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Synthesis and molecular structure of an unusual –Ga–Ga–Ga– linked organometallic

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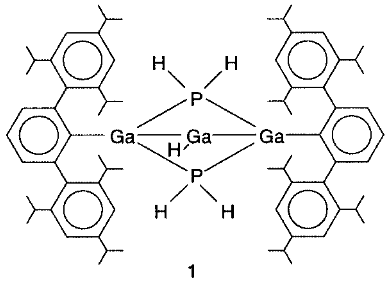
Reaction of [(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$]$GaCl_2$ with $P(SiMe_3)_3$ affords the unusual organometallic compound [(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$]Ga{$H_2PGa(H)PH_2$}Ga[$C_6H_3(C_6H_2$-Pr^i_3-2,4,6)$_2$] 1 characterized by multinuclear NMR, complete (C, H, Ga and P) elemental analyses, IR spectroscopy and single crystal X-ray diffraction; 1 is significant as it contains a rare Ga–Ga–Ga [2.5145(13) and 2.7778(14) Å] linkage even as its formation is facilitated by the unusual stripping of the sterically demanding *m*-terphenyl ligand from the central gallium atom.

One of the most extensively studied reactions in organo-group 13 chemistry of the past decade has been that of organometallic moieties with various phosphines.[1] The preference for tris(trimethylsilyl)phosphine, $P(SiMe_3)_3$, as a phosphorus source may largely be traced to the considerable steric demands (*i.e.* large cone angle) of this compound coupled with the robust nature of the trimethylsilyl leaving groups.[2] Herein, we report the synthesis[3] and molecular structure[4] of [(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$]Ga{$H_2PGa(H)PH_2$}Ga[$C_6H_3(C_6H_2$-Pr^i_3-2,4,6)$_2$] **1** isolated from reaction of [(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$]$GaCl_2$[5] with $P(SiMe_3)_3$. Compound **1**, characterized by multinuclear NMR, complete elemental (C, H, Ga and P) analyses IR spectroscopy, and single crystal X-ray diffraction, is significant as it contains a rare –Ga–Ga–Ga– linkage even as its formation is facilitated by the unusual stripping of the sterically demanding *m*-terphenyl ligand from the central gallium atom.



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The laboratory has had an interest in the organogallium chemistry of $P(SiMe_3)_3$ for some time having previously reported the synthesis and molecular structure of the phosphinogallane dimer $[Me_2Ga–P(SiMe_3)_2]_2$, isolated from reaction of $GaMe_3$ with $P(SiMe_3)_3$.[6] This compound contained a planar Ga_2P_2 four-membered ring with an independent Ga–P bond distance of 2.456(1) Å. Reaction of the Lewis acid–base adduct $Me_3Ga–PMe_3$ [Ga–P 2.455(4) Å] with $P(SiMe_3)_3$ was shown by this laboratory to afford $[(Me_3Si)_2P\{Me_2Ga\}_2PMe]_2$– a novel bicyclic phosphinogallane consisting of two fused Ga_2P_3 five-membered rings sharing a common P–P base at a distance of 2.25(3) Å with a mean Ga–P bond distance of 2.44(4) Å.[7] Relative to sterically demanding ligands the *m*-terphenyl moiety (2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$ has been most prominently utilized in the stabilization of Na_2[{(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$}–Ga≡Ga–{$C_6H_3(C_6H_2Pr^i_3$-2,4,6)$_2$}], a novel gallyne possessing a short Ga–Ga bond distance of 2.319(3) Å.[8–10] Thus, as described herein, we endeavored to examine the organogallium chemistry of this ligand as a function of $P(SiMe_3)_3$.

The formation of **1** is at once both surprising and interesting. Although the stripping of a large organic moiety from a gallium center, as with the central gallium atom of **1**, is noteworthy, it is not unprecedented as a $Pr^i_3C_6H_2$ ligand has been shown to be stripped from a gallium atom.[11] While it may be reasonable to consider the five hydrogen atoms, two on each of the two phosphorus atoms and one on the central gallium atom, as having originated from the stripped *m*-terphenyl ligand, there are other possibilities. It is also possible, for example, that the ligand stripping may have initiated hydride abstraction from the solvent (or *vice versa*). It is noteworthy that the title compound has been repeatedly isolated in this laboratory under a number of conditions.[3] The phosphine hydrogen atoms and the gallium hydride are prominently manifest in IR and NMR spectroscopy. IR spectroscopic data for **1** indicate the presence of phosphine hydrogen atoms with bands at 2371 cm^{-1} [$\nu_{P–H}$ (m)] and 2337 cm^{-1} [$\nu_{P–H}$ (m)]. These values compare well to 2314 cm^{-1} [$\nu_{P–H}$ (m)] for {$[Me_2Ga]_4[(\mu\text{-}PH)_2(C_6H_4)]_2$}[12] and to 2343 cm^{-1} [$\nu_{P–H}$ (sym)] and 2335 cm^{-1} [$\nu_{P–H}$ (asym)] for the phosphinogallane trimer $[Bu^t_2Ga(\mu\text{-}PH_2)]_3$.[13] The gallium hydride IR bands at 1801 cm^{-1} [$\nu_{Ga–H}$ (vw)] and 1849 cm^{-1} [$\nu_{Ga–H}$ (vw)] of **1** are comparable to previously reported gallium hydride IR bands: $Me_2N–GaH_3$,[14] 1829 cm^{-1} [$\nu_{Ga–H}$ (vw)]; $[(PhCH_2(Me)_2NGaH_3]$,[15] 1835 cm^{-1} ($\nu_{Ga–H}$) and $(Et_2O)_2Li$-$[\mu\text{-}As(SiMe_3)_2]_2GaH_2$,[16] 1834 cm^{-1}. Similar to **1** which exhibits two Ga–H IR bands, the organometallic (mono)hydride $K[Ga(H)(CH_2SiMe_3)_3]$ also exhibits two Ga–H IR bands at 1915 cm^{-1} [$\nu_{Ga–H}$ (vw)] and 1840 cm^{-1} [$\nu_{Ga–H}$ (vw)].[17] It is important to note that our calculated IR spectrum agrees well with the experimental results of **1** reported herein.[18] A theoretical study of the model molecule $CH_3Ga\{H_2PGa(H)PH_2\}GaCH_3$ at the DZP B3LYP level of theory in this laboratory reveals harmonic vibrational frequencies corresponding to P–H stretches of 2441, 2441, 2418 and 2415 cm^{-1}. Moreover, the calculated Ga–H IR band appears at 1882 cm^{-1}. In sum, these theoretical predictions are in good agreement (within 5%) with the experimentally observed IR spectrum. Although the Ga–H bond could not be unambiguously assigned in the ^{1}H NMR spectrum, P–H was clearly observed as a multiplet at δ 3.25; moreover the integration is indicative of two hydrogen atoms on each of the two phosphorus atoms. Consistent with its diamagnetic nature, the title compound did not prove to be EPR active.

A number of points are noteworthy relative to structure (Fig. 1) and bonding in the title compound. Compound **1** may be considered as a Ga_3P_2 trigonal bipyramidal core bridging the two *m*-terphenyl ligands. The Ga–C bonds in **1** of 1.969(6) and 1.982(6) Å are longer than the value reported for [(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$]$GaCl_2$ [1.949(8) Å] and yet are considerably shorter than that reported for the Na_2[{(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$}–Ga≡Ga–{$C_6H_3(C_6H_2Pr^i_3$-2,4,6)$_2$}] gallyne (2.06 Å). The angles about the {–P–Ga–P–} core connecting the

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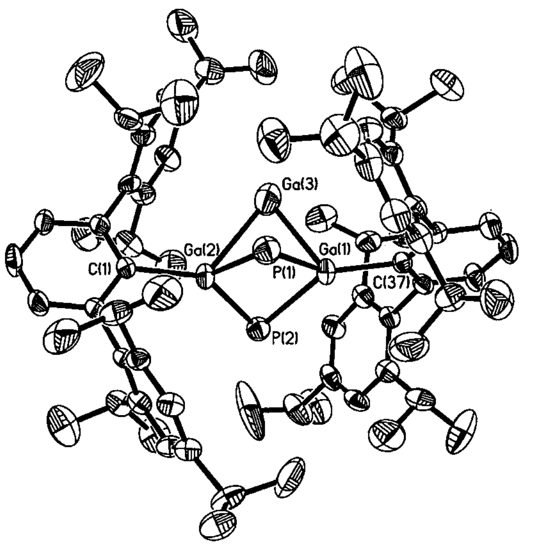

Fig. 1 Molecular structure of **1** (all hydrogen atoms, including that on Ga(3) and the two each on P(1) and P(2), have been omitted for clarity and only one position for each disordered phosphorus atoms is shown. Ellipsoids are shown at the 30% probability level): Bond distances (Å) and angles (°): Ga(1)–C(37) 1.969(6), Ga(2)–C(1) 1.982(6), Ga(1)–P(2) 2.564(5), Ga(1)–P(1) 2.660(6), Ga(1)–Ga(3) 2.5145(13), Ga(2)–P(1) 2.449(5), Ga(2)–P(2) 2.455(4), Ga(2)–Ga(3) 2.7778(14), Ga(1)···Ga(2) 3.031, Ga(3)···P(1) 3.327, Ga(3)···P(2) 3.314, P(1)···P(2) 3.930; C(37)–Ga(1)–P(2) 129.98(19), C(37)–Ga(1)–P(1) 130.3(2), P(2)–Ga(1)–P(1) 97.58(10), C(37)–Ga(1)–Ga(3) 115.97(18), P(2)–Ga(1)–Ga(3) 81.48(15), P(1)–Ga(1)–Ga(3) 79.96(18), C(1)–Ga(2)–P(1) 124.0(2), C(1)–Ga(2)–P(2) 128.1(2), P(1)–Ga(2)–P(2) 106.5(3), C(1)–Ga(2)–Ga(3) 119.69(18), P(1)–Ga(2)–Ga(3) 78.78(15), P(2)–Ga(2)–Ga(3) 78.33(13), Ga(1)–Ga(3)–Ga(2) 69.68(4), Ga(2)–P(1)–Ga(1) 72.65(17), Ga(2)–P(2)–Ga(1) 74.27(14).

two $[(2,4,6\text{-}Pr^i_3C_6H_2)_2C_6H_3]Ga$ fragments are particularly acute at angles of 69.68(4), 72.65 and 74.27° for Ga(1)–Ga(3)–Ga(2), Ga(1)–P(1)–Ga(2) and Ga(1)–P(2)–Ga(2), respectively. The Ga(1)–Ga(3)–Ga(2) linkage is asymmetric at distances of 2.5145(13) and 2.7778(14) Å for Ga(1)–Ga(3) and Ga(2)–Ga(3), respectively. It should be noted, however, that compound **1** is not governed by a plane of symmetry or a twofold axis which would demand a symmetrical –Ga–Ga–Ga– linkage. Even though these Ga–Ga distances in **1** are rather long, they compare with a Ga–Ga range of 2.678–2.702 Å for the Ga_4-tetrahedral based $[Ga\{C(SiMe_3)_3\}]_4$.[19] Indeed, the Ga–Ga bond distances of **1** compare favorably with the Ga–Ga distances of 2.440(1) and 2.790(1) Å for the recently reported 'silicon-capped' Ga_4Si trigonal bipyramidal anion.[20]

The mean Ga–P distance in **1** is 2.461 Å. With Ga···P contacts of 3.327 and 3.314 Å for Ga(3)···P(1) and Ga(3)···P(2), respectively, the possibility of meaningful gallium–phosphorus interactions would appear to be remote. Likewise, the P(1)···P(2) approach of 3.930 Å is far beyond the realm of a phosphorus–phosphorus bond as typical P–P single bond distances are normally in the range 2.25(3)–2.35 Å.[21] Lastly, the Ga(1)···Ga(2) approach of 3.031 Å virtually rules out significant metal–metal interaction.

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Notes and references

1 A. M. Arif, B. L. Benac, A. H. Cowley, R. Geerts, R. A. Jones, K. B. Kidd, J. M. Power and S. T. Schwab, *J. Chem. Soc., Chem. Commun.*, 1986, 1543.

2 R. L. Wells, S. R. Aubuchon, M. F. Self, J. P. Jasinski, R. C. Woudenberg and R. J. Butcher, *Organometallics*, 1992, **11**, 3370.

3 Compound **1** was prepared by a number of methods under a variety of conditions. All syntheses afforded **1** in comparable yields. *Method A*: inside a drybox (M Braun LabMaster 130), a Schlenk flask was charged with $[(2,4,6\text{-}Pr^i_3C_6H_2)_2C_6H_3]GaCl_2$ (1.30 g, 2.08 mmol), diethyl ether (40 mL) and a stirring bar. The resulting colorless solution was cooled to −78 °C. To this flask a solution of $P(SiMe_3)_3$ (0.52 g, 2.08 mmol) in diethyl ether (30 mL) was added *via* syringe over a period of 10 min. The solution was allowed to stir for 3 h at low temperature, after which it was allowed to slowly warm to room temperature and continued to stir for 72 h resulting in a slightly yellow solution. After filtration, the volume of the solution was reduced to *ca.* 20 mL *in vacuo*. Cooling the solution to −25 °C for one week gave colorless crystals of **1** (0.25 g, 0.20 mmol). Yield: 30%. mp: 191 °C (decomp.). Anal. Calc. (found) for $C_{72}H_{103}P_2Ga_3$ (E + R Microanalytical Laboratory, Corona, NY): C, 69.80 (70.30); H, 8.40 (8.19); Ga, 16.90 (16.88); P, 5.00 (4.86%). ^1H NMR (300 MHz, 298 K, C_6D_6): δ 0.87–1.31 [m, 72H, $CH(CH_3)_2$], 2.92 [m, 12H, $-CH(CH_3)_2$], 3.25 (m, 4H, PH_2), 7.10–7.21 [m, 14H, CH (aromatic)]. ^{13}C NMR (300 MHz, 298 K, THF-d_8): δ 23.5, 31.3, 35.4 (isopropyl); 120.0, 121.5, 128.8, 129.3, 140.6, 146.9, 148.0, 149.6 (aromatic carbon atoms). $^{31}P\{^1H\}$ NMR (300 MHz, 298 K, THF-d_8): δ −167.95 (s). Compound **1** was EPR inactive, thereby confirming its diamagnetic nature. IR (Perkin Elmer Paragon 1000PC FT-IR Spectrometer) (Nujol mull): 2371 [ν_{P-H} (m)], 2337 [ν_{P-H} (m)], 1801 [ν_{Ga-H} (vw)], 1849 cm^{-1} [ν_{Ga-H} (vw)].

4 A number of crystals of **1** were mounted and sealed in a glass capillaries under an atmosphere of nitrogen inside the drybox. The X-ray intensity data on an appropriate sample were collected at room temperature on a Bruker SMART TM CCD-based X-ray diffractometer system with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using the ω-scan technique to a maximum 2θ value of 46.7°. *Crystallographic data*: $C_{72}H_{103}P_2Ga_3$: monoclinic, space group $P2_1/n$ (no. 14), a = 18.7040(16), b = 18.4955(16), c = 20.3393(17) Å, β = 92.588(2)°, V = 7029.0(10) Å^3, Z = 4, M = 1239.64, μ = 1.224 mm^{-1}, D_c = 1.171 g cm^{-3}. Of the 9812 independent reflections collected, 4427 were observed [$I > 2\sigma(I)$]. A routine absorption correction was applied by using SADABS and any decay correction was made with the SAINT program. The structure was solved by direct methods using the SHELXTL 5.1 Software Package. Each of the two bridging phosphorus atoms was found to be disordered over two adjacent positions with a refined occupancy factor of 0.50 for each position. The non-hydrogen atoms (except for the disordered phosphorus atoms) were refined anisotropically while hydrogen atoms were placed in ideal positions with their coordinates and thermal parameters riding on the attached carbon atoms (C–H 0.98 Å), the phosphorus atoms (P–H 1.50 Å) and the bridging gallium atom (Ga–H 1.50 Å). The final residual values based on 695 variable parameters and 4427 observed reflections [$I > 2\sigma(I)$] and $R1$ = 0.0637, $wR2$ = 0.1359 and those for all 9812 unique reflections are $R1$ = 0.1665, $wR2$ = 0.1711. CCDC 182/1538. See http://www.rsc.org/suppdata/cc/a9/a909451b/ for crystallographic files in .cif format.

5 J. Su, X.-W. Li and G. H. Robinson, *Chem. Commun.*, 1998, 2015.

6 M. D. B. Dillingham, J. A. Burns, W. T. Pennington and G. H. Robinson, *Inorg. Chim. Acta*, 1994, **216**, 267.

7 J. A. Burns, W. T. Pennington and G. H. Robinson, *Organometallics*, 1995, **14**, 1533.

8 J. Su, X.-W. Li, R. C. Crittendon and G. H. Robinson, *J. Am. Chem. Soc.*, 1997, **119**, 5471.

9 J. Xie, R. S. Grev, J. Gu, H. F. Schaefer III, P. v. R. Schleyer, J. Su, X.-W. Li and G. H. Robinson, *J. Am. Chem. Soc.*, 1998, **120**, 3773.

10 G. H. Robinson, *Acc. Chem. Res.*, 1999, **32**, 773.

11 K. M. Waggoner, S. Parkin, D. C. Pestana, H. Hope and P. P. Power, *J. Am. Chem. Soc.*, 1991, **113**, 3597.

12 R. L. Wells, H. Rahbarnoohi, P. B. Glaser, L. M. Liable-Sands and A. L. Rheingold, *Organometallics*, 1996, **15**, 3204.

13 A. H. Cowley, P. R. Harris, R. A. Jones and C. M. Nunn, *Oranometallics*, 1991, **10**, 652.

14 D. O'Hare, J. S. Ford, T. C. M. Page and T. J. Whitaker, *J. Chem. Soc., Chem. Commun.*, 1991, 1445.

15 P. C. Andrews, M. G. Gardiner, C. L. Raston and V.-A. Tolhurst, *Inorg. Chim. Acta*, 1997, **259**, 249.

16 J. F. Janik, R. L. Wells, V. G. Young Jr. and H. A. Halfen, *Organometallics*, 1997, **16**, 3022.

17 R. B. Hallock, O. T. Beachley Jr., Y.-J. Li, W. M. Sanders, M. R. Churchill, W. E. Hunter and J. L. Atwood, *Inorg. Chem.*, 1983, **22**, 3683.

18 H. F. Schaefer III and Y. Xie, unpublished results.

19 W. Uhl, W. Hiller, M. Layh and W. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1364.

20 G. Linti, W. Köstler, H. Piotrowski and A. Rodig, *Angew. Chem., Int. Ed.*, 1998, **37**, 2209.

21 *Compounds Containing Phosphorus–Phosphorus Bonds*, ed. A. H. Cowley, Dowden, Hutchinson and Ross, Inc., Stroudsburg, PA, 1973. A listing of typical P–P single bond values is found on p. 6 and references cited therein.

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