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Preliminary communication

Surprising stability of a monomeric bis azide of gallium(III)

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Abstract

The intramolecularly base-stabilized arylgallium diazide $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(N_3)_2$ (**1**) has been prepared by a metathetical reaction of the corresponding arylgallium dichloride with NaN_3. Compound **1** was found not only to be air stable, but also to survive vapor phase heating at 400°C or UV irradiation at 254 nm. The X-ray crystal structure of **1** has been determined; triclinic, $P\bar{1}$, with $a = 8.861(2)$, $b = 10.445(4)$, $c = 11.562(4)$ Å, $\alpha = 107.07(3)$, $\beta = 105.92(2)$, $\gamma = 101.35(3)°$, $V = 937.9(5)$ Å^3 and $Z = 2$. Compound **1** is monomeric in the solid state.

Keywords: Gallium; Azides; Aryls; X-ray crystal structure

Monoazides of gallium(III) constitute a well documented class of compounds [1] and have been used as single-source precursors for the growth of GaN film by OMCVD [2,3]. Interestingly however, diazides of gallium(III) remain unknown. In spite of the low stability of main group diazides such as $Me_2Si(N_3)_2$ and $(2,4,6\text{-}{}^tBu_3C_6H_2)P(N_3)_2$, which decompose to generate the corresponding silylene [4] and phosphinidene [5] respectively, we decided to attempt the synthesis of a diazide of gallium(III). Herein, we report the synthesis, characterization, and X-ray crystal structure of an intramolecularly base stabilized arylgallium diazide featuring two terminal azide groups.

The dichloride $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaCl_2 \cdot C_6H_6$ [6] (1.23 g, 3.0 mmol) and an excess of NaN_3 (0.58 g, 9.0 mmol) were mixed in 30 ml of MeCN at 25°C. After the reaction mixture had been stirred for 12 h at this temperature the solvent was removed under reduced pressure affording a white residue. Addition of 40 ml of hexane to the residue, followed by filtration and removal of the volatiles from the filtrate under vacuum, resulted in an 81% yield (0.89 g) of microcrystalline $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Ga(N_3)_2$ (**1**), m.p. 75°C. Elemental analysis for $C_{12}H_{19}GaN_8$: calculated C 41.77%, H 5.55%, N 32.48%; found C 41.98%, H 5.59%, N 32.24%.

Preliminary information on the structure of **1** was derived from ^1H NMR [7] and IR spectroscopic data. Examination of the ^1H NMR spectrum (C_6D_6) of **1** revealed the presence of a single N–Me resonance (δ 2.09 ppm) as well as a single $N\text{–}CH_2$ resonance (δ 2.95 ppm) thus indicating that the two Me_2NCH_2 arms of the aryl ligand are arranged in a symmetrical fashion. The detection of two sets of bands in the IR spectrum of **1** (KBr) at 1345, 1288 cm^{-1} and 2135, 2065 cm^{-1}, which correspond with $\nu_{sym}[N_3]$ and $\nu_{asym}[N_3]$ respectively, indicated the presence of a terminal $Ga(N_3)_2$ moiety. Definitive structural insights (e.g. connectivity of the dimethylamino groups) were gained from an X-ray analysis. Cooling of a saturated toluene solution of **1** to −20°C overnight afforded suitable single crystals of **1** · 0.5 toluene which undergo solvent loss at 25°C.

Crystal data: $C_{12}H_{19}GaN_8 \cdot 0.5(C_7H_8)$, $M = 391.14$, triclinic, space group $P\bar{1}$, $a = 8.861(2)$, $b = 10.445(4)$, $c = 11.562(4)$ Å, $\alpha = 107.07(3)$, $\beta = 105.92(2)$, $\gamma = 101.35(3)°$, $V = 937.9(5)$ Å^3, $D_c = 1.385$ g/cm^3, $Z = 2$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 1.482$ mm^{-1}. A total of 3899 independent reflections was collected on a Siemens P4 diffractometer at 193 K with 2θ between 4.6 and 55.0° using the $\theta\text{–}2\theta$ scan mode and a graphite monochromator.

The structure was solved by direct methods and refined (full-matrix least-squares) on F^2 to $wR = 14.45\%$ for 3894 reflections and 235 parameters. For

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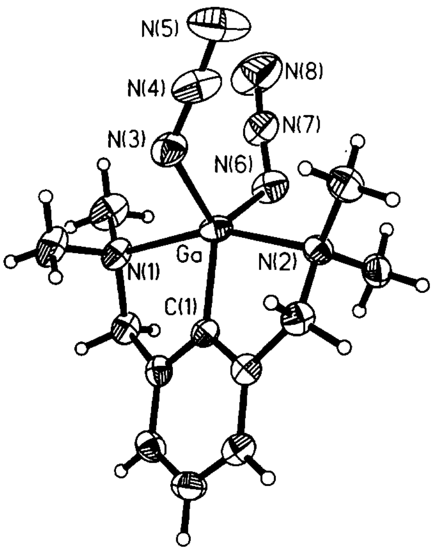

Fig. 1. View of the structure of **1**. Important bond lengths (Å) and angles (deg): Ga–C(1) 1.922(4), Ga–N(1) 2.315(4), Ga–N(2) 2.303(3), Ga–N(3) 1.914(4), Ga–N(6) 1.928(4), N(3)–N(4) 1.212(5), N(4)–N(5) 1.139(6), N(6)–N(7) 1.181(5), N(7)–N(8) 1.130(6), C(1)–Ga–N(3) 125.2(2), C(1)–Ga–N(6) 126.6(2), N(3)–Ga–N(6) 108.2(2), N(1)–Ga–N(2) 158.7(1), Ga–N(3)–N(4) 123.0(3), Ga–N(6)–N(7) 122.3(3), N(3)–N(4)–N(5) 173.5(6), N(6)–N(7)–N(8) 176.1(5).

comparison, the conventional $R(F_o) = 5.38\%$ for 2887 reflections with $F_o > 4\sigma(F_o)$. The X-ray analysis revealed that **1** is monomeric (Fig. 1) and that there are no unusually short intermolecular contacts. Examination of the cell packing diagram (Fig. 2) indicates that the disordered toluene molecules are interstitial and located between pairs of molecules of **1**. Both CH_2NMe_2 arms of the aryl ligand are coordinated to the gallium atom. The overall geometry at the pentacoordinate gallium center is trigonal bipyramidal. However, while the $CGa(N_3)_2$ moiety is planar within experimental error (sum of angles at Ga = 360.0(2)°), the axial ligands are distinctly non-linear (N(1)–Ga–N(2) = 158.7(1)°) owing to the constraints of the ligand system. The two terminal azide groups, which are quasi linear (N(3)–N(4)–N(5) = 173.5(6) and N(6)–N(7)–N(8) = 176.1(5)), are arranged in an open scissors-like fashion. It is noteworthy that such an arrangement minimizes the lone-pair repulsive interactions which could in principle occur between N3 and N5 as well as between N6 and N8. This particular geometry may contribute to the stability of **1**. The gallium azide bond distances in **1**, which are equal within experimental error, average to 1.92 Å. To our knowledge, no previous structural data are available for terminal GaN_3 groups. However, the average $Ga–N_3$ distance in **1** (1.92 Å) is shorter than that in polymeric Me_2GaN_3 (2.05 Å) [3]. This shortening, rather than reflecting any π bonding interaction between the gallium and the azide groups, may result from the terminal location of the azide groups in **1**.

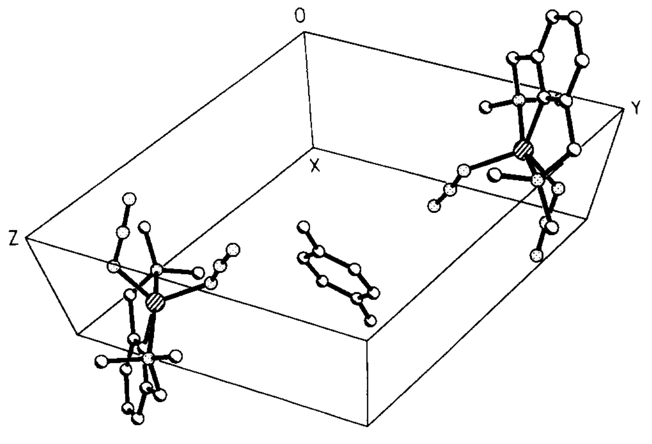

Fig. 2. Cell packing diagram for **1** · 0.5 toluene.

As the percentage by weight of azide nitrogen in **1** is equal to 24.4%, extremely low stability or even explosive behavior was expected [8]. Instead, we found that **1** is surprisingly stable. For instance, **1** survives vapor phase heating at 400°C or UV irradiation at 254 nm. The use of **1** as a precursor for the growth of GaN film by OMCVD was investigated. However, even at a substrate (GaAs) temperature of 600°C no growth was obtained and **1** was detected intact by MS.

In conclusion, the base stabilization effect provided by the 2,6-bis(dimethylaminomethyl)phenyl ligand, together with a favorable arrangement of the azide functionalities, may be responsible for significant stabilization of a species that otherwise might be expected to be explosive. Tables of crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

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[7] ^{1}H NMR (300.15 MHz, 298 K, C_6D_6): 1, $\delta = 2.09$ (s, 12H, NMe_2), 2.95 (s, 4H, CH_2), 6.71 (d, 2H, 3,5 H-ring, $J = 7.2$ Hz), 7.14 (t, 1H, 4 H-ring, $J = 7.2$ Hz). $^{13}C\{^1H\}$ NMR (75.67 MHz, 298 K, C_6D_6): 1, δ 45.6 (NMe_2), 64.1 (CH_2), 124.7 (3,5 C-ring), 130.6 (4 C-ring), 143.8 (2,6 C-ring). The *ipso* carbon was not detected. MS (CI, CH_4): 1: m/z 345 ($M^+ + H$, 10%), 302 ($M^+ - N_3$, 100%). HRMS (CI, CH_4): calculated for $C_{12}H_{20}GaN_8$ 345.1066; found 345.1063.

[8] The empirical lower limit for the explosivity of covalent azides is 25% by weight of azide nitrogen. S. Patai (ed.), *The Chemistry of the Azide Group,* Interscience, London, 1971.