Synthesis and molecular structure of $[Bu^t{}_2Ga\{\mu\text{-}O_2P(Ph)OGaBu^t{}_2\}]_2$: a novel three-coordinate gallium compound

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The reaction of $GaBu^t{}_3$ with phenylphosphonic acid results in the formation of the unusual phosphonate bridged dimer, $[Bu^t{}_2Ga\{\mu\text{-}O_2P(Ph)OGaBu^t{}_2\}]_2$, whose molecular structure consists of two four- and two three-coordinate gallium centres; while $[Bu^t{}_2Ga\{\mu\text{-}O_2P(Ph)OGaBu^t{}_2\}]_2$ exists as the *trans* isomer in the solid state, it undergoes a *trans* to *cis* isomerization in solution, ΔH = 7 ± 1 kJ mol^{-1} and ΔS = 25 ± 4 J mol^{-1} K^{-1}.

The chemical design of controlled interfacial and surface chemistry has become a major research area in both inorganic and organic chemistry.[1] Langmuir–Blodgett (LB) monolayers have long been known, especially with relevance to lipid layers, while in 1946 Bigelow *et al.*[2] reported the phenomenon of self assembly of molecular films on surfaces. Since this time self-assembled monolayers (SAMs) have been extensively studied, in particular those on gold,[3] Al_2O_3[4] and SiO_2.[5] We have recently become interested in the chemical modification of the surface of the new cubic phase of GaS[6] for microelectronic chemical sensor applications.[7] Based upon analogy with the work of Mallouk and coworkers[8] we have investigated alkylphosphonate, $[RPO_3]^{2-}$, as a potential linkage moiety. In order to facilitate spectroscopic characterization of the SAM on GaS (and GaAs), we have prepared low molecular mass model compounds of the inorganic surface–organic absorbate interface. However, the chemistry of group 13 alkylphosphonate compounds has been little explored.[9] This is curious since group 13 dialkylphosphinate and arsinate compounds $[R_2M(O_2ER'_2)]_2$ (E = P, As) have been extensively characterized,[10–12] and group 13 phosphates represent an important group of porous and mesoporous materials. The paucity of structural information on gallium alkylphosphonates has led us to investigate their synthesis and characterization.

To a hexane solution of phenylphosphonic acid under an inert atmosphere was added 3 mol equiv. of $GaBu^t{}_3$ at −78 °C with rapid stirring. After warming to room temperature and removal of the volatiles under vacuum, the resulting white powder was recrystallized from toluene (−25 °C) to give large colourless crystals of $[Bu^t{}_2Ga\{\mu\text{-}O_2P(Ph)OGaBu^t{}_2\}]_2$ **1** in high yield. The mass spectrum of **1** is consistent with its dimeric formulation.†

The molecular structure of *trans*-$[Bu^t{}_2Ga\{\mu\text{-}O_2P(Ph)OGaBu^t{}_2\}]_2$ (*trans*-**1**) has been confirmed by X-ray crystallography,‡ see Fig. 1, and exists as a centrosymmetric dimer of two $[Bu^t{}_2Ga]^+$ units bridged by two organogallium phosphonate moieties, $[O_2P(Ph)OGaBu^t{}_2]^-$. The resulting $Ga_2O_2P_2$ cycle is isostructural with the core observed in $[Bu^t{}_2Ga(\mu\text{-}O_2PPh_2)]_2$ and $[Bu^t{}_2Ga\{\mu\text{-}O_2P(Ph)OH\}]_2$ **I**.[12,13] Furthermore, its chair-like conformation is typical of eight-membered rings containing a group 13 metal.[14] The intra-ring Ga–O distances [Ga(1)–O(2) 1.909(8), Ga(1)–O(2) 1.883(8) Å] are significantly longer than the exocyclic Ga–O distances [Ga(2)–O(3) 1.804(8) Å]. Both of these observations are consistent with the relative hybridization about the gallium atoms, *i.e.* Ga(1) sp^3; Ga(2) sp^2. The intra-ring distances are slightly shorter than the equivalent distances in $[Bu^t{}_2Ga(\mu\text{-}O_2PPh_2)]_2$ [1.950(8), 1.969(7) Å]; however, the P(1)–O distances are within experimental error of the values found in $[Bu^t{}_2Ga(\mu\text{-}O_2PPh_2)]_2$ [1.485(8), 1.497(8) Å]. In addition, the exocyclic distances in *trans*-**1** are shorter than those observed for $Bu^t{}_2Ga(OCPh_3)$ [1.831(4) Å].[15] The Ga(2)–O(3)–P(1) angle [152.9(5)°] is less acute than has been previously observed for terminal gallium alkoxides [127.5(3)–132.3(4)°]. It has previously been observed that for group 13 metals (M), more linear M–O–E units are exhibited for heteroatom oxo ligands (*e.g.* E = Si) than the corresponding alkoxides (E = C).[16] The Ga···Ga distances (4.76, 5.07, 6.00 Å) are suitable to allow the phenylphosphonate ligand to bind to the (100) surface of both GaAs (Ga···Ga 2.82, 5.65 Å)[17] and cubic GaS (Ga···Ga 3.88, 5.50 Å).[6]

The ^1H NMR of crystals of **1** shows the two *tert*-butyl resonances expected for the *trans*-isomer (*i.e. trans*-**1**), which by comparison with previously reported compounds[15,18] may be assigned as those attached to the four- (δ 1.42) and three-coordinate (δ 1.03) gallium centres. However, three additional resonances are present, one (δ 0.99) associated with the three-

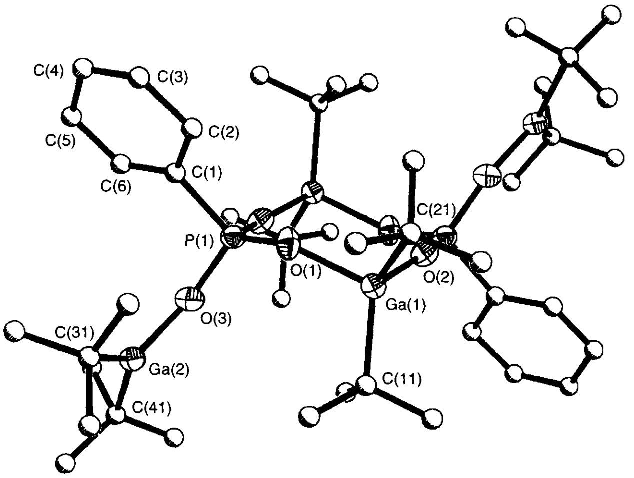
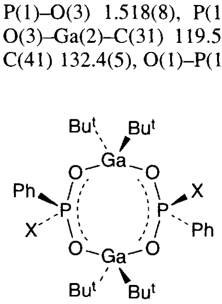
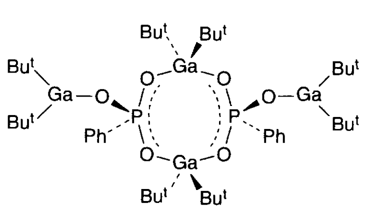


Fig. 1 Molecular structure of *trans*-$[Bu^t{}_2Ga\{\mu\text{-}O_2P(Ph)OGaBu^t{}_2\}]_2$. Thermal ellipsoids are shown at the 30% level. Carbon atoms are shown as shaded spheres, and all hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (°): Ga(1)–O(1) 1.909(8), Ga(1)–O(2) 1.883(8), Ga(1)–C(11) 1.96(1), Ga(1)–C(21) 2.01(1), Ga(2)–O(3) 1.804(8), Ga(2)–C(31) 1.97(1), Ga(2)–C(41) 1.98(1), P(1)–O(1) 1.516(7), P(1)–O(2) 1.489(3), P(1)–O(3) 1.518(8), P(1)–C(1) 1.79(1) Å; O(1)–Ga(1)–O(2) 102.1(3), O(3)–Ga(2)–C(31) 119.5(4), O(3)–Ga(2)–C(41) 107.9(4), C(31)–Ga(2)–C(41) 132.4(5), O(1)–P(1)–O(3) 111.2(5), O(3)–P(1)–O(2a) 113.8(4)°.



I X = Ph, OH



cis-**1**

coordinate gallium, and two resonances (δ 1.59, 1.26) consistent with a four-coordinate centre. Similar additional resonances are observed in the ^{13}C and ^{31}P NMR spectra.† The presence of these additional peaks in the NMR spectra may be explained by the presence of either *cis–trans* or a dimer–trimer equilibria; the lack of concentration dependence of the spectra rules out the latter. *Cis–trans* mixtures have been observed for group 13 amido compounds, $[R_2M\{\mu\text{-}N(H)R'\}]_2$.[19–21] The additional peaks may therefore be assigned to the *cis* isomer (*cis*-**1**).† The *cis*/*trans* ratio is temperature dependent and the equilibrium constants (K_{eq}) may be measured for the isomerization *trans*-**1** → *cis*-**1**. The plot of ln K_{eq} *vs.* $1/T$ yields $\Delta H = 7 \pm 1$ kJ mol^{-1} and $\Delta S = 25 \pm 4$ J mol^{-1} K^{-1}.§ The *trans* isomer is therefore thermodynamically more stable, but the positive entropy change favours the *cis* isomer. This may be due to a reduction in symmetry from *trans*-**1** to *cis*-**1**. The $T\Delta S$ term is therefore responsible for the conversion of *trans*-**1** to *cis*-**1** with increased temperature. Conversely, reduction of the solution temperature results in the maximization of the concentration of *trans*-**1** which subsequently crystallizes out of solution.

It is interesting to note the structural relationship between compound **1** and the alkyl alumoxane $[Bu^t_2Al(\mu\text{-}OAlBu^t_2)]_2$ **II**, in which the phenylphosphonate ligand has been replaced by the isolobal oxo ligand.[22] We note that this analogy has been further demonstrated by Mason *et al.* with the synthesis of the alkylphosphonate analogues of the alkyl alumoxanes, $[RAl(\mu_3\text{-}O)]_n$, *i.e.* $[RAl(\mu_3\text{-}O_3PR')]_n$.[13]

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Footnotes

† *Selected physical data* for $[Bu^t_2Ga\{\mu\text{-}O_2P(Ph)OGaBu^t_2\}]_2$: colourless blocks; mp 176–178 °C. MS, *m/z* (EI, %) 1033 ($M^+ - Me$, 100%), 991 ($M^+ - Bu^t$, 20%), 933 ($M^+ - Bu^t - HBu^t$, 26%), 919 ($M^+ - Bu^t - Me$, 100%), 877 ($M^+ - 3\ Bu^t$, 10). IR (Nujol mull); 3501.7s, 2922.5br (sh) 2359s, 1458.7m, 1376.6s (sh), 1260.6s (sh), 1144.3, 1105.0, 1038.8, 1022.1vs br, 802.8s br, 750.1s (sh); 723.5s (sh); 694.1s (sh), 548.0s br cm^{-1}. NMR (C_6D_6, relative to external $SiMe_4$): *trans*-**1**; ^1H δ 8.13 (4 H, m, *o*-CH), 7.08 (6 H, m, *o*-CH), 1.42 [36 H, s, λ^4-GaC(CH$_3$)$_3$], 103 [36 H, s, λ^3-GaC(CH$_3$)$_3$]. ^{13}C δ 30.58 [λ^4-GaC(*C*H$_3$)$_3$], 30.14 [λ^3-GaC(*C*H$_3$)$_3$], phenyl peaks not assignable. ^{31}P δ −12.73. *cis*-**1**; ^1H δ 8.13 (4 H, m, *o*-CH), 7.08 (6 H, m, *o*-CH), 1.59 [18 H, s, λ^4-GaC(CH$_3$)$_3$], 1.26 [18 H, s, λ^4-GaC(CH$_3$)$_3$], 0.99 [36 H, s, λ^3-GaC(CH$_3$)$_3$]. ^{13}C δ 31.4 [λ^4-GaC(*C*H$_3$)$_3$], 30.9 [λ^4-GaC(*C*H$_3$)$_3$], 30.2 [λ^3-GaC(*C*H$_3$)$_3$], phenyl peaks not assignable. ^{31}P δ −12.63.

‡ *Crystal data* for $C_{44}H_{82}Ga_4O_6P_2$, $M = 1047.97$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.662(4)$, $b = 13.619(2)$, $c = 17.832(4)$ Å, $\beta = 103.64(2)°$. $U = 2752(1)$ Å^3, $D_c = 1.264$ g cm^{-3}, $Z = 2$, $F(000) = 1096$, Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 2.025$ mm^{-1}. Enraf-Nonius CAD-4 automated diffractometer, 3667 reflections collected, $2 \leqslant 2\theta \leqslant 44°$, absorption (DIFABS) correction, 3482 unique reflections and 1760 having with $F > 6\sigma(F)$. Structure solved by direct methods (SHELX-86), and Fourier difference synthesis. Refinement by full-matrix least squares with Ga, P, O, C anisotropic. Hydrogen atoms were placed in calculated positions [d(C–H) = 0.95 Å, $U(H) = 1.2\ U_{eq}$ (attached carbon)], converged $R = 0.0475$, $R_w = 0.0523$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/221.

§ These values are slightly higher than reported for the *cis*/*trans* isomerization of $[Me_2Ga(\mu\text{-}NHBu^t)]_2$, see ref. 21.

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