

Reactions of  $\text{AlH}_3 \cdot \text{NMe}_3$  with Nitriles: Structural Characterization and Substitution Reactions of Hexameric Aluminum Imides<sup>†</sup>

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The reaction of  $\text{AlH}_3 \cdot \text{NMe}_3$  with RCN proceeds with the evolution of trimethylamine and affords  $(\text{HAINCH}_2\text{R})_6$  ( $\text{R} = \text{Ph}$  (**1**),  $p\text{-MeC}_6\text{H}_4$  (**2**),  $p\text{-CF}_3\text{C}_6\text{H}_4$  (**3**)). Compounds **1** and **3** are characterized by single-crystal structural analysis. Compound **1** reacts with  $\text{Me}_3\text{SiBr}$  as well as with  $\text{PhC}\equiv\text{CH}$  to give  $(\text{XAINCH}_2\text{Ph})_6$  ( $\text{X} = \text{Br}$  (**4**),  $\text{PhC}\equiv\text{C}$  (**5**)). Structural data and other characterization data of compounds **4** and **5** show that all the hydridic hydrogen atoms in **1** have been replaced by bromine atoms and  $\text{PhC}\equiv\text{C}$  groups, respectively. Compounds **1**–**5** are potential precursors for the preparation of aluminum nitride. Crystals of **1** are rhombohedral, space group  $R\bar{3}$ , with  $a = 15.7457(13)$  Å,  $b = 15.7457(13)$  Å,  $c = 14.949(2)$  Å,  $V = 3209.8(5)$  Å<sup>3</sup>, and  $Z = 3$ . Crystals of  $3 \cdot 3/4\text{C}_7\text{H}_8$  are triclinic, space group  $P\bar{1}$ , with  $a = 17.527(11)$  Å,  $b = 18.894(12)$  Å,  $c = 19.246(15)$  Å,  $\alpha = 96.11(7)^\circ$ ,  $\beta = 102.23(4)^\circ$ ,  $\gamma = 106.79(3)^\circ$ ,  $V = 5867(7)$  Å<sup>3</sup>, and  $Z = 4$ . Compound **4** crystallizes in the monoclinic space group  $P2_1/c$ , with  $a = 14.175(4)$  Å,  $b = 16.678(5)$  Å,  $c = 10.731(3)$  Å,  $\beta = 106.82(2)^\circ$ ,  $V = 2428.6(11)$  Å<sup>3</sup>, and  $Z = 2$ . Compound  $5 \cdot \text{C}_7\text{H}_8$  crystallizes in the monoclinic space group  $C2/c$ , with  $a = 25.842(5)$  Å,  $b = 15.443(3)$  Å,  $c = 20.699(4)$  Å,  $\beta = 105.88(3)^\circ$ ,  $V = 7945(3)$  Å<sup>3</sup>, and  $Z = 4$ .

## Introduction

Aluminum imides and amides, containing the  $(\text{AlN})_n$  skeleton, are potential precursors for the chemical vapor deposition of aluminum nitride.<sup>1</sup> The physical and chemical properties of aluminum nitride strongly depend on its purity. Aluminum nitride is one of the best electrical insulators for microelectronic applications.<sup>2</sup> In addition to the utility in industry the complex structural features of the Al–N systems make them an interesting class of compounds from an academic point of view.<sup>3</sup> The reaction of methylamine and alane dates back to 1955.<sup>4</sup> An Al–N polymer, insoluble in

organic solvents and containing an equivalent of hydridic hydrogen per Al atom, was reported but not characterized. Reactions of alanes and alanates with various amines leading to aluminum imides and amides have been well-documented.<sup>3,5</sup> There have been reports on the formation of aluminum imides from reactions 1–3<sup>4,5c,6</sup> (Scheme 1). A few crystal structures of aluminum imides ( $n = 4, 6, \text{ or } 8$ )

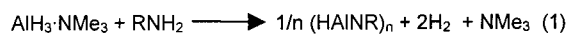
<sup>†</sup> Dedicated to Professor Karl Wieghardt on the occasion of his 60th birthday.

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- (1) (a) Haussonne, J.-M. *Mater. Manuf. Processes* **1995**, *10*, 717. (b) Interrante, L. V. *Gov. Rep. Announce. Index (U. S.)* **1995**, *95*, Abstr. No. 508,364 (CAS: **1996**, *124*, 41572). (c) Interrante, L. V. *Gov. Rep. Announce. Index (U. S.)* **1993**, *93*, Abstr. No. 350,504 (CAS: **1994**, *121*, 89550). (d) Jensen, J. L. U.S. Pat., US 5,276,105.
- (2) (a) Boyd, D. C.; Haasch, R. T.; Mantell, P. R.; Schulze, R. K.; Evans, J. F.; Gladfelder, W. L. *Chem. Mater.* **1989**, *1*, 119. (b) Bolt, J. D.; Tebbe, F. N. *Adv. Ceram.* **1989**, *26*, 69. (c) Bertalet, D. C.; Liu, H.; Rogers, J. W. *J. Appl. Phys.* **1994**, *75*, 5385. (d) Jones, A. C. *J. Cryst. Growth* **1993**, *129*, 728. (e) Rockensüss, W.; Roesky, H. W. *Adv. Mater.* **1993**, *5*, 443.

- (3) (a) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem.* **1988**, *100*, 1765; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699. (b) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385. (c) Cesari, M.; Cucinella, S. *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol I, p 167. (d) Gilbert, J. K.; Smith, J. D. *J. Chem. Soc.* **1968**, 233. (e) Al-Wassil, A.-A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc., Dalton. Trans.* **1985**, 1929, and references therein. (f) Ruff, J. K.; Hawthorne, F. J. *Am. Chem. Soc.* **1960**, *82*, 2141. (g) Wiberg, E.; May, A. *Z. Naturforsch. B* **1955**, *10*, 230.
- (4) Wiberg, E.; May, A. *Z. Naturforsch. B* **1955**, *10*, 232.
- (5) (a) Wehmschulte, R. J.; Power, P. P. *Polyhedron* **2000**, *19*, 1649, and references therein. (b) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791. (c) Ehrlich, R.; Young, A. R., II; Lichstein, B. M.; Perry, D. D. *Inorg. Chem.* **1964**, *3*, 628. (d) Montero, M. L.; Wessel, H.; Roesky, H. W.; Teichert, M.; Usón, I. *Angew. Chem.* **1997**, *109*, 644; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 629. (e) Linti, G.; Nöth, H.; Rahm, P. *Z. Naturforsch. B* **1988**, *43*, 53. (f) Heine, A.; Stalke, D. *Angew. Chem.* **1992**, *104*, 941; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854.
- (6) Cucinella, S.; Salvatori, T.; Busetto, C.; Cesari, M. *J. Organomet. Chem.* **1976**, *121*, 137, and references therein.

## Scheme 1



obtained from reactions 1 and 2 have also been reported. The influence of the nature of the amine on the structure and extent of oligomerization of these imides has also been established. Even though the reactions of trialkylamine alanes with acetonitrile and propionitrile have been reported almost 4 decades ago, to the best of our knowledge so far there is no structural evidence for the formation of aluminum imides from reaction 3. Power et al. have reported that the reaction of a bulky alane  $[\text{Mes}^* \text{AlH}_2]_2$  ( $\text{Mes}^* = 2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$ ) with nitriles  $\text{RCN}$  ( $\text{R} = \text{Me}, t\text{-Bu}, \text{Mes}$ ) gives the *ortho*-metalated dimers, *cis*- and *trans*- $[\text{AlC}_6\text{H}_2\text{-}2,4\text{-}t\text{-Bu}_2\text{-}6\text{-CMe}_2\text{-CH}_2\{\mu^2\text{-N(H)CH}_2\text{R}\}]_2$ . However, the formation of an aluminum imide  $[\text{Mes}^* \text{AlNCH}_2\text{R}]_n$  was not observed.<sup>7</sup> Recent studies by our group on the reaction of  $\text{AlH}_3 \cdot \text{NMe}_3$  with C–C and C–N multiple bond systems have resulted in structurally interesting, highly stable polyhedral aluminum clusters.<sup>8</sup>

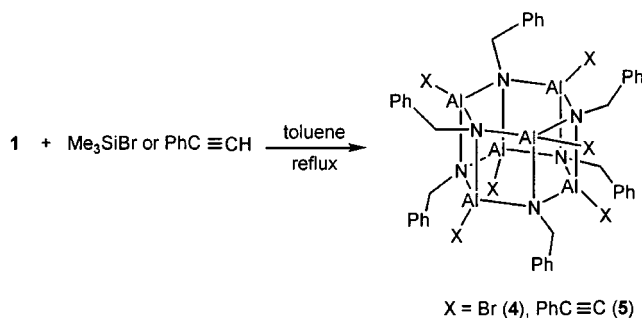
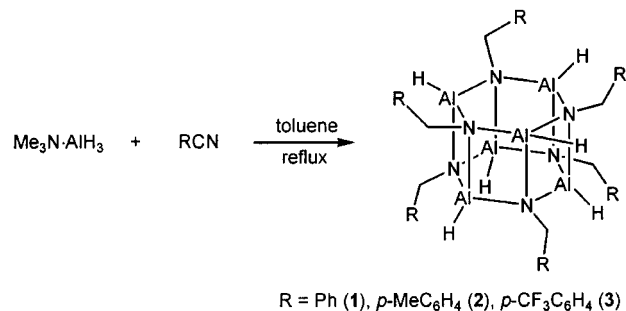
In this contribution, we report the synthesis and structural characterization of reaction products from the treatment of  $\text{AlH}_3 \cdot \text{NMe}_3$  with  $\text{PhCN}$ ,  $p\text{-MeC}_6\text{H}_4\text{CN}$ , and  $p\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$ . We also report for the first time on the functionalization reactions of one of the products,  $(\text{HAINCH}_2\text{Ph})_6$ , with  $\text{Me}_3\text{-SiBr}$  and  $\text{PhC}\equiv\text{CH}$ . These reactions are summarized in Scheme 2.

## Experimental Section

**General Procedures.** All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a drybox. Solvents were purified according to conventional procedures and were freshly distilled prior to use.  $\text{AlH}_3 \cdot \text{NMe}_3$  was prepared as described in the literature.<sup>9</sup>  $\text{PhCN}$  (Aldrich) was distilled over  $\text{P}_4\text{O}_{10}$ .  $p\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$ ,  $p\text{-MeC}_6\text{H}_4\text{CN}$ ,  $\text{Me}_3\text{SiBr}$ , and  $\text{PhC}\equiv\text{CH}$  were procured from Aldrich and used as such. NMR spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument, and the chemical shifts are reported with reference to tetramethylsilane (TMS). IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer. Melting points were obtained on a HWS-SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen, Germany.

**Reaction of  $\text{AlH}_3 \cdot \text{NMe}_3$  with  $\text{PhCN}$  (Synthesis of 1).**  $\text{AlH}_3 \cdot \text{NMe}_3$  (30 mL, 0.5 M solution in toluene) was added to a solution of  $\text{PhCN}$  (1.00 g, 9.7 mmol) in toluene (15 mL) at  $-78^\circ\text{C}$ . The mixture was stirred at this temperature for an hour and brought to

## Scheme 2



room temperature before it was refluxed until the evolution of  $\text{NMe}_3$  ceased. Reducing the volume to 10 mL and cooling to  $0^\circ\text{C}$  afforded colorless crystals of **1**. These were separated from the mother liquor by decantation and dried well under vacuum. Yield 0.60 g (46%). Mp:  $245^\circ\text{C}$  (decomp). NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ ,  $\delta$  4.20 (s, 12H,  $\text{CH}_2$ ), 7.14 (m, 30H,  $\text{C}_6\text{H}_5$ );  $^{13}\text{C}$ ,  $\delta$  49.49 ( $\text{CH}_2$ ), 126.96 ( $p\text{-C}_6\text{H}_5$ ), 127.52 ( $m\text{-C}_6\text{H}_5$ ), 128.81 ( $o\text{-C}_6\text{H}_5$ ), 142.40 ( $\text{CH}_2\text{-C}$ ). IR: 1855s, 1494m, 1310w, 1201w, 1031m, 1009s, 903w, 819m, 748s, 730s, 663s, 524m, 481m,  $436\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{48}\text{Al}_6\text{N}_6$ : C, 63.15; H, 6.06; Al, 20.27; N, 10.52. Found: C, 62.77; H, 5.99; Al, 19.12; N, 10.41.

**Reaction of  $\text{AlH}_3 \cdot \text{NMe}_3$  with  $p\text{-MeC}_6\text{H}_4\text{CN}$  (Synthesis of 2).** The reaction between  $\text{AlH}_3 \cdot \text{NMe}_3$  (25 mL, 0.5 M solution in toluene) and  $p\text{-MeC}_6\text{H}_4\text{CN}$  (1.00 g, 8.5 mmol) was carried out in the same way as the reaction between  $\text{AlH}_3 \cdot \text{NMe}_3$  and  $\text{PhCN}$ . Yield: 0.82 g (65%). Mp:  $233^\circ\text{C}$  (decomp). NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ ,  $\delta$  2.39 (s, 18H,  $\text{CH}_3$ ), 4.15 (s, 12H,  $\text{CH}_2$ ), 6.89 (m, 12H,  $m\text{-C}_6\text{H}_4$ ), 7.23 (m, 12H,  $o\text{-C}_6\text{H}_4$ ).  $^{13}\text{C}$ ,  $\delta$  21.23 ( $\text{CH}_3$ ), 49.10 ( $\text{CH}_2$ ), 125.30 ( $p\text{-C}_6\text{H}_4$ ), 127.53 ( $m\text{-C}_6\text{H}_4$ ), 129.42 ( $o\text{-C}_6\text{H}_4$ ), 139.60 ( $\text{CH}_2\text{-C}$ ). IR: 1887w, 1855s, 1515w, 1316w, 1261w, 1202w, 1183w, 1004m, 985m, 935w, 842w, 808m, 758s, 730s, 672s, 505m,  $470\text{cm}^{-1}$ . Anal. Calcd for  $(2 \cdot \text{C}_7\text{H}_8)$   $\text{C}_{55}\text{H}_{68}\text{Al}_6\text{N}_6$ : C, 67.75; H, 7.03; N, 8.62. Found: C, 67.40; H, 6.37; N, 8.58.

**Reaction of  $\text{AlH}_3 \cdot \text{NMe}_3$  with  $p\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$  (Synthesis of 3).** The reaction between  $\text{AlH}_3 \cdot \text{NMe}_3$  (20 mL, 0.5 M solution in toluene) and  $p\text{-CF}_3\text{C}_6\text{H}_4\text{CN}$  (0.85 g, 5.0 mmol) was carried out in the same way as the reaction between  $\text{AlH}_3 \cdot \text{NMe}_3$  and  $\text{PhCN}$ . Yield: 0.63 g (63%). Mp:  $240^\circ\text{C}$  (decomp). NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ ,  $\delta$  4.25 (s, 12H,  $\text{CH}_2$ ), 7.21 (m, 24H,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}$ ,  $\delta$  49.18 ( $\text{CH}_2$ ), 123.83 (m,  $\text{CF}_3$ ,  $J_{\text{C-F}} = 272\text{ Hz}$ ) 126.89 ( $m\text{-C}_6\text{H}_4$ ) 127.96 ( $o\text{-C}_6\text{H}_4$ ), 130.34 (m,  $p\text{-C}_6\text{H}_4$ ,  $J_{\text{C-F}} = 33\text{ Hz}$ ), 145.61 ( $\text{CH}_2\text{-C}$ ). IR: 1877s, 1618w, 1419w, 1326s, 1262w, 1168m, 1131s, 1068s, 1033w, 982w, 860w, 820m, 740s, 693m, 632w, 550w, 499w,  $445\text{cm}^{-1}$ . Anal. Calcd for  $(3 \cdot \text{C}_7\text{H}_8)$   $\text{C}_{53.25}\text{H}_{48}\text{Al}_6\text{F}_{18}\text{N}_6$ : C, 50.13; H, 3.79; F, 26.80; N, 6.59. Found: C, 50.62; H, 3.94; F, 26.43; N, 6.51.

**Reaction of 1 with  $\text{Me}_3\text{SiBr}$  (Synthesis of 4).** To a suspension of **1** (0.30 g, 0.4 mmol) in toluene (20 mL) was added  $\text{Me}_3\text{SiBr}$  (0.40 g, 2.6 mmol) at room temperature. The reaction mixture was

(7) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, *37*, 6906.  
 (8) (a) Zheng, W.; Stasch, A.; Prust, J.; Roesky, H. W.; Cimpoesu, F.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem.* **2001**, *113*, 3569; *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3461. (b) Stasch, A.; Ferbinteanu, M.; Prust, J.; Zheng, W.; Cimpoesu, F.; Roesky, H. W.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *J. Am. Chem. Soc.*, accepted for publication.  
 (9) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141.

stirred overnight and refluxed for an hour. The solution was filtered after cooling to room temperature and stored at 0 °C overnight to obtain colorless crystals of  $(\text{PhCH}_2\text{NAlBr})_6$ , **4**. The crystals were dried under vacuum after decanting the mother liquor. Yield: 0.40 g, (83%). Mp: 296 °C (decomp). IR: 1560w, 1307w, 1262w, 1203w, 1030w, 977m, 962m, 817m, 741s, 722s, 691m, 660m, 549w, 512w  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{42}\text{Al}_6\text{Br}_6\text{N}_6$ : C, 39.65; H, 3.33; N, 6.61. Found: C, 39.43; H, 3.61; N, 6.37.

**Reaction of 1 with  $\text{PhC}\equiv\text{CH}$  (Synthesis of 5).** The reaction between **1** (0.42 g, 0.5 mmol) and  $\text{PhC}\equiv\text{CH}$  (0.33 g, 3.2 mmol) was carried out in the same way as the reaction between **1** and  $\text{Me}_3\text{SiBr}$ . The amount of filtrate was reduced to 10 mL and stored at 0 °C. Colorless crystals of  $(\text{PhCH}_2\text{NAlC}\equiv\text{CPh})_6$ , **5**, were obtained after a week. Yield: 0.52 g (70%). Mp: 293 °C (decomp). NMR ( $\text{C}_6\text{D}_6$ ):  $^1\text{H}$ ,  $\delta$  4.83 (s, 12H,  $\text{CH}_2$ ), 6.96 (m, 30H,  $\text{CH}_2\text{C}_6\text{H}_5$ ), 7.37 (m, 18H, *p*- and *m*- $\text{C}_6\text{H}_5\text{C}\equiv\text{C}$ ), 7.74 (m, 12H, *o*- $\text{C}_6\text{H}_5\text{C}\equiv\text{C}$ );  $^{13}\text{C}$ ,  $\delta$  47.25 ( $\text{CH}_2$ ), 77.78 (Al–C), 83.87 (Al– $\text{C}\equiv\text{C}$ ), 122.79, 125.64, 127.80, 128.41, 124.48, 128.76, 132.4 ( $\text{C}\equiv\text{CC}_6\text{H}_5$  and  $\text{CH}_2\text{C}_6\text{H}_5$ ). IR: 2127m, 1951w, 1882w, 1804w, 1595m, 1496m, 1262m, 1212m, 1070m, 1026s, 914w, 800s, 755s, 690s, 647s, 611s, 537m  $\text{cm}^{-1}$ .

**X-ray Structure Determination of 1 and 3–5.** A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data for **1**, **3**, and **4** were collected on a Siemens-Stoe AED2 four-circle instrument (at 200 K for **1** and **3**, and at 203 K for **4**; data for **5** were collected on a Bruker AXS CCD diffractometer at 133 K). All measurements were made with graphite-monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods using SHELXS-97<sup>10</sup> and refined against  $F^2$  on all data by full-matrix least squares with SHELXL-97.<sup>11</sup> All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors (including anomalous scattering) were taken from ref 12. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model.

## Results and Discussion

The major objective of the work described here was the structural characterization of the products of a reaction between RCN and  $\text{AlH}_3\cdot\text{NMe}_3$  and their stability toward nucleophilic reagents. Addition of  $\text{AlH}_3\cdot\text{NMe}_3$  to PhCN in toluene at  $-78 \text{ }^\circ\text{C}$  resulted in a yellow colored solution, which turned colorless upon refluxing. Keeping the solution at 0 °C overnight yielded colorless crystals of **1**. In a similar way, *p*- $\text{MeC}_6\text{H}_4\text{CN}$  and *p*- $\text{CF}_3\text{C}_6\text{H}_4\text{CN}$  react with  $\text{AlH}_3\cdot\text{NMe}_3$  and give **2** and **3**. Compounds **1–3** are air-/moisture-sensitive and decompose at 245, 233, and 240 °C, respectively, with the evolution of a gas. Compound **1** smoothly reacts with an excess of  $\text{Me}_3\text{SiBr}$  in toluene, and all the hydridic hydrogen atoms are replaced by bromine atoms. Compound **4** is the sole product of the reaction. However, a complex mixture of products (based on  $^{19}\text{F}$  NMR) was formed when  $\text{Me}_3\text{SnF}$  was employed in place of  $\text{Me}_3\text{SiBr}$ . The reaction of compound **1** with  $\text{PhC}\equiv\text{CH}$ , which reacts with  $\text{AlH}_3\cdot\text{NMe}_3$  and forms an Al–C network,<sup>8b</sup> is straightforward with the

evolution of hydrogen. All the hydridic hydrogen atoms were substituted by the acetylide moieties forming compound **5**. Compound **5** is extremely air-/moisture-sensitive, and hence our attempts to obtain a proper analytical data were unsuccessful. The results were inconsistent.

The IR spectra of compounds **1–3** exhibit a strong band around  $1860 \text{ cm}^{-1}$  due to  $\nu(\text{Al–H})$ .<sup>13</sup> The absence of this band in **4** and **5** proves that all Al–H bonds are substituted. A sharp band of medium intensity at  $2127 \text{ cm}^{-1}$  in the IR spectrum of **5** can be attributed to  $\nu(\text{C}\equiv\text{C})$ .<sup>14</sup> The base peak in the EI mass spectra of compounds **1–5** corresponds to the organic substituent on the nitrogen. In addition to EI spectra, FAB, ES, and FD techniques were also applied on compounds **1–5**. However, no molecular ion peak is observed.

The mechanism of the reaction between PhCN and  $\text{AlH}_3\cdot\text{NMe}_3$  is not fully understood at present. However, IR and NMR spectral analyses of an initial product of the reaction show the involvement of the imide,  $\text{PhCH}=\text{N–AlH}_2\cdot\text{NMe}_3$  as an intermediate. A pale yellow colored product was obtained by the addition of 1.5 equiv of  $\text{AlH}_3\cdot\text{NMe}_3$  in toluene to a solution of PhCN (in toluene) at room temperature followed by evaporation of all volatiles under high vacuum. The IR spectrum of the product shows two absorptions, one in the  $\nu(\text{C}=\text{N})$  region ( $1653 \text{ cm}^{-1}$ ) and another in the  $\nu(\text{Al–H})$  region ( $1791 \text{ cm}^{-1}$ ) in addition to the absorptions of **1**. No absorptions related to  $\nu(\text{C}\equiv\text{N})$  are observed. The  $^1\text{H}$  NMR spectrum at 30 °C in toluene- $d_8$  shows three doublet resonances in the phenyl region in addition to the multiplet related to **1**. In agreement with the unsaturated nature of the intermediate the doublets appear in the more deshielded region ( $\delta$  7.31, 7.41, and 7.65 in a 2:2:1 ratio) compared to the multiplet of **1** ( $\delta$  7.14). Upon heating the sample to 90 °C the doublets distinctively diminish as the multiplet related to **1** becomes more prominent. These observations are in accordance with the proposed intermediate,  $\text{PhCH}=\text{N–AlH}_2\cdot\text{NMe}_3$ , which can be expected to form by the transfer of a hydride to the nitrilic carbon atom. Upon heating  $\text{PhCH}=\text{N–AlH}_2\cdot\text{NMe}_3$  the elimination of  $\text{NMe}_3$  and the formation of **1** are observed.

Crystallographic data for the structural analyses of compounds **1** and **3–5** are given in Table 1, and the important bond parameters are listed in Table 2. The molecular structure of **1** is shown in Figure 1. Compound **1** crystallizes in the rhombohedral space group  $R\bar{3}$  with one-sixth of the molecule in the asymmetric unit. Compound **1** basically contains an hexagonal drum with the top and bottom faces of the polyhedron being made of two six-membered  $(\text{AlN})_3$  rings, which are almost planar. These six-membered rings are joined by six transverse Al–N bonds forming six rectangular side faces of the drum. As with the previously studied structures, the Al–N bonds in the six-membered rings are significantly shorter than the transverse bonds joining

(10) Sheldrick, G. M. SHELXS-90/96, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

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

(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1969; Vol. IV, pp 55, 99, 149.

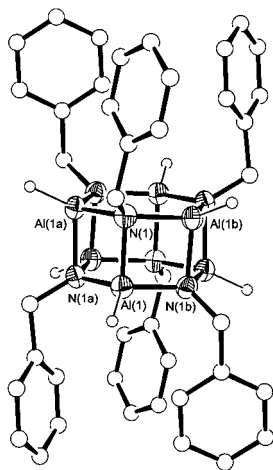
(13) (a) Gardiner, M. G.; Koutsantonis, G. A.; Lawrence, S. M.; Lee, F.-C.; Raston, C. L. *Chem Ber.* **1996**, *129*, 545. (b) Jones, C.; Lee, F.-C.; Koutsantonis, G. A.; Gardiner, M. G.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1996**, 829.

(14) Szymanski, H. A. *Interpreted Infrared Spectra*; Plenum Press Data Division: New York, 1966; Vol 2, p 5.

**Table 1.** Crystallographic Data for the Structural Analyses of **1**,  $3 \cdot 3/4 C_7H_8$ , **4**, and  $5 \cdot C_7H_8$ 

	<b>1</b>	$3 \cdot 3/4 C_7H_8$	<b>4</b>	$5 \cdot C_7H_8$
empirical formula	$C_{42}H_{48}Al_6N_6$	$C_{53.25}H_{48}Al_6F_{18}N_6$	$C_{42}H_{42}Al_6Br_6N_6$	$C_{97}H_{80}Al_6N_6$
fw	798.74	1275.86	1272.16	1491.55
<i>T</i> /K	200(2)	200(2)	203(2)	133(2)
$\lambda/\text{\AA}$	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	rhombohedral	triclinic	monoclinic	monoclinic
space group	$R\bar{3}$	$P\bar{1}$	$P2_1/c$	$C2/c$
<i>a</i> /\AA	15.7457(13)	17.527(11)	14.175(4)	25.842(5)
<i>b</i> /\AA	15.7457(13)	18.894(12)	16.678(5)	15.443(3)
<i>c</i> /\AA	14.949(2)	19.246(15)	10.731(3)	20.699(4)
$\alpha$ /deg	90	96.11(7)	90	90
$\beta$ /deg	90	102.23(4)	106.82(2)	105.88(3)
$\gamma$ /deg	120	106.79(3)	90	90
<i>V</i> /\AA <sup>3</sup>	3209.8(5)	5867(7)	2428.6(11)	7945(3)
<i>Z</i>	3	4	2	4
<i>D</i> (calcd)/(g·cm <sup>-3</sup> )	1.240	1.444	1.740	1.247
$\mu$ (Mo K $\alpha$ )/cm <sup>-1</sup>	0.187	0.209	5.106	0.134
<i>F</i> (000)	1260	2598	1248	3128
cryst size/mm <sup>3</sup>	0.80 × 0.70 × 0.70	1.00 × 0.60 × 0.30	0.50 × 0.40 × 0.30	1.00 × 0.80 × 0.60
$\theta$ range/deg	4.18–24.97	3.51–22.20	3.73–25.02	2.38–27.73
index range	–17 ≤ <i>h</i> ≤ 17 –12 ≤ <i>k</i> ≤ 12 –17 ≤ <i>l</i> ≤ 17	–18 ≤ <i>h</i> ≤ 18 –19 ≤ <i>k</i> ≤ 19 –19 ≤ <i>l</i> ≤ 20	–16 ≤ <i>h</i> ≤ 16 –19 ≤ <i>k</i> ≤ 12 –12 ≤ <i>l</i> ≤ 12	–33 ≤ <i>h</i> ≤ 32 0 ≤ <i>k</i> ≤ 20 0 ≤ <i>l</i> ≤ 27
reflns collected	2020	17 020	7655	8878
independent reflns	848	14 183	4265	8878
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>			
data/restraints/params	848/0/86	14183/1044/1497	4265/0/271	8878/501/508
<i>R</i> 1, <i>R</i> 2 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0334, 0.0861	0.1125, 0.3108	0.0528, 0.1197	0.0896, 0.1964
<i>R</i> 1, <i>R</i> 2 (all data) <sup>a</sup>	0.0365, 0.0890	0.1637, 0.3831	0.0839, 0.1380	0.0978, 0.2019
<i>S</i>	1.120	1.429	1.033	1.213
$\Delta\rho$ (min), $\Delta\rho$ (max)/(e <sup>-</sup> \AA <sup>3</sup> )	0.150, –0.190	1.760, –0.706	0.890, –0.888	0.891, –0.819

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .  $R2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$ .



**Figure 1.** Crystal structure of compound **1**. All hydrogen atoms except those on Al are excluded for clarity.

the rings.<sup>3e,15</sup> The benzyl groups are oriented toward each other, blocking the top and bottom faces of the hexagonal drum and thereby exposing the hydridic hydrogens. This can be seen in the reactivity of compound **1** with nucleophiles such as  $Me_3SiBr$  and  $PhC\equiv CH$ .

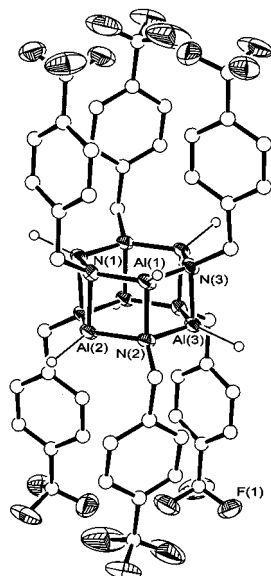
Compound **3** crystallizes in the triclinic space group  $P\bar{1}$  with two halves of the molecule and another independent molecule along with 1.5 molecules of toluene in the asymmetric unit. The molecular structure of **3** is shown in Figure 2. Bond parameters and other features of the molecule are similar to those of compound **1**. A plot of **4** is given in

**Table 2.** Selected Bond Lengths and Bond Angles of Compounds **1** and **3–5**

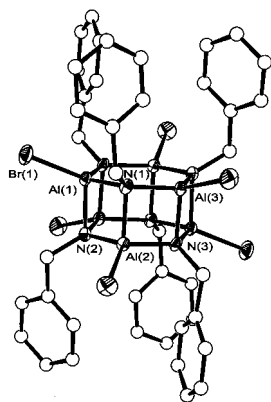
bond distances (\AA)		bond angles (deg)	
<b>Compound 1</b>			
N(1a)–Al(1)	1.886(2)	Al(1a)–N(1)–Al(1b)	124.37(8)
Al(1)–N(1b)	1.893(2)	N(1)–Al(1)–Al(1b)	88.77(6)
Al(1)–N(1)	1.9736(14)	N(1a)–Al(1)–N(1)	91.26(6)
		N(1a)–Al(1)–N(1b)	115.25 (8)
		Al(1a)–N(1)–Al(1)	88.57(6)
		N(1)–Al(1)–N(1b)	91.05(6)
<b>Compound 3</b>			
Al(1)–N(1)	1.880(10)	N(1)–Al(1)–N(3)	115.3(5)
Al(1)–N(3)	1.902(11)	N(3)–Al(1)–N(2)	90.8(4)
Al(1)–N(2)	1.980(10)	Al(3)–N(2)–Al(1)	88.4(4)
Al(2)–N(2)	1.900(10)	N(1)–Al(1)–N(2)	91.1(4)
Al(3)–N(3)	1.959(10)	Al(3)–N(2)–Al(2)	124.0(5)
		Al(2)–N(2)–Al(1)	88.1(4)
<b>Compound 4</b>			
Al(1)–N(1)	1.889(5)	N(1)–Al(1)–N(2)	91.9(2)
Al(1)–N(2)	1.972(6)	N(1)–Al(1)–Br(1)	120.2(2)
Al(1)–Br(1)	2.245(2)	Al(3)–N(1)–Al(1)	123.5(3)
Al(2)–N(3)	1.873(5)	N(3)–Al(2)–N(2)	116.4(2)
Al(2)–N(1)	1.982(6)	N(2)–Al(1)–Br(1)	113.9(2)
<b>Compound 5</b>			
Al(1)–N(3)	1.876(3)	N(3)–Al(1)–N(1)	114.33(13)
Al(1)–N(1)	1.884(3)	N(1)–Al(1)–C(11)	120.24(15)
Al(1)–C(11)	1.912(4)	Al(1)–N(1)–Al(2)	88.34(12)
Al(1)–N(2)	1.972(3)	C(11)–C(12)–C(13)	178.7(4)
C(11)–C(12)	1.196(5)	C(22)–C(21)–Al(2)	178.3(3)
C(12)–C(13)	1.444(5)	C(32)–C(31)–Al(3)	171.2(3)
		N(3)–Al(1)–C(11)	116.65(15)
		N(3)–Al(1)–N(2)	91.66(12)
		Al(2)–N(2)–Al(3)	122.12(16)
		C(12)–C(11)–Al(1)	174.6(3)
		C(21)–C(22)–C(23)	178.6(4)
		C(31)–C(32)–C(33)	176.7(4)

**Figure 3.** Compound **4** crystallizes in the monoclinic space group  $P2_1/c$  with half of the molecule in the asymmetric unit.

(15) Cesari, M.; Perego, G.; Del Piero, G.; Cucinella, S.; Cernia, E. *J. Organomet. Chem.* **1974**, *78*, 203.

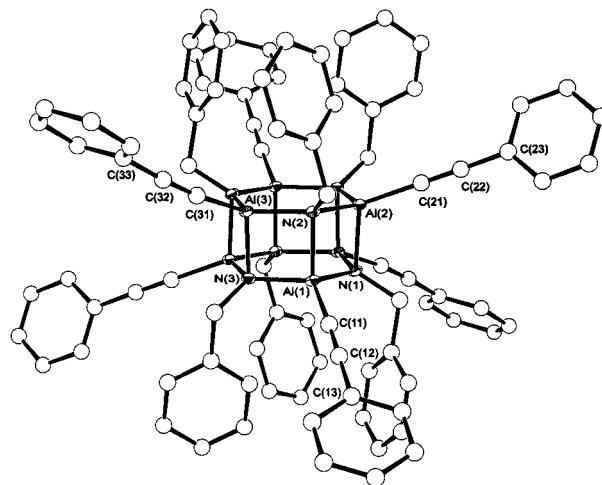


**Figure 2.** Crystal structure of compound **3**. All hydrogen atoms except those on Al are excluded for clarity.



**Figure 3.** Crystal structure of compound **4**. All hydrogen atoms are excluded for clarity.

A comparison of bond distances and bond angles with those of **1** shows that the cage structure is not disturbed by the replacement of the hydrogen atoms by the bulky bromine atoms. A plot of compound **5** is given in Figure 4. Compound **5** crystallizes in the monoclinic space group  $C2/c$  with half of the molecule along with half of a molecule of toluene in the asymmetric unit. An interesting feature of the structure is that the  $C\equiv C-Al$  bond angles deviate from the expected



**Figure 4.** Crystal structure of compound **5**. All hydrogen atoms are excluded for clarity.

$180^\circ$  and vary significantly from each other ( $C(12)-C(11)-Al(1) = 174.6(3)^\circ$ ,  $C(22)-C(21)-Al(2) = 178.3(3)^\circ$ , and  $C(32)-C(31)-Al(3) = 171.2(3)^\circ$ ). In a similar way,  $C\equiv C-C$  bond angles also deviate slightly from linearity ( $C(11)-C(12)-C(13) = 178.7(4)^\circ$ ,  $C(21)-C(22)-C(23) = 178.6(4)^\circ$ , and  $C(31)-C(32)-C(33) = 176.7(4)^\circ$ ).

## Conclusion

The products of general formula  $(HAlNCH_2R)_6$  resulting from the reaction between nitriles and  $AlH_3 \cdot NMe_3$  have been structurally characterized. It has been shown that they basically contain an hexagonal drum made of an  $(AlN)_6$  network and a hydridic hydrogen per Al atom. The stability of one of these  $(AlN)_6$  clusters toward nucleophilic reagents such as  $PhC\equiv CH$  and  $Me_3SiBr$  has been demonstrated. Presently we are investigating the preparation of aluminum nitride from compounds **1** and **2**.

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**Supporting Information Available:** Single-crystal X-ray structural data of compounds **1** and **3–5** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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