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Formation of a gallium triphosphorus heterocycle by reaction of the alkylgallium(I) compound $Ga_4[C(SiMe_3)_3]_4$ with tri(*tert*-butyl)cyclotriphosphane

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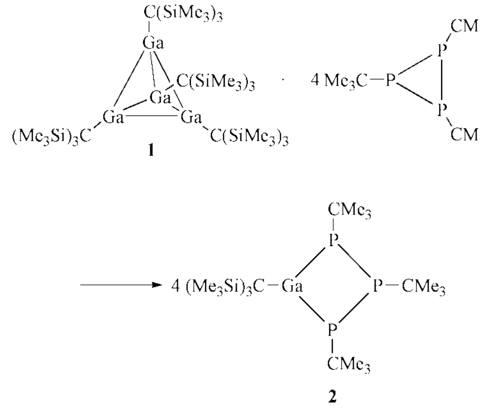
Tri(*tert*-butyl)cyclotriphosphane reacted with $Ga_4[C(SiMe_3)_3]_4$ **1** by the insertion of a monomeric GaR fragment into one of its P–P bonds. A four-membered, slightly folded GaP_3 heterocycle was formed which has a co-ordinatively unsaturated gallium atom and all substituents in *trans* positions.

Introduction

The dark red, air-stable alkylgallium(I) compound $Ga_4[C(SiMe_3)_3]_4$ **1** is easily available by reduction of the corresponding lithium alkyltrichlorogallate with freshly prepared Rieke magnesium.[1] It possesses an almost undistorted tetrahedron of four gallium atoms in its molecular center, but dissociation occurred upon dissolution in benzene. The monomeric, highly unsaturated fragment GaR was characterized in the gas phase by an electron diffraction experiment.[2] Compound **1** showed a remarkable chemical reactivity,[3] similar to that of the analogous tetraindium derivative.[4] Complete oxidation was achieved by treatment with elemental chalcogens and gave heterocubane type molecules,[4,5] while transfer of only one sulfur atom and partial oxidation yielded cluster compounds containing mixed-valent gallium or indium atoms.[6] The monomeric fragment GaR is isolobal to carbon monoxide, and we isolated transition metal complexes bearing bridging[7] or terminally co-ordinated GaR ligands.[8] An outstanding example of this type of compound is the $Ni(CO)_4$ analogous derivative $Ni[GaC(SiMe_3)_3]_4$, for which a bonding situation similar to that of the carbonyl complexes with σ-donor π-acceptor interactions was verified by quantum-chemical calculations.[8] White phosphorus reacted with **1** by the insertion of three monomeric GaR fragments into three P–P bonds of its P_4 tetrahedron.[9] A Ga_3P_4 cage compound resulted, the structure of which is similar to that of $[P_7]^{3-}$ or P_4Se_3. Although the last P_3 ring was not attacked by GaR fragments, it seemed clear that the reaction and the opening of the P–P bonds was favored by the ring strain of the P_4 molecule. Therefore, we treated the tetragallium compound **1** with tri(*tert*-butyl)cyclotriphosphane, which contains a three-membered P_3 ring in its molecular center. This cyclotriphosphane should possess a ring strain similar to that of white phosphorus and should allow the insertion of GaR fragments to obtain novel heterocyclic compounds.

Results and discussion

A solution of the tetragallane(4) **1** and four equivalents of tri(*tert*-butyl)cyclotriphosphane in *n*-hexane was heated under reflux for 13 h completely to consume the gallium starting compound, eqn. (1). A dark orange-red mixture was formed, from which the product **2** was isolated after recrystallization in a yield of 75%. The bright red crystals have a melting point of 174 °C.



(1)

The ^{31}P NMR spectrum of compound **1** showed a typical A_2X spectrum with a doublet and a triplet and clearly separated chemical shifts of δ 81.7 and −21.6, respectively. Both resonances were shifted to lower field in comparison with those of the starting compound $P_3(CMe_3)_3$, which had two resonances at δ −70.1 and −108.5.[10,11] That resonance of **2** which is at the lower field was attributed to the phosphorus atoms attached to gallium. To the best of our knowledge, similar low-field shifts have not been observed before with Ga–P derivatives, for which chemical shifts in a wide range between about $\delta = +50$ and -200[12] are usually observed (δ −522 for the Ga_3P_4 cage compound cited above[9]). The heterocyclic triphosphorus compounds $i\text{-}Pr_2NB(PCMe_3)_3$[13] and $Ph_2Ge(PCMe_3)_3$,[14] which both have a structure quite similar to that of **2**, have ^{31}P NMR shifts at a higher field at δ −30 and −35. Deshielded phosphorus atoms similar to **2** were observed in some compounds possessing co-ordinatively unsaturated gallium atoms such as $(TMP)_2Ga{-}P(CMe_3)_2$ (δ 48.6; TMP = 2,2,6,6-tetramethylpiperidino)[15,16] or in some four-membered Ga_2P_2 heterocycles possessing di(*tert*-butyl)gallium groups (δ 28 to 33).[16] The coupling constant $^1J_{PP} = 185$ Hz detected for **2** is in the range usually observed for cyclotriphosphanes with a *trans* arrangement of the substituents.[10] Smaller ones were obtained for the four-membered BP_3 and GeP_3 heterocycles cited above (127[13] and 153 Hz,[14] respectively). Owing to the complicated spin system with chemically and magnetically non-equivalent phosphorus atoms in the molecular center, the ^1H and ^{13}C NMR spectra cannot be interpreted by a first order approach. In the ^1H NMR spectrum two pseudo doublets were obtained for the *tert*-butyl groups with an intensity ratio of 1 to 2, while the resonance of the tris(trimethylsilyl)methyl group attached to gallium was not affected by the phosphorus atoms and gave a

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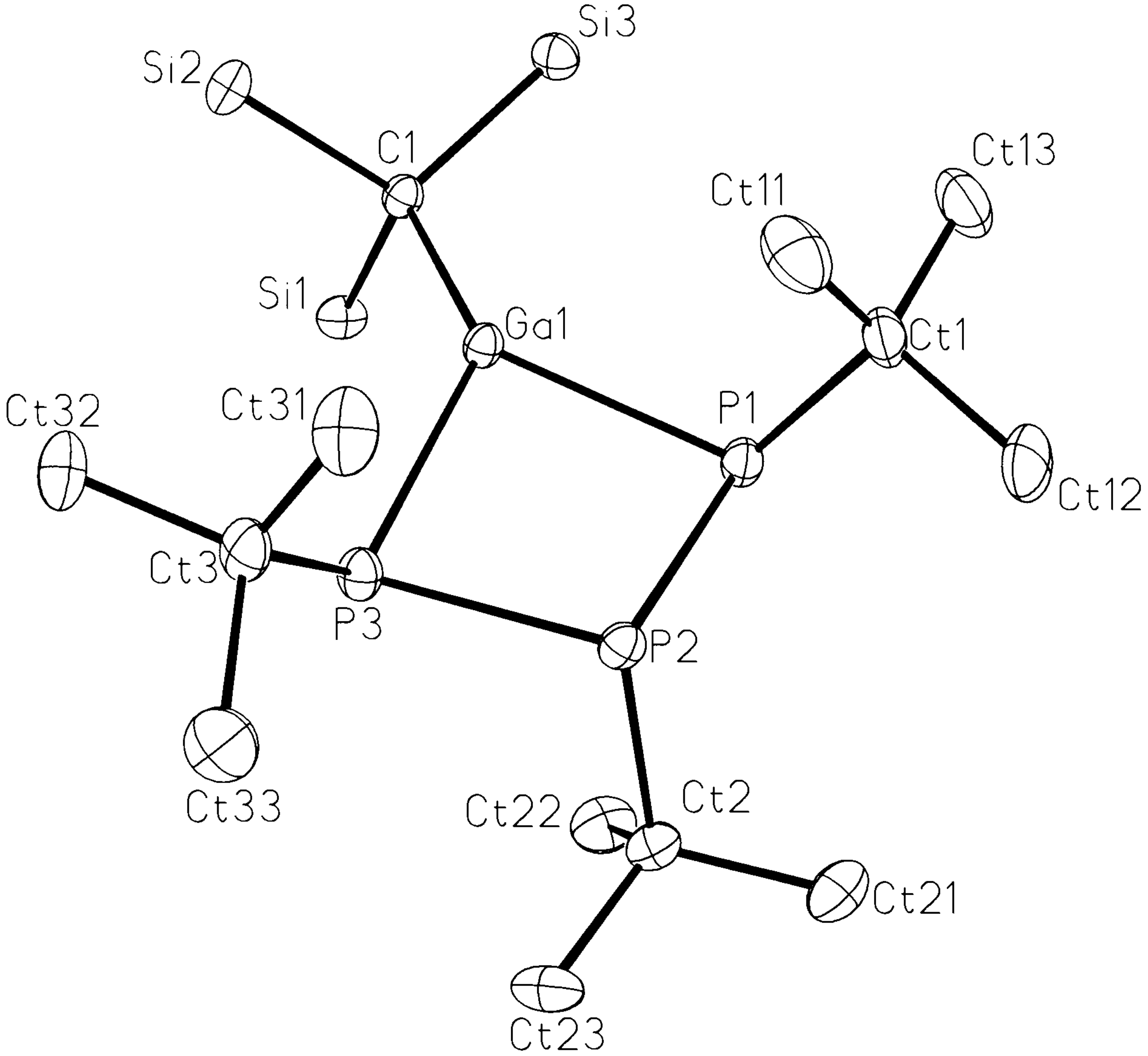

Fig. 1 Molecular structure of compound **2**. Only one of the two independent molecules is shown; a similar numbering scheme holds for the second molecule. Thermal ellipsoids are drawn at the 40% probability level. Methyl groups of the $C(SiMe_3)_3$ substituent and hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): Ga1–C1 200.4(2), Ga1–P1 235.77(7), Ga1–P3 237.00(7), P1–P2 221.72(9), P2–P3 221.73(9), Ga2–C2 199.9(2), Ga2–P4 236.22(7), Ga2–P6 235.02(6), P4–P5 221.85(9) and P5–P6 221.69(9); Ga1–P1–P2 84.91(3), P1–P2–P3 98.12(3), P2–P3–Ga1 84.62(3), P1–Ga1–P3 90.23(2), Ga2–P4–P5 84.47(3), P4–P5–P6 98.15(3), P5–P6–Ga2 84.78(3) and P4–Ga2–P6 90.66(2).

sharp singlet. The intensity ratio gave one $C(SiMe_3)_3$ substituent per three *tert*-butyl groups. A pseudo quartet resulted in the ^{13}C NMR spectrum for the methyl groups of both equivalent *tert*-butyl substituents near the gallium atoms, while a more complicated splitting pattern was observed for the CMe_3 substituent attached to the middle phosphorus atom.

The molecular structure of compound **2** is depicted in Fig. 1; only one of the two crystallographically independent molecules is shown. **2** contains four-membered GaP_3 heterocycles which are not planar, but folded across the P1 ··· P3 axis by 16.2° and across the P4 ··· P6 axis by 15.6° in the second molecule. The gallium atoms are located 46.7 and 44.4 pm above the plane of the remaining three atoms of the heterocycle. The phosphorus atoms have a pyramidal environment with very similar sums of the bond angles between 296.54 (P1) and 306.21° (P3), and the *tert*-butyl groups adopt a *trans* arrangement. The co-ordination sphere of the gallium atoms deviates slightly from planarity (sum of the angles 354.63 and 354.10°), which may be caused by steric repulsion between both neighboring *tert*-butyl groups and the bulky tris(trimethylsilyl)methyl group at Ga.

The Ga–P bond lengths (236.0 pm on average) are in the lower range of known distances in organogallium phosphides, which often have co-ordinatively saturated gallium atoms as, for instance, in heterocubane type molecules.[12,17] Shorter distances down to 225 pm were reported for some compounds possessing co-ordinatively unsaturated gallium atoms.[15] A significant π interaction between Ga and P was not verified up to now by quantum chemical calculations, but in a few cases a hindered rotation detected by NMR spectroscopy was interpreted in terms of a π contribution to the Ga–P bonds. The P–P bond lengths (221.7 pm on average) are similar to those of white phosphorus[18] or to those of cyclic compounds such as the starting cyclotriphosphane[10] and the four-membered BP_3 heterocycle[13] described above. The most acute angles of the GaP_3 heterocycles are found at the phosphorus atoms attached to gallium (Ga–P–P 84.7° on average), the angles at the gallium atoms are near 90° (90.4°), and the largest angles were observed at the inner phosphorus atoms (98.1°).

The insertion of a second GaR group into a P–P bond was not observed, even when a large excess of compound **1** was employed with a very long reaction time. Treatment of the tetraindium analogue of **1**, $In_4[C(SiMe_3)_3]_4$,[4] with tri(*tert*-butyl)cyclotriphosphane in boiling *n*-hexane according to eqn. (1) gave no reaction after a period of 8 h; longer heating led to complete decomposition of the indium compound and the formation of $HC(SiMe_3)_3$. Tetra(*tert*-butyl)cyclotetraphosphane[10] possessing a four-membered P_4 ring in its molecular center did not react with compound **1** at all in boiling solvents, which may be due to its smaller ring strain. Upon UV irradiation of a solution of both components in hexane complete decomposition occurred with the formation of a multitude of unknown products. The related cyclic pnicogen compounds tetra(*tert*-butyl)cyclotetraarsane and the corresponding cyclic antimony derivative reacted with the aluminium(I) cyclopentadienide $Al_4Cp^*_4$[19] by loss of the *tert*-butyl groups and formation of the cage compounds $(Cp^*Al)_3As_2$[20] and $(Cp^*Al)_3Sb_2$,[21] which possess trigonal bipyramidal molecular cores. Compound **1** and its tetraindium analogue did not react with $Sb_4(CMe_3)_4$[22] at all in boiling *n*-hexane, while complete decomposition was observed upon irradiation or heating in boiling toluene.

Experimental

All procedures were carried out under purified argon. *n*-Hexane was dried over $LiAlH_4$, toluene over sodium–benzophenone. Tri(*tert*-butyl)cyclotriphosphane[10] and the tetragallium compound **1**[1] were obtained according to literature procedures.

Synthesis

Compound 2. A mixture of 0.312 g (0.259 mmol) of compound **1** and 0.278 g (1.053 mmol) of tri(*tert*-butyl)cyclotriphosphane in 50 mL of *n*-hexane was heated under reflux for 13 h, changing to strawberry-red. The solvent was removed *in vacuo*, and the residue thoroughly evacuated to remove unchanged cyclotriphosphane. The residue was recrystallized from toluene (−50 °C for some days) to obtain bright red crystals of the product **2**. Yield: 0.439 g (75%). mp. (argon, sealed capillary): 174 °C (Found: Ga, 12.0%; *M* 540 cryoscopically in benzene. $C_{22}H_{54}GaP_3Si_3$ requires Ga, 12.3%; $M = 565.6$). δ_H (C_6D_6, 300 MHz) 1.55 (pseudo-d, 18 H, CMe_3 at P1, P3), 1.48 (pseudo-d, 9 H, CMe_3 at P2) and 0.40 (s, 27 H, $SiMe_3$). δ_C (C_6D_6, 75.5 MHz) 38.6 (pseudo-q, P–C at P1, P3), 34.1 (pseudo-q, CMe_3 at P1, P3), 31.0 (m, P–C at P2), 29.6 (m, CMe_3 at P2) and 6.7 ($SiMe_3$); GaC not detected. δ_P (C_6D_6, 202.5 MHz) 81.7 (d, $^1J_{PP} = 185$ Hz, GaP) and −21.6 (t, P2). $\tilde{\nu}_{max}$/cm^{-1} (CsBr, paraffin) 1304w, 1260s, 1252s δCH_3; 1202vw, 1165m, 1120w, 1080w, 1026m, 1012m νCC; 932vw, 918vw, 853vs; 812w, 783w, 721s $\rho CH_3(Si)$; 677w, 658w, 625w, 600w νSiC, νPC. λ_{max}/nm (*n*-hexane) (ε/M^{-1} cm^{-1}): 240 (11000), 310 (2000) and 480 (300).

Crystal structure determination of compound 2

Single crystals of compound **2** were obtained on cooling of a saturated solution in toluene to −50 °C. $C_{22}H_{54}GaP_3Si_3$, $M = 565.6$, monoclinic, $a = 933.71(4)$, $b = 2088.5(1)$, $c = 1644.4(1)$ pm, $\beta = 94.534(7)°$, $U = 3196.6(3)$ Å^3, $T = 193(2)$ K, space group $P2_1$ (no. 4[23]), $Z = 4$, μ(Mo-Kα) = 1.132 mm^{-1}, 11183 unique reflections (R(int) = 0.038) which were used in all calculations. 10288 Reflections $I > 2\sigma(I)$. The final $wR(F^2)$ was 0.0700, $R1 = 0.0243$, SHELXL 97.[24]

CCDC reference number 186/2108.

See http://www.rsc.org/suppdata/dt/b0/b003760p/ for crystallographic files in .cif format.

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