Chloride and Phosphide-substituted Gallium Hydrides: [Cy$_3$PGaH$_{3-n}$Cl$_n$], n = 1 or 2, and Trimeric [{H$_2$Ga(μ-PCy$_2$)}$_3$]

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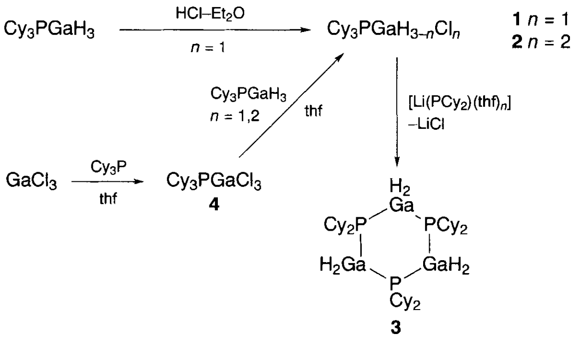
Thermally robust chlorogallanes, Cy$_3$PGaH$_2$Cl **1** and Cy$_3$PGaHCl$_2$ **2**, accessible by redistribution reactions involving Cy$_3$PGaH$_3$ and Cy$_3$PGaCl$_3$ (Cy = cyclohexyl) or **1** *via* anhydrous HCl reaction with Cy$_3$PGaH$_3$, show phosphine but not chloride–hydride exchange in aromatic solvents; treatment of **1** with [Li(PCy$_2$)(thf)$_n$] affords trimeric [{H$_2$Ga(μ-PCy$_2$)}$_3$] **3**, which crystallises in a twist-boat conformation.

The generation of thin films of group 13/15 semiconductor materials is the driving force for the development of single-source precursors of the general type L$_n$MEL′$_n$ that feature the desired 1 : 1 stoichiometry of the elements.[1,2] Deposition studies of selected alkylated precursors have yielded favourable results.[1,3,4] The incorporation of hydride ligands in preference to carbon-based ligands ensures a reduction in the amount of carbonaceous contaminant in the deposited films. While the synthesis of donor adducts of group 13 metal hydrides is well developed[5,6] and the trialkylamine adducts of alane and gallane have been used in the successful production of metal and semiconductor thin films,[7,8] there have been only limited studies on generating group 13/15 compounds, H$_n$MEL$_n$. These deal with dialkylaminoalanes,[9] a trimeric aluminium phosphide [{H$_2$Al(μ-PEt$_2$)}$_3$],[10] two monomeric base-stabilised phosphino- and arsino-alanes, Me$_3$NAl(EMes$_2$)H$_2$ (Mes = mesityl, E = P or As),[5] and for gallium, amidogallane [(H$_2$GaNH$_2$)$_3$].[4]



Scheme 1 Cy = C$_6$H$_{11}$

In developing suitable reagents to gain access to gallane analogues of the type H$_n$GaEL$_n$, phosphine adducts of chlorogallane have been targeted. Trimethylamine adducts of a number of halogenogallanes have been prepared, but none have been structurally authenticated. These compounds were prepared by the reaction of Me$_3$NGaH$_3$ with hydrogen halide gas[11] and *via* redistribution of Me$_3$NGaH$_3$ and Me$_3$NGaCl$_3$. Lewis base-free chlorogallane, [(GaH$_2$Cl)$_2$], is accessible from GaCl$_3$ and Me$_3$SiH, but it suffers from stringent synthetic requirements including exclusion of air, and decomposes at room temperature.[12] Herein, we report the synthesis‡ and properties of thermally robust, moderately air-stable tricyclohexylphosphine adducts of mono- and di-chlorogallane, Cy$_3$PGaH$_2$Cl **1** (decomp. > 164 °C), and Cy$_3$PGaHCl$_2$ **2** (decomp. > 185 °C), and show the synthetic utility of **1** in the synthesis of thermally robust trimeric phosphidogallane [{H$_2$Ga(μ-PCy$_2$)}$_3$], **3** (decomp. > 150 °C).

Compound **1** was prepared by the reaction of Cy$_3$PGaH$_3$ with 1 equiv. of HCl, or more conveniently *via* redistribution involving Cy$_3$PGaH$_3$ and Cy$_3$PGaCl$_3$ **4**, in the appropriate ratio, which was the method of synthesis of **2** (Scheme 1);‡ the reaction of Cy$_3$PGaH$_3$ with HgCl$_2$ (ratio 1 : 2) afforded a mixture of compounds, Cy$_3$PGaH$_n$Cl$_{3-n}$ (n = 1–3) (NMR, IR). In contrast the aluminium analogue of **1**, Cy$_3$PAlH$_2$Cl, is readily

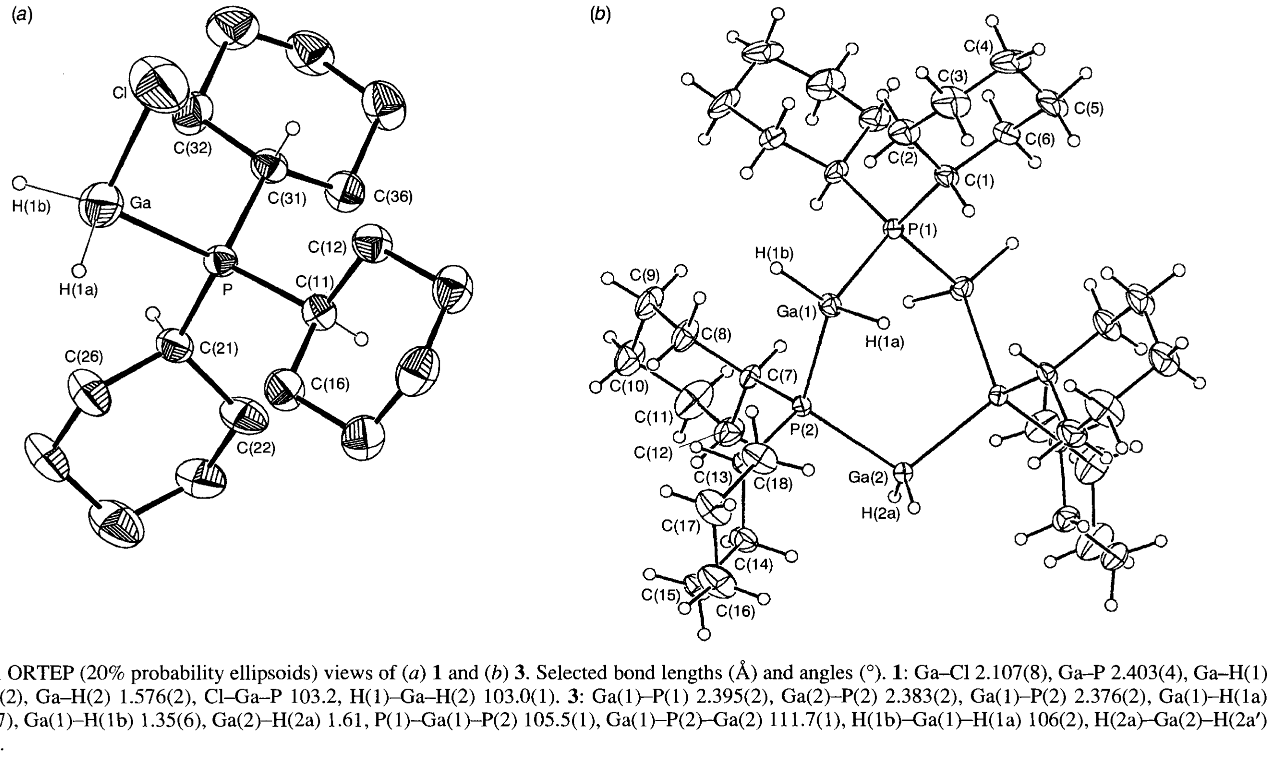


Fig. 1 ORTEP (20% probability ellipsoids) views of (*a*) **1** and (*b*) **3**. Selected bond lengths (Å) and angles (°). **1**: Ga–Cl 2.107(8), Ga–P 2.403(4), Ga–H(1) 1.608(2), Ga–H(2) 1.576(2), Cl–Ga–P 103.2, H(1)–Ga–H(2) 103.0(1). **3**: Ga(1)–P(1) 2.395(2), Ga(2)–P(2) 2.383(2), Ga(1)–P(2) 2.376(2), Ga(1)–H(1a) 1.56(7), Ga(1)–H(1b) 1.35(6), Ga(2)–H(2a) 1.61, P(1)–Ga(1)–P(2) 105.5(1), Ga(1)–P(2)–Ga(2) 111.7(1), H(1b)–Ga(1)–H(1a) 106(2), H(2a)–Ga(2)–H(2a′) 109.4.

prepared from Cy_3PAlH_3 with $HgCl_2$.[13] Compound **1** reacts with $[Li(PCy_2)(thf)_n]$, prepared *in situ*, to give compound **3**.

Compounds **1**–**4** were characterised by NMR, IR, microanalysis and X-ray structure determinations on **1** and **3**. The chlorogallane derivatives **1** and **2** gave characteristic broad ^1H NMR hydride resonances (δ 5.46 and 4.86, respectively). Indeed, the purity of these compounds and the presence of Cy_3PGaH_3 (δ 4.23) can be easily determined from the ^1H NMR spectra (and IR). In benzene solvents containing **1**, **2**, **4** and Cy_3PGaH_3 there is no chloride–hydride redistribution between the MH_3Cl_{3-n} moieties, unlike in thf. However, in benzene and also in toluene, phosphine exchange prevails. The ^{31}P NMR spectrum for an equimolar mixture of **1** and Cy_3PGaH_3 in toluene comprises a single resonance at δ 6.8. On warming coalescence occurs at $-50\,°C$ with two resonances at $-80\,°C$ corresponding to **1** and Cy_3PGaH_3[14] [eqn. (1), $k = 3.1 \times 10^3\ s^{-1}$, $\Delta G^\ddagger = 9.4\ kcal\ mol^{-1}$ (1 cal = 4.184 J)].

$$Cy_3PGaH_3 + Cy_3P'GaH_2Cl \overset{k}{\rightleftharpoons} Cy_3P'GaH_3 + Cy_3PGaH_2Cl \quad (1)$$

The hydride resonance in the ^1H NMR spectrum of **3** appears to be a poorly resolved triplet (δ 4.68) consistent with coupling of the hydrides to two equivalent P centres. The proton-coupled ^{31}P NMR shows a broad singlet (full width half height 56 Hz) at a similar shift to the $^{31}P\{^1H\}$ NMR spectrum, δ −33.

The structures of **1** and **3** are shown in Fig. 1,§ and represent the first solid state structures of a chlorogallane and a phosphido gallium dihydride species. Molecules of **1** comprise the asymmetric unit, revealing a distorted tetrahedral metal centre. The Ga–P distance of 2.403(4) Å is significantly shorter than those established for the related phosphine adducts of gallane [2.460(2) Å, Cy_3PGaH_3; 2.444(6) Å, $Bu^t{}_3PGaH_3$],[14,15] consistent with the expected higher Lewis acidity of GaH_2Cl relative to GaH_3. The Ga–Cl distance of 2.107(8) Å is shorter than those in the addition compound Me_3PGaCl_3 [2.171(2) and 2,176(2) Å],[16] and predicted values established for GaH_2Cl.[17,18] In compound **3** the asymmetric unit is half the molecule, the other half being generated by a crystallographic C_2 axis. Thus, there are two independent Ga–P distances, 2.395(2) and 2.383(2) Å, which are not unusual. Overall, the inner core of the complex adopts a twist-boat conformation similar to that observed for the related complex, $[\{Me_2Ga(\mu\text{-}PPr^i{}_2)\}_3]$,[19] which has comparable Ga–P distances of 2.442 and 2.428 Å.

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Footnotes

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‡ **1**: A solution of **4** (0.16 g, 0.35 mmol) in thf (30 ml) was added to a solution of H_3GaPCy_3 (0.25 g, 0.71 mmol) in thf (30 ml) at 0 °C, the solvent was removed *in vacuo* after stirring for 16 h, to give a white powder which was recrystallised from Et_2O (*ca.* −30 °C); 0.34 g, yield 84%; mp 164–166 °C (decomp.); ^1H NMR (200 MHz, C_6D_6): δ 5.46 (br s, GaH), 1.84, 1.57, 1.37, 1.02, (3H, 3H, 2H, 3H, m, C_6H_{11}); ^{13}C NMR (50.3 MHz, C_6D_6): δ 31.3 (d, PCH, $^1J_{C-P}$ 15.0 Hz), 29.8 (s, CCH_2), 27.5 (d, CCH_2, $^2J_{C-P}$ 10.4 Hz), 26.3 (s, CCH_2); ^{31}P NMR (81 MHz, C_6D_6): δ 1.9 (*cf.* 9.2 free ligand); IR ν(Ga–H)/cm^{-1} 1880 (br).

2: A solution of H_3GaPCy_3 (0.09 g, 0.24 mmol) dissolved in thf (30 ml) was added to a solution of Cl_3GaPCy_3 (0.22 g, 0.48 mmol) in thf (50 ml) at 0 °C. The solvent was removed *in vacuo* after stirring for 16 h, to give a white powder which was recrystallised from Et_2O at −26 °C to give white cubic crystals; mp 174–176 °C; ^1H NMR (200 MHz, C_6D_6): δ 4.86 (br s, GaH), 2.00, 1.83, 1.51, 0.98, (3H, 3H, 2H, 3H, m, C_6H_{11}); ^{13}C NMR (50.3 MHz, C_6D_6): δ 28.8 (s, CH), 28.0 (s, CH_2), 26.4 (d, CH_2), 25.3 (s, CH_2); ^{31}P NMR (81 MHz, C_6D_6): δ 0.7 (*cf.* 9.2 free ligand); IR: ν(Ga–H)/cm^{-1} 1925.

3: A solution of $[Li(PCy_2)(thf)_n]$ (2.3 mmol), prepared *in situ* from $HPCy_2$ and Bu^nLi, in thf (20 ml) was added to a solution of Cy_3PGaH_2Cl (0.88 g, 2.3 mmol) in thf (30 ml) at 0 °C, after 10 min the mixture was stirred at ambient temperature for 24 h. Filtration and cooling to *ca.* −30 °C yielded some H_3GaPCy_3 (X-ray, IR and ^1H NMR). The mother liquor was concentrated and cooled to *ca.* −30 °C to yield colourless crystals of **3**; 0.31 g, yield 50%; mp > 150 °C (decomp.); ^1H NMR (200 MHz, C_6D_6): $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): δ −32.7; IR ν(Ga–H)/cm^{-1} 1844s, 1818s.

4: A solution of PCy_3 (0.45 g, 1.60 mmol) dissolved in Et_2O (30 ml) was added to a solution of $GaCl_3$ (0.28 g, 1.60 mmol) in Et_2O (30 ml) with stirring at room temperature. A white precipitate formed immediately. The reaction mixture was stirred for 2 h. The solvent was removed *in vacuo* to give a white crystalline powder which was recrystallised from thf at −26 °C to give colourless cubic crystals, 0.65 g, yield 89%; mp 189 °C; ^1H NMR (200 MHz, C_6D_6): δ 2.05, 1.84, 1.72, 1.35, (3H, 3H, 2H, 3H, m, C_6H_{11}); ^{13}C NMR (50.3 MHz, C_6D_6); δ 32.0 (d, CH), 28.7 (s, CH_2), 27.9 (d, CH_2), 26.8 (s, CH_2); ^{31}P NMR (81.0 Hz, C_6H_6): δ 10.8 (*cf.* 9.2 free ligand).

Satisfactory elemental analyses were obtained for **1**, **3** and **4**.

§ *Crystal data*: for **1** (T = 297 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries, λ = 0.71069 Å), $C_{18}H_{35}ClGaP$, M = 387.67, monoclinic, space group $P2_1/c$, a = 8.207(6), b = 13.580(3), c = 18.84(1) Å, β = 97.27(4)°, U = 1031.5 Å^3, $F(000)$ = 824, Z = 4. D_c = 1.236 g cm^{-1}, μ(Mo-Kα) = 15.2 mm^{-1}, specimen 0.25 × 0.30 × 0.30 mm, 4031 unique reflections, 1979 with $I > 2.5\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°. The hydride atoms were located in difference Fourier maps and fixed in those positions.

For **3** (T = 297 K; Rigaku AFC7R diffractometer, crystals, mounted in capillaries, λ = 0.71069 Å) $C_{36}H_{72}Ga_3P_3$, M = 807.05, monoclinic, space group $C2/c$, a = 21.734(6), b = 10.930(3), c = 20.146(5) Å, β = 119.33(2)°, U = 4172(1) Å^3. $F(000)$ = 1704, Z = 4, D_c = 1.285 g cm^{-1}, μ(Mo-Kα) = 20.6 cm^{-1}, specimen 0.45 × 0.50 × 0.70 mm, 1486 unique reflections, 957 with $I > 3\sigma(I)$ used in the refinement, $2\sigma_{max}$ = 40.1°. Hydride H(2a) was located in a difference map and fixed. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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