Mono- and digallane complexes of a tridentate amido-diamine ligand†

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Bis(2-dimethylaminoethyl)amido gallane, $H_2GaN(CH_2CH_2NMe_2)_2$, that melts at 27 °C and remains stable upon heating at 55 °C for two days, was synthesized either from the reaction of the quinuclidine adduct of monochlorogallane with the lithium salt of the corresponding amine, or from the reaction of trimethylamine gallane and the amine; the latter affords an unusual co-product with both GaH_2 and GaH_3 bonded to the same amido nitrogen.

For the chemical vapor deposition of gallium-containing films, there is interest in developing nonpyrophoric, alternative precursors to trimethyl or triethyl gallium. It is also desirable for these precursors to minimize carbon contamination. Gallium hydride complexes that do not contain direct gallium–carbon bonds are attractive candidates.[1] Gallane itself, a hydrogen-bridged dimer $[GaH_3]_2$, decomposes above −30 °C.[2] Room-temperature isolable gallium hydride derivatives are generally stabilized with bulky ligands or they exist as oligomers as exemplified by $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaH_2$,[3] $[H_2GaNMe_2]_3$,[4] $H_2GaN(SiMe_3)_2(quin)$ (where quin = quinuclidine),[5] and $[^tBu(H)GaNEt_2]_2$.[6] The increase in molecular mass renders them less volatile. Although several hydrides with smaller ligands including $[H_2GaNH_2]_3$,[7] $[H_2GaNHNMe_2]_2$,[8] $H_3Ga(quin)$[9] and $[H_2GaN_3]_n$[10] have been used to prepare GaN and GaAs nanocrystals or films at low temperatures, hydride-based precursors with the merits of long-shelf life and high volatility have yet to be discovered. To address these problems, we used a tridentate nitrogen ligand to prepare gallium hydride complexes, and herein report the synthesis and characterization of thermally robust, volatile bis(2-dimethylaminoethyl)amido gallane, $H_2GaN(CH_2CH_2NMe_2)_2$ (**1**), which is a liquid above 27 °C. Along with the synthesis of **1**, an unusual complex in which the amido nitrogen bridges between a gallium dihydride and a trihydride was isolated and structurally characterized.

Compound **1**[11] was initially synthesized from the reaction shown in eqn. 1. A solution of $LiN(CH_2CH_2NMe_2)_2$[12] (1.21 g, 7.33 mmol) in 40 mL of Et_2O was added to a solution of $H_2GaCl(quin)$[13] (1.60 g, 7.33 mmol) in 40 mL of Et_2O at room temperature. The mixture was stirred for 14 h and filtered. The solvent and volatile quinuclidine were removed from the filtrate under vacuum affording a pale-yellow liquid. Fractional distillation under reduced pressure afforded **1** (1.26 g, 75% yield) as a colorless, mobile liquid, which slowly solidified at ambient temperature to form a colorless, crystalline solid.

$$H_2GaCl(quin) + LiN(CH_2CH_2NMe_2)_2 \rightarrow H_2GaN(CH_2CH_2NMe_2)_2 + quin + LiCl \qquad (1)$$

Compound **1** melted at 27 °C. Its vapor pressures, obtained from multiple distillation experiments, were 0.20, 0.37, 0.69 and 0.91 Torr at 40, 48, 57 and 61 °C, respectively. While heating **1** under vacuum at 80 °C resulted in evaporation without decomposition, it started to decompose under N_2 at 100 °C forming $HN(CH_2CH_2NMe_2)_2$ and gray particles that were presumably elemental gallium. Under 1 atm of N_2, **1** survived for 48 h at 55 °C in a glass vial, or 24 h at 50 °C when in contact with stainless steel, and then gradually decomposed as evidenced by the formation of gray particles. Although **1** is air sensitive, it is not pyrophoric. These results suggest that **1** may have practical utility as a gallium precursor in vapor deposition processes (CVD, MOCVD, *etc.*).

The structure of **1**,[14] as shown in Fig. 1, was monomeric with a crystallographically imposed two-fold axis passing through the Ga(1)–N(2) bond. The gallium adopted a distorted trigonal bipyramidal geometry with the two NMe_2 groups occupying the axial positions. The hydrides were located from the electron density map. In the literature, similar structures were found for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaH_2$[3] and $H_2GaCl(quin)_2$.[13] It is noteworthy that $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]GaH_2$ also exhibited a very high thermal stability; its vapor survived up to 350 °C.[3] We speculate that the high thermal stability of these chelating five-coordinate gallium compounds arises from the blocking of the fifth gallium coordination site that otherwise might be used in a decomposition reaction.

A second route to **1** was explored and is shown in Scheme 1. In a typical run, an Et_2O solution (20 mL) of $HN(CH_2CH_2NMe_2)_2$[12]

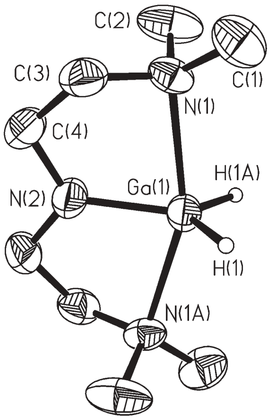

Fig. 1 Structure of **1** showing 50% thermal ellipsoids. The hydrogen atoms except for those on Ga are omitted for clarity. Selected bond distances (Å) and angles (°): Ga(1)–N(2) 1.874(2), Ga(1)–N(1) 2.2826(16), Ga(1)–H(1) 1.47(2); N(1)–Ga(1)–N(2) 79.04(4), N(2)–Ga(1)–H(1) 121.0(8), N(1A)–Ga(1)–H(1) 97.2(8), N(1)–Ga(1)–H(1) 94.0(8).

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† Dedicated to the memory of Ian P. Rothwell

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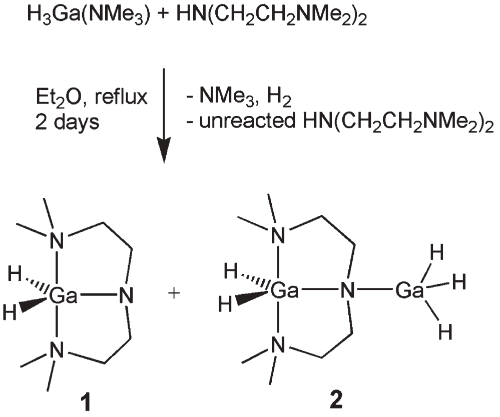

Scheme 1

(9.05 g, 56.8 mmol) was added to a dry ice–2-propanol cooled Et_2O solution (200 mL) of approximately 1 equivalent of freshly prepared $H_3Ga(NMe_3)$.[15] The reaction mixture was refluxed for two days followed by evaporation of Et_2O to give a colorless mixture of **1**, a new compound (**2**) and unreacted $HN(CH_2CH_2NMe_2)_2$ as measured by NMR. Pentane (70 mL) was added to the mixture, which was then filtered. Upon cooling, **2** was isolated from the filtrate as a colorless crystalline solid (1.85 g, 22% yield based on gallium). A liquid mixture of **1**, $HN(CH_2CH_2NMe_2)_2$ and a residue of **2** was obtained after removal of pentane from the mother liquor. Distillation at reduced pressures afforded 6.55 g of **1** (50% yield based on gallium).

Crystalline **2** was stable at low temperatures, but gradually decomposed over a period of a few days at room temperature. For a freshly prepared sample, it decomposed at 69 °C. The IR spectrum (KBr pellet) exhibited ν_{Ga-H} absorptions at 1797, 1871 and 1888 cm^{-1}. The structure of **2** (Fig. 2)[16] was unprecedented in the sense that the bonding of N(2) was covalent to the GaH_2 and dative to the GaH_3. The corresponding N(2)–Ga(1) and N(2)–Ga(2) bond lengths were 1.9922(17) and 2.0582(18) Å, respectively. This is significantly different from that observed in cyclic $(R_2GaNR'_2)_n$ and $(R_2GaNHR')_n$ (where R, R′ = H, alkyl or aryl groups, and n = 2 or 3) compounds, where the bridging Ga–N bond lengths were essentially equal.[17] At room temperature the ^{13}C NMR spectrum of **2** in toluene-d_8 consisted of resonances at 47.7 (NMe_2), 55.3 (CH_2) and 58.0 ppm (CH_2). The inability to resolve distinct methyl resonances was also reflected in the ^1H NMR spectrum. The spectrum, however, displayed broad singlets at 4.51 and 4.78 ppm attributable to the GaH_3 and GaH_2 groups. At −83 °C the proton methyl resonances were resolved consistent with the solid state structure.

It was intriguing that **2** was isolated nearly quantitatively from the reaction of **1** with one equivalent of $H_3Ga(NMe_3)$ in Et_2O at temperatures up to room temperature. This result demonstrated the strong Lewis basicity of the amido ligand in **1**. This strong basicity was further confirmed by the inability to displace $H_2GaN(CH_2CH_2NMe_2)_2$ from **2** with quinuclidine: no reaction occurred after **2** and quinuclidine were stirred in a 1 : 1 molar ratio in Et_2O at room temperature for 4 h.

The stability of **1** does not preclude reactions with Group 15 reagents. At 150 °C in an autoclave, **1** reacted under 12 atm of NH_3 in a period of 40 min to give mainly $[HGaNH]_n$ which exists as oligomeric rods and forms GaN when reacted at higher temperatures.[18] We are applying the $-N(CH_2CH_2NMe_2)_2$ ligand to a number of other metals and using **1** to deposit III–V semiconductor films. These results will be reported in subsequent publications.

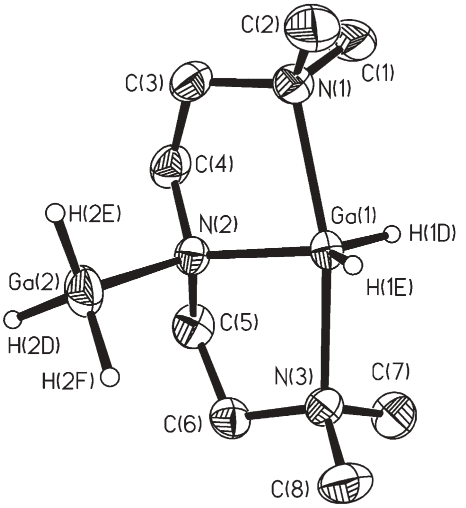

Fig. 2 Structure of **2** showing 50% thermal ellipsoids. The hydrogen atoms except for those on Ga are omitted for clarity. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 2.3140(18), Ga(1)–N(2) 1.9922(17), Ga(1)–N(3) 2.2730(17), Ga(2)–N(2) 2.0582(18), Ga(1)–H(1D) 1.42(3), Ga(1)–H(1E), 1.43(2); N(1)–Ga(1)–N(2) 82.15(7), N(1)–Ga(1)–N(3) 162.93(7), N(2)–Ga(1)–N(3) 82.68(7), N(2)–Ga(1)–H(1D) 114.5(11), N(3)–Ga(1)–H(1D) 88.9(11), N(1)–Ga(1)–H(1D) 90.3(11), N(2)–Ga(1)–H(1E) 119.9(10), N(3)–Ga(1)–H(1E) 96.6(10), N(1)–Ga(1)–H(1E) 97.7(10), H(1D)–Ga(1)–H(1E) 125.6(15), Ga(1)–N(2)–Ga(2), 113.67(9).

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11 Compound **1**. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 2.08 (12H, s, NMe_2), 2.36 (4H, t, $NCH_2CH_2NMe_2$), 3.10 (4H, t, $NCH_2CH_2NMe_2$), 4.90 (2H, br s, GaH_2); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 45.71 (s,

NMe_2), 50.56 (s, CH_2), 61.04 (s, CH_2). MS (CI): $[H_2GaN(CH_2CH_2NMe_2)_2 + H]^+$ (230 amu, 31.3% of the total ion abundance). IR (NaCl window): ν_{GaH}, 1781 cm^{-1}. Anal. calc. for $C_8H_{22}GaN_3$: C, 41.78; H, 9.64; N, 18.27%. Found: C, 41.22; H, 8.69; N, 18.06%.

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14 **Crystal data of 1**. $C_8H_{22}GaN_3$, M = 230.01, orthorhombic, a = 11.010(2), b = 11.706(2), c = 9.4523(19) Å, U = 1218.2(4) $Å^3$, T = 173 K, space group *Pbcn* (no. 60), Z = 4, μ(Mo-Kα) = 2.221 mm^{-1}, 13559 reflections measured, 1412 unique (R_{int} = 0.0362) which were used in all calculations. The final $wR(F^2)$ was 0.0771 (all data). CCDC 266262. See http://www.rsc.org/suppdata/cc/b5/b503705k/ for crystallographic data in CIF or other electronic format.

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16 **Crystal data of 2**. $C_8H_{25}Ga_2N_3$, M = 302.75, orthorhombic, a = 6.1939(14), b = 12.977(3), c = 17.601(4) Å, U = 1414.8(6) $Å^3$, T = 173 K, space group $P2_12_12_1$ (no. 19), Z = 4, μ(Mo-Kα) = 3.779 mm^{-1}, 17128 reflections measured, 3255 unique (R_{int} = 0.0376) which were used in all calculations. The final $wR(F^2)$ was 0.0531 (all data). CCDC 266261. See http://www.rsc.org/suppdata/cc/b5/b503705k/ for crystallographic data in CIF or other electronic format.

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