

Reaction of the Primary Alane (2,4,6-*t*-Bu₃H₂C₆AlH₂)₂ with Nitriles, Isonitriles, and Primary Amines

Rudolf J. Wehmschulte[†] and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

Received September 11, 1998

The reactions of the sterically encumbered primary alane (Mes*AlH₂)₂ (Mes* = C₆H₂-2,4,6-*t*-Bu₃) with the nitriles *t*-BuCN, MesCN (Mes = C₆H₂-2,4,6-Me₃) or MeCN lead eventually to dimeric amido alane products in which one of the ortho *t*-Bu groups of the Mes* ligand is metalated and the nitrile is reduced to the amide ligand N(H)CH₂R (R = *t*-Bu, Mes, or Me). The compounds [AlC₆H₂-2,4-*t*-Bu₂-6-CMe₂CH₂{μ²-N(H)CH₂R}]₂ (R = *t*-Bu, **2** (cis), **3** (trans); Mes, **4** (cis), **5** (trans); Me, **6** (cis)) have been isolated and characterized spectroscopically and also by X-ray crystallography in the cases of **4** and **5**. The intermediate, dimeric iminato complex [Mes*Al(H){μ²-NC(H)*t*-Bu}]₂ (**1**), can also be isolated under carefully controlled, mild conditions. Reaction of (Mes*AlH₂)₂ with the isonitrile *t*-BuNC affords the cyclic species {Mes*AlN(*t*-Bu)CH₂}₂ (**7**) featuring a six-membered (AlNC)₂ ring which, when heated, affords the cyclometalated species [AlC₆H₂-2,4-*t*-Bu₂-6-CMe₂CH₂{N(*t*-Bu)H}(CH₂)]₂ (**8**). Recognition that the products **2**–**6** and **8** were derivatives of primary amides led to an investigation of synthetic approaches to these product types via the direct reaction of (Mes*AlH₂)₂ with some primary amines. Treatment of (Mes*AlH₂)₂ with H₂NCH₂Mes affords the dimeric amido alane [Mes*(H)Al{μ²-N(H)CH₂Mes}]₂ as a mixture of trans (**9**) and cis (**10**) isomers. Further heating of **9** and **10** affords the ortho-metalated compounds **4** and **5**. The reaction of (Mes*AlH₂)₂ with H₂NSiPh₃ furnishes the bis amido aluminum compound Mes*Al{N(H)SiPh₃}₂ (**11**) and [Mes*(H)Al{N(H)SiPh₃}]₂. The latter yields the dimeric imide {Mes*AlNSiPh₃}₂ (**12**) at elevated temperature.

Introduction

(Mes*AlH₂)₂,¹ a bulky primary alane, has been shown to react smoothly with PhEH₂ (E = N, P, As) and (Me₂SiO)₃ to form the novel, formally unsaturated ring systems (Mes*AlEPh)_{*n*} (E = N, *n* = 2; E = P, As, *n* = 3) and (Mes*AlO)₄.³ In addition, reaction with azobenzene (i.e., Ph–N=N–Ph) affords an isoelectronic analogue of a cyclopentadienide anion, [Mes*Al(μ²-PhNNPh)Al(Mes*)(μ²-NPh)]₂.⁴ The reactivity of (Mes*AlH₂)₂ toward the polar, formally triply or doubly bonded nitrile or isonitrile groups has not been investigated, however. Reduction of nitriles by using aluminum hydrides was first reported in 1957⁵ and it is a well-known procedure in organic synthesis. It was hoped that the bulky Mes* group would allow the isolation and characterization of intermediates of this hydride reduction. It seems that only one such intermediate, the compound [(*i*-Bu)₂Al{μ²-N=C(H)(C₆H₃-2,6-Me₂)}]₂, has been characterized by X-ray crystallography.⁶ This species was obtained from the reaction of 2,6-Me₂H₃C₆CN with HAl(*i*-Bu)₂. In addition, it was possible that reduction of RCN with a bulky alane such as (Mes*AlH₂)₂ would be an alternative, nonprotic approach to the synthesis of aluminum imides. In this paper the synthesis

and characterization of several reaction products from the treatment of (Mes*AlH₂)₂ with the nitriles RCN (R = *t*-Bu, Mes, or Me), the isonitrile *t*-BuNC, and the amines H₂NCH₂-Mes and H₂NSiPh₃ are described. These reactions are summarized in Scheme 1.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or a Vacuum Atmospheres HE43-2 drybox. MeCN, *t*-BuCN, *t*-BuNC, and MesCN were obtained from commercial suppliers and dried by standard procedures. (Mes*AlH₂)₂¹ and H₂NSiPh₃⁷ were synthesized by literature methods, and H₂NCH₂Mes (which was originally synthesized by the reaction of MesCH₂Cl with potassium amide⁸) was obtained by the reduction of MesCN with LiAlH₄. Solvents were freshly distilled under N₂ from Na/K alloy and degassed twice prior to use. NMR spectra were recorded on a General Electric GE-300 spectrometer, and IR spectra were obtained on a Perkin-Elmer PE-1430 spectrometer.

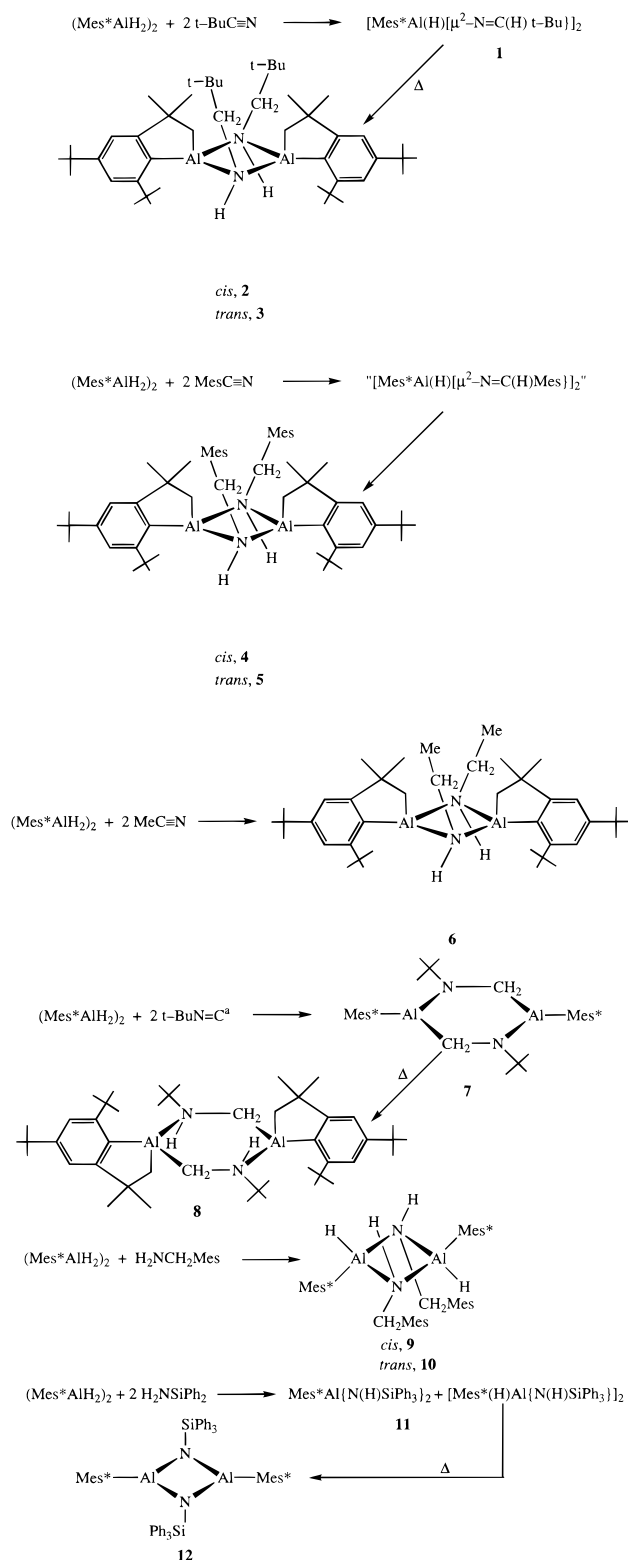
[Mes*Al(H){μ²-N=C(H)-*t*-Bu}]₂ (**1**). A solution of (Mes*AlH₂)₂ (0.59 g, 1.1 mmol) in *n*-pentane (60 mL) was treated with *t*-BuCN (0.24 mL, 0.18 g, 2.15 mmol) at room temperature. After ca. 1 min, a fine, colorless precipitate formed. The solution was stirred for 1 h, after which the solid was collected on a sintered glass frit and dried under reduced pressure. Yield: 0.53 g, 60%. Mp: 265–270 °C. Calcd for C₂₃H₄₀Al₂N₂: C, 77.26; H, 11.28; N, 3.92. Found: C, 77.33; H, 11.02; N, 3.84. ¹H NMR (C₆D₆): 8.52 (s, N=CH, 2H), 7.54, 7.48 (AB system, *m*-H, 4H), ⁴J_{HH} = 1.5 Hz, 5.1 (s, broad, Al–H, 2H), 1.80, 1.52, 1.39 (s, *o*-, *p*-Me, 18H each), 0.67 (s, *t*-Bu, 18H). ¹³C{¹H} NMR (C₆D₆): 190.6 (N=C), 162.3, 160.5 (*o*-C), 149.5 (*p*-C), 121.3, 120.7 (*m*-C), 41.2, 38.9, 38.6, 34.9 (C(CH₃)₃), 34.6, 33.4, 31.5 (*o*-, *p*-CH₃), 24.3 (*t*-Bu). IR: 1828 (st, ν_{Al–H}), 1668 (sh), 1642 (st, ν_{N=C}).

(7) Kraus, C. A.; Rosen, R. *J. Am. Chem. Soc.* **1925**, 47, 2739.

(8) Hauser, C. R.; Brasen, W. R.; Skell, P. S.; Kantor, S. W.; Brodhag, A. E. *J. Am. Chem. Soc.* **1956**, 78, 1653.

[†] Present address: Room 208, Department of Chemistry & Biochemistry, 620 Parrington Oval, Norman, OK 73019.

- (1) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, 33, 5611.
- (2) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, 118, 791.
- (3) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, 119, 8387.
- (4) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1996**, 35, 2717.
- (5) (a) Zakharkin, L. I.; Khorlina, I. M. *Proc. Acad. Sci. USSR* **1957**, 116, 879. (b) Zakharkin, L. I.; Khorlina, I. M. *Bull. Acad. Sci. USSR (Engl. Transl.)* **1959**, 523. (c) Andreoli, P.; Billi, L.; Carnelli, G.; Panunzio, M.; Martelli, G.; Spunta, G. *J. Org. Chem.* **1990**, 55, 4199.
- (6) Jensen, J. A. *J. Organomet. Chem.* **1993**, 456, 161.

Scheme 1. Summary of the Reactions Leading to **1–12**^a

^a The formula for *t*-BuNC is given as the doubly bonded canonical form although it is also possible to write it with an NC triple bond.

cis- and trans-[AlC₆H₂-2,4-*t*-Bu₂-6-CMe₂CH₂{μ²-N(H)CH₂(*t*-Bu)}]₂ (2 and 3). A solution of **1** in benzene (15 mL) was heated to 80 °C for 40 h. Removal of the solvent followed by crystallization from *n*-hexane (15 mL) at −20 °C for 6 days afforded 0.9 g of a 1:1 mixture of **2** and **3**. Yield: 75%. Mp: 303–310 °C. Calcd for C₂₃H₄₀NAl: C, 77.26; H, 11.28; N, 3.92. Found: C, 77.81, H, 11.41; N, 3.76. ¹H NMR (**2**, **3**) (C₆D₆): 7.70, 7.68, 7.61, 7.58 (s, *m*-H, 2H ea), 2.87

(dd, N—CH₂, 2H, **3**), ²J_{HH} = 11.1 Hz, ³J_{HH} = 11.1 Hz, 2.75 (d, N—CH₂, 4H, **2**), ³J_{HH} = 6.3 Hz, 2.55 (d, N—CH₂, 2H, **3**), 1.90 (s, C(CH₃)₂, 6H, **3**), 1.75 (s, C(CH₃)₂, 12H, **2**), 1.63, 1.60 (s, *o*-C(CH₃)₃, 18H ea), 1.58 (s, C(CH₃)₂, 6H, **3**), 1.35, 1.33 (s, *p*-C(CH₃)₃, 18H ea), 0.82 (d, Al—CH₂, 2H, **3**), ²J_{HH} = 14.7 Hz, 0.66 (s, Al—CH₂, 4H, **2**), 0.60 (d, Al—CH₂, 2H, **3**), 0.55 (s, CH₂—C(CH₃)₃, 36H). ¹³C{¹H} NMR (**2**, **3**) (C₆D₆): 168.1, 167.0 (6-C), 157.4, 156.7 (2-C), 151.3 (*p*-C), 126.5, 120.0, 119.7, 119.4 (*m*-C), 56.7, 56.5 (N—CH₂), 41.5, 41.3 (C—Me₂), 38.9 (CMe₂, **3**), 38.0 (CMe₂, **2**), 36.6 (CMe₂, **3**), 34.1 (*o*-C(CH₃)₃), 31.7 (*p*-C(CH₃)₃), 27.3, 27.4 (N—C—C(CH₃)₃), 26.0 (broad, Al—CH₂), 20.1 (broad, Al—CH₂). IR: 3295 (w, ν_{N—H}).

cis- and trans-[AlC₆H₂-2,4-*t*-Bu₂-6-CMe₂CH₂{μ²-N(H)CH₂Mes}]₂ (cis, **4; trans, **5**).** A solution of MesCN (0.20 g, 1.38 mmol) in hexane (10 mL) was added to a rapidly stirred solution of (Mes*AlH₂)₂ (0.38 g, 0.69 mmol) in hexane (30 mL) at room temperature. The mixture was warmed to reflux temperature (ca. 70 °C), at which point stirring was discontinued and the mixture was maintained at 70 °C for 3 days. Upon cooling of the mixture to room temperature, a small amount of white insoluble solid precipitated. This was removed by filtration, and the resulting clear colorless solution was concentrated to ca. 25 mL and cooled in a −20 °C freezer overnight to give 0.14 g of the trans isomer **5** as a fine colorless powder. Yield: 24%. Mp: 245–255 °C, melts partially with color change to orange, does not melt completely under 300 °C. ¹H NMR (C₆D₆): 7.68 (d, *m*-H, 2H), ⁴J_{HH} = 1.5 Hz, 7.57 (d, *m*-H, 2H), 6.50 (s, *m*-H (Mes), 4H), 4.12 (t, NH, 2H), ³J_{HH} = 4.0 Hz, 4.04 (d, N—CH₂, 2H), ²J_{HH} = 12.3 Hz, 3.96 (d, N—CH₂, 2H) (ABX system), 1.94 (s, *p*-CH₃(Mes), 6H), 1.84 (s, *o*-CH₃ (Mes), 12H), 1.71, 1.54 (2s, C(CH₃)₂, 12H), 1.46 (s, *o*-C(CH₃)₃, 18H), 1.41 (s, *p*-C(CH₃)₃, 18H), 0.91 (d, Al—CH₂, 2H) ²J_{HH} = 15.3 Hz, 0.43 (d, Al—CH₂, 2H). ¹³C NMR (C₆D₆): 166.9 (6-C), 157.1 (2-C), 151.5 (*p*-C), 137.2, 135.2 (*i*-, *p*-C(Mes)), 136.3 (*o*-C(Mes)), 129.7 (*m*-C(Mes)), 120.5, 119.8 (*m*-C), 42.2 (N—CH₂), 41.4 (CMe₂), 38.4, 36.9 (CMe₂), 35.0 (*p*-C(CH₃)₃), 33.9 (*o*-C(CH₃)₃), 31.7 (*p*-C(CH₃)₃), 25.1 (broad, Al—CH₂), 20.7 (*p*-CH₃(Mes)), 19.9 (*o*-CH₃(Mes)). IR: ν_{NH} = 3305 cm^{−1} (m). The colorless supernatant liquor from **5** was concentrated to ca. 3 mL and cooled in a −20 °C freezer for 1 week to give 0.15 g of the cis isomer **4** as the adduct **4**·hexane in the form of large colorless plates. Yield: 23%. Mp: 222–225 °C, turns opaque at 50 °C, softens at 210 °C. ¹H NMR (C₇D₈, 20 °C): 7.71 (d, 5-H, 2H), ⁴J_{HH} = 1.5 Hz, 7.50 (d, 3-H, 2H), 6.42 (s, *m*-H(Mes), 4H), 4.01 (d, N—CH₂, 4H), ³J_{HH} = 4.5 Hz, 1.91 (s, *p*-CH₃(Mes)), 6H, 1.85 (s, *o*-CH₃(Mes), 12H), 1.84 (s, C(CH₃)₂, 12H) or vice versa, 1.40 (s, *o*-C(CH₃)₃, 18H), 1.20 (s, *p*-C(CH₃)₃, 18H), 0.87 (s, Al—CH₂, 4H). ¹³C NMR (C₆D₆, 20 °C): 167.7 (6-C), 156.9 (2-C), 151.4 (4-C), 137.0, 134.8 (*i*-, *p*-C(Mes)), 136.2 (*o*-C(Mes)), 129.5 (*m*-C(Mes)), 119.5 (*m*-C), 41.5 (CMe₂), 41.3 (N—CH₂), 38.0 (CMe₂), 35.0 (*p*-CMe₃), 33.5 (*o*-CMe₃), 20.7 (*p*-CH₃(Mes)), 20.2 (Al—CH₂; broad), 20.0 (*o*-CH₃(Mes)). IR: ν_{NH} = 3295 cm^{−1} (m). Crystals of **4**·toluene and **5**·benzene suitable for X-ray diffraction studies were grown from concentrated toluene (in a −20 °C freezer) and benzene (at ca. +6 °C) solutions over a period of several days.

cis-[AlC₆H₂-2,4-*t*-Bu₂-6-CMe₂CH₂{μ²-N(H)CH₂CH₃}]₂ (6). MeCN (0.079 mL, 0.061 g, 1.5 mmol) was added to a solution of (Mes*AlH₂)₂ (0.41 g, 0.75 mmol) in *n*-hexane (30 mL) at room temperature. The MeCN phase disappeared after 3–4 min, and the resulting clear, colorless solution turned pale yellow after ca. 15 min. After stirring for ca. 3 h, the solution was concentrated to ca. 10 mL and cooled in a −20 °C freezer overnight. As no crystals were formed, all the volatile materials were removed under reduced pressure. The solid was then redissolved in *n*-hexane, and the solution was heated to reflux for 18 h. Small amounts of a fine colorless solid were precipitated and removed by filtration. Concentration of the filtrate to ca. 20 mL and cooling in a −20 °C freezer for 1 week afforded 0.09 g of **6** as a colorless, microcrystalline solid. Yield: 19%. Mp: softens at 264 °C, melts at 266–269 °C. Calcd for C₂₀H₃₄NAl: C, 76.14; H, 10.86; N, 4.44. Found: C, 76.01, H, 10.59; N, 4.31. ¹H NMR (C₆D₆): 7.70 (d, *m*-H, 2H), ⁴J_{HH} = 1.5 Hz, 7.58 (d, *m*-H, 2H), 2.68 (dq, N—CH₂, 4H), ³J_{HH} = 7.2 Hz (d and q), 1.70 (s, C(CH₃)₂, 12H), 1.49 (s, *o*-C(CH₃)₃, 18H), 1.41 (s, *p*-C(CH₃)₃, 18H), 0.62 (t, N—C—CH₃, 6H), 0.56 (s, Al—CH₂, 4H). ¹³C{¹H} NMR (C₆D₆, 60 °C): 168.2 (6-C), 157.1 (2-C), 151.3 (*p*-C), 119.5, 119.1 (*m*-C), 41.5 (N—CH₂), 38.8, 38.0, 35.1 (quaternary

carbons), 37.6 (C(CH₃)₂), 34.1 (*o*-C(CH₃)₃), 31.8 (*p*-C(CH₃)₃), 19.4 (N-C-CH₃). IR: 3290 cm⁻¹ (w, $\nu_{\text{N-H}}$).

{Mes*AlN(*t*-Bu)CH₂}(7). A slurry of (Mes*AlH₂)₂ (0.43 g, 0.75 mmol) in *n*-pentane (20 mL) was treated with *t*-BuNC (0.17 mL, 0.12 g, 1.5 mmol) at 0 °C to give, almost immediately, a clear solution. After ca. 5 min the solution was cooled slowly in a ca. -20 °C freezer for 5 days to give 0.19 g of colorless, microcrystalline 7. A second crop of 7 (0.12 g) was obtained by concentration of the mother liquor to ca. 2–3 mL followed by cooling to ca. -20 °C for 1 week. Crystals of 7 suitable for X-ray crystallographic studies were grown from a saturated pentane solution at ca. -20 °C. Yield: 58%. Mp: disintegrates into a powder at 113 °C; becomes yellow orange at 265 °C, melts with gas evolution at 286–287 °C. ¹H NMR (C₆D₆): 7.52 (s, *m*-H, 4H), 2.46 (s, Al-CH₂, 4H), 1.74 (s, *o*-C(CH₃)₃, 36H), 1.34 (s, *p*-C(CH₃)₃, 18H), 1.16 (s, N-C(CH₃)₃, 18H). ¹³C{¹H} NMR (C₆D₆): 156.4 (*o*-C), 149.6 (*p*-C), 135.7 (*i*-C), 122.0 (*m*-C), 54.1 (N-C(CH₃)₃), 38.4 (Al-CH₂), 36.6 (*o*-C(CH₃)₃), 34.7 (*p*-C(CH₃)₃), 33.4 (*o*-C(CH₃)₃), 31.5 (*p*-C(CH₃)₃), 30.0 (N-C(CH₃)₃).

[AlC₆H₂-2,4-*t*-Bu₂-6-CMe₂CH₂{N(*t*-Bu)H}(CH₂)₂](8). 7 (0.14 g, 0.2 mmol) in benzene (25 mL) was heated to 80 °C for 1 h. Standing at room temperature overnight afforded a microcrystalline solid, which was recrystallized from 10 mL of benzene at ca. 6 °C for 1 week. Yield: 0.02 g (14%). Mp: turns orange and melts with slight gas evolution at 284–285 °C. Calcd for C₂₃H₄₀NAl: C, 77.26; H, 11.28; N, 3.92. Found: C, 77.93; H, 11.46; N, 3.68. ¹H NMR (C₆D₆, 80 °C): 7.68 (d, *m*-H, 2H), ⁴J_{HH} = 1.7 Hz, 7.59 (d, *m*-H, 2H), 2.80 (d, N-H, 2H), ³J_{HH} = 12 Hz, 2.20 (dd, N-CH, 2H), ²J_{HH} = 13.8 Hz, 1.99 (d, N-CH, 2H), 1.95 (s, C(CH₃)₂, 6H), 1.53 (s, *o*-C(CH₃)₃, 18H), 1.50 (s, C(CH₃)₂, 6H), 1.41 (s, *p*-C(CH₃)₃, 18H), 0.82 (s, N-C(CH₃)₃, 18H), 0.65, 0.57 (AB system, Al-CH₂, 4H), ²J_{HH} = 14.4 Hz. ¹³C{¹H} NMR (C₆D₆, 80 °C): 121.0, 119.0 (*m*-C), 57.8, 41.8, 40.1, 37.6, 36.4, 35.0; 33.4 (*o*-C(CH₃)₃), 31.8 (*p*-C(CH₃)₃), 28.3 (N-C(CH₃)₃). IR: 3225 cm⁻¹ (m, $\nu_{\text{N-H}}$).

cis- and *trans*-[Mes*Al(H){ μ^2 -N(H)CH₂Mes}]₂ (9 and 10). A solution of (Mes*AlH₂)₂ (0.30 g, 0.54 mmol) in *n*-pentane (20 mL) was treated dropwise with a solution of MesCH₂NH₂ (0.16 g, 1.07 mmol) in *n*-pentane (10 mL) at 0 °C. After the initial formation of a clear colorless solution, a fine colorless precipitate began to form at the end of the addition. The mixture was brought to room temperature and stirred for another 14 h. The colorless precipitate was collected on a sintered glass frit and dried under reduced pressure. Yield: 86%. Mp: melts with gas evolution at 161–162 °C. Calcd for C₂₈H₄₄NAl: C, 79.76; H, 10.52; N, 3.32. Found: C, 80.08; H, 10.96; N, 3.19. ¹H NMR (C₆D₆): 7.51 (s, *m*-H (10), 2H), 7.31 (s, *m*-H (9), 4H), 7.19 (s, *m*-H (10), 2H), 6.63 (s, *m*-H(Mes), 4H), 6.61 (s, *m*-H(Mes), 4H), 4.95 (s, broad, Al-H, 2H), 4.73 (s, broad, Al-H, 2H), 4.46 (d, N-CH₂ (9), 4H), ³J_{HH} = 6.6 Hz, 4.12 (dd, N-CH₂ (10), 2H), ²J_{HH} = 12.9 Hz, ³J_{HH} = 10.5 Hz, 3.77 (d, N-CH₂ (9), 2H), 2.23 (s, *o*-CH₃(Mes), 12H), 2.14 (s, *o*- and *p*-CH₃(Mes), 18H), 2.10 (s, *p*-CH₃(Mes), 6H), 1.77 (s, *o*-C(CH₃)₃ (10), 18H), 1.43 (s, C(CH₃)₃, 18H), 1.36 (s, C(CH₃)₃, 18H), 1.35 (s, C(CH₃)₃, 18H), 1.28 (s, *o*-C(CH₃)₃ (9), 36H). IR: 2297 cm⁻¹ (w, $\nu_{\text{N-H}}$), 1841 cm⁻¹ (st, $\nu_{\text{Al-H}}$).

Mes*Al{N(H)SiPh₃}₂ (11). A solution of H₂NSiPh₃ (0.41 g, 1.5 mmol) in ethylbenzene (20 mL) was added dropwise to a solution of (Mes*AlH₂)₂ (0.41 g, 0.75 mmol) in ethylbenzene (20 mL) at room temperature, which resulted in vigorous gas evolution, which stopped a few minutes after the addition was complete. After 2 h at room temperature the clear colorless solution was placed in a preheated oil bath at 125–130 °C and maintained at that temperature for 4 h. After cooling to room temperature, a small amount of colorless solid was removed and the solution was cooled to -20 °C for 4 days. As no crystals were obtained, all volatile materials were removed under reduced pressure and the resulting glass was recrystallized in a -20 °C freezer from *n*-hexane (ca. 2 mL) to afford 0.21 g of a colorless, microcrystalline solid in spherical aggregates. Yield: 34% (based on H₂NSiPh₃). ¹H NMR (C₆D₆): 7.58 (m, SiPh, 12H), 7.35 (s, *m*-H(Mes*), 2H), 7.12 (m, SiPh, 18H), 1.44 (s, *o*-C(CH₃)₃, 18H), 1.32 (s, *p*-C(CH₃)₃, 9H), 0.75 (s, N-H, 2H). ¹³C{¹H} NMR (C₆D₆): 158.2 (*o*-C(Mes*)), 150.5 (*p*-C(Mes*)), 138.4 (*i*-C), 135.9, 129.4, 127.9 (tertiary carbons, SiPh₃), 121.3 (*m*-C(Mes*)), 37.8 (*o*-C(CH₃)₃), 34.8 (*p*-C(CH₃)₃), 33.3

Table 1. Crystallographic Data for 4-toluene, 5-3benzene, 7, and 12

| | 4-toluene | 5-3benzene | 7 | 12 |
|-----------------------------------------------------------------------|---------------------------------------------------------------------|----------------------------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| formula | C ₆₃ H ₉₂ - Al ₂ N ₂ | C ₇₉ H ₁₀₂ - Al ₂ N ₂ | C ₄₆ H ₈₀ - Al ₂ N ₂ | C ₇₂ H ₈₈ - Al ₂ N ₂ Si ₂ |
| fw | 931.35 | 1073.54 | 715.08 | 1091.58 |
| space group | P1 | P1 | P2 ₁ /c | P1 |
| <i>a</i> , Å | 11.896(4) | 10.927(2) | 11.317(2) | 10.110(2) |
| <i>b</i> , Å | 14.315(4) | 11.160(1) | 9.668(2) | 11.988(3) |
| <i>c</i> , Å | 18.354(4) | 14.231(2) | 20.651(4) | 13.937(3) |
| α , Å | 78.53(2) | 89.228(8) | | 108.61(2) |
| β , Å | 71.60(2) | 89.546(10) | 90.17(2) | 95.16(2) |
| γ , Å | 84.69(2) | 72.469(9) | | 104.36(2) |
| <i>V</i> , Å ³ | 2905.2(14) | 1654.6(3) | 2259.4(7) | 1524.3(6) |
| <i>Z</i> | 2 | 1 | 2 | 1 |
| <i>T</i> , K | 130 | 130 | 130 | 123 |
| λ , Å | 1.541 78 | 1.541 78 | 1.541 78 | 1.541 78 |
| <i>d</i> _{calc} , g cm ⁻³ | 1.065 | 1.077 | 1.051 | 1.189 |
| μ , mm ⁻¹ | 0.724 | 0.695 | 0.794 | 1.132 |
| <i>R</i> 1 (for <i>I</i> > 2 σ (<i>I</i>) data) ^a | 0.071 | 0.042 | 0.0559 | 0.0606 |
| wR2 ^a | 0.144 | 0.102 | 0.1566 | 0.1645 |

$$^a R1 = \sum ||F_o - F_c|/|\sum F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}.$$

(*o*-C(CH₃)₃), 31.5 (*p*-C(CH₃)₃). IR: ν_{NH} = 3350 (w), 3297 (w), rel intensity \approx 1:2.

(Mes*AlNSiPh₃)₂ (12). The synthesis was identical to that of 11 except that the reaction mixture was heated to 135 °C for 17.5 h. Concentration to ca. 15 mL followed by dissolution of microcrystalline solid at reflux temperature and slow cooling to room temperature afforded 0.12 g of 12 as colorless crystals of sufficient quality for X-ray crystallography. Yield: 15%. Mp: >300 °C. ¹H NMR (C₆D₆, 80 °C): 7.57 (dd, SiPh, 12H), *J*_{HH} = 8.1 Hz, *J*_{HH} = 1.5 Hz, 7.41 (s, *m*-H(Mes*), 4H), 6.97 (m, SiPh, 18H), 1.56 (s, *o*-C(CH₃)₃, 36H), 1.35 (s, *p*-C(CH₃)₃, 18H). The low solubility of 12 did not allow the recording of a ¹³C NMR spectrum. Removal of the solvent from the mother liquor and recrystallization of the sticky residue from *n*-pentane (5 mL, -20 °C) for 1 week afforded 0.25 g of 11.

X-ray Crystallographic Studies. X-ray quality crystals of 4-PhMe, 5-3C₆H₆, 7, or 12 were removed from the Schlenk tube and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in a low-temperature N₂ stream as previously described.⁹ All data were collected at 130 K on a Syntex P2₁ or Siemens P4/RA diffractometer equipped with a low-temperature device and a graphite (Syntex P2₁) or nickel foil (Siemens P4/RA) monochromator. Calculations were carried out with SHELXTL-PLUS programs.^{10a} Scattering factors and the correction for anomalous scattering were taken from common sources.^{10b} The structures were solved by direct methods and refined by full-matrix least squares refinement. An absorption correction was applied by using the program XABS2.¹¹ Crystal data for 4, 5, 7, and 12 are given in Table 1. Selected bond distances and angles are provided in Table 2.

Discussion

The reaction between (Mes*AlH₂)₂ and *t*-BuCN in pentane at room temperature affords in the first instance the dimeric species [Mes*Al(H){ μ^2 -N=C(H)-*t*-Bu}]₂ (1). Unfortunately, crystals of 1 have not yet been obtained that have proven suitable for X-ray crystallography. The ¹H and ¹³C{¹H} NMR spectra

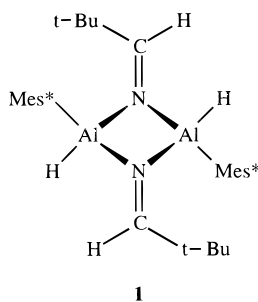
- (9) This method is described by Hope: Hope, H. A Practicum in Synthesis and Characterization. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.
- (10) (a) SHELXTL, A Program for Crystal Structure Determinations, version 5.03; Siemens Analytical Instruments: Madison, WI, 1994. (b) International Tables for X-ray Crystallography, D. Reidel Publishing Co.; Dordrecht, The Netherlands, 1993; Vol. C.
- (11) Parkin, S. R.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

Table 2. Selected Bond Distances (Å) Angles (deg) for **4**, **5**, **7**, and **12**

| | 4 , cis isomer | | 5 , trans isomer |
|--------------------------|-----------------------|----------|-------------------------|
| Al–N | 1.941(4) | 1.945(4) | 1.950(2) |
| | 1.970(4) | 1.969(4) | 1.963(2) |
| Al–C(Ar) | 1.970(4) | 1.959(4) | 1.971(2) |
| Al–C(CH ₃) | 1.950(5) | 1.952(5) | 1.954(2) |
| N–C | 1.509(6) | 1.512(6) | 1.511(2) |
| Al–Al | 2.763(2) | | 2.8172(11) |
| N–Al–N | 85.7(2) | 85.6(2) | 87.92(7) |
| Al–N–Al | 89.8(2) | 89.9(2) | 93.2(4) |
| N–Al–C(Ar) | 137.0(2) | 138.8(2) | 131.52(7) |
| | 115.4(2) | 114.4(2) | 117.69(7) |
| N–Al–C(CH ₃) | 112.9(2) | 112.5(2) | 112.26(8) |
| | 111.2(2) | 112.2(2) | 116.31(9) |
| C–Al–C | 95.1(2) | 95.5(2) | 93.18(8) |

| | 7 | | 12 |
|-------------------|-----------|-------------------|-----------|
| Al(1)–N(1) | 1.796(2) | Al(1)–N(1) | 1.842(2) |
| Al(1)–C(1) | 1.986(2) | Al(1)–N(1A) | 1.841(2) |
| Al(1)–C(19) | 1.988(2) | N(1)–Si(1) | 1.705(2) |
| N(1)–C(19A) | 1.472(3) | Al(1)–C(1) | 1.975(3) |
| N(1)–C(20) | 1.490(3) | Al(1)–Al(1A) | 2.528(2) |
| N(1)–Al(1)–C(1) | 127.26(9) | N(1)–Al(1)–N(1A) | 93.3(1) |
| N(1)–Al(1)–C(19) | 119.7(1) | Al(1)–N(1)–Al(1A) | 86.7(1) |
| C(1)–Al(1)–C(19) | 113.0(1) | C(1)–Al(1)–N(1) | 133.3(1) |
| Al(1)–N(1)–C(19A) | 110.9(1) | C(1)–Al(1)–N(1A) | 133.5(1) |
| Al(1)–N(1)–C(20) | 132.6(1) | Si(1)–N(1)–Al(1) | 135.7(1) |
| C(19A)–N(1)–C(20) | 114.5(2) | Si(1)–N(1)–Al(1A) | 136.4(1) |
| C(2)–C(1)–C(6) | 117.0(2) | | |

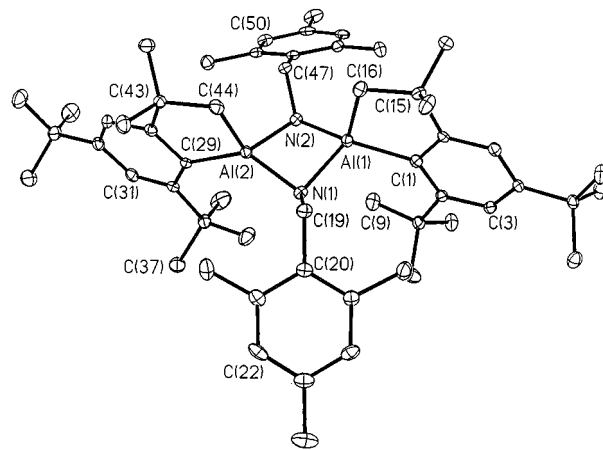
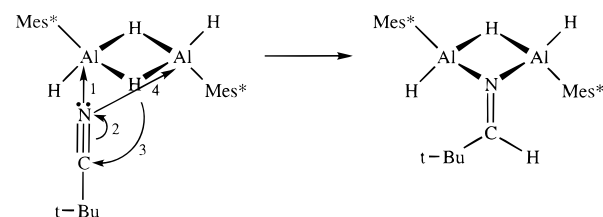
of **1** display two sets of signals for the ortho *t*-Bu groups, meta hydrogens, and the ortho and meta carbons indicating hindered rotation around the Al–C bonds. The ¹H and ¹³C NMR chemical shifts of the imide hydrogen and carbon (N=CH; 8.52 and 190.6 ppm) are in the expected region. In addition, the IR spectrum displays a strong Al–H stretching absorption at 1828 cm^{−1} and a strong N=C stretch at 1642 cm^{−1}. The most likely structure of **1** is probably a dimer featuring bridging iminato groups and terminal hydrogens as given by



This proposal is consistent with the spectroscopic data, and addition of the hydrogen to the nitrilic carbon is consistent with X-ray data on related systems such as **4** and **5** (see below) and the structure of the complex [(*i*-Bu)₂Al{μ²-N=C(H)(C₆H₃-2,6-Me₂)}₂]₂⁶ featuring bridging iminato groups.

The exact mechanism of the reduction of nitriles to imines by aluminum hydrides is unknown. However, it is probable that the first step involves coordination of nitrile nitrogen to an aluminum center whereupon the electron density removed from nitrogen induces a corresponding drift of electrons toward nitrogen from the nitrilic carbon, which is then attacked by a bridging hydrogen to generate an intermediate in which the aluminums are bridged by hydrogen and an iminato group as shown in Scheme 2.

Heating of **1** at ca. 80 °C for 40 h leads to the activation of an ortho *t*-Bu group on each Mes* ring to afford the products

**Figure 1.** Thermal ellipsoid plot (30%) of **4** with hydrogen atoms omitted for clarity.**Scheme 2.** Possible Initial Sequence for the Interaction of (Mes*AlH₂)₂ with *t*-BuC≡N

2 and **3** as depicted in Scheme 1. This also results in the addition of two hydrogens to each bridging iminato group to afford primary amido ligands N(H)CH₂(*t*-Bu) which bridge the aluminums. It is possible that this reaction occurs via an aluminum iminato intermediate of formula {Mes*AlNCH₂(*t*-Bu)}_n which, under the reaction conditions, proceeds further to give the aluminum amide complexes **2** and **3**.

The reaction of (Mes*AlH₂)₂ with 2 equiv of MesCN in refluxing hexane yields the ortho-metallated species **4** and **5** in moderate yield. Monitoring of the reaction by ¹H NMR shows that signals at 8.9 and 9.3 ppm are detectable after mixing of the reactants. These signals may be assigned to the N=C(H)-Mes moiety of the iminato complex (analogous to **1**) which is initially produced, but which could not be isolated. Reaction of (Mes*AlH₂)₂ with 4 equiv of MesCN at room temperature in an attempt to synthesize the bisiminato complex Mes*Al{N=C(H)Mes}₂ led only to **4** and **5** and unreacted MesCN. Apparently, ortho metalation is preferred to reaction with more than 1 equiv of MesCN by each aluminum center. The structures of **4** and **5** are depicted in Figures 1 and 2. The cis isomer **4** has no crystallographically imposed symmetry restrictions, and it can be seen that both the nitrogen CH₂Mes substituents and the ortho-metallated “*t*-Bu” groups are mutually cis to each other. In the trans isomer **5** there is an inversion center in the center of the Al₂N₂ ring. The data in Table 2 show that the structural parameters for **4** and **5** differ only slightly. Moreover, the bond distances are quite close to those previously observed for bonding involving aluminum amide dimers.¹² Apart from their different isomeric forms, the most obvious structural difference between the two compounds is the fact that the Al₂N₂ core in **4** is folded whereas in **5** it is strictly planar. This bending results

(12) (a) Hess, A.; Hinderer, A.; Steinhäuser, S. Z. *Anorg. Allg. Chem.* **1970**, 377, 1. (b) Gosling, K.; McLaughlin, G. M.; Sim, G. A.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2719. (c) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Swastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood-Wiley: Chichester, 1979.

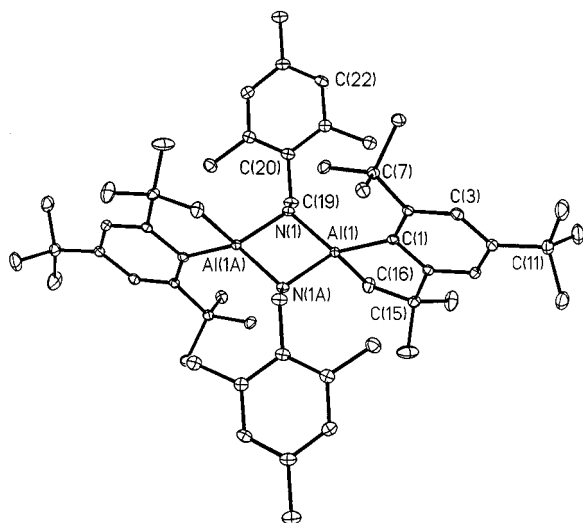


Figure 2. Thermal ellipsoid plot (30%) of **5** with hydrogen atoms omitted for clarity.

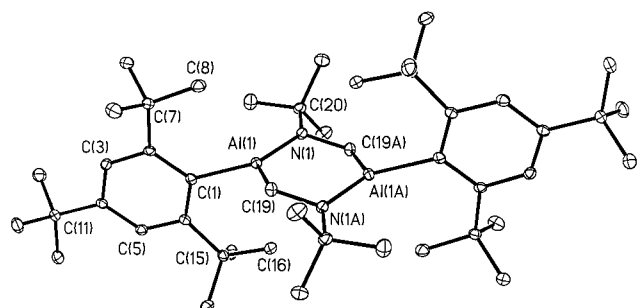


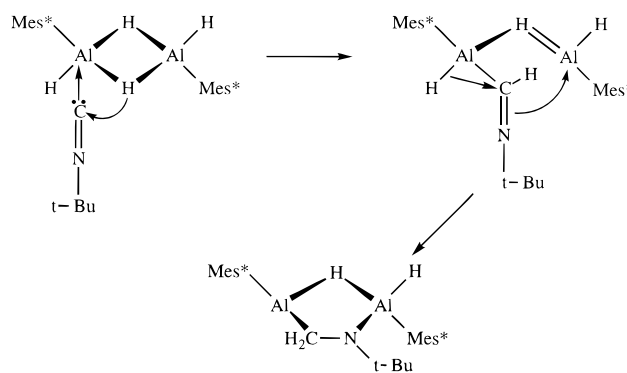
Figure 3. Thermal ellipsoid plot (30%) of **7** with hydrogen atoms omitted for clarity.

in a slightly closer approach of the aluminums in **4**. The Al–N distances in the cores are essentially equivalent with an average value near 1.96 Å.

Treatment of $(\text{Mes}^*\text{AlH}_2)_2$ with 2 equiv of acetonitrile and refluxing in hexane solution results in the compound **6**. Monitoring of this reaction by ^1H NMR showed that ortho metalation had already begun after ca. 15 min at room temperature. Refluxing in hexane completed this process in a few hours. The dimeric **6** was the only isolable product from the reaction. Strong positive NOE interactions of the Al–CH₂ and N–CH₂ moieties suggest that **6** exists in the cis form with a structure similar to that of **4**.

The addition of the isonitrile *t*-BuNC to $(\text{Mes}^*\text{AlH}_2)_2$ resulted in a vigorous reaction to afford **7** in good yield. In fact, care has to be taken so that the reaction temperature does not exceed ca. 10 °C since ortho-metalated side products are rapidly produced above this temperature. Refluxing **7** in hexane leads to the ortho-metalated product **8**, which can be isolated in low yield as a colorless microcrystalline solid. ^1H and ^{13}C NMR studies indicate that it exists in the all-trans isomer as shown in Scheme 1. The structure of **7** is illustrated in Figure 3. It may be noted that it is an isomer of **1**. Consistent with the spectroscopic data, two hydrogens have been added to the carbon of the isonitrile to afford units of formula $\text{Mes}^*\text{AlN}(t\text{-Bu})\text{CH}_2$ which are dimerized in the solid. The mechanism whereby this process occurs is currently unknown, but it probably involves initial coordination of isonitrile carbon to aluminum (or its insertion into an Al–(μ-H) bond) followed by hydrogen transfer and rearrangement as proposed in Scheme 3.

Scheme 3. Possible Initial Sequence for the Interaction of $(\text{Mes}^*\text{AlH}_2)_2$ with *t*-BuN=C



Molecules of **7** are characterized by a crystallographically required center of symmetry in the middle of the six-membered (AlCN)₂ ring. The ring has a chairlike structure with a planar N(1) C(19) N(1A) C(19A) array. The aluminums are ca. 0.4 Å above or below this plane such that there is a 25.1° angle between the plane defined by C(1) C(19) Al(1) N(1) and the averaged N(1) C(19) N(1A) C(19A) plane. The Mes* ring plane subtends an angle of 86.4° with respect to the averaged coordination plane at aluminum. The aluminum has almost trigonal planar coordination, $\Sigma^\circ\text{Al}(1) = 358.1(1)^\circ$, and the N(1) coordination geometry also shows a slight deviation from planarity, $\Sigma^\circ\text{N}(1) = 357.99(16)^\circ$, with N(1) ca. 0.12 Å out of the Al(1) C(20) C(19A) plane. The ring may be regarded as a formal analogue of 1,4-cyclohexadiene if π -delocalization of the nitrogen lone pair onto aluminum is assumed. Indeed, the “short” Al–N bond length of 1.796(2) Å is consistent with this view. Nonetheless, the preponderance of theoretical and experimental data show that the shortening in Al–N bonds of this type is mostly due to the low aluminum coordination number and ionic factors rather than delocalization.¹³ Refluxing **7** in benzene for 1 h results in the ortho-metalated product **8**. Unfortunately, no single crystals large enough for X-ray crystallography could be obtained. ^1H NMR spectroscopy indicates that **8** probably has an all-trans structure owing to the AMX pattern for the Al–CH₂–N–H moiety and an AB pattern seen for the Al–CH₂–C(Me)₂ hydrogens. The IR spectrum displays an N–H absorption at 3225 cm^{−1}.

Isolation of the amide products **2–6** and **8** led to the investigation of the direct reaction of some primary amines with $(\text{Mes}^*\text{AlH}_2)_2$. Thus, the treatment of $(\text{Mes}^*\text{AlH}_2)_2$ with 2 equiv of H₂NCH₂Mes led to the dimeric primary amide $[\text{Mes}^*\text{Al}(\text{H})\{\mu^2\text{-N}(\text{H})\text{CH}_2\text{Mes}\}]_2$ as a 50:50 mixture of cis (**9**) and trans (**10**) isomers. Heating of this mixture of **9** and **10** to 150–200 °C for 30 min does not lead to the iminato complex $\{\text{Mes}^*\text{Al}(\mu^2\text{-NCH}_2\text{Mes})\}_n$ but to a 50:50 mixture of the ortho-metalated derivatives **4** and **5**. This transformation can also be effected in solution, but it requires ca. 3 days to complete at a temperature of ca. 70 °C. Reaction of $(\text{Mes}^*\text{AlH}_2)_2$ with H₂NSiPh₃ at room temperature affords a mixture of the bisamide $\text{Mes}^*\text{Al}\{\text{N}(\text{H})\text{-SiPh}_3\}_2$ (**11**) and amide/hydride $[\text{Mes}^*(\text{H})\text{Al}\{\text{N}(\text{H})\text{SiPh}_3\}]_2$ as well as some unreacted $(\text{Mes}^*\text{AlH}_2)_2$. This result is very similar to that obtained in the corresponding reaction of $(\text{Mes}^*\text{AlH}_2)_2$ with H₂NPh, which affords the analogous bisamide $\text{Mes}^*\text{Al}\{\text{N}(\text{H})\text{Ph}\}_2$, whose structure has been determined.² At higher temperatures (ca. 125–130 °C), H₂ is eliminated from the

(13) (a) Brothers, P. J.; Power, P. P. *Adv. Organomet. Chem.* **1996**, 39, 1. (b) Knabel, K.; Krossing, I.; Nöth, H.; Schwenk-Kircher, H.; Schmidt-Amelunxen, M.; Seifert, T. *Eur. J. Inorg. Chem.* **1998**, 1095.

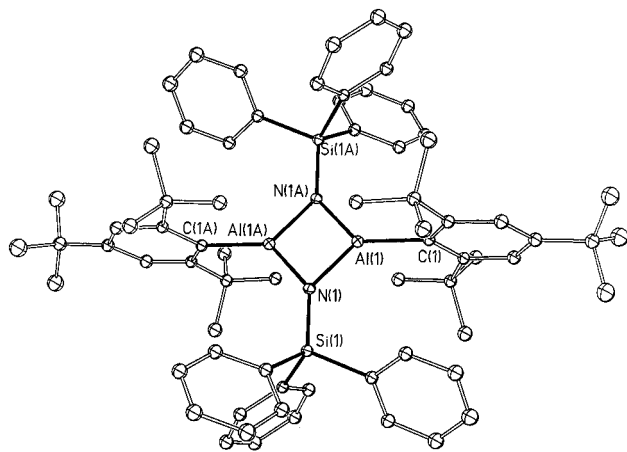


Figure 4. Thermal ellipsoid plot (30%) of **12** with hydrogen atoms omitted for clarity.

monoamide coproduct $[\text{Mes}^*(\text{H})\text{Al}\{\text{N}(\text{H})\text{SiPh}_3\}]_2$ and the dimeric imide $(\text{Mes}^*\text{AlNSiPh}_3)_2$ **12** is obtained. This compound has the centrosymmetric, dimeric structure depicted in Figure 4, which is similar to that obtained for $(\text{Mes}^*\text{AlNPh})_2$.

The planar Al_2N_2 core has essentially equal Al–N distances (cf. Table 2) with a slightly wider internal ring angle at aluminum ($93.27(1)^\circ$) than at nitrogen ($86.73(10)^\circ$). The coordination at aluminum is planar, but the nitrogen geometry is slightly pyramidal, $\Sigma^\circ\text{N} = 358.83(13)^\circ$. The Al–Al separation is only $2.528(2)$ Å, which is shorter than that in many compounds known to have aluminum–aluminum bonds.¹⁴ The plane of the Mes^* ring is oriented almost perpendicular to the Al_2N_2 core. Compound **12** is the newest member of a very small group of dimeric imidoalanes. Known examples include $\text{Cp}^*\text{-}\{(\text{Me}_3\text{Si})_2\text{N}\}\text{AlN}(\mu^2\text{-AlCp}^*)(\mu^2\text{-}\{\text{Al}\{\text{N}(\text{SiMe}_3)_2\}\})\text{AlCp}^*$,¹⁵ $\text{Cp}^*\text{-AlNC}_6\text{H}_3\text{-2,6-i-Pr}_2$,¹⁶ ($\text{Cp}^* = \text{C}_5\text{Me}_5$), and the previously mentioned $(\text{Mes}^*\text{AlNPh})_2$ species. The Al–N and Al–C

distances in **12** are marginally (ca. 0.015 Å) longer than those observed in $(\text{Mes}^*\text{AlNPh})_2$. In addition, the internal ring angle at aluminum in **12** is 4.5° wider than it is in $(\text{Mes}^*\text{AlNPh})_2$, whereas the internal angle at nitrogen is a corresponding amount narrower. It is probable that these structural differences are due to the increased size of the nitrogen substituent.

Conclusion. The reaction of $(\text{Mes}^*\text{AlH}_2)_2$ with nitriles or an isonitrile results in hydrogen addition to the unsaturated carbon. The reaction appears to proceed in a stepwise manner with addition of the first hydrogen producing an iminato species as an intermediate. A second hydrogen addition to carbon readily takes place in the reaction with the isonitrile *t*-BuNC to generate the compound **7**. However, with nitriles the addition of the second hydrogen to carbon proceeds only at elevated temperatures, which also results in ortho metalation to give the amide products **2–6**. These species are also accessible through the direct reaction of $(\text{Mes}^*\text{AlH}_2)_2$ with the appropriate amines. However, direct reaction of $(\text{Mes}^*\text{AlH}_2)_2$ with H_2NSiPh_3 or (as previously reported) H_2NPh results in the diamides $\text{Mes}^*\text{Al}\{\text{N}(\text{H})\text{R}\}_2$ ($\text{R} = \text{Ph}$ or SiPh_3) and the monoamides $\{\text{Mes}^*(\text{H})\text{-AlN}(\text{H})\text{R}\}_2$, which upon further heating afford the dimeric imides $(\text{Mes}^*\text{AlNR})_2$ with no ortho metalation. The different susceptibility to ortho metalation of the compounds at high temperature is probably connected to the different types of precursors (i.e., a bisamide species such as **11** versus an iminato species such as **1**) involved although a more detailed explanation is not possible at present.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supporting Information Available: Tables giving full data collection parameters and further details of refinement, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, hydrogen coordinates, and isotropic thermal parameters (44 pages). Ordering information is given on any current masthead page.

IC9810992

- (14) (a) Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386. (b) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 124. (c) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939.
- (15) Schultz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969.

- (16) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 271.