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Gallane/Phosphine Adducts: Air-Stable $H_3Ga{\cdot}P(C_6H_{11})_3$ and Gallane Rich $2H_3Ga{\cdot}(PMe_2CH_2)_2$

Alane, AlH_3, forms stable mono(tertiary amine) adducts which can be four-coordinate monomeric species in the solid state and vapor phase[1] or dimeric five-coordinate species in the solid state with two bridging hydrides.[2] Gallane, GaH_3, forms mono(tertiary amine) adducts of lower thermal stability,[3] with metal centers exclusively four-coordinate in the gas phase[4] and in the solid state.[3,5] While alane/phosphine adducts can decompose under mild conditions,[6,7] gallane forms relatively stable tertiary phosphine adducts,[8,9] yet none of these compounds have been structurally authenticated. Herein we report the synthesis, properties, and structures of some new, remarkably stable compounds of this type, viz. $H_3Ga{\cdot}PCy_3$ (**1**; Cy = cyclohexyl) and $2H_3Ga{\cdot}(PMe_2CH_2)_2$ (**2**), together with theoretical investigations of the model compound $H_3Ga{\cdot}PH_3$ and for comparison $H_3Ga{\cdot}NH_3$.

Compounds **1** and **2** were both readily obtained from either $H_3Ga{\cdot}NMe_3$ or $LiGaH_4$ by ligand displacement or lithium hydride elimination, respectively (Scheme I).[10] Earlier syntheses of gallane/phosphine adducts involved the treatment of $LiGaH_4$ with phosphine and HCl ($GaH_3{\cdot}PMe_3$ (**3**) and $H_3Ga{\cdot}PPh_3$ (**4**)). There was no evidence for the formation of an intermediate 1:1 compound $H_3Ga{\cdot}(PMe_2CH_2)_2$ of the type previously found in the analogous ligand displacement reaction involving TMEDA (=*N,N,N′,N′*-tetramethylethylenediamine).[3] Polydentate diaryl tertiary phosphines failed to react with $H_3Ga{\cdot}NMe_3$ ($PPh_2(CH_2)_nPPh_2$, $n = 1$ and 2, and $(PPh_2CH_2CH_2)_2PPh$) or with $LiGaH_4$ ($PPh_2(CH_2)_2PPh_2$), which probably relates to their lower basicity and/or the tendency for gallane to form four-coordinate species. For example, the gallane/bis(trimethylamine) adduct, $H_3Ga{\cdot}2NMe_3$, yields the mono(trimethylamine) adduct, $H_3Ga{\cdot}NMe_3$, above −22.8 °C.[11] Related to this work is the recent synthesis of a borane-rich polydentate phosphine adduct.[12]

Both **1** and **2** have high thermal stability, decomposing at temperatures >130 and 100 °C, respectively (cf. >77 °C for **3** and 20 °C for **4**),[8] which are comparable with the best stability for gallane/tertiary amine adducts, notably decomposition >100 °C for $H_3Ga{\cdot}N(CH_2CH_2)_3CH$ (**5**).[3] Compound **1** sublimes in vacuo (120 °C, 0.1 mbar), and remarkably it is stable indefinitely in air, most likely because of the large "cone angle" of the phosphine, whereas **2** rapidly decomposes in air.

Results of the X-ray structure determinations of **1** and **2**[13] are presented in Figure 1. The hydrides were located in **1**, mean Ga–H = 1.48 Å, and with the P-center, Ga–P = 2.460 (2) Å, the metal centers have tetrahedral geometry, as in **5** and $2H_3Ga{\cdot}(NMe_2CH_2)_2$ (**6**).[3] The latter compound is isolobal with **2**, yet the compounds are not isostructural, crystallizing in different cells and with the methylene atoms disordered only in **2**, where no hydride atoms were located. This may be a consequence of the disorder and/or less steric hindrance of the phosphine compared to the phosphine in **1** resulting in libration about the Ga–P vector; in **6**, the hydrides were located and the metal–donor group distance is as expected considerably shorter, 2.094 (4) Å;[3] cf. 2.399 (4) Å in **2**. Even in the absence of locating the hydrides, the Ga···Ga separations rule out bridging interactions and thus the metal centers most likely have tetrahedral geometry. The Ga–P distances are within the limits established for a variety of four-coordinate complexes of gallium containing a neutral donor phosphine, 2.353

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(10) Compound **1** was prepared as follows. $P(C_6H_{11})_3$ (1.01 g, 3.57 mmol) was slowly added to a solution of $LiGaH_4$ with stirring at −30 °C. When the mixture was warmed to room temperature, a white solid formed which was removed by filtration, and concentrating the mother liquor in vacuo followed by cooling to −30 °C gave colorless crystals of **1**: 0.92 g, yield 72% (cf. 44% from $H_3Ga{\cdot}NMe_3$ and $(C_6H_{11})_3P$); mp dec >130 °C; ^1H NMR (250 MHz, C_6D_6) δ 4.32 (br s, Ga*H*), 1.88, 1.81, 1.67, 1.57, 1.41, 1.10 (2 H, 1 H, 2 H, 1 H, 2 H, 3 H, m, C_6H_{11}); ^{13}C NMR (62.8 MHz, C_6D_6) δ 26.0 (s, CH_2), 27.2 (d, CH_2, $^2J_{C\text{-}P} = 10.5$ Hz), 29.2 (s, CH_2), 31.0 (d, CH, $^1J_{C\text{-}P} = 14.5$ Hz); ^{31}P NMR (121.47 Hz, C_6H_6) δ 11.8; IR ν(Ga–H) 1800 br cm^{-1}. Anal. Calcd for $C_{18}H_{36}PGa$: C, 61.18; H, 10.19. Found: C, 60.94; H, 10.15. Compound **2** was prepared as follows. To a stirred solution of $H_3Ga{\cdot}NMe_3$ (0.56 g, 4.25 mmol) in diethyl ether (30 cm^3) at 0 °C was added $(Me_2PCH_2)_2$ (0.4 mL, 0.36 g, 2.40 mmol). After 10 min, the mixture was warmed to ambient temperature and stirred for a further 1 h. The slightly turbid solution was then filtered and the filtrate cooled to −30 °C, giving colorless needles of **2**, 0.31 g. The cold supernatant was decanted and concentrated in vacuo. Cooling at −30 °C gave a further crop of **2**: 0.18 g; total yield 78% (cf. 20% from $LiGaH_4$ and $(Me_2PCH_2)_2$); mp 107 °C dec; ^1H NMR (250 MHz, C_6D_6) δ 1.67 (12 H, virtual t, PCH_3, $J = 3.4$ Hz), 2.28 (4 H, s, PCH_2), 4.67 (6 H, br s, Ga*H*); ^{13}C NMR (62.8 MHz, C_6D_6) δ 9.6 (t, PCH_3, $^1J_{C\text{-}P} = 9$ Hz), 21.7 (t, PCH_2, $^1J_{C\text{-}P} = 10$ Hz); ^{31}P NMR (121.47, C_6D_6) δ −29.5; IR ν(Ga–H) 1982 br cm^{-1}. Anal. Calcd for $C_6H_{22}P_2Ga_2$: C, 24.38; H, 7.50. Found: C, 23.93; H, 6.93.

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(13) Crystal structure data are as follows ($T = 296$ K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries). Compound **1**: $C_{18}H_{36}GaP$, $M = 353.2$, triclinic, space group $P\bar{1}$, $a = 8.226$ (3) Å, $b = 11.011$ (3) Å, $c = 11.444$ (3) Å, $\alpha = 75.33$ (2)°, $\beta = 88.63$ (3)°, $\gamma = 81.91$ (3)°, $V = 993$ Å^3, $F(000) = 374$, $Z = 2$, D_c = g·cm^{-3}, μ(Cu Kα) = 25.8 cm^{-1}, $A = 0.90$–0.99, specimen 0.2 × 0.3 × 0.4 mm, 2291 unique reflections, 2200 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max} = 110°$. Compound **2**: $C_6H_{22}Ga_2P_2$, $M = 295.6$, monoclinic, space group $P2_1/c$, $a = 6.231$ (1) Å, $b = 11.485$ (1) Å, $c = 10.249$ (1) Å, $\beta = 102.2$ (1)°, $V = 716.9$ Å^3, $F(000) = 600$, $Z = 2$, $D_c = 1.37$ g·cm^{-3}, μ(Cu Kα) = 63.78 cm^{-1}, $A = 0.88$–0.99, specimen 0.4 × 0.4 × 0.4 mm, 1055 unique reflections, 768 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max} = 110°$. R,R': 0.072, 0.084 (**1**); 0.069, 0.078 (**2**).

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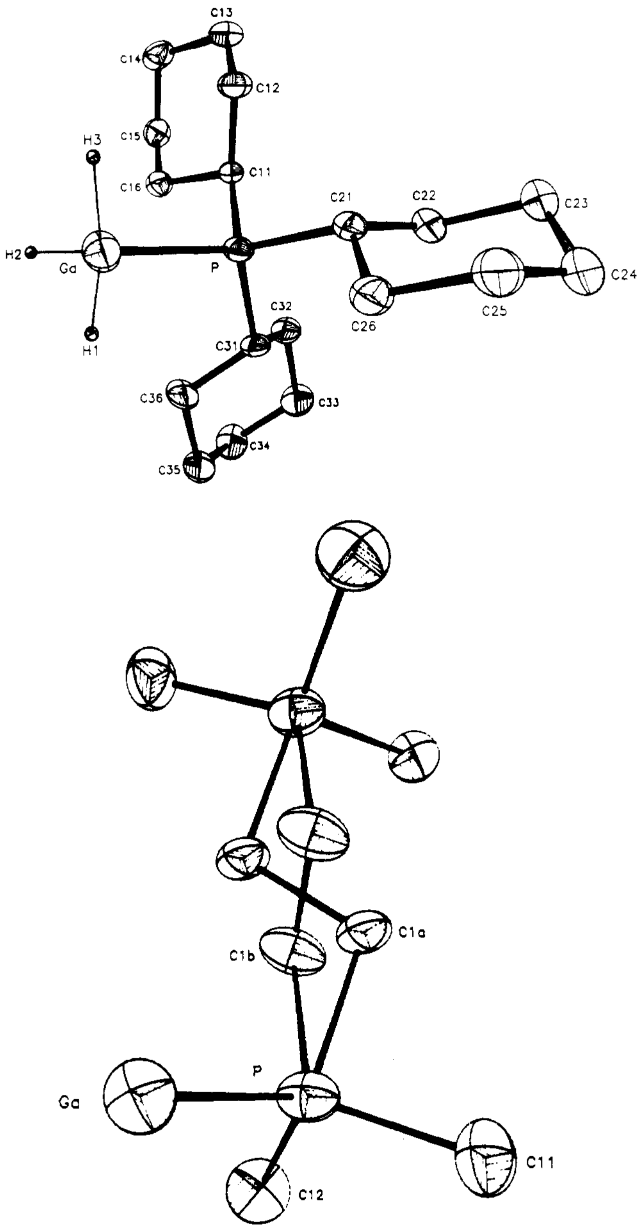
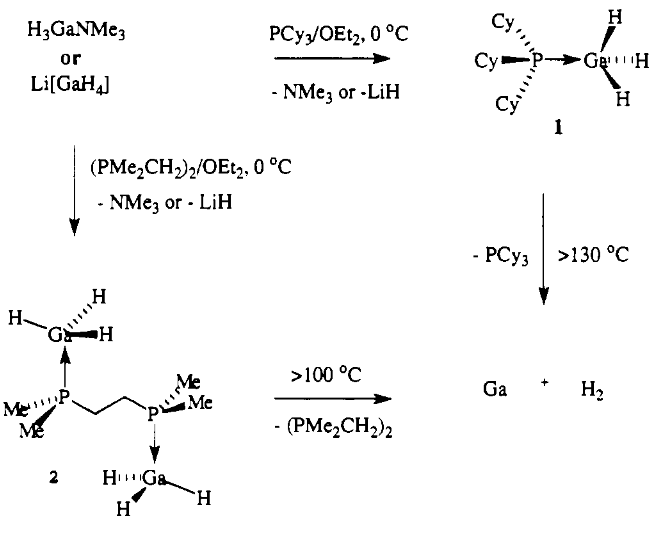


Figure 1. Projections of (top) $H_3Ga\cdot P(C_6H_{11})_3$ (**1**) and (bottom) $2H_3Ga\cdot(PMe_2CH_2)_2$ (**2**) (centrosymmetric molecule) with 20% thermal ellipsoids and arbitrary radii for H atoms. Selected bond distances (Å) and angles (deg): compound **1**, Ga–P 2.460 (2), P–C(11, 12, 13) 1.805 (8), 1.853 (8), 1.868 (8), Ga–H(1, 2, 3) 1.35, 155, 1.54, P–Ga–H(1, 2, 3) 111, 108, 109, Ga–P–C(11, 12, 13) 111.4 (3), 110.6 (3), 113.6 (3); compound **2**, Ga–P 2.399 (4), P–C(1)A,B 1.87 (3), 1.93 (4), P–C(11, 12) 1.82 (1), 1.83 (1), Ga–P–C(1)A,B 113 (1), 113 (2), Ga–P–C(11, 12) 113.7 (5), 114.8 (6).

(2)–2.683 (5) Å.[14] It is noteworthy that uncomplexed gallane is dimeric in the vapor phase, $H_2Ga(\mu\text{-}H)_2GaH_2$,[15] as for $Me_2Ga(\mu\text{-}H)_2GaMe_2$, but is oligomeric in the solid state,[16] and the 1:1 gallane/borane is also dimeric.[17] Moreover, theory yields bridging hydride structures for trigallane, Ga_3H_9.[18]

Scheme I[a]



[a] Cy = C_6H_{11}.

Ab initio molecular orbital calculations have been carried out on $H_3Ga\cdot PH_3$ and $H_3Ga\cdot NH_3$ using Gaussian 88[19] on an IBM RS6000-540 platform. Structures were found initially with a STO-3G minimal basis set using the effective core potential (ECP) approximation on the heavy atoms. These geometries were then refined using a double-ζ (DZ) basis with a core potential retained on the heavy atoms (ECP-DZ), before the geometries were refined using an all-electron double-ζ plus polarization basis, and finally a Møller–Plesset second-order correction was made. At the highest level calculation for both monomers, optimized geometries and energies are as follows. $H_3Ga\cdot PH_3$, $H_3Ga\cdot NH_3$: Ga–P,N = 2.576, 2.074 Å; H–P,N = 1.398, 1.027 Å; Ga–H = 1.561, 1.570 Å; H–P,N–Ga = 118.878, 110.087°; H–Ga–P,N = 96.708, 99.574°; –2267.8893, –1980.6464 hartrees. While the Ga–P distance is longer than those found in **1** and **2**, it is within the range of Ga–P distances found in phosphine adducts of trialkylgalliums;[15] the computed Ga–N distance is within the range found in tertiary amine adducts of gallane.[3] A substantial survey of the potential energy hypersurfaces with the ECP-DZ basis showed no evidence for the existence of a stable dimer of either of the two model molecules. This contrasts with calculations on $H_3Al\cdot NH_3$, which show the dimer to be of comparable energy to the monomer, in accordance with structures of tertiary amine adducts of alane.[2]

Note Added in Proof. Since submission of this paper the synthesis and structure of **2** have been reported.[20]

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Supplementary Material Available: Tables of final atomic parameters, anisotropic thermal parameters, bond lengths, and bond angles for **1** and **2** and optimized computed geometries and energies for $H_3Ga\cdot PH_3$ and $H_3Ga\cdot NH_3$ (7 pages); listings of structure factor amplitudes for **1** and **2** (18 pages). Ordering information is given on any current masthead page.

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