# Gallane Adducts of Bifunctional Group V Ligands; Crystal Structures of $(GaH_3)_2$(tmen) and $(GaH_3)_2$(dmpe)†

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Treatment of $GaH_3NMe_3$ with either tmen or dmpe yields $(GaH_3)_2$(tmen) **1** and $(GaH_3)_2$(dmpe) **2**; the X-ray structure of **2** is the first structure determination of a phosphine adduct of a gallium hydride.

Although the epitaxial growth of semiconductors by metal organic vapour phase epitaxy (MOVPE) or chemical beam epitaxy (CBE) has developed rapidly in recent years, a reduction in the amount of carbon incorporated into the films over current levels achievable still represents an important research target in many instances.[1,2] $AlH_3(NMe_3)$ and $GaH_3(NMe_3)$ have recently been reported as excellent sources for the growth of high purity metal films on both silicon and gallium arsenide substrates *via* CBE[3–5] and MOVPE.[6] Electronic grade samples of $AlH_3(NMe_3)$ are now commercially available and are being used in device fabrication whereas the relatively lower thermal stability of $GaH_3(NMe_3)$ means that its very favourable surface chemistry may not be commercially exploited. In this paper we report the synthesis, characterisation and X-ray structure determinations of some novel volatile gallane derivatives with relatively high thermal stability.

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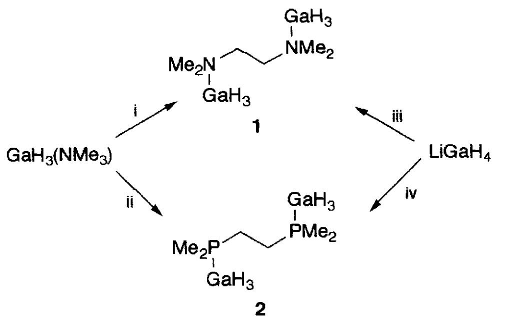
† tmen = *N,N,N′,N′*-tetramethylethylenediamine; dmpe = 1,2-bis-(dimethylphosphino)ethane.



**Scheme 1** *Reagents and conditions*: i, tmen, room temp., $-NMe_3$; ii, dmpe, room temp., $-NMe_3$; iii, tmen·2HCL, tmen, 0 °C, $-H_2$, $-LiCl$: iv, dmpe·2HCl, −10 °C, $-H_2$, $-LiCl$

Condensation of an excess of either tmen or dmpe onto $GaH_3(NMe_3)$[7] at −196 °C followed by warming to room temperature leads to the efficient loss of $NMe_3$ and formation of $(GaH_3)_2$(tmen) **1** and $(GaH_3)_2$(dmpe) **2**, respectively.‡ Alternatively $LiGaH_4$ can be treated with the hydrochloride salts dmpe·2HCl in diethyl ether or tmen·2HCl (Scheme 1). X-Ray-quality crystals of both **1** and **2** were obtained by slow crystallisation from toluene solutions at −20 °C. Compounds **1** and **2** have been characterised by NMR and IR spectroscopy, mass spectrometry, elemental microanalysis and X-ray crystal structure determinations.§

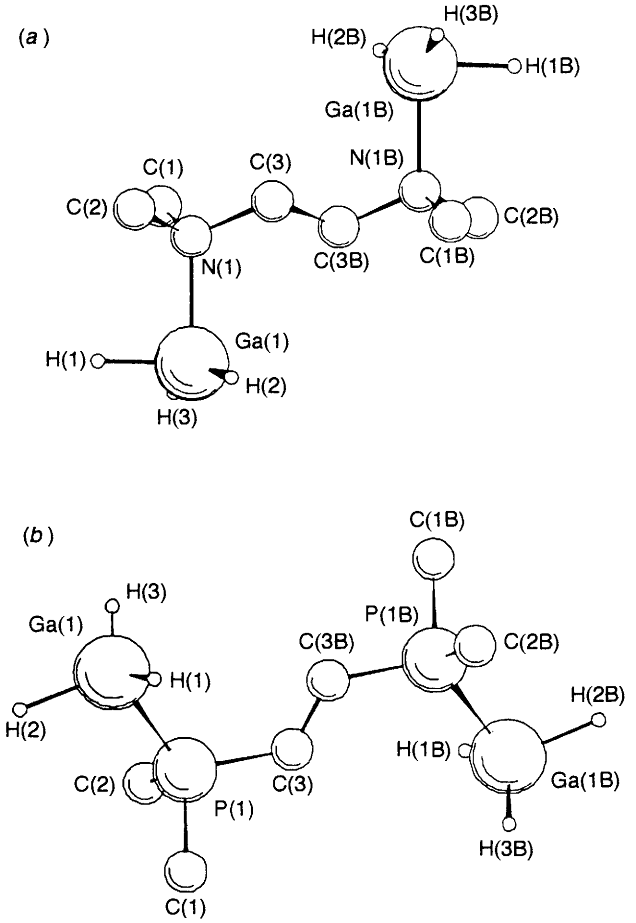


**Fig. 1** (*a*) The structure of $(GaH_3)_2$(tmen) **1**: selected bond lengths (Å) and angles (°): Ga(1)–N(1) 2.085(3), Ga(1)–H(1) 1.54(6), Ga(1)–H(2) 1.32(7), Ga(1)–H(3) 1.45(7), N(1)–C(1) 1.480(5) N(1)–C(2) 1.492(5), N(1)–C(3) 1.498(4), C(3)–C(3B) 1.508(7), C(1)–N(1)–Ga(1) 109.7(2), C(2)–N(1)–Ga(1) 107.4(2), C(2)–N(1)–C(1) 108.4(3), C(3)–N(1)–Ga(1) 113.1(2), C(3)–N(1)–C(1) 111.8(3), C(3)–N(1)–C(2) 106.2(3), H(1)–Ga(1)–H(2) 88.1(16), H(1)–Ga(1)–H(3) 99.7(30), H(2)–Ga(1)–H(3) 109.5(30), C(3B)–C(3)–N(1) 112.7(3). (*b*) The structure of $(GaH_3)_2$(dmpe) **2**: selected bond lengths (Å) and angles (°): Ga(1)–P(1) 2.403(1), Ga(1)–H(1) 1.40(8), Ga(1)–H(2) 1.59(6), Ga(1)–H(3) 1.35(9), P(1)–C(1) 1.798(6), P(1)–C(2) 1.796(6), P(1)–C(3) 1.787(7), C(3)–C(3B) 1.29(1), C(1)–P(1)–Ga(1) 112.9(2), C(2)–P(1)–Ga(1) 115.2(2), C(2)–P(1)–C(1) 104.4(3), C(3)–P(1)–Ga(1) 115.0(2), C(3)–P(1)–C(1) 102.9(5), C(3)–P(1)–C(2) 105.2(4), H(1)–Ga(1)–H(2) 102.0(30), H(1)–Ga(1)–H(3) 102.5(24), H(2)–Ga(1)–H(3) 101.7(39), C(3B)–C(3)–P(1) 126.1(9).

Compared with their $NMe_3$ or $PMe_3$ analogues respectively, which decompose over several hours at room temperature, both **1** and **2** appear to be significantly more thermally stable. NMR studies showed that a solid sample of neither complex decomposes significantly after 2 days at room temperature, but over a period of weeks substantial decomposition does occur. However, solutions in toluene decompose completely after standing for 1–2 days at room temperature. Compounds **1** and **2** are less volatile than their $NMe_3$ or $PMe_3$ analogues which sublime readily at room temperature; **2** may be sublimed *in vacuo* at 50 °C ($<10^{-5}$ Torr) but decomposes rapidly at 65 °C, whereas **1** sublimes with decomposition at *ca.* 70 °C ($<10^{-5}$ Torr).

Results of the X-ray structure determinations for both **1** and **2** are shown in Fig. 1. The crystal structures are consistent with all the spectroscopic data and show that both didentate ligands bridge between two gallane moieties rather than forming five-coordinate chelate complexes. This contrasts dramatic-

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‡ *Synthesis and characterisation*: Method (*i*); in the absence of any solvent, *N,N,N′,N′*-tetramethylethylenediamine (tmen) (0.61 $cm^3$, 4.02 mmol) or 1,2-bis(dimethylphosphino)ethane (dmpe) (0.72 $cm^3$, 3.84 mmol) was condensed *in vacuo* at −196 °C onto $GaH_3(NMe_3)$ (0.502 g, 3.8 mmol). The solution was allowed to warm slowly to room temperature. After 0.5 h, excess of ligand was removed *in vacuo* at 10 °C leaving a white solid which was taken up in toluene. The resulting solution was reduced in volume and cooled very slowly to −20 °C, affording crystals of **1** and **2** (32% yield).

Method (*ii*): tmen (7.5 $cm^3$, 50 mmol) was condensed *in vacuo* at −196 °C onto a solid mixture of $LiGaH_4$ (1.02 g, 12.6 mmol) and tmen·2HCl (1.64 g, 8.7 mmol). The mixture was warmed slowly to room temeprature, stirred for 0.5 h and filtered. Excess of tmen was removed *in vacuo* at −20 °C leaving a white solid **1** (0.74 g, 44% yield). A solution of $LiGaH_4$ (0.324 g, 4.0 mmol) in diethyl ether (50 $cm^3$) was added to a stirred suspension of dmpe·2HCl (0.66 g, 2.96 mmol) in diethyl ether (50 $cm^3$) during 1 h at −30 °C. After stirring for 1 h at −10 °C the solution was filtered and the solvent removed *in vacuo* forming a white solid **2** (0.22 g, 37% yield).

For **1**: $^1H$ NMR (300 MHz, $CD_3C_6D_5$, −80 °C), δ 4.93 (6H, s, GaH), 2.45 (4H, s, $CH_2$) and 1.68 (12H, s, $NMe_2$); IR: $\nu_{Ga\text{-}H}$ 1804 $cm^{-1}$; *m/z* 187 ($M^+$-$GaH_2$). For **2**; $^1H$ NMR (300 MHz, $CD_3C_6D_5$, −50 °C), δ 4.28 (6H, s, GaH), 1.25 (4H, s, $CH_2$) and 0.42 (12H, s, $PMe_2$); IR: $\nu_{Ga\text{-}H}$ 1829 $cm^{-1}$; MS: *m/z* 295 ($M^+$) and 223 ($M^+ - GaH_3$). Satisfactory elemental analysis results were obtained.

§ *Crystal data* for **1**: $C_6H_{22}Ga_2N_2$, $M = 261.69$, monoclinic, space group $P2_1/n$, $a = 6.724(3)$, $b = 17.067(2)$, $c = 5.893(1)$ Å, $\beta = 114.70(3)°$, $Z = 2$, $D_c = 1.41$ g $cm^{-3}$, $U = 617.0$ Å$^3$, $\mu$(Mo-$K\alpha$) = 43.07 $cm^{-1}$, $F(000) = 268$. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-Kα X-rays. Data were corrected for Lorentz–polarisation and absorption effects. Full-matrix least-squares refinement of 60 parameters gave $R = 0.041$, $R_w = 0.0465$ for 1075 reflections with $I > 3\sigma(I)$.

*Crystal data* for **2**: $C_6H_{22}Ga_2P_2$, $M = 295.63$, monoclinic, space group $P2_1/a$, $a = 10.262(2)$, $b = 11.494(3)$, $c = 6.232(2)$ Å, $\beta = 102.20(2)°$, $Z = 2$, $D_c = 1.36$ g $cm^{-3}$, $U = 718.51$ Å$^3$, $\mu$(Mo-Kα) = 43.07 $cm^{-1}$, $F(000) = 300$. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-Kα X-rays. Data were corrected for Lorentz–polarisation and absorption effects. Full-matrix least-squares refinement of 60 parameters gave $R = 0.0347$, $R_w = 0.0436$ for 885 reflections with $I > 3\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ally with $AlH_3$(tmen) which has been shown to have a polymeric chain structure in the solid state.[8] In the solid state both **1** and **2** lie on crystallographic twofold axes bisecting the C(3)–C(3B) bond of the tmen and dmpe ligands, respectively. The gallium coordination in both **1** and **2** is as expected pyramidal with Ga–N and Ga–P bond lengths of 2.085(3) and 2.403(1) Å, respectively. The Ga–N bond length is in good agreement with the Ga–N bond length of 1.97(7) Å found for $GaH_3(NMe_3)$.[9] No phosphine adducts of complexes containing Ga–H bonds have been previously structurally characterized; however, $(GaMe_3)_2(Ph_2PCH_2CH_2PPh_2)$ has a Ga–P bond length of 2.546(4) Å.[10] The X-ray diffraction data were of sufficiently high quality to allow the location and refinement of both the positional and isotropic thermal parameters of the gallium hydrides. The mean Ga–H distances were 1.44(7) and 1.45(7) Å for **1** and **2**, respectively. These distances are comparable to those found in the electron-diffraction studies on $[H_2Ga(NMe_2)]_2$ [Ga–H 1.487(4) Å][11] and $Ga(BH_4)_2H$ [Ga–H 1.774(2) Å].[12]

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