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Examination of dibenzyl aluminum and gallium azides as potential precursors to AlN and GaN☆

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Abstract

This publication summarizes our attempts to prepare precursor molecules of formula Bn_2MN_3-THF [where Bn = benzyl, M = Ga (**3**) and Al (**8**)] and to use them in the low-temperature synthesis of AlN and GaN. Compound **3** was prepared from Bn_2GaCl-THF (**2**) and Me_3SiN_3. Compound **8** was obtained by a different route which requires the combination of Cl_2AlN_3 and BnMgCl in toluene. During the course of this work two new amides, $[Bn_2AlNMe_2]_2$ (**4**) and $Bn_2AlN(SiMe_3)_2$-THF (**5**) were prepared and structurally characterized by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aluminum; Azide; Benzyl; Gallium; Nitride

1. Introduction

The motivation behind this work is the preparation of precursor molecules that can decompose at low temperature (< 260°C) to form the important electronic materials, AlN and GaN [1]. It is based upon a combination of two recent developments related to unimolecular approaches to materials. The first is the use of benzyl as a supporting ligand on the metal to be incorporated in the solid-state material. It can be easily eliminated as a radical under thermal conditions [2]. Indeed, the homolytic bond dissociation energy for this group ($PhCH_2$–H, 368 kJ mol^{-1}) is lower than for other alkyls such as CH_3–H and CH_3CH_2–H (438 kJ mol^{-1} and 420 kJ mol^{-1}, respectively) [3]. This has been demonstrated for 14/16 compounds such as $[Bn_2SnS]_3$ [4]. At temperatures as low as 200°C this and related molecules have been used to produce fairly pure SnS.

The second development involves the use of azide, N_3, as the source of nitride. Early work demonstrated that complexes having the formula, $[R_2MN_3]_n$ [5] could be converted to AlN [6] and GaN [7]. Subsequent expanded efforts with this group have led to many other new unimolecular precursors [8] including some monomeric intramolecularly stabilized derivatives [9].

This publication summarizes our attempts to combine these two advantages in the preparation of precursor molecules of formula Bn_2MN_3-THF [where Bn = benzyl, M = Ga (**3**) and Al (**8**)] and to use them in the low-temperature synthesis of AlN and GaN. During the course of this work two new amides, $[Bn_2AlNMe_2]_2$ (**4**) and $Bn_2AlN(SiMe_3)_2$-THF (**5**) were prepared and structurally characterized.

2. Results and discussion

2.1. Synthesis and characterization

The first route explored to obtain the dibenzyl azides Bn_2MN_3-THF (M = Al, Ga) made use of the dibenzyl chlorides Bn_2MCl-THF [M = Al (**1**) and Ga (**2**) [10]] as

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☆ Dedicated to Alan H. Cowley on the occasion of his 65th birthday.

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a starting material. These dibenzyl chlorides can be readily obtained from Bn_3M-THF and MCl_3 in toluene as outlined by Eq. (1). Compounds **1** and **2** were combined with NaN_3 at ambient temperatures in THF (Eq. (2)). From these reactions the Bn_2MCl-THF starting material was apparent. Attempts to increase any formation of the targeted compounds by increasing the temperature of the reaction led to the formation of a gray precipitate and a solution containing primarily bibenzyl (Bn–Bn). In the case of **1** after exposure to air, the gray precipitate turned white and was determined to be Al_2O_3 by XRD. The use of Me_3SiN_3 instead of NaN_3 in toluene presented the same results as described above for **1** (Eq. (3)). Conversely, **2** reacts with Me_3SiN_3 in toluene to produce mainly Bn_2GaN_3-THF (**3**) (Eq. (4)) as a light-green viscous liquid. Bn–Bn is an unavoidable but minor impurity (from ^{1}H-NMR). Further evidence of the identity of **3** stems from the azido absorbance at 2130 cm^{-1} in the IR and the elemental analysis with the appropriate formulation.

$$2Bn_3M\text{-}THF + MCl_3 \xrightarrow{\text{Toluene}} 3Bn_2MCl\text{-}THF \qquad (1)$$

$M = Al, Ga$

$$Bn_2MCl\text{-}THF + NaN_3 \xrightarrow{\text{THF}} \text{no reaction} \qquad (2)$$

$M = Al, Ga$

$$Bn_2AlCl\text{-}THF + Me_3SiN_3 \xrightarrow{\text{Toluene}} \text{no reaction} \qquad (3)$$

$$Bn_2GaCl\text{-}THF + Me_3SiN_3 \xrightarrow{\text{Toluene}} Bn_2GaN_3\text{-}THF\ (\mathbf{3}) + Me_3SiCl \qquad (4)$$

In order to demonstrate that the $[Bn_2MCl]_2$ reagents could indeed undergo salt elimination reactions (despite the results obtained for NaN_3) the combination of **1** with $LiNMe_2$ and $LiN(SiMe_3)_2$ was explored. These two reactions (Eqs. (5) and (6)) led to high yields of the respective amides **4** and **5**. In solution the benzyl CH_2 resonances for **4** appear as a singlet (δ 1.73 ppm) while those of **5** appear as a doublet (δ 1.97 ppm). This indicates that these groups in **4** undergo rotation in solution which leads to an averaged signal. In **5** however, these groups are either diastereotopic (both Bn groups equivalent with CH_aH_b) or in two distinct environments.

$$2Bn_2AlCl\text{-}THF + 2LiNMe_2 \xrightarrow[-\text{THF}]{\text{Toluene}} [Bn_2AlNMe_2]_2\ (\mathbf{4}) + 2LiCl \qquad (5)$$

$$Bn_2AlCl\text{-}THF + LiN(SiMe_3)_2 \xrightarrow{\text{Toluene}} Bn_2AlN(SiMe_3)_2\text{-}THF\ (\mathbf{5}) + LiCl \qquad (6)$$

Suitable crystals for X-ray crystallography were obtained for compounds **4** and **5** from toluene and hexane solutions. The molecular structures and atom numbering schemes are shown in Figs. 1 and 2. As observed for many other Group 13 amides [11], **4** exists as a nitrogen-bridged dimer in the solid (Fig. 1). The Al-μ-N bonds are 1.970(5)Å while the Al–C bonds are 1.97(1)Å. By comparison, monomeric **5** (Fig. 2), with a terminal amide group has a much shorter Al–N bond, 1.850(5)Å and similar Al–C bonds, 1.98 (1)Å.

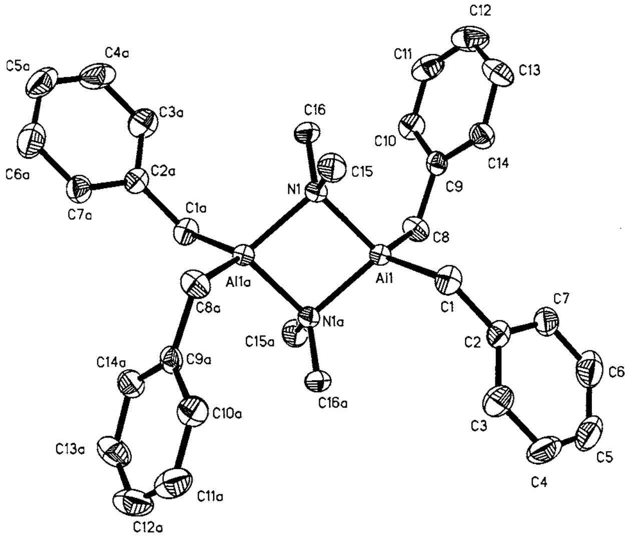


Fig. 1. Molecular structure and atom numbering scheme for **4**. Selected bond distances (Å) and angles (°) are as follows: Al(1)–N(1) 1.970(5), Al–C(1) 1.983(6), Al(1)–C(8) 1.968(6), Al(1)–N(1A) 1.954(5); N(1)–Al(1)–C(1) 109.1(2), C(1)–Al(1)–C(8) 115.0(3), N(1)–Al(1)–N(1A) 88.5(2), C(8)–Al(1)–N(1A) 114.1(2), Al(1)–N(1)–C(15) 112.5(4), N(1)–Al(1)–C(8) 114.1(2), C(1)–Al(1)–N(1A) 113.0(2), Al(1)–N(1)–C(16) 115.7(4), Al(1)–N(1)–Al(1A) 91.5(2).

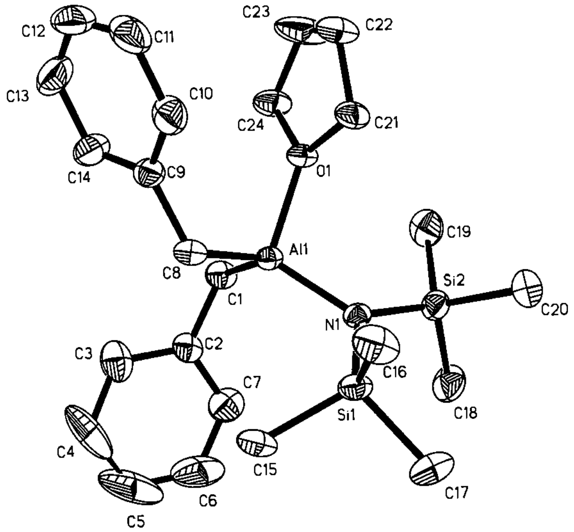


Fig. 2. Molecular structure and atom numbering scheme for **5**. Selected bond distances (Å) and angles (°) are as follows: Al(1)–O(1) 1.900(4), Al(1)–C(1) 1.990(7), Al(1)–N(1) 1.850(5), Al(1)–C(8) 1.987(7); O(1)–Al(1)–N(1) 106.0(2), N(1)–Al(1)–C(1) 116.0(3), N(1)–Al(1)–C(8) 115.7(3), Al(1)–O(1)–C(21) 121.6(4), Al(1)–N(1)–Si(2) 123.2(3), O(1)–Al(1)–C(1) 102.3(3), O(1)–Al(1)–C(8) 102.2(2), C(1)–Al(1)–C(8) 112.3(3), Al(1)–O(1)–C(24) 126.9(4), Al(1)–N(1)–Si(1) 116.4(3).

Monomeric aluminum amides are not rare, for example, the silylamide Al[N(SiMe$_3$)$_2$]$_3$ is monomeric and has a planar trigonal geometry [12]. The C–Al–C angles in **5** and **6** are nearly the same 115.0(3)° (3) and 112.3(3)° (4) due to the increased s character of the Al–C bond compared to the Al–N (or O) bonds which have more p character and are thus more acute.

It was clear that the use of heat to assist in the formation of an azide-M linkage resulted in decomposition of the reactants and/or products (Eq. (2)). In order to avoid this, starting materials which already contained this bond, Cl$_2$MN$_3$ (M = Al (**6**) [13] and Ga (**7**) [14], were used instead. Compounds **6** and **7** were prepared from the metallic chlorides and azidotrimethylsilane in dichloromethane as shown in Eq. (7). The combination of **6** with BnMgCl in toluene at ambient temperature led to the formation of the desired compound Bn$_2$AlN$_3$-THF (**8**) as a yellow viscous liquid with a small amount of impurities in a minor proportion (from ^{1}H-NMR), the azido absorbances for **8** appear at 2137 and 2180 cm^{-1} (Eq. (8)). A similar reaction with **7** produced a complex mixture of products including Bn$_3$Ga-THF (characterized by ^{1}H-NMR). It is worth noting that although the precursor molecules **3** and **8** are similar, two distinct routes of synthesis have to be used to obtain them. Eqs. (4) and (8) outline the differences in the syntheses.

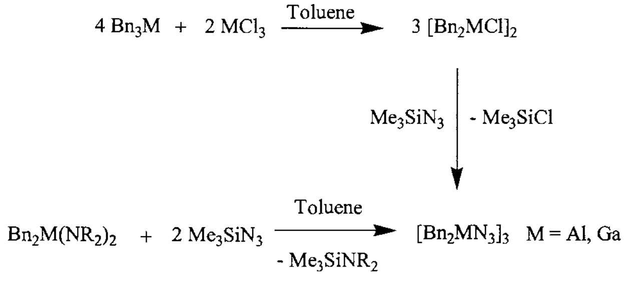
$$\mathrm{MCl_3 + Me_3SiN_3 \xrightarrow{CH_2Cl_2} Cl_2MN_3 + Me_3SiCl} \tag{7}$$

M = Al, Ga

$$\mathrm{Cl_2AlN_3 + 2BnMgCl \xrightarrow{Toluene} Bn_2AlN_3\text{-}THF\ (\mathbf{8}) + 2MgCl_2} \tag{8}$$

2.2. Decomposition studies

Thermogravimetric analysis of **3** indicated that the compound began to lose weight at temperatures near 50°C. A total of 69% loss of weight was registered at 210°C at a rate of 5°C min^{-1}. The pyrolysis of **3** (200 mg) was performed up to 230°C for 12 h in a quick distillation apparatus under nitrogen. A colorless liquid was distilled and collected in the cup of the apparatus, the IR of the product showed a high content of Bn–Bn. After removal of the distilled liquid the remaining yellow liquid was heated slowly up to 300°C in the same apparatus under dynamic vacuum (10^{-3} Torr) resulting in a bright black solid which showed a 20% carbon content from elemental analyses. Similar conditions for **8** at 50–80°C produced crystalline Bn–Bn (confirmed by IR and ^{1}H-NMR) on the walls of the apparatus. Subsequent heating at 300°C under dynamic vacuum led to a black powder which elemental analyses indicated had more than 10% carbon content. From these results it would appear that compounds **3** and **8** decompose before becoming volatile.



Scheme 1. Proposed routes to non-coordinated [Bn$_2$Mn$_3$]$_3$ (M = Al, Ga).

3. Conclusions

The results presented in this manuscript are the first involving the use of compounds that contain both benzyl and azide groups on a Group 13 element (Bn$_2$MN$_3$). These compounds were specifically designed as precursors to AlN and GaN. The adducts Bn$_2$MN$_3$-THF were originally targeted since they could potentially form the monomers Bn$_2$MN$_3$ in the gas phase. Based upon the poor pyrolysis results this is apparently not the case. Current efforts are directed at the use of systems that do not contain a coordinating solvent as shown in Scheme 1. It is expected that these compounds will be trimeric based upon the trimeric formulation found for other Group 13 dialkyl azides, [R$_2$M(N$_3$)]$_3$ (R = Me, Et) [15]. Furthermore, it has previously been shown that Me and Bn provide similar trimer structures for indium halide complexes [16].

4. Experimental

4.1. General considerations

All manipulations were conducted using Schlenk techniques in conjunction with an inert atmosphere glove box. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 and 399.78 MHz (^{1}H) and are reported relative to SiMe$_4$ (in ppm). Elemental analyses were obtained on a Perkin–Elmer 2400 Analyzer and were satisfactory for all compounds. IR data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. Thermogravimetric analyses were run on a Perkin–Elmer 7 Series Thermal Analysis System. The reagents, Me$_3$SiN$_3$, NaN$_3$, LiNMe$_2$ and LiN(SiMe$_3$)$_2$ were purchased from Aldrich and used without further purification. The compounds Bn$_2$AlCl-THF (**1**), Bn$_2$GaCl-THF (**2**) [10] were prepared from the redistribution reaction with Bn$_3$M-THF and MCl$_3$ in toluene according to reported procedures. Compounds ClAl(N$_3$)$_2$ (**6**), ClGa(N$_3$)$_2$ (**7**) were prepared according to the literature procedures [13,14]. X-ray data for **4** and **5** were collected on a Siemens P-4 diffractometer using graphite-monochromated Mo–K_α radiation. The structures were refined using the Siemens software package SHELXTL 4.0. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were put into calculated positions. Absorption corrections were not employed. Further details of the structure analyses are given in Table 1.

*4.2. Bn_2GaN_3-THF (**3**)*

To a 40 ml solution of **2** (2.6 g, 7.23 mmol) in toluene was added Me_3SiN_3 (0.86 g, 7.5 mmol) at 25°C. The reaction mixture was stirred for 24 h, then the volatiles were removed under vacuum. The resultant liquid was redissolved in toluene, cannula filtered and after evaporation of the solvent, a light-green viscous liquid was obtained (2.23 g, 84%). ^{1}H-NMR (C_6D_6): δ 0.86 (m, 4H, THF), 2.16 (s, 4H, PhC$\underline{H}_2$), 3.17 (m, 4H, THF), 7.09 (m, 10H, Ph$\underline{H}$). IR: ν 3412 m, 3059 s, 3023 s, 2951 s, 2905 s, 2130 s, 1944 w, 1809 w, 1869 w, 1597 s, 1491 s, 1369 w, 1348 w, 1248 m, 1208 s, 1111 s, 1051 s, 756 s, 702 s, 652 w. Anal. Calc.: C, 59.05; H, 6.06. Found: C, 59.09; H, 5.62.

Table 1
Crystal data for **4** and **5**

	4	**5**
Empirical formula	$C_{16}H_{20}AlN$	$C_{24}H_{40}AlNOSi$
Formula weight	253.30	441.70
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	9.313(2)	11.100(3)
b (Å)	11.703(5)	16.897(3)
c (Å)	13.944(3)	14.774(6)
α (°)	90.0	90.0
β (°)	105.75(2)	94.64(3)
γ (°)	90.0	90.0
V (Å^3)	1461.8(8)	2761.7(14)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.151	1.062
Crystal size (mm)	$0.6\times0.6\times0.4$	$1.6\times0.4\times0.4$
Radiation, K_α; λ(Å)	Mo; 0.71073	Mo; 0.71073
Temperature (K)	298	298
2θ range (°)	3.5–45	3.5–45
Scan type	2θ-θ	2θ-θ
Scan speed (° min^{-1})	12–60	8–60
Scan range (°)	0.47	0.60
Reflections collected	2034	4603
Independent reflections	1837 [$R_{int}=0.04$]	3599 [$R_{int}=0.1197$]
Reflections observed [$F>4.0\sigma(F)$]	1062	1953
Number of parameters	163	262
R	0.0581	0.0630
R_w	0.0600	0.0640
Goodness of fit on F^2	1.31	1.71
Largest difference electron density (e Å^{-3})	0.23 and −0.18	0.26 and −0.22

*4.3. $[Bn_2AlNMe_2]_2$ (**4**)*

Compound **1** (prepared in situ from Bn_3Al and $AlCl_3$) (3.16 mmol, 1.00 g) was suspended in toluene (10 ml) then $LiNMe_2$ (3.16 mmol, 0.166 g, 95%) was added as a solid at 25°C. The reaction was stirred for 12 h, then volatiles were removed and the residual solid extracted with 40 ml of toluene. Filtration, followed by evaporation of the solvent yielded a white solid (0.755 g, 94%). Crystals suitable for X-ray analysis were grown from a supersaturated solution in hot toluene slowly cooled to ambient temperature. M.p. 119–121°C. ^{1}H-NMR (C_6D_6): δ 1.73 (s, 4H, PhC$\underline{H}_2$), 1.92 (s, 6H, NC$\underline{H}_3$), 6.99–7.16 (m, 10H, Ph$\underline{H}$); IR: ν 3021 m, 2903 s, 1595 s, 1487 w, 1459 s, 1199 m, 1087 w, 1032 w, 897 w, 801 w, 748 w, 698 w, 665 w, 609 w, 530 w, 474 w. Anal. Calc.: C, 75.89; H, 7.91; N,5.53. Found: C, 75.83; H, 8.01; N, 5.66.

*4.4. $Bn_2AlN(SiMe_3)_2$-THF (**5**)*

Compound **1** (prepared in situ from Bn_3Al and $AlCl_3$) (4.75 mmol, 1.50 g) was suspended in toluene (20 ml) then $LiN(SiMe_3)_2$ (4.75 mmol, 0.795 g) was added as a solid at 25°C. The reaction was stirred for 12 h, then volatiles were removed and the residual solid extracted with 40 ml of toluene. Filtration, followed by evaporation of the solvent yielded a white solid (1.65 g, 79%). Crystals suitable for X-ray analysis were grown from a hexane solution stored at −30°C for 2 days. M.p. 99–101°C. ^{1}H-NMR (C_6D_6): δ 0.29 (s, 18H, Si$\underline{Me}_3$), 0.85, 3.30 (m, 8H, THF), 1.97 (br d, 4H, Ph$\underline{CH}_2$) 7.00, 7.21 (m, 10H, Ph$\underline{H}$); IR: ν 3001 s, 2923 m, 1692 m, 1458 w, 1450 s, 1191 m, 1062 w, 898 w, 811 w, 745 w, 683 w, 672 w, 60 w, 474 w. Anal. Calc.: C, 65.31; H, 9.07; N, 3.17. Found: C, 65.33; H, 9.33; N, 3.22.

*4.5. Bn_2AlN_3-THF (**8**)*

To a solution of Cl_2AlN_3 (2.1 g, 15 mmol) in toluene (50 ml) at 0°C was added BnMgCl (15 ml, 2.0 M solution in THF) slowly (30 min). After the addition was completed the reaction mixture was left to reach r.t. and stirred for 12 h more. The volatiles were removed under vacuum, and then the residual solids were extracted with 150 ml of toluene. The solution was filtered with a glass frit followed by removal of volatiles under vacuum which afforded a yellow liquid (3.82 g, 81%). ^{1}H-NMR (C_6D_6): δ 0.85 (br s, 4H, THF), 1.81 (s, 4H, PhC$\underline{H}_2$), 3.23 (br s, 4H, THF), 7.13 (m, 10H, Ph$\underline{H}$). IR: ν 3073 s, 3015 s, 2905 s, 2180 s, 2137 s, 1592 s, 1489 s, 1451 w, 1412 m, 1202 s, 1044 s, 855 s.

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