.068
final max/min $\Delta\rho$ (e Å^{-3})	0.381/−0.321	0.209/−0.257	0.688/−0.587	0.214/−0.308	0.416/−0.553

[a] R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$ (for $I > 2\sigma(I)$). [b] wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goodness of fit = $\{\sum[w(|F_o^2| - |F_c^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$. [d] The coordinated Et_2O molecule is disordered. [e] One *i*-Pr group of the terminal NHDipp substituent is disordered.

squares on F^2 (SHELXL-97).[29] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. The crystallographic data of **2**−**4**, **6**, and **8** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-144769 (**2**), CCDC-144769 (**3**), CCDC-144768 (**4**), CCDC-144767 (**6**), and CCDC-144770 (**8**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Telefax, (+44) 1223/336033; E-mail, deposit@ccdc.cam-ak.uk).

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **2**−**4**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Sheldrick, G. M. SHELXS-97, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(29) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen: Göttingen, Germany, 1997.