Johnson Matthey plc for generous loans of ruthenium trichloride.

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Tertiary Amine Adducts of Gallane: Gallane-Rich $[\{GaH_3\}_2(TMEDA)]$ (TMEDA = *N,N,N′,N′*-Tetramethylethylenediamine) and Thermally Robust $[GaH_3(quinuclidine)]$

There has been renewed interest in gallane with the synthesis of digallane, $H_2Ga(\mu\text{-}H)_2GaH_2$,[1] and gallaborane, $H_2Ga(\mu\text{-}H)_2BH_2$,[2] and the use of tertiary amine adducts of gallane in the presence of nitrogen for chemical vapor deposition of gallium nitride.[3] While gallane readily forms adducts with tertiary amines, only an imprecise structure of one of them, H_3GaNMe_3, has been studied in the solid,[4] possibly because of their tendency to decompose to gallium metal, amine, and hydrogen close to room temperature.[5]

Herein we report (i) the synthesis of some new gallane/tertiary amine adducts; (ii) studies on varying the nature of the amine, either the alkyl substituents on the amine or the number of tertiary amine centers/Lewis base, where the thermal stability of the adducts is affected and (iii) the first complete crystal structure determinations of gallane/tertiary amine adducts, viz the 2:1 gallane/TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) and 1:1 gallane/quinuclidine adducts.

Treatment of H_3GaNMe_3[6] with excess TMEDA in diethyl ether gave a 1:1 gallane/TMEDA adduct, $H_3Ga(TMEDA)$, as a white solid, which rapidly lost $^1/_2$ equiv of Lewis base in vacuo (weight loss), via a colorless oil, affording solid $[\{H_3Ga\}_2\{(NMe_2CH_2)_2\}]$ (**1**) in high yield. This and the synthesis of the quinuclidine adduct $[H_3Ga\{N(CH_2CH_2)_3CH\}]$ (**2**) are shown in Scheme I.[7] The instability of the 1:1 gallane/TMEDA adduct with respect to loss of one tertiary amine center/metal center is similar to that established for the gallane/bis(trimethylamine) adduct, which exists only between −45.4 and −22.8 °C, decomposing at higher temperatures to H_3GaNMe_3.[8] In contrast, the corresponding alane/bis(trimethylamine) can be purified as a crystalline solid in the presence of excess trimethylamine.[9] Furthermore, the 1:1 alane/TMEDA adduct is thermally stable, sublimable in vacuo without decomposition.[10]

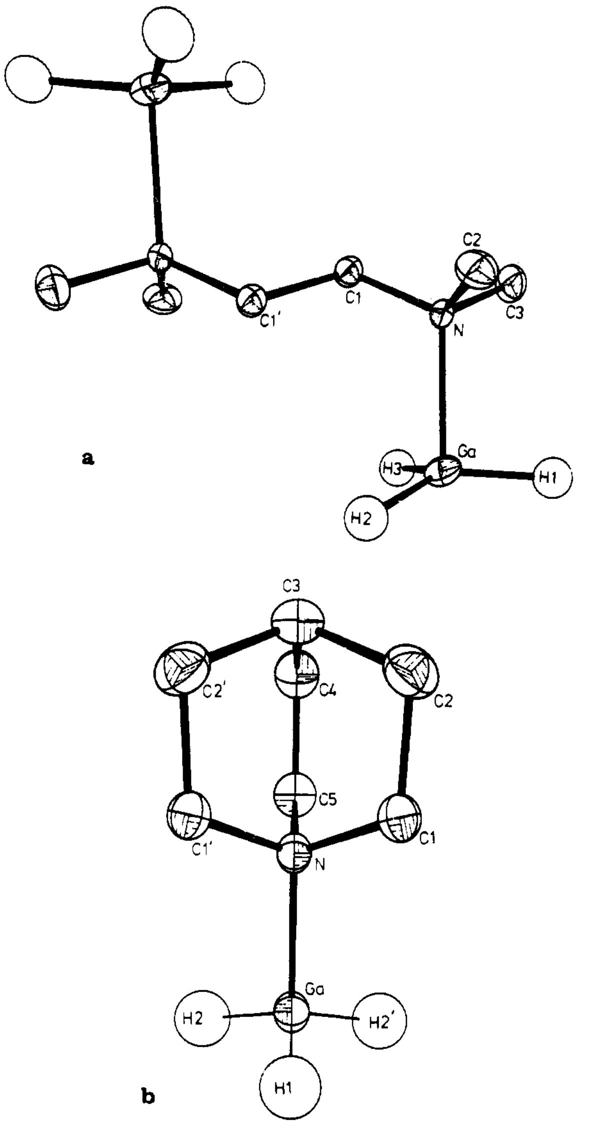

Figure 1. Molecular projections of (a) $[\{H_3Ga\}_2\{(NMe_2CH_2)_2\}]$ (**1**) and (b) $[H_3Ga\{N(CH_2CH_2)_3CH\}]$ (**2**) with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms shown. Bond distances [Å] and angles (deg) are as follows. Compound **1**: Ga–N = 2.094 (4), Ga–H(1,2,3) = 1.36, 1.40, 1.57, N–C(1) = 1.476 (7), N–C(2) = 1.481 (7), N–C(3) = 1.478 (7), C(1)–C(1)′ = 1.51 (1); N–Ga–H(1,2,3) = 103, 99, 97, H(1)–Ga–H(2,3) = 125, 114, H(2)–Ga–H(3) = 112, Ga–N–C(1,2,3) = 113.2 (3), 108.6 (4), 106.9 (4), C(1)–N–C(2,3) = 112.7(5), 106.6 (4), C(2)–N–C(3) = 108.5 (5), N–C(1)–C(1)′ = 113.8 (6). Compound **2**: Ga–N = 2.063 (4), Ga–H(1,2) = 1.69 (6), 1.55 (5), N–C(5) = 1.507 (6), C(1)–C(2) = 1.529 (5), C(2)–C(3) = 1.525 (5), C(3)–C(4) = 1.514 (7), C(4)–C(5) = 1.514 (7); N–Ga–H(1,2) = 100 (2), 105 (2), H(1)–Ga–H(2) = 117 (2), H(2)–Ga–H(2)′ = 110 (2), Ga–N–C(1,5) = 110.7 (2), 110.6 (3), C(1)–N–C(1)′ = 108.1 (3), C(1)–N–C(5) = 108.3 (3), N–C(1)–C(2) = 111.9 (3), C(1)–C(2)–C(3) = 108.7 (3), C(2)–C(3)–C(2)′ = 108.3 (3), C(2)–C(3)–C(4) = 109.1 (3), C(3)–C(4)–C(5) = 109.6 (4), N–C(5)–C(4) = 114.4 (4).

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(7) Compounds **1** and **2** were synthesised as follows. To synthesize **1**, a solution of TMEDA (1.3 mL, 8.64 mmol) in OEt_2 (5 mL) was added over 30 min to H_3GaNMe_3 (0.95 g, 7.20 mmol, prepared by a variation of the literature procedure)[6] in OEt_2 (15 mL) at 0 °C. After 1 h at room temperature, volatiles were removed in vacuo, to yield initially a white solid, then after 1 min a colourless oil followed by a white solid of **1** after 3–5 min. This was recrystallized as colorless prisms overnight at −20 °C from OEt_2 (15 mL) (0.88 g, 95% yield). Mp: 74–76 °C dec. ^1H NMR (300 MHz, toluene-d_8, 243 K): δ (relative to TMS) 1.49 (12 H, s, CH_3) 2.55 (4 H, s, CH_2), 4.78 (6 H, broad s, GaH_3); ^{13}C NMR (243 K): δ 46.64 (s, CH_3) 56.7 (s, CH_2). IR: ν_{Ga-H} 1840 cm^{-1}. To synthesize **2**, quinuclidine hydrochloride (1.96 g, 13.4 mmol) was added over 30 min to a solution of $Li[GaH_4]$ (1.08 g, 13.4 mmol, prepared by a variation of the literature procedure)[6] in OEt_2 (100 ml) at −80 °C, resulting in an immediate evolution of gas. After warming to room temperature, the mixture was stirred for 2 h and then filtered and the volatiles removedc in vacuo to yield a white solid. Sublimation of the resulting white solid (0.2 mmHg, 65–70 °C) afforded colorless prisms of **2** (2.32 g, 94% yield). Mp: 100–101 °C dec. ^1H NMR (250 MHz, C_6D_6): δ (relative to TMS) 0.93 (6 H, m, CH_2), 1.12 (1 H, m, CH) 2.60 (6 H, t, NCH_2) 4.80 (3 H, broad s, GaH_3); ^{13}C NMR, δ 19.26 (s, CH) 25.0 (s, CH_2) 48.87 (s, CH_2N). IR: ν_{Ga-H} 1810 cm^{-1}. Anal. Calcd for $C_7H_{16}GaN$: C, 45.7; H, 8.8; N, 7.6. Found: C, 46.1; H, 8.7; N, 7.7.

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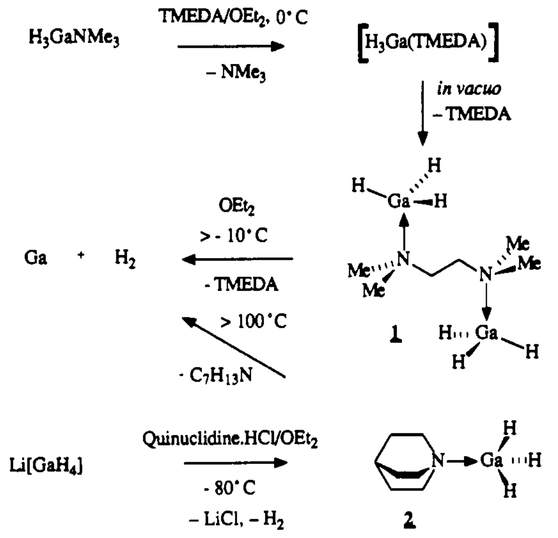
Scheme I



Compound **1** slowly decomposes in solution above −10 °C and in the solid at ca 20 °C to gallium metal, hydrogen and amine, as for the related compound, H_3GaNMe_3.[8] In contrast, the 1:1 adduct is stable for days at room temperature in solution and in the solid. We have also attempted to prepare other gallane/polydentate tertiary amine adducts, namely those based on (−)-sparteine and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine. Although adducts are formed at low temperatures they rapidly decompose to gallium close to ca. 20 °C. Overall, polydentate amines seemingly destabilize gallane; the opposite prevails for alane.[10] Quinuclidine is a unidentate amine that enhances the stability of gallane relative to H_3GaNMe_3, most likely because it is a stronger base. Its adduct, **2**, has remarkable thermal stability, being stable for months at room temperature, subliming in vacuo at 65–70 °C, and decomposing only above ca. 100 °C.

Results of the X-ray structure determinations of **1** and **2**[11] are presented in Figure 1. Both are comprised of discrete molecules possessing a crystallographic inversion center, **1**, or mirror plane, **2**, so that the metal centers in **1** are remote, ruling out intramolecular hydride bridging. The Ga–N distances, 2.094 (4) Å in **1** and 2.063 (4) Å in **2**, reflect the differences in thermal stability of the two compounds and amine base strength, and compare with 2.124 (7) Å for the analogous distance derived from the gas-phase structure determination of H_3GaNMe_3.[12] (An inaccurate and incomplete X-ray structure determination on this compound yielded Ga–N = 1.97 (9) Å.[4]) Given that aluminum and gallium have the same covalent radius, it is interesting to note that an Al–N distance of 2.063 (8) Å in the related compound H_3AlNMe_3 (2.063 (8) Å gas phase)[13] is consistent with it possessing similar thermal stability relative to **2** yet greater thermal stability relative to **1**. The hydrido groups and *N*-alkyl substituents are staggered in both compounds.

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council.

Supplementary Material Available: Tables listing atomic positional parameters, ligand hydrogen atom parameters, anisotropic thermal parameters, extended metal core geometries, and ligand non-hydrogen geometries (5 pages); tables of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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[11] Crystallographic data ($T = 296$ K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries): for compound **1**, $C_6H_{22}Ga_2N_2$, $M = 261.7$, monoclinic, space group $P2_1/n$, $a = 5.891$ (6) Å, $b = 17.073$ (2) Å, $c = 6.728$ (1) Å, $\beta = 114.161$ (9)°, $V = 617.5$ (27) Å^3, $F(000) = 268$, $Z = 2$, $D_c = 1.413$ g·cm^{-3}, μ(Cu Kα) = 49.5 cm^{-1}, $A^* = 0.71$–0.92, specimen dimensions 0.08 × 0.31 × 0.42 mm, 821 unique reflections, 737 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max} = 110°$; for compound **2**, $C_7H_{16}GaN$, $M = 184.0$, monoclinic, space group $P2_1/m$, $a = 6.1276$ (7) Å, $b = 9.058$ (1) Å, $c = 8.226$ (1) Å, $\beta = 98.24$ (1)°, $V = 451.9$ (6) Å^3, $F(000) = 192$, $Z = 2$, $D_c = 1.357$ g·cm^{-3}, μ(Cu Kα) = 29.7 cm^{-1}, $A^* = 0.75$–0.98, specimen dimensions 0.06 × 0.21 × 0.24 mm, 861 unique reflections, 680 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max} = 110°$. The structures were solved with the heavy-atom method and refined by full-matrix least-squares refinement with non-hydrogen atoms anisotropic. Hydrogen atoms were located on difference maps and included as invariants for **1** or refined in *x*, *y*, *z* for **2**. Unit weights were used and the final residuals were $R = 0.042$ and 0.029 and $R' = 0.046$ and 0.030, for **1** and **2**, respectively.

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Synthesis and X-ray Crystal Structure of a C_2B_4 "Carbons Apart" Carborane Dianion. 2,4-Bis(trimethylsilyl)-2,4-dicarba-*nido*-hexaborate(2−): A New Synthon in Organometallics

The dianions of the *nido*-carboranes, particularly of the C_2B_4, C_2B_9, and C_2B_{10} systems, have been the building blocks of a wide variety of metallacarboranes of main group and transition metals.[1] However, X-ray structural information is available for only a few selected monoanions[2–6] and for an unusual bis[triphenylmethylphosphonium] salt of the bis(carborane), which is, in fact, closely related to the structure of the most stable isomer of [*nido*-$C_2B_{10}H_{13}$]$^-$ anion with 0941 *styx* topology.[7] Unlike the *nido*-C_2B_9 and *nido*-C_2B_{10} carborane systems, only the dilithium and sodium lithium salts of the "carbons adjacent" *nido*-C_2B_4 carborane dianions have been synthesized, and the corresponding disodium salt could not be made.[8] However, the new dianion [*nido*-2,4-$(Me)_2$-2,4-$C_2B_4H_4$]$^{2-}$ (I) was made recently via the two-electron reduction of *closo*-1,6-$(Me)_2$-1,6-$C_2B_4H_4$ (II) in the presence of lithium naphthalide in THF, and its "carbons apart" geometry was assigned on the basis of ^{11}B NMR spectroscopy and ab initio/IGLO calculations.[9] Nevertheless, the crystal structures

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