

The insertion of alkylgallium(I) groups [Ga–C(SiMe₃)₃] into P–P bonds of P₄: formation of a P₄(GaR)₃ cage

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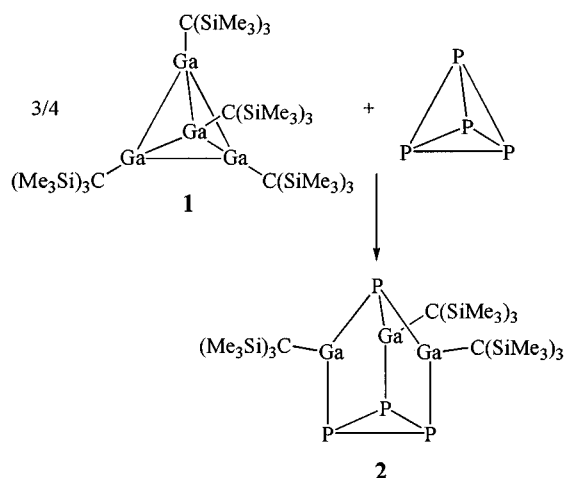
The tetrahedral gallium(I) compound Ga₄[C(SiMe₃)₃]₄ **1** reacted with white phosphorus by the threefold insertion of its monovalent gallium atoms into P–P bonds of the P₄ tetrahedron with formation of a novel P₄(GaR)₃ cage possessing a structure similar to P₄S₃.

Recently, we succeeded in synthesizing the first known alkylgallium(I) compound (**1**), which in the solid state adopted the tetrahedral structure Ga₄[C(SiMe₃)₃]₄, but dissociated into monomeric GaR fragments in dilute solutions.¹ Compound **1** is available now in a high yield by the reduction of the corresponding alkyltrichlorogallate with Rieke magnesium,² and shows a remarkable and unprecedented chemical reactivity similar to the up to now more intensively investigated indium analogue In₄[C(SiMe₃)₃]₄.³ The chalcogens sulfur, selenium and tellurium gave heterocubane type molecules,⁴ the insertion of a GaR fragment into one P–P bond of tri(*tert*-butyl)cyclo-triphosphane was observed,⁵ and the monomers are able to replace carbonyl groups in transition metal carbonyl complexes to yield novel transition metal gallium compounds.⁵ The reaction of **1** with white phosphorus is reported here.

Tetragallane(4) **1** and P₄ reacted slowly in boiling *n*-hexane to yield yellow crystals of the novel trigallium tetraphosphorus compound **2** in a yield of 52%. The formation of **2** can be described by the insertion of three monomeric GaR fragments into three of the six P–P bonds of the P₄ tetrahedron. A similar reaction has not been observed before. The cyclopentadienyl-aluminum(I) derivative (AlCp*)₄ gave the electron deficient cage compound (AlCp*)₆P₄, which consists of two face-sharing heterocubanes with two opposite corners unoccupied.⁶ The indium analogue of **1** yielded another product probably containing four indium atoms and only one phosphorus atom, which, however, could not, as yet, be characterized completely. As expected, singlets were observed for the SiMe₃ groups in the ¹H and ¹³C NMR spectra of **2**, and the resonance of the α carbon atoms attached to gallium (δ 27.8) was in the characteristic range of compounds containing coordinatively unsaturated

tricoordinated gallium atoms. Two resonances were detected in the ³¹P NMR spectrum at δ –202.8 and –521.9. The first is in the expected range and splits into a doublet due to the coupling with the phosphorus atom at the apex of the cage. It was assigned to the P₃ group, of which each member is further coordinated by only one gallium atom. The apical phosphorus atom attached to three gallium atoms showed a quite unusual chemical shift to a very high field and gave a quartet caused by the coupling to the equivalent phosphorus atoms of the P₃ ring. To the best of our knowledge, similar high field shifts have been observed for only very few compounds such as P₄ itself (δ –488), tin(II) derivatives (SnPR)_x and BaSn₃P₄R₄ (up to δ –529).⁷

The molecular structure of the Ga₃P₄ cage (Fig. 1) contains a homocycle of three phosphorus atoms, of which each is further attached to one gallium atom. The fourth phosphorus atom resides at the apex of the cage and is pyramidally coordinated by three gallium atoms, which are coordinatively unsaturated and bind to one carbon atom and two phosphorus atoms in an ideal planar arrangement (Ga2 due to its special position on a crystallographic mirror plane, Ga1: sum of angles 360.0°). The structure is, thus, quite similar to the structures of [P₇]^{3–} or P₄S₃,⁸ which have, however, electronically saturated atoms in the bridging positions. The Ga–P distances to the single phosphorus atom P1 (234.2 pm) are little shorter than those to the P₃ ring (237.8 pm), which may be caused by the higher negative charge at P1 and a stronger ionic contribution to its bonds. All Ga–P bonds are in the lower range usually observed for organogallium phosphides, in which generally the phosphorus atoms are further attached to alkyl groups as in heterocubane type molecules (RGaPR)₄.⁹ The P–P distances (218.1 pm, average) are in the usual range and only a little shorter than in



Scheme 1

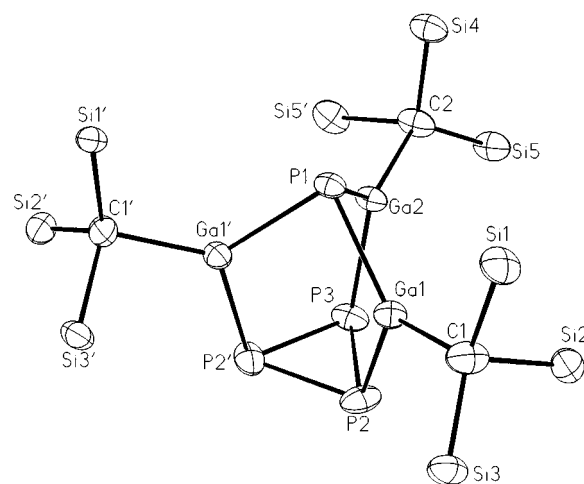


Fig. 1 Molecular structure of **2**. Selected bond lengths (pm) and angles (°): P1–Ga1 234.2(1), P1–Ga2 234.2(2), P2–Ga1 236.9(2), P3–Ga2 237.8(2), P2–P2' 217.8(3), P2–P3 218.3(2), Ga1–C1 197.5(5), Ga2–C2 198.1(7); Ga1–P1–Ga1' 86.43(6), Ga1–P1–Ga2 85.91(5), Ga1–P2–P2' 102.54(4), Ga1–P2–P3 102.20(8), Ga2–P3–P2 102.33(7), P2'–P2–P3 60.08(5), P2–P3–P2' 59.8(1), P1–Ga1–P2 113.76(5), P1–Ga2–P3 113.53(7).

P₄. The cage geometry forces the Ga atoms to approach to a distance of 319.7 pm on average, which is much shorter than the sum of the van der Waals radii (380 pm),¹⁰ but longer than the Ga–Ga separation in the Ga₄ tetrahedron of **1** (268.8 pm).¹ These structural parameters suggest the treatment of **2** with a strong reducing agent in order to transfer electron density to the unsaturated gallium atoms and to obtain a delocalized σ bond in the cage. The Ga–C bonds (197.7 pm) are much shortened compared to those of the starting compound **1** (208 pm). The shortening is more pronounced than observed previously, and even in heterocubanes with the more electronegative chalcogen atoms longer distances were observed.⁴ Several reasons may account for this observation such as the increase of oxidation state of the Ga atoms from +1 in **1** to +3 in compound **2**, the lower steric strain in the molecule and the low coordination number of the Ga atoms with an increased s character of the Ga–C bond.

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Notes and references

† A solution of compound **1** (469 mg, 0.390 mmol, small excess) in 40 ml of *n*-hexane (dried over *n*-butyllithium) was added under argon to 56 mg of white phosphorus (0.452 mmol). The mixture was refluxed for 14 h, and the color changed from red to orange. After cooling, filtration and evaporation the product was recrystallized from toluene or cyclopentane (20/–30 °C). Yield: 240 mg (52%, based on P₄); yellow, air-sensitive crystals (decomp. 215 °C). ¹H NMR (300 MHz, C₆D₆): δ 0.42. ¹³C NMR (75.5 MHz, C₆D₆): δ 27.8 (GaC), 6.7 (SiMe₃). ³¹P NMR (202 MHz, C₆D₆): δ –202.8 (d), –521.9 (q, ²J_{PP} 31 Hz). IR (paraffin, cm^{–1}): 1304w, 1260m (δ CH₃); 1169vs, 1157vw, 1117vw, 1078w, 1045m; (pentane) 856vs, 783w, 721m (ρ CH₃); 675w, 654w, 627w (ν SiC); 521w, 463w (ν GaC), 380vw (δ SiC). UV–VIS (hexane): λ_{max} (log ϵ) = 225 (sh, 3.7), 255 (3.9), 295 (sh, 3.5), 380 nm (3.0). Molar mass (cryoscopically in benzene): obs. 980, calc. 1027.8 g mol^{–1}.

‡ *Crystal data*: single crystals from cyclopentane; not evacuated; handled in perfluorinated polyether; four solvent molecules each formula unit; C₃₀H₈₁Ga₃P₄Si₉·4C₅H₁₀; orthorhombic; space group *Pnma* (no. 62), *a* = 13.132(3), *b* = 32.368(6), *c* = 17.233(3) pm, *U* = 7325(3) Å³, *Z* = 4, *D_c*

= 1.186 g cm^{–3}, crystal dimensions 0.5 × 0.4 × 0.2 mm, *T* = 213 K; $\mu(\text{Mo-K}\alpha)$ = 1.359 mm^{–1}; STOE IPDS diffractometer; 266 exposures, $\Delta\phi$ = 0.7°, $-16 \leq h \leq 16$, $-39 \leq k \leq 39$, $-21 \leq l \leq 21$; 7293 independent reflections; 4973 reflections with $F > 4\sigma(F)$; structure solved by direct methods and refined with all independent structure factors based on F^2 ;¹¹ 414 parameters; *R*1 = 0.058; *wR*2 = 0.165; max., min. residual electron density 1.437 (near the disordered silyl group at Si5A), –0.611 e Å^{–3}. The molecule is located on a crystallographic mirror plane with the atoms P1, P3, Ga2, C2, Si4 and C41 on special positions. All C(SiMe₃)₃ groups were statistically disordered, their atoms were refined by restrictions of bond lengths and angles. CCDC 182/1192. See <http://www.rsc.org/suppdata/cc/1999/771/> for crystallographic files in .cif format.

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