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Detection of a Rotation Barrier around a Bond between Heavier Main Group 3 and 5 Elements

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Multiple bonding between main group 3 and 5 elements has been well-known for many years in the case of B–N compounds.[1,2] In contrast, examples of multiple bonding for the corresponding B–P[3,4] and B–As[5] species have only been recently established. Another recent report has featured the structures of the Zintl anions $M_2E_4^{6-}$ (M = Al, Ga; E = P, As), which have planar M_2E_2 cores with each metal also bound to a terminal E and display shortened bonds (e.g. Ga–P = 2.247 (5) Å) that are suggestive of considerable multiple character.[6] A number of molecular compounds have also been reported that display bonding between three-coordinate heavier main group 3 and 5 elements in which a multiple interaction is conceivable. Among these are $Ga(AsMes_2)_3$, (Ga–As = ~2.49 Å),[7] $Ga(PHMes^*)_3$ (Ga–P = 2.34 (1) Å),[8] $(\eta^1\text{-}C_5Me_5)_2GaAs(SiMe_3)_2$ (Ga–As = 2.433 (4) Å),[9] $(Ph_3C_6H_2GaPC_6H_{11})_3$ (Ga–P = 2.279 (4)–2.338 (5) Å),[10] $t\text{-}BuGa(PHMes^*)_2$ (Ga–P = 2.32 Å),[11] $(t\text{-}BuGaPMes^*)_2$ (Ga–P = 2.274 (4) Å),[11] and $In[P(t\text{-}Bu)_2]_3$ (In–P = 2.574–2.613 Å),[12] all of which have been structurally characterized. These molecules are not thought to involve significant main group element 3–5 multiple bonding since such interactions are precluded by large angles between the pnictide lone pair and empty metal p-orbitals and, in addition, a near normal pyramidal coordination at the pnictide. No doubt, the large inversion barriers normally observed in trivalent phosphorus and arsenic compounds play a significant role in determining their molecular architecture and represent a formidable obstacle to multiple bonding. Nonetheless, recent experiments on boron–phosphorus[3,4] or boron–arsenic[5] compounds in this laboratory have conclusively demonstrated that multiple bonding may be induced by introducing bulky and/or electropositive substituents on phosphorus or arsenic that lower the inversion barrier and enable π-overlap to occur. In this paper the application of similar principles to induce multiple Ga–P bonding in a compound of the general formula $R_2GaPR'R''$ is described.

The compound $t\text{-}Bu_2GaPMes^*(SiPh_3)$ (**1**) was synthesized[13] in good yield by the reaction of $t\text{-}Bu_2GaCl$ with $LiPMes^*(SiPh_3)$ in ether solution. The product **1** was isolated as colorless crystals and characterized structurally (X-ray) and spectroscopically (IR, ^1H, and ^{31}P NMR). The X-ray crystal structure[14] depicted in Figure 1 consists of well-separated phosphinogallane monomers.

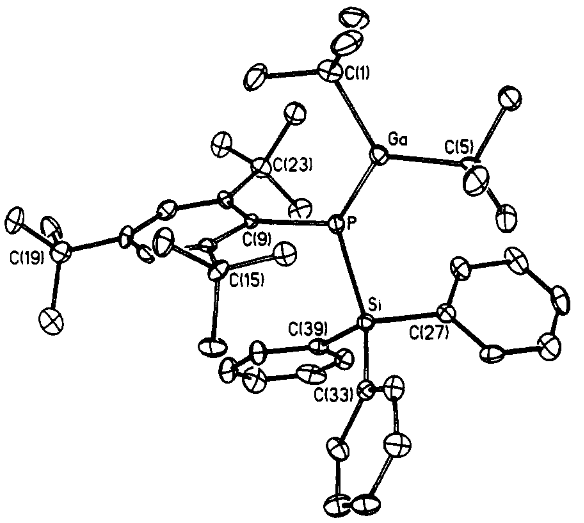

Figure 1. Important bond distances (Å) and angles (deg) for **1**: Ga–P = 2.295 (3), Ga–C(1) = 2.01 (1), Ga–C(5) = 2.01 (1), P–Si = 2.259 (4), P–C(9) = 1.890 (8), Si–C(27) = 1.890 (9), Si–C(33) = 1.899 (8), Si–C(39) = 1.895 (8); P–Ga–C(1) = 118.9 (3), P–Ga–C(5) = 121.2 (3), C(1)–Ga–C(5) = 119.1 (4), Ga–P–Si = 125.3 (1), Ga–P–C(9) = 112.5 (3), Si–P–C(9) = 108.6 (3).

The most important structural features are the flattened pyramidal (Σ°P = 346.2°) geometry at phosphorus and the very small angle (3.2°) between the perpendiculars to the GaC_2 and PCSi planes. This geometrical arrangement is very different from those observed in $(\eta^1\text{-}C_5Me_5)_2GaAs(SiMe_3)_2$[9] or $Ga(AsMes_2)_3$,[7] where there are large twist angles (~50–60°) between the lone pair and metal p-orbitals. The "eclipsed" geometry in **1** is also remarkable in view of the large substituent sizes, which, for steric reasons, tend to favor a twisted geometry similar to that observed in $(\eta^1\text{-}C_5Me_5)_2GaAs(SiMe_3)_2$.[9] The Ga–P distance is somewhat short, 2.295 (3) Å (cf. 2.34 (1) Å in $Ga(PHMes^*)_3$),[8] although it is not significantly different from the Ga–P distances observed in $(TriphGaPC_6H_{11})_3$[10] or $(t\text{-}BuGaPMes^*)_2$.[11] It may be that, because of the large substituent groups, the Ga–P distance in **1** is longer than it would be in a hypothetical planar $R_2GaPR'_2$ species with less crowding R and R′ groups.

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(13) Under anaerobic and anhydrous conditions and with cooling in an ice bath, Ph_3SiCl (1.17 g, 4 mmol) in Et_2O (20 mL) was added dropwise to a solution formed by the dropwise addition of *n*-BuLi (2.5 mL of a 1.6 M hexane solution, 4 mmol) to Mes^*PH_2[18] (1.11 g, 4 mmol) in Et_2O (30 mL), and the mixture was stirred for 12 h. The resultant colorless solution was filtered and treated dropwise with *n*-BuLi (2.5 mL of 1.6 M hexane solution, 4 mmol). After the mixture was stirred for 3 h at room temperature, $t\text{-}Bu_2GaCl$ (0.86, 4 mmol)[19] in Et_2O (15 mL) was added dropwise and the solution was stirred for a further 4 h. The volatile materials were removed under reduced pressure, and the residue was taken up in pentane (30 mL). Filtration and concentration to ca. 10 mL and cooling to −78 °C gave a white solid which may be recrystallized from a minimum volume of hexane or Et_2O in a −20 °C freezer. Yield: 2.07 g, 72%. Mp = 154–158 °C dec. ^1H NMR (C_7D_8): δ = 1.12 ($Ga(t\text{-}Bu)_2$, 18 H), 1.58 (*o*-*t*-Bu, 18 H), 1.3 (*p*-*t*-Bu, 9 H), 7.05 (d, *m*-H of $SiPh_3$, 6 H), 7.09 (mm, *o*- and *p*-H of $SiPh_3$, 9 H). ^{31}P NMR (C_6D_6): δ = −119. IR: ν(Ga–P) = 318 cm^{-1}.

(14) Crystal data at 130 K with Mo Kα (λ = 0.710 69 Å): *a* = 10.133 (4) Å, *b* = 17.199 (9) Å, *c* = 23.861 (9) Å, β = 92.07 (2)°, monoclinic, $P2_1/c$, *Z* = 4, 3264 unique observed ($I > 3\sigma(I)$) data, *R* = 0.077.

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The most important characteristic of **1** arises from its variable-temperature ^{1}H NMR behavior. At room temperature well-resolved peaks characteristic of Mes* and $SiPh_3$ are observed in addition to a peak at δ 1.12 due to the $-Ga(t\text{-}Bu)_2$ moiety. Cooling the solution results in a broadening of the $Ga(t\text{-}Bu)_2$ peak and its separation into two signals at ca. −27 °C. Substitution of the parameters $T_c = 246$ K and $\Delta\nu = 12$ Hz into an approximate formula[15] affords a ΔG value of 12.7 kcal mol^{-1} for the dynamic process. The magnetic inequivalence of the $Ga(t\text{-}Bu)_2$ groups at low temperature may be explained on the basis of restricted rotation around the Ga–P bond owing, most probably, to a Ga–P π-interaction.[16] This observation apparently represents the first direct experimental evidence of a rotational barrier in a bond between heavier main group 3 and 5 elements. Most likely, there is a weak π-interaction in **1** owing to the reduction of the phosphorus inversion barrier by the presence of (i) bulky substituents and (ii) the electropositive groups $-SiPh_3$ and $-Ga(t\text{-}Bu)_2$. In other words, conditions have been created whereby adjacent empty and lone pair orbitals may overlap more effectively to form a weak Ga–P π-bond which is similar in strength to those on the lower end of the scale in comparable B–N[17] and B–P[4] compounds. However, a greater range of Ga–P π-bonded species will have to be synthesized before a more accurate overall comparison with the B–N and B–P systems can be made.

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Supplementary Material Available: Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and a figure showing NMR spectra (10 pages). Ordering information is given on any current masthead page.

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(16) It could be argued that restricted rotation around the Ga–P bond is a result of steric effects. Two considerations are contrary to this argument: first the substituents on Ga and P are in the eclipsed configuration and second the structure of $t\text{-}Bu_2GaOMes^*$ (which is also eclipsed and would be expected to have similar steric interference between the Mes* and *t*-Bu groups) displays no inequivalence of the Ga–*t*-Bu groups at temperatures as low as −90 °C. A reviewer has, however, suggested that the lack of *t*-Bu group splitting in $t\text{-}Bu_2GaOMes^*$ may be due to rapid wagging of the –OMes* in the C_2GaOC molecular plane. We think that this explanation is unlikely because no inequivalence could be detected in related amido derivatives for which wagging of this type is impossible.

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