Syntheses and X-ray Structures of Base-Stabilized Iminoalanes§

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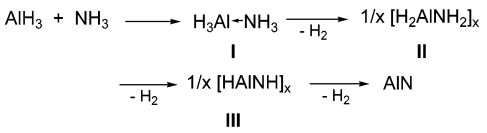
Reactions between low-valent $[Cp^*Al]_4$ and trialkylsilyl azides RR'_2SiN_3 proceed with N_2 elimination and subsequent formation of iminoalanes $[Cp^*AlNSiRR'_2]_x$ (R, R′ = Et **1**, *i*-Pr **2**, *t*-Bu **3**; R = *t*-Bu R′ = Me **4**), which further react with an equimolar amount of 4-(dimethylamino)pyridine (dmap) with formation of dmap-stabilized iminoalanes of the general type $[dmap\text{-}Al(Cp^*)NSiRR'_2]_2$ (R, R′ = Et **5**, *i*-Pr **6**; R = *t*-Bu R′ = Me **7**). No reaction was observed for $[Cp^*AlNSi(t\text{-}Bu)_3]_2$, **3**. In contrast, Cp*Al and RR'_2SiN_3 react in the presence of dmap at elevated temperatures with C−H activation of the ortho-H_{dmap} and formation of dihydroanthracene-type compounds of the type $[o\text{-}Al(Cp^*)N(H)SiRR'_2\text{-}dmap]_2$ (R, R′ = Et **8**, *i*-Pr **9**, *t*-Bu **10**; R = *t*-Bu R′ = Me **11**). The reaction of Cp*Al and *t*-Bu_3SiN_3 with 2 equiv of dmap proceeds with *o*-C−H_{dmap} activation of only one dmap molecule and formation of the dmap-stabilized monomeric aminoalane [*o*-Al(dmap)(Cp*)N(H)Si(*t*-Bu)$_3$-dmap], **12**. Compounds **3** and **5**−**12** were characterized by IR, mass, and multinuclear NMR spectroscopy (^1H, ^{13}C), and **3**, **7**, **8**, **9**, **11**, and **12** also by single-crystal X-ray structure analysis.

Introduction

Compounds containing Al−N bonds have a long-standing history in main group organometallic chemistry due to their fascinating structures, interesting bonding properties, and versatility in organic and inorganic syntheses.[1] In addition, their potential application to serve as precursors for the synthesis of aluminum nitride, AlN, which finds several applications as ceramic material, has stimulated their synthesis. Early studies by Wiberg et al. perfectly illustrate some general reaction patterns in aluminum−nitrogen chemistry. AlH_3 and NH_3 react with formation of the Lewis acid−base adduct $H_3Al{-}NH_3$, which is stable only at very low temperature. At higher temperatures, H_2 is eliminated with stepwise formation of aminoalane $[H_2AlNH_2]_x$ and iminoalane $[HAlNH]_x$. Finally, aluminum nitride, AlN, is formed.[2] Comparable findings have been observed for reactions of trialkylalanes with primary, secondary, and tertiary amines. Numerous adducts (type I) and aminoalanes (type II), which typically form four- or six-membered rings, have been prepared in the last decades,[3] whereas iminoalanes $[RAlNR']_x$ have been structurally characterized to a far lesser extent.[4] They typically adopt oligomeric structures in the solid state ($x = 4$, 6, 7, 8, and higher) with the central aluminum and nitrogen atoms featuring tetrahedral coordination environments. The degree of oligomerization is controlled by the steric demand of the organic substituents (R, R′). In addition, a very few lower aggregated species such as monomeric,[5] dimeric,[6] and trimeric iminoalanes[7] containing 2- and 3-fold coordinated Al and N centers have been synthesized. These are of particular interest due to their bonding properties. Six-membered rings are isoelectronic to benzene (C_6H_6) and borazine ($B_3N_3H_6$), sometimes referred to as "*inorganic benzene*". Monomeric compounds RAlNR′ are also a challenging goal since they should exhibit multiple bonding character, as was observed for iminoboranes. Unfortunately, they have a strong oligomerization tendency. Theoretical calculations for HAlNH demonstrated that dimerization is strongly exothermic (140 kcal/mol) and occurs without any activation barrier.[8]

Scheme 1. General Reaction Sequence of the AlH_3/NH_3 Reaction



§ Dedicated to Prof. Hansgeorg Schnöckel on the occasion of his 65th birthday.

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

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

(3) See the following and references therein: (a) Chang, C.-C.; Ameerunisha, M. S. *Coord. Chem. Rev.* **1999**, *189*, 199. (b) Bauer, T.; Schulz, S.; Hupfer, H.; Nieger, M. *Organometallics* **2002**, *21*, 2931.

(4) (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.

(5) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2172.

(6) (a) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969. (b) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271. (c) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791. (d) Schulz, S.; Voigt, A.; Roesky, H. W.; Häming, L.; Herbst-Irmer, R. *Organometallics* **1996**, *15*, 5252. (e) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, *37*, 6906. (f) Uhl, W.; Molter, J.; Koch, R. *Eur. J. Inorg. Chem.* **1999**, 2021.

(7) (a) Wagonner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed.* **1988**, *27*, 1699. (b) Wagonner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

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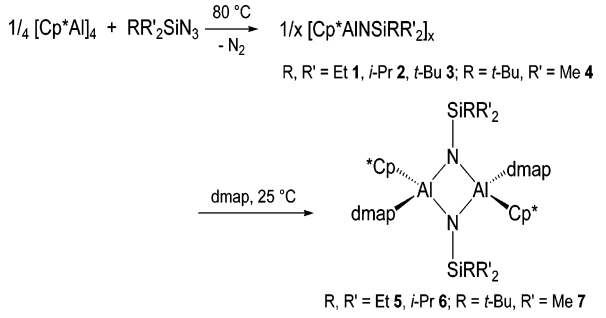
Scheme 2. Formation of dmap-Stabilized Four-Membered Iminoalanes



Dimerization of $[HAlNH]_2$ to the heterocubane $[HAlNH]_4$ again occurs with an energy release of 66 kcal/mol.

The most common principles for the stabilization of monomeric group 13-imides are kinetic (bulky organic substituents) and electronic stabilization (electron-withdrawing substituents at Al, electron-donating substituents at N (*push*−*pull* substitution pattern)).[9] These general principles have been successfully applied for the synthesis of $[\{HC(MeCDippN)_2\}Al{=}NR]$ (R = 2,6-$Trip_2C_6H_3$) by reaction of the low-valent Al(I) compound $\{HC(MeCDippN)_2\}Al$ with the sterically encumbered azide N_3R at ambient temperature.[5] In contrast, comparable reactions between $[Cp^*Al]_4$ and $N_3SiR'_3$ (R′ = Me, Et, Ph, *i*-Pr, *t*-Bu) between 60 and 80 °C yielded dimeric iminoalanes.[6a,d] Obviously, the mild reaction conditions and the high degree of steric crowding favor the formation of monomeric species. In addition, the increase of the coordination number of the Al center from two ("normal" iminoalane RAl═NR′) to three ([{HC(MeCDippN)$_2$}Al═NR]) by use of the *β*-ketiminato ligand seems to play a key role for the stabilization of low-aggregated iminoalanes. Comparable findings have been reported very recently for the synthesis of base-stabilized, dimeric iminoalanes containing sterically less hindered substituents. Coordination of a Lewis base such as NMe_3[3b] or THF[6f] increases the coordination number of a dimeric iminoalane $[RAlNR']_2$ from three to four and hence decreases its oligomerization tendency.

In an attempt to stabilize low-aggregated iminoalanes, we became interested in their general reactivity toward strong Lewis bases, and we re-examined reactions of univalent $[Cp^*Al]_4$ with trialkylsilyl azides RR'_2SiN_3. Unlike the studies reported previously,[6a,d] the reactions were performed in the presence of the strong Lewis base 4-(dimethylamino)pyridine (dmap). The resulting compounds **3**−**12** were characterized by elemental analyses, IR, mass, and multinuclear NMR spectroscopy (^{1}H, ^{13}C), and **3**, **7**, **8**, **9**, **11**, and **12** also by single-crystal X-ray structure analysis.

Results and Discussion

Reactions of $[Cp^*Al]_4$ and trialkylsilyl azides RR'_2SiN_3 between 60 and 80 °C proceed with smooth elimination of N_2 and subsequent formation of iminoalanes $[Cp^*AlNSiRR'_2]_x$ (R, R′ = Et **1**, *i*-Pr **2**, *t*-Bu **3**; R = *t*-Bu R′ = Me **4**), which further react at ambient temperature with an equimolar amount of dmap with formation of dmap-stabilized dimeric iminoalanes of the general type $[dmap\text{-}Al(Cp^*)NSiRR'_2]_2$ (R, R′ = Et **5**, *i*-Pr **6**; R = *t*-Bu, R′ = Me **7**). Only $[Cp^*AlNSi(t\text{-}Bu)_3]_2$ (**3**) did not react with dmap under these conditions, most likely due to the steric crowding of the *t*-Bu groups. The ^{1}H and ^{13}C NMR spectra of

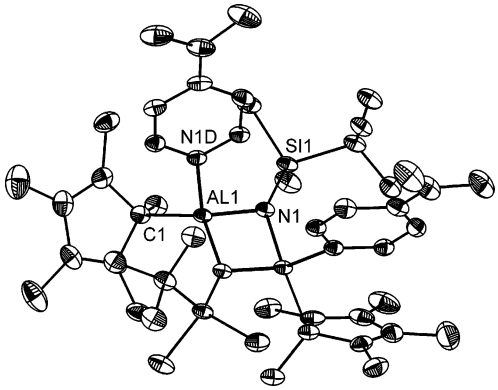


Figure 1. Molecular structure and atom-numbering scheme of compound **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

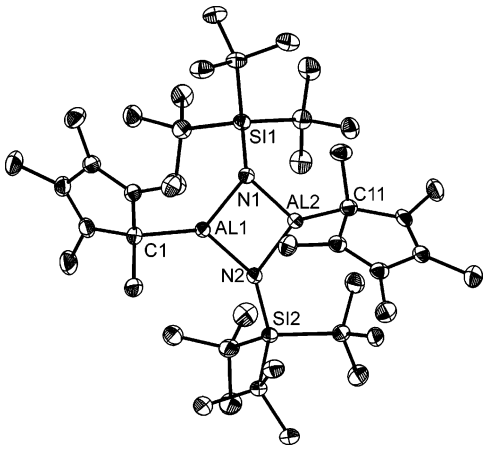


Figure 2. Molecular structure and atom-numbering scheme of compound **7**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

5−**7** show resonances due to the trialkylsilyl group, the Cp* substituent, and the dmap base.[10] The Cp* substituents in **5**−**7** show different numbers of resonances in the ^{1}H NMR spectra, indicating an expressed bonding flexibility (η^1−η^5) in solution. The EI mass spectra of **5**−**7** show peaks due to typical fragmentation reactions. In contrast, the molecular ion peak was observed for **3**.

The solid-state structures of **3** and **7** were determined by single-crystal X-ray diffraction. Suitable crystals were obtained after storage of solutions of **3** and **7** in toluene at 4 °C for 48 h. Figures 1 and 2 show their solid-state structures. **3** crystallizes in the orthorhombic space group *Pbcn* (No. 60) and **4** in the monoclinic space group *C*2/*c* (No. 15), both with one toluene molecule per formula unit (**3**: 1 toluene per molecule (no crystallographic symmetry); **7**: 1/2 toluene per 1/2 molecule (crystallographic C_2 symmetry)). Since **3** has been described previously,[6d] the bonding parameters will not be discussed in detail. It should only be mentioned that the central, noncentrosymmetric Al_2N_2 ring in **3** adopts a butterfly-type conformation (19.5° along the Al···Al axis), in contrast to previously described four-membered heterocyclic iminoalanes, which typically exhibit planar Al_2N_2 ring geometries. This is most likely due to the presence of very bulky *t*-Bu_3Si substituents at the N centers. The N centers in **7** adopt a trigonal-planar coordination sphere (sum of bond angles = 360°), whereas the Al centers adopt slightly distorted tetrahedral coordination environments.

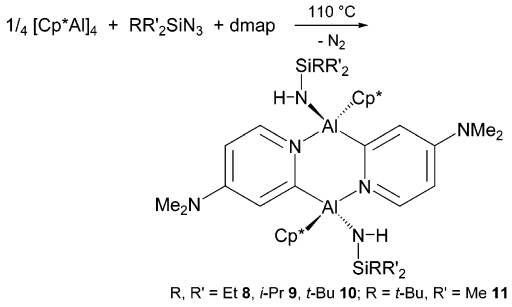
(8) Hamilton, T. P.; Shaikh, A. W. *Inorg. Chem.* **1997**, *36*, 754.
(9) See for instance: Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.
(10) ^{13}C NMR spectra of some compounds could not be recorded due to their poor solubility in organic solvents.

Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] of 3 and 7

	[Cp*AlNSi(*t*-Bu)$_3$]$_2$ (**3**)		
Al1−N1	1.840(1)	N1−Al1−N2	93.3(1)
Al1−N2	1.837(1)	N1−Al2−N2	93.0(1)
Al2−N1	1.841(1)	Al1−N1−Al2	85.1(1)
Al2−N2	1.841(1)	Al1−N2−Al2	85.2(1)
Al1−C1	2.025(1)	C1−Al1−N1	130.8(1)
Al2−C11	2.034(2)	C1−Al1−N2	125.4(1)
N1−Si1	1.730(1)	C11−Al2−N1	125.9(1)
N2−Si2	1.732(1)	C11−Al2−N2	131.4(1)
		Si1−N1−Al1	129.2(1)
		Si1−N1−Al2	138.8(1)
		Si2−N2-A1	138.9(1)
		Si2−N2−Al2	130.1(1)
	[dmap-Al(Cp*)NSi(*t*-Bu)Me$_2$]$_2$ (**7**)		
Al1−N1#[a]	1.856(2)	N1−Al1−N1#[a]	92.2(1)
Al1−N1	1.863(2)	Al1−N1−Al1#[a]	87.7(1)
Al1−N1D	2.007(2)	N1−Al1−N1D	106.1(1)
Al1−C1	2.083(2)	C1−Al1−N1D	108.3(1)
N1−Si1	1.699(2)	C1−Al1−N1	117.6(1)
		Si1−N1−Al1	129.7(1)
		Si1−N1−Al1#[a]	142.7(1)

[a] Symmetry operator: $-x+1, y, -z+0.5$.

Scheme 3. Formation of Dihydroanthracen-Type Compounds



R, R' = Et **8**, *i*-Pr **9**, *t*-Bu **10**; R = *t*-Bu, R' = Me **11**

The central four-membered ring in **7** also deviates from planarity (5.1° along the Al···Al axis) due to the coordination of the dmap bases. The Al−N distances within the Al_2N_2 ring of **7** (1.856(2), 1.863(2) Å) are slightly elongated compared to those of **3** (av 1.839 Å) as a result of the higher coordination number of the Al centers (4 vs 3). The Al−N_{dmap} distance in **7** (2.007(2) Å) is significantly longer, as is typical for dative Al−N bonds. The Cp* substituents in **3** and **7** are σ-bonded to the Al centers with Al−C distances of 2.034(2) [2.025(2)] Å (**3**) and 2.083(2) Å (**7**), respectively, again reflecting the different coordination numbers of the Al centers. The endocyclic Al−N−Al bond angles (av 85.2° **3**; 87.7(1)° **7**) are smaller than the N−Al−N bond angles (av 93.2° **3**; 92.2(1)° **7**), consequently leading to relatively short *transannular* Al···Al distances (2.490(1) Å **3**; 2.575(1) Å **7**; for comparison 2.60 Å in Al_2Me_6). Reactions of $[Cp^*Al]_4$ and RR'_2SiN_3 in refluxing toluene in the presence of an equimolar amount of dmap also proceed with smooth N_2 elimination. However, in contrast to the previously described reactions, dark-colored solutions were formed, from which colorless crystals of dihydroanthracene-type compounds of the general type [*o*-Al(Cp*)N(H)SiRR′$_2$-dmap]$_2$ (R, R′ = Et **8**, *i*-Pr **9**, *t*-Bu **10**; R = *t*-Bu R′ = Me **11**) were isolated after storage at −60 °C. Compounds **8**, **9**, and **11** were also formed when dmap-stabilized iminoalanes **5**−**7** were heated in toluene at 110 °C for 1 h. The ^{1}H and ^{13}C NMR spectra of **8**−**11** again show resonances due to the trialkylsilyl group and the Cp* substituent. In contrast, the aromatic protons of the dmap molecules in **8**−**11** no longer show the typical AA′XX′ peak pattern as was observed for **5**−**7**. Instead, three sets of resonances are observed,

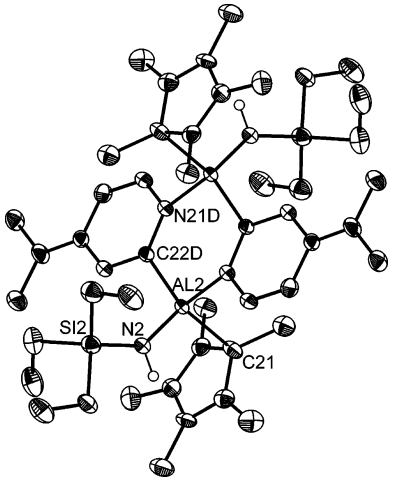


Figure 3. Molecular structure and atom-numbering scheme of compound **8** (one independent molecule). Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N, have been omitted for clarity.

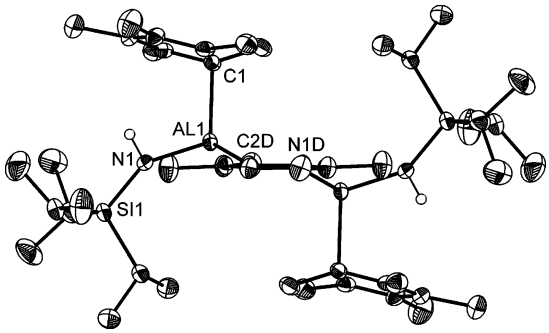


Figure 4. Molecular structure and atom-numbering scheme of compound **9**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N, have been omitted for clarity.

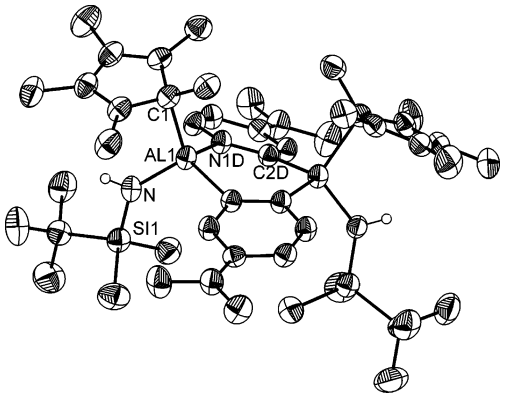


Figure 5. Molecular structure and atom-numbering scheme of compound **11**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N, have been omitted for clarity.

indicating the presence of three nonequivalent ring protons. These results were confirmed by ^{13}C NMR spectroscopy, also demonstrating the ring-C_{dmap} atoms to be chemically nonequivalent. The ^{1}H NMR spectra of **8**−**11** also show additional resonances at very high field (−0.30 to −0.60 ppm) for the N-H group. IR spectra of **8**−**11** also show typical absorption bands between 3100 and 3300 cm^{-1}. The EI mass spectra of **8**−**11** do not show the molecular ion peak. However, the central dihydroanthracene-type core was found to be thermally very

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] of 8, 9, and 11

	[*o*-Al(Cp*)N(H)SiEt$_3$-dmap]$_2$ (**8**) [second molecule]		
Al1−N11D	1.935(3) [1.943(3)]	N1−Al1−N11D	107.2(1) [109.1(2)]
Al1−C12D#[a]	2.013(3) [2.021(4)]	N1−Al1−C12D#[a]	113.6(1) [114.6(1)]
Al1−N1	1.811(3) [1.801(3)]	N1−Al1−C11	115.3(1) [110.3(1)]
Al1−C11	2.121(4) [2.128(4)]	N11D-Al1−C11	111.8(1) [99.6(2)]
N11D−C12D	1.381(4) [1.382(4)]	C11−Al1−C12D#[a]	102.3(1) [115.4(1)]
N1−Si1	1.706(3) [1.715(3)]	Al1−N11D−C12D	123.5(2) [124.4(2)]
		Al1#[a]−C12D−N11D	125.0(2) [123.7(2)]
N11D−Al1−C12D#[a]	104.4(1) [106.4(1)]	Al1−N1−Si1	137.3(2) [142.2(2)]
	[*o*-Al(Cp*)N(H)Si(*i*-Pr)$_3$-dmap]$_2$ (**9**)		
Al1−N1D	1.936(2)	N1−Al1−N1D	110.0(1)
Al1−C2D#[b]	2.020(2)	N1−Al1−C2D#[b]	118.4(1)
Al1−N1	1.814(2)	N1−Al1−C1	109.5(1)
Al1−C1	2.101(2)	N1D−Al1−C1	109.8(1)
N1D−C2D	1.390(3)	C1−Al1−C2D#[b]	103.6(1)
N1−Si1	1.714(2)	Al1−N1D−C2D	123.5(2)
		Al1#[b]−C2D−N1D	123.2(2)
N1D−Al1−C2D#[b]	105.2(1)	Al1−N1−Si1	146.3(2)
	[*o*-Al(Cp*)N(H)Si(*t*-Bu)Me$_2$-dmap]$_2$ (**11**)		
Al1−N1D	1.933(2)	N1−Al1−N1D	105.4(1)
Al1−C2D#[c]	2.028(3)	N1−Al1−C2D#[c]	113.9(1)
Al1−N1	1.819(3)	N1−Al1−C1	110.1(1)
Al1−C1	2.701(3)	N1D−Al1−C1	113.9(1)
N1D−C2D	1.375(3)	C1−Al1−C2D#[c]	107.9(1)
N1−Si1	1.696(3)	Al1−N1D−C2D	124.5(2)
		Al1#[c]−C2D−N1D	126.2(2)
N1D−Al1−C2D#[c]	105.7(1)	Al1−N1−Si1	135.5(2)

[a] Symmetry operator: $-x+1, -y+1, -z+1$ (first molecule); $-x+2, -y+2, -z$ (second molecule). [b] Symmetry operator: $-x, -y+1, -z+1$. [c] Symmetry operator: $-x+1, y, -z+0.5$.

robust since peaks with the highest mass typically correspond to the molecular ion peak *minus* one alkyl substituent from the silyl group or *minus* one Cp* group.

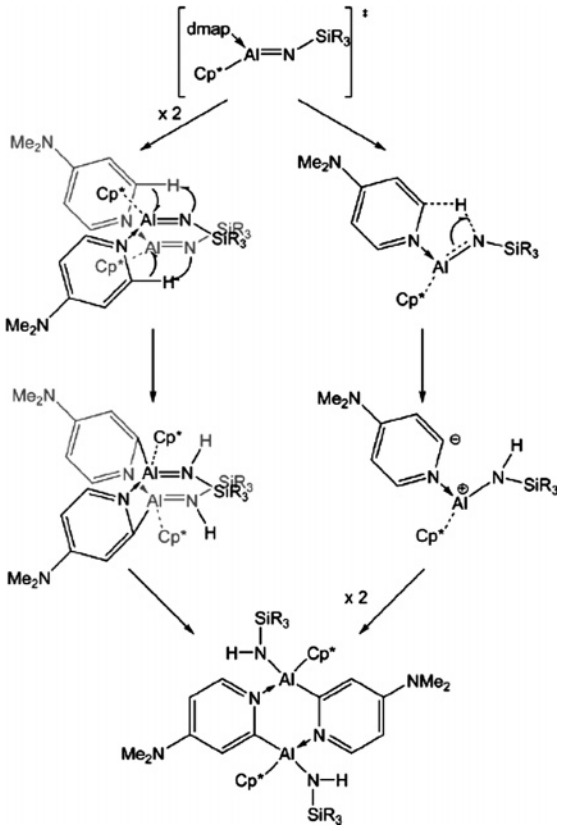
Colorless crystals of **8**, **9**, and **11** suitable for X-ray structure analyses were grown from solutions in toluene at −60 °C. Figures 3−5 show their solid-state structures. They crystallize in different space groups ($P\bar{1}$ (No. 2), two half independent molecules in the asymmetric unit **8**, *C*2/*c* (No. 15) **9**, *C*2/*c* (No. 15) **11**). The central skeleton of **8**, **9**, and **11** contains three annelated six-membered rings, which adopt a dihydroanthracene-type conformation.

8 and **9** show crystallographic C_i symmetry, whereas **11** exhibits C_2 symmetry. The structures can alternatively be described as dimers of ortho-metalated dmap (*head-to-tail* Al−N$_{imin}$ adducts). The central (AlCN)$_2$ six-membered rings in **8** and **9** both adopt a flattened chair-like conformation (convolution degree 24.1° (**8**), 25.3° (**9**); for comparison 55° in cyclohexane) with the Cp* and N(H)SiR′$_2$ groups in *transoid* orientations. The annelated dmap rings are in plane with the plane of the (AlCN)$_2$ chair (Figures 3 and 4), and the Cp* rings adopt an almost coplanar orientation to the central dihydroanthracene-type system. In contrast, the (AlCN)$_2$ ring of **11** forms a distorted envelope-type conformation. The Cp* rings and the N(H)Si(*t*-Bu)$_3$ groups adopt a *cisoid* orientation, most likely due to the higher steric demand of the *t*-Bu groups. As a consequence, the central dihydroanthracene-type ring system significantly deviates from planarity, as can be seen in Figure 5. The endocyclic Al−N bond lengths (1.935(3) Å [1.943(3) Å] **8**, 1.936(2) Å **9**, 1.933(2) Å **11**) are longer than the exocyclic ones (1.811(3) Å [1.801(3) Å] **8**, 1.814(2) Å **9**, 1.819(3) Å **11**), indicating a rather dative bonding character of the endocyclic Al−N$_{dmap}$ bond, even though these bond lengths are significantly shorter compared to that in dmap-AlMe$_3$ (av 201.4 Å).[11] The Cp* substituents in **8**, **9**, and **11** are σ-bonded (Al−C: 2.121-(4) Å [2.128(4) Å] **8**, 2.101(2) Å **9**, 2.071(3) Å **11**), as was observed for **3** and **7**. The endocyclic bond angles [deg] within the central (AlCN)$_2$ rings (N−Al−C: 106.4(1) [106.4(1)] **8**, 105.2(1) **9**, 105.7(1) **11**; Al−C−N: 125.0(2), [123.7(2)] **8**, 123.2(2) **9**, 125.0(2) **11**; C−N−Al: 123.5(2), [124.4(2)] **8**, 123.5(2) **9**, 124.5(2) **11**) clearly reflect the different coordination numbers (Al 4, C 3, N 3) and hybridization states (Al sp^3, C sp^2, N sp^2) of the central ring atoms. Ortho-C−H activation of dmap has been described twice in the literature.[12] In both reaction types, the presence of a very strong basic reaction center, which was formed as a result from the coordination of the Li cation of the metalation reagent (*n*-BuLi, tmpLi (tmp = 2,2,6,6-tetramethylpiperidyl)) to the heteroatom (O, F) of the BF$_3$- or LiOC$_2$H$_4$NMe$_2$-mediated reaction, was found to be essential. According to these findings, the formation of **8**−**11** most likely proceeds through the intermediate formation of monomeric iminoalanes Cp*AlNSiRR′$_2$, which are expected to be highly reactive species due to the presence of both coordinatively and electronically unsaturated central atoms. Reactions with dmap yield monomeric, dmap-stabilized iminoalanes dmap-Al(Cp*)NSiRR′$_2$, which contain a very strong basic imine center. Ortho-C−H$_{dmap}$ activation occurs either through the formation of a weakly bonded dimer (pathway I), which subsequently undergoes intermolecular N−H and Al−C bond formation reactions, or by intramolecular deprotonation and formation of a monomeric, zwitterionic compound (pathway II), which dimerizes with formation of the dihydroanthracene-type compounds **8**−**11**. To investigate the role of dmap in more detail, the reaction of Cp*Al, *t*-Bu$_3$SiN$_3$, and 2 equiv of dmap in refluxing toluene was investigated, yielding the dmap-stabilized monomer [*o*-Al(dmap)(Cp*)N(H)Si(*t*-Bu)$_3$-dmap], **12**. The ^{1}H NMR spectrum of **12** shows two different sets of resonances due to the aromatic H atoms of the dmap molecule. The signal patterns indicate the presence of both an activated and a nonactivated dmap molecule. These results were con-

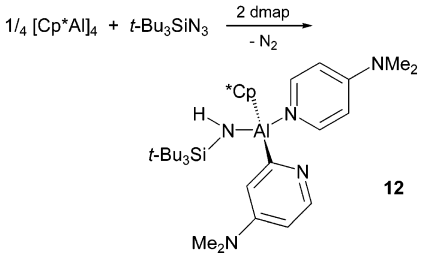
(11) Thomas, F.; Bauer, T.; Schulz, S.; Nieger, M. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2018.

(12) (a) Vedejs, E.; Chen, X. *J. Am. Chem. Soc.* **1996**, *118*, 1809. (b) Cuperly, D.; Gros, P.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 238.

Scheme 4. Proposed Reaction Pathway for the Activation of o−C−H



Scheme 5. Formation of dmap-Stabilized Monomer 12



firmed by ^{13}C NMR spectroscopy. The IR spectra also show the formation of an N-H group (3315 cm^{-1}). The EI mass spectrum of **12** shows the molecular ion peak with almost 20% intensity, indicating **9** to be thermally very stable.

Colorless crystals of **12** were obtained from a solution in toluene at −60 °C. Figure 6 shows the solid-state structure of **12**, which crystallizes in the triclinic space group $P\bar{1}$ (No. 2). The central Al atom in **12** is coordinated by one Cp* substituent, one amido group (NH(Si*t*-Bu_3)), and one activated (ortho-position) dmap molecule. The tetrahedral coordination sphere is completed by one additional dmap molecule. Obviously, the strong Lewis base dmap disaggregates the dihydroanthracene-type dimer **10**, which can be described as a *head-to-tail* adduct, with subsequent formation of **12**. Comparable findings have been previously observed for the reactions of four- and six-membered Al/group15 heterocycles $[R_2AlER'_2]_x$ (E = P, As, Sb, Bi) with dmap, yielding the base-stabilized monomers dmap-$AlR_2ER'_2$.[13] The Al−C_{Cp^*} bond length (2.098(2) Å) is significantly longer than the Al−C_{dmap} distance (2.004(2) Å), as was observed for **8**, **9**, and **11**. The Al−N_{amido} bond distance (1.829(2) Å) is in the typical range as observed for 3-fold-coordinated

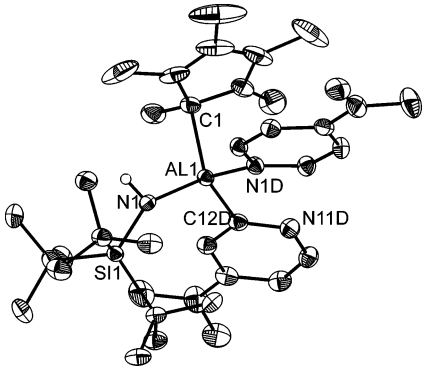
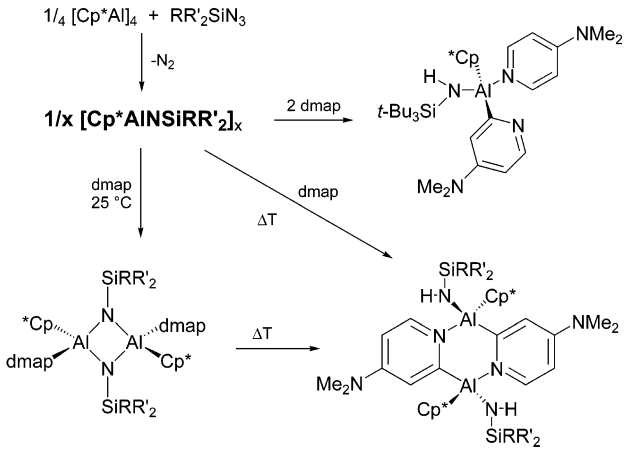


Figure 6. Molecular structure and atom-numbering scheme of compound **12**. Thermal ellipsoids are drawn at the 50% probability level. H atoms, except those attached to N, have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−N1 1.829(2), Al1−N1D 1.942(2), Al1−C1 2.098(2), Al1−C12D 2.004(2), N1−Si1 1.725(2); N1−Al1−N1D 107.9(1), N1−Al1−C12D 115.7(1), N1−Al1−C1 109.3(1), N1D−Al1−C12D 108.4(1), N1D−Al1−C1 105.1(1), C12D−Al1−C1 110.0(1), Al1−N1−Si1 149.0(1).

Scheme 6. Summary of the Reactions of $[Cp^*Al]_4$ with Trialkylsilyl Azides RR'_2SiN_3 and dmap



N centers, and the Al−N_{dmap} bond distance (1.942(2) Å) is relatively short, as was observed for **8**, **9**, and **11**.

Conclusions. Reactions of equimolar amounts of $[Cp^*Al]_4$, trialkylsilyl azides RR'_2SiN_3, and 4-(dimethylamino)pyridine (dmap) were investigated. The reactions proceed with elimination of N_2 and subsequent formation of dmap-stabilized dimers or dihydroanthracene-type compounds. The latter are formed by ortho-C−H activation of the coordinating dmap base. In addition, the reaction of Cp*Al, *t*-Bu_3SiN_3, and 2 equiv of dmap yielded a base-stabilized, monomeric aluminum amide.

Experimental Section

General Procedures. 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. 4-(Dimethylamino)pyridine was purchased from Aldrich and sublimed prior to use. $[Cp^*Al]_4$[14] and silyl azides RR'_2SiN_3[15] were prepared according to literature methods. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^1H and

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

(14) Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729.

$^{13}C\{^1H\}$ NMR spectra were referenced to internal C_6D_5H (^1H: $\delta = 7.154$; ^{13}C: $\delta = 128.0$) or internal toluene-d_8 (^1H: $\delta = 2.03$ (q), 6.98 (m), 7.00 (br), 7.09 (m); ^{13}C: $\delta = 20.4$ (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 and a Finnigan MAT 8230. 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 Elementaranalyse Labor der Universität Paderborn. Yields are given for the pure products.

General Synthesis of [dmap-Al(Cp*)NSiRR′$_2$]$_2$. A suspension of 1 mmol of RR′$_2$SiN$_3$ and 0.16 g (0.25 mmol) of [Cp*Al]$_4$ in 30 mL of toluene was heated for 30 min between 60 and 80 °C until gas evolution has stopped. The resulting clear solution was cooled to ambient temperature, combined with a solution of 1 mmol (0.12 g) of dmap in 5 mL of toluene, and stirred for 5 min, yielding yellowish to brownish suspensions. Addition of THF (20−30 mL) gave clear solutions (**5**, **6**), which were stored at −30 °C. **5** and **6** were obtained as colorless solids. **7** was obtained as a colorless crystalline solid after slow cooling of a hot solution in 40 mL of toluene. **3** did not react with dmap under these conditions.

[Cp*AlNSi(*t*-Bu)$_3$]$_2$ (3). Yield: 0.64 g (85%). Mp: 244 °C (dec). Anal. Found (calcd) for $C_{44}H_{84}Al_2N_2Si_2-C_7H_8$ (843.4 g/mol): H: 10.76 (10.91); C: 72.28 (72.66); N: 3.23 (3.32). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 1.08 (s, 6H, Cp*), 1.17 (s, 27H, *t*-Bu), 1.91 (s, 6H, Cp*), 2.09 (s, 3H, Cp*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 15.1 (C_5*Me*$_5$), 22.8 (*t*-Bu), 32.2 (*t*-Bu), 122.4 (C_5Me$_5$). EI-MS (35 eV, 200 °C): *m*/*z* (%) 750 (3) [M]$^+$, 693 (8) [M − *t*-Bu]$^+$, 558 (34) [M − Cp* − *t*-Bu]$^+$, 375 (21) [M/2]$^+$, 135 (85) [Cp*]$^+$, 57 (100) [*t*-Bu]$^+$.

[dmap-Al(Cp*)NSiEt$_3$]$_2$ (5). Yield: 0.50 g (60%). Mp: 145 °C. Anal. Found (calcd) for $C_{46}H_{80}Al_2N_6Si_2$ (827.3 g/mol): H: 9.65 (9.75); C: 66.68 (66.81); N: 10.09 (10.16). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.47 (q, $^3J_{HH} = 7.9$ Hz, 6H, CH_2CH_3), 0.94 (t, $^3J_{HH} = 7.7$ Hz, 9H, CH_2CH_3, 1.69 (s, 6H, C_5Me_5), 1.75 (s, 9H, C_5Me_5), 2.49 (s, 6H, NMe_2), 6.21 (d, $^3J_{HH} = 5.7$ Hz, 2H, C3/C5-H-dmap), 8.27 (d, $^3J_{HH} = 6.3$ Hz, 2H, C2/C6-H-dmap). ^{13}C NMR (75 MHz, toluene-d_8, 30 °C): δ 6.5 (CH_2CH_3) 11.6 (C_5Me_5), 14.3 (CH_2CH_3), 35.4 (NMe_2), 95.6 (C_5Me_5), 107.2 ($C3_{dmap}$), 121.9 ($C2_{dmap}$), 138.0 ($C4_{dmap}$). EI-MS (12 eV, 350 °C): *m*/*z* (%) 797 (1) [M − Et]$^+$, 691 (42) [M − Cp*]$^+$, 553 (80) [M − 2dmap − Et]$^+$, 122 (100) [dmap]$^+$.

[dmap-Al(Cp*)NSi(*i*-Pr)$_3$]$_2$ (6). Yield: 0.82 g (90%). Mp: 160−165 °C (dec). Anal. Found (calcd) for $C_{52}H_{92}Al_2N_6Si_2$ (911.5 g/mol): H: 10.12 (10.17); C: 68.37 (68.52); N: 9.16 (9.22). ^1H NMR (300 MHz, toluene-d_8, 95 °C): δ 1.15 (m, 21H, *i*-Pr), 1.71 (s), 1.83 (s), 2.19 (s) (15H, C_5Me_5), 2.27 (s, 6H, NMe_2), 6.24 (d, $^4J_{HH} = 5.9$ Hz, 2H, C3/C5-H-dmap), 8.74 (d, $^4J_{HH} = 4.7$ Hz, 2H, C2/C6-H-dmap). ^{13}C NMR (75 MHz, toluene-d_8, 95 °C): δ 1.4 ($CHMe_2$), 9.3, 10.9, 17.0 (C_5Me_5), 15.0 ($CHMe_2$), 38.4 (NMe_2), 106.6 ($C3_{dmap}$), 109.7 (C_5Me_5), 121.7 ($C2_{dmap}$), 137.8 ($C4_{dmap}$). EI-MS (12 eV, 150−250 °C): *m*/*z* (%) 667 (1) [M − 2dmap]$^+$, 623 (1) [M − 2dmap − *i*-Pr]$^+$, 532 (6) [M − 2dmap − Cp*]$^+$, 489 (6) [M − 2dmap − *i*-Pr − Cp*]$^+$, 135 (35) [Cp*]$^+$, 122 (100) [dmap]$^+$.

[dmap-Al(Cp*)NSi(*t*-Bu)Me$_2$]$_2$ (7). Yield: 0.53 g (64%). Mp: 184−187 °C (dec). Anal. Found (calcd) for $C_{46}H_{80}Al_2N_6Si_2-C_7H_8$ (919.4 g/mol): H: 9.43 (9.57); C: 69.03 (69.27); N: 9.08 (9.14). ^1H NMR (300 MHz, toluene-d_8, thf-d_8 (2:1), 65 °C): δ −0.04 (s, 6 H, Si(*t*-Bu)Me_2), 0.64 (s, 9 H, Si(*t*-Bu)Me_2), 1.96 (s, 15 H, Cp*), 2.70 (s, 6 H, NMe_2), 6.34 (br, 2 H, C3/C5-H-dmap), 8.49 (br, 2 H, C2/C6-H-dmap). A ^{13}C NMR spectrum could not be recorded due to the very poor solubility of **7** in organic solvents. EI-MS (16 eV, 350 °C): *m*/*z* (%) 628 (14) [Cp*(dmap)AlN(Si(*t*-Bu)Me$_2$)$_2$N-(Si(*t*-Bu)H)]$^+$), 391 (100) [Cp*AlN(Si(*t*-Bu)Me$_2$)N(Si(H)*t*-Bu)]$^+$, 268 (21) [$C_5Me_4CH_2$]$_2^+$, 162 (4) [Cp*Al]$^+$, 135 (63) [Cp*]$^+$, 134 (60) [$C_5Me_4CH_2$]$^+$.

General Synthesis of [*o*-Al(Cp*)N(H)SiRR′$_2$-dmap]$_2$. A suspension of 1 mmol of RR′$_2$SiN$_3$, 0.16 g (0.25 mmol) of [Cp*Al]$_4$, and 0.12 g (1 mmol) of dmap was heated in 50 mL of toluene to reflux for 30 min. The resulting solution was stored at −50 °C, yielding colorless crystals.

[*o*-Al(Cp*)N(H)SiEt$_3$-dmap]$_2$ (8). Yield: 0.58 g (71%). Mp: 232−240 °C (dec). Anal. Found (calcd) for $C_{46}H_{80}Al_2N_6Si_2$ (827.3 g/mol): H: 9.62 (9.75); C: 66.61 (66.81); N: 10.04 (10.16). ^1H NMR (300 MHz, toluene-d_8, 30 °C): δ −0.31 (s, 1H, NH), 0.79 (q, $^3J_{HH} = 7.8$ Hz 6H, CH_2CH_3), 1.23 (t, $^3J_{HH} = 7.8$ Hz, 9H, CH_2CH_3), 1.79 (s, 15H, C_5Me_5), 2.49 (s, 6H, NMe_2), 6.09 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 3.4$ Hz, 1H, C5-H-dmap), 7.25 (d, $^4J_{HH} = 3.4$ Hz, 1H, C3-H-dmap), 8.23 (d, $^3J_{HH} = 7.0$ Hz, 1H, C6-H-dmap). A ^{13}C NMR spectrum could not be recorded due to the very poor solubility of **8** in organic solvents. IR (Nujol): $\bar{\nu}$ 3243, 3232 (N−H) cm^{-1}. EI-MS (12 eV, 450 °C): *m*/*z* (%) 797 (2) [M − Et]$^+$, 691 (76) [M − Cp*]$^+$, 278 (8) [M/2 − Cp*]$^+$, 206 (100) [M/2 − Cp* − Et − NMe_2]$^+$, 135 (48) [Cp*]$^+$, 122 (64) [dmap]$^+$.

[*o*-Al(Cp*)N(H)Si(*i*-Pr)$_3$-dmap]$_2$ (9). Yield: 0.67 g (74%). Mp: 270−275 °C (dec). Anal. Found (calcd) for $C_{52}H_{92}Al_2N_6Si_2$ (911.5 g/mol): H: 10.09 (10.17); C: 68.43 (68.52); N: 9.19 (9.22). ^1H NMR (300 MHz, toluene-d_8, 30 °C): δ −0.60 (br, 1H, N-H), 0.90−1.17 (m, 21H, *i*-Pr), 1.64 (s, 15H, C_5Me_5), 2.55 (s, 6H, NMe_2), 6.18 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 3.3$ Hz, 2H, C5-H-dmap), 7.31 (s, $^4J_{HH} = 3.1$ Hz, 2H, C3-H-dmap), 8.41 (dd, $^3J_{HH} = 6.9$ Hz, $^5J_{HH} = 0.4$ Hz, 2H, C6-H-dmap). $^{13}C\{^1H\}$ NMR (75 MHz, toluene-d_8, 95 °C): δ 1.4 ($CH(CH_3)_2$), 13.0 (C_5Me_5), 15.0 ($CH(CH_3)_2$), 38.5 (NMe_2), 104.8 ($C3/C5_{dmap}$), 118.5 (C_5Me_5), 119.6 ($C6_{dmap}$), 149.0 ($C2_{dmap}$), 153.5 ($C4_{dmap}$). IR (Nujol): $\bar{\nu}$ 3179, 3236 (N−H) cm^{-1}. EI-MS (16 eV, 400 °C): *m*/*z* (%) 868 (1) [M − *i*-Pr]$^+$, 776 (49) [M − Cp*]$^+$, 640 (2) [M − 2Cp*]$^+$, 135 (40) [Cp*]$^+$, 130 (100) [(*i*-Pr)$_2$SiNH$_2$]$^+$, 121 (65) [dmap − H]$^+$.

[*o*-Al(Cp*)N(H)Si(*t*-Bu)$_3$-dmap]$_2$ (10). Yield: 0.82 g (85%). Mp: 250−255 °C (dec). Anal. Found (calcd) for $C_{58}H_{104}Al_2N_6Si_2$ (995.6 g/mol): H: 10.37 (10.53); C: 69.72 (69.97); N: 8.31 (8.43). ^1H NMR (300 MHz, toluene-d_8, 95 °C): δ −0.53 (s, 1H, NH), 1.29 (s, 27H, *t*-Bu), 1.74 (s, 15H C_5Me_5), 2.63 (s, NMe_2), 6.36 (dd, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 3.2$ Hz, 1H, C5-H-dmap), 7.56 (d, $^4J_{HH} = 3.2$ Hz, 1H, C3-H-dmap), 8.81 (d, $^3J_{HH} = 7.2$ Hz, 1H, C6-H-dmap). A ^{13}C NMR spectrum could not be recorded due to the very poor solubility of **10** in organic solvents. IR (Nujol): $\bar{\nu}$ 3215, 3304 (N−H) cm^{-1}. EI-MS (16 eV, 400 °C): *m*/*z* (%) 820 (5) [M − Cp*]$^+$, 342 (16) [M/2 − Cp*]$^+$, 214 (21) [N(H)Si(*t*-Bu)$_3$]$^+$, 135 (84) [Cp*]$^+$, 121 (35) [dmap − H]$^+$, 57 (100) [*t*-Bu]$^+$.

[*o*-Al(Cp*)N(H)Si(*t*-Bu)Me$_2$-dmap]$_2$ (11). Yield: 0.58 g (71%). Mp: 225−230 °C (dec). Anal. Found (calcd) for $C_{46}H_{80}Al_2N_6Si_2-2C_7H_8$ (1011.8 g/mol): H: 9.31 (9.49); C: 71.07 (71.21); N: 8.21 (8.31). ^1H NMR (300 MHz, toluene-d_8, 30 °C): δ −0.36 (s, 1H, NH), 0.18 (s, 3H, Si(*t*-Bu)Me_2), 0.21(s, 3H, Si(*t*-Bu)Me_2), 1.14 (s, 9H, Si(*t*-Bu)Me_2), 1.72 (s, 15H, C_5Me_5), 2.63 (s, 6H, NMe_2), 6.19 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 3.2$ Hz, 1H, C5-H-dmap), 7.27 (d, $^4J_{HH} = 3.1$ Hz, 1H, C3-H-dmap), 8.26 (d, 1H, $^3J_{HH} = 6.8$ Hz, C6-H-dmap). $^{13}C\{^1H\}$ NMR (75 MHz, toluene-d_8, 30 °C): δ 1.6 (Si(*t*-Bu)Me_2), 13.1 (C_5Me_5), 23.5 (Si(CMe_3)Me$_2$), 30.2 (Si(CMe_3)Me$_2$), 38.7 (NMe_2), 104.6 ($C3/C5_{dmap}$), 117.2 (C_5Me_5), 119.0 ($C6_{dmap}$), 148.1 ($C2_{dmap}$), 153.6 ($C4_{dmap}$). IR (Nujol): $\bar{\nu}$ 3101, 3330 (N−H) cm^{-1}. EI-MS (12 eV, 400−500 °C): *m*/*z* (%) 812 (1) [M − Me]$^+$, 771 (1) [M − *t*-Bu]$^+$, 691 (100) [M − Cp*]$^+$, 135 (5) [Cp*]$^+$, 57 (35) [*t*-Bu]$^+$.

[*o*-Al(dmap)(Cp*)N(H)Si(*t*-Bu)$_3$-dmap] (12). A 0.24 g amount of *t*-Bu$_3$SiN$_3$ (1 mmol), 0.16 g (0.25 mmol) of [Cp*Al]$_4$, and 0.24 g (2 mmol) of dmap were heated in 50 mL of toluene at 75 °C,

(15) Moberg, C.; Adolfson, H. In *Catalysis 1: Organometallics, Vol. 4: Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds*; Flemming, I. (Hrsg.); Science of Synthesis: Houben-Weyl, Methods of Molecular Transformations, Thieme, 2001.

Table 3. Crystallographic Details for 3, 7, 8, 9, and 11

	3	**7**	**8**	**9**	**11**	**12**
empirical formula	$C_{44}H_{84}Al_2N_2Si_2$−toluene	$C_{46}H_{80}Al_2N_6Si_2$−toluene	$C_{46}H_{80}Al_2N_6Si_2$	$C_{52}H_{92}Al_2N_6Si_2$	$C_{46}H_{80}Al_2N_6Si_2$−2 toluene	$C_{36}H_{62}AlN_5Si$
molecular mass	843.4	919.4	827.3	911.5	1011.8	620.0
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	*Pbcn* (no. 60)	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)
a [Å]	28.6468(3)	15.2494(2)	11.0466(5)	30.6476(6)	15.8746(9)	8.5764(1)
b [Å]	17.3400(2)	24.9648(4)	13.0505(7)	9.1764(2)	14.8353(8)	12.7498(1)
c [Å]	20.9183(2)	14.5470(3)	17.4302(10)	24.2053(7)	25.8986(15)	17.4072(2)
α [deg]	90	90	102.797(2)	90	90	101.112(1)
β [deg]	90	100.894(1)	95.132(3)	127.180(1)	92.351(3)	96.038(1)
γ [deg]	90	90	97.467(3)	90	90	93.532(1)
V [Å^3]	10390.9(2)	5438.2(2)	2411.4(2)	5423.7(2)	6094.1(6)	1843.9(1)
Z	8	4	2 = 4 × 0.5	4	4	2
T [K]	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
radiation (*λ* [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ [mm^{-1}]	0.136	0.137	0.147	0.137	0.128	0.118
D_{calcd} [g cm^{-3}]	1.078	1.123	1.139	1.116	1.103	1.117
$2\theta_{max}$ [deg]	50	50	50	50	50	50
cryst dimens [mm]	0.25 × 0.20 × 0.15	0.55 × 0.35 × 0.20	0.30 × 0.20 × 0.10	0.40 × 0.15 × 0.10	0.30 × 0.25 × 0.15	0.50 × 0.30 × 0.10
no. of reflns	78 227	29 093	22 391	17 829	14 167	31 599
no. of unique reflns	9157	4785	8386	4728	4879	6497
R_{merg}	0.0450	0.0373	0.0409	0.0613	0.0377	0.0438
no. params refined/ restraints	523/0	276/14	517/0	289/1	297/57	399/1
R1[a]	0.0367	0.0447	0.0794	0.0438	0.0583	0.0380
wR2[b]	0.1058	0.1350	0.2281	0.0967	0.1705	0.1113
goodness of fit[c]	1.058	1.069	1.033	0.900	1.053	1.038
final max./min. $\Delta\rho$, e Å^{-3}	0.277/−0.264	0.797/−0.491	1.856/−0.551	0.252/−0.206	0.463/−0.453	0.420/−0.220

[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 $= \{\sum[w(|F_o^2| - |F_c^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

until gas evolution was finished. The resulting blue solution was stored at −50 °C for 5 days, yielding colorless crystals of **12**. Yield: 0.25 g (41%). Mp: 175−185 °C (dec). Anal. Found (calcd) for $C_{36}H_{62}AlN_5Si$ (620.0 g/mol): H: 9.97 (10.08); C: 69.53 (69.74); N: 11.18 (11.29). ^{1}H NMR (300 MHz, toluene-d_8, 30 °C): δ −0.51 (s, 1H, NH), 1.02 (s, 27H, *t*-Bu), 1.68 (s, 15H, C_5Me_5), 2.65 (s, 6H, NMe_2), 2.77 (s, 6H, NMe_2), 6.22 (dd, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 3.0 Hz, 1H, C5-H-dmap), 6.31 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C3′/C5′-H-dmap), 7.24 (d, $^4J_{HH}$ = 2.8 Hz, 1H, C3-H-dmap), 8.34 (d, $^3J_{HH}$ = 5.8 Hz, 1H, C6-H-dmap), 8.90 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C2′/C6′-H-dmap). ^{13}C{^{1}H} NMR (75 MHz, toluene-d_8, 30 °C; [a] = activated dmap, [b] = nonactivated dmap): 13.1 (C_5Me_5), 23.6 (CMe_3), 30.5 (CMe_3), 38.5, 41.1 (2 × NMe_2), 105.3 (C3/C3′$_{dmap}$[b]), 107.1 (C3/C5$_{dmap}$[a]), 118.4 (C_5Me_5), 119.8 (C6$_{dmap}$[a]), 127.7 (C2$_{dmap}$[b]), 137.4 (C4$_{dmap}$[b]), 149.3 (C2$_{dmap}$[a]), 167.7 (C4$_{dmap}$[a]). IR (Nujol): $\bar{\nu}$ 3315 (N−H) cm^{-1}. EI-MS (12 eV, 450 °C): *m*/*z* (%) 618 (20) [M]$^+$, 562 (11) [M − *t*-Bu]$^+$, 484 (100) [M − Cp*]$^+$, 441 (14) [M − *t*-Bu − dmap]$^+$, 427 (9) [M − *t*-Bu − Cp*]$^+$, 135 (28) [Cp*]$^+$, 122 (31) [dmap]$^+$, 57 (100) [*t*-Bu]$^+$.

X-ray Structure Solution and Refinement. Crystallographic data of **3**, **7**, **8**, **9**, **11**, and **12** are summarized in Table 3. Figures 1−6 show ORTEP diagrams of the solid-state structures of **3**, **7**, **8**, **9**, **11**, and **12**. Data were collected on a Nonius Kappa-CCD diffractometer. The structures were solved by direct methods (SHELXS-97)[16] and refined by full-matrix least-squares on F^2 (SHELXL-97).[17] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (H(N) free). The crystallographic data of **3**, **7**, **8**, **9**, **11**, and **12** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-285233 (**3**), CCDC-285231 (**7**), CCDC-285236 (**8**), CCDC-285232 (**9**), CCDC-285234 (**11**), and CCDC-285235 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: (+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 **3**, **7**, **8**, **9**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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

(17) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Universität Göttingen, 1997.