

The synthesis of phosphorus heterocycles from tetra-*tert*-butyltetraphosphacubane

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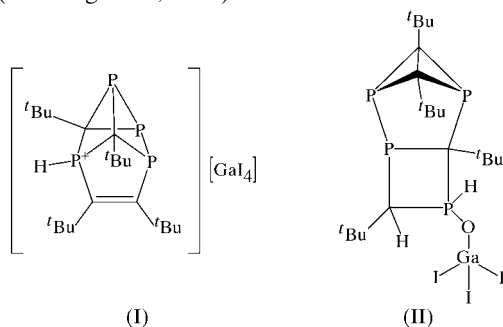
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Tetra-*tert*-butyltetraphosphacubane, $P_4C_4tBu_4$, reacts with water in the presence of 'GaI' to yield two products, namely 4,6,7,8-tetra-*tert*-butyl-1,2,3-triphospha-5-phosphoniatetracyclo[3.2.1.0^{2,4}.0^{3,8}]oct-6-ene tetraiodogallate(III), $(C_{20}H_{37}P_4)[GaI_4]$, and triiodo(3,5,7,8-tetra-*tert*-butyl-1,2,4λ⁵,6-tetraphosphatetracyclo[4.1.1.0^{2,5}.0^{7,8}]octan-4-one)gallium(III), $[GaI_3(C_{20}H_{38}OP_4)]$, both of which have been structurally characterized. The X-ray crystal structure determination of the former compound shows it to be an ion-separated salt, while the latter compound is a neutral phosphinite complex of GaI_3 .

Comment

There is much interest in the reactivity of compounds derived from the cyclo-oligomerization of phosphalkynes, RCP , especially the cyclotetramer of $tBuCP$ (Hitchcock *et al.*, 1995). This compound is of interest because a strong interaction between the P-atom lone-pair electrons and the $P-C \sigma^*$ antibonding orbitals considerably reduces the nucleophilicity of the P atoms (Wettling *et al.*, 1989).



We have recently published a study on the reactivity of secondary phosphines towards 'GaI' (Baker *et al.*, 2003). These reactions have yielded Ga—Ga bonded dimers with the coordination of one phosphine molecule per Ga^{II} centre. Therefore, we thought it worthwhile to investigate the reaction of 'GaI' towards the relatively poorly nucleophilic tetraphosphacubane $P_4C_4tBu_4$. No reaction occurred, but in the

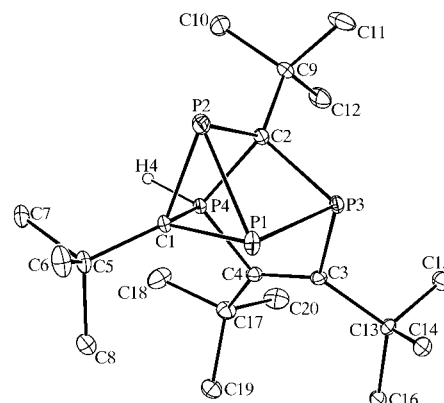


Figure 1

The molecular structure of the cation of (I). Displacement ellipsoids are drawn at the 50% probability level and methyl H atoms have been omitted for clarity.

presence of trace water, a rearrangement of the P_4C_4 skeleton was observed, yielding two products, both of which have been structurally characterized and are reported here.

The molecular structure of $(C_{20}H_{37}P_4)[GaI_4]$, (I), is shown in Fig. 1. The bond lengths and angles around the gallium centre of the anion are unremarkable. The tetraphosphabis(homoprismane) framework of the cation is comparable to the neutral analogue that forms a complex with two $W(CO)_5$ moieties, *viz.* $[(C_{20}H_{36}P_4)\{W(CO)_5\}_2]$ (Hitchcock *et al.*, 1995). The only significant differences between these species are in the bond lengths around atom P4, which are slightly longer in (I). The bond angles around atom P4 are also greater in (I); the sum of the $C-P-C$ angles is 314.1° in (I) (Table 1) and 289° in $[(C_{20}H_{36}P_4)\{W(CO)_5\}_2]$. There is no specific directional interaction between the cation and anion in (I).

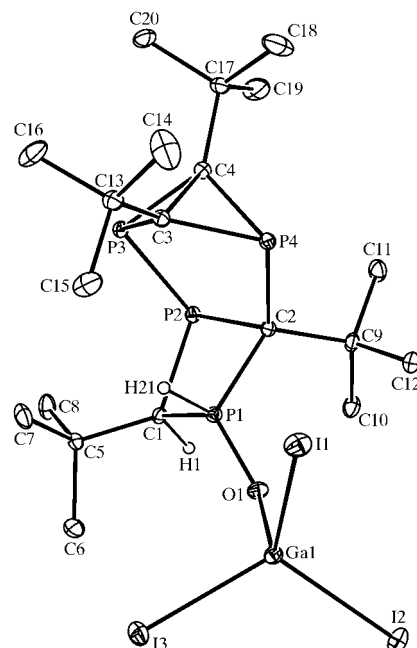


Figure 2

The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level and methyl H atoms have been omitted for clarity.

The molecular structure of $[\text{GaI}_3(\text{C}_{20}\text{H}_{38}\text{OP}_4)]$, (II), is shown in Fig. 2. The 2,4-diphosphabicyclo[1.1.0]butane fragment is a rare structural motif and only three examples have been reported previously. The P—C and C—C bond lengths of the bicyclic framework (Table 2) are similar to those in previous examples (Niecke *et al.*, 1999; Jones *et al.*, 2001; Mack *et al.*, 2002), and the P—O and Ga—O bond lengths of the phosphinite function are also in keeping with previously reported examples of phosphinite–gallium adducts (Barron *et al.*, 1996).

The mechanisms of formation of (I) and (II) are unknown, but in both cases, the rearrangement of the tetraphosphabicyclic framework in the presence of water is mediated by 'GaI', since no reaction occurs in its absence.

Experimental

'GaI' was prepared by the ultrasonic activation of Ga (0.07 g, 0.99 mmol) and I_2 (0.24 g, 0.98 mmol) in toluene (10 ml) for a period of 2 h. To the resulting green suspension, a solution of $\text{P}_4\text{C}_4\text{tBu}_4$ (0.10 g, 0.25 mmol) in toluene (10 ml) was added. The reaction mixture was stirred for 30 min and a few drops of water were added. The suspension was then stirred overnight, after which the solvent was removed *in vacuo*. The residue was extracted with hexane, concentrated and stored at 243 K, yielding crystals of (I) in low yield (<5%). Compound (II) was isolated (yield < 5%) by extraction of the residue with Et_2O , and the solution was concentrated *in vacuo*. Storage at 243 K yielded crystals suitable for X-ray diffraction analysis.

Compound (I)

Crystal data

$(\text{C}_{20}\text{H}_{37}\text{P}_4)[\text{GaI}_4]$
 $M_r = 978.70$
 Triclinic, $P\bar{1}$
 $a = 9.6290$ (19) Å
 $b = 12.459$ (3) Å
 $c = 13.867$ (3) Å
 $\alpha = 82.91$ (3)°
 $\beta = 81.28$ (3)°
 $\gamma = 83.65$ (3)°
 $V = 1624.6$ (6) Å³

$Z = 2$
 $D_x = 2.001$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 18 935 reflections
 $\theta = 2.9$ – 27.5 °
 $\mu = 4.85$ mm⁻¹
 $T = 150$ (2) K
 Plate, yellow
 $0.15 \times 0.15 \times 0.07$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans to fill Ewald sphere
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.471$, $T_{\max} = 0.712$
 25 682 measured reflections
 7382 independent reflections

5661 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.131$
 $\theta_{\max} = 27.5$ °
 $h = -12 \rightarrow 12$
 $k = -16 \rightarrow 16$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.151$
 $S = 1.04$
 7382 reflections
 277 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 4.243P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.15$ e Å⁻³
 $\Delta\rho_{\min} = -2.69$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

I1—Ga1	2.5442 (11)	P2—C2	1.950 (6)
I2—Ga1	2.5590 (10)	P3—C2	1.875 (6)
I3—Ga1	2.5290 (12)	P3—C3	1.882 (6)
I4—Ga1	2.5513 (10)	P4—C2	1.781 (6)
P1—C1	1.869 (6)	P4—C4	1.801 (6)
P1—P2	2.214 (3)	P4—C1	1.807 (7)
P1—P3	2.249 (2)	C3—C4	1.366 (9)
P2—C1	1.893 (6)		
I3—Ga1—I1	110.29 (4)	C5—C1—P4	124.4 (4)
I3—Ga1—I4	106.99 (3)	C5—C1—P1	119.8 (5)
I1—Ga1—I4	110.60 (4)	P4—C1—P1	108.4 (3)
I3—Ga1—I2	109.85 (4)	C5—C1—P2	126.6 (4)
I1—Ga1—I2	107.91 (4)	P4—C1—P2	92.2 (3)
I4—Ga1—I2	111.21 (4)	P1—C1—P2	72.1 (2)
C1—P1—P2	54.46 (19)	C9—C2—P4	124.3 (5)
C1—P1—P3	94.8 (2)	C9—C2—P3	118.2 (4)
P2—P1—P3	81.26 (9)	P4—C2—P3	95.5 (3)
C1—P2—C2	81.5 (3)	C9—C2—P2	122.1 (4)
C1—P2—P1	53.5 (2)	P4—C2—P2	91.2 (3)
C2—P2—P1	85.4 (2)	P3—C2—P2	98.9 (3)
C2—P3—C3	98.9 (3)	C4—C3—C13	135.0 (5)
C2—P3—P1	86.2 (2)	C4—C3—P3	116.6 (4)
C3—P3—P1	100.8 (2)	C13—C3—P3	108.3 (4)
C2—P4—C4	107.6 (3)	C3—C4—C17	134.0 (5)
C2—P4—C1	88.8 (3)	C3—C4—P4	105.7 (4)
C4—P4—C1	117.7 (3)	C17—C4—P4	120.3 (5)

Compound (II)

Crystal data

$[\text{GaI}_3(\text{C}_{20}\text{H}_{38}\text{OP}_4)]$
 $M_r = 868.80$
 Monoclinic, $P2_1/c$
 $a = 12.082$ (2) Å
 $b = 17.522$ (4) Å
 $c = 14.615$ (3) Å
 $\beta = 101.47$ (3)°
 $V = 3032.2$ (10) Å³
 $Z = 4$
 $D_x = 1.903$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 66 215 reflections
 $\theta = 2.9$ – 27.5 °
 $\mu = 4.18$ mm⁻¹
 $T = 150$ (2) K
 Square prism, yellow
 $0.30 \times 0.30 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans to fill Ewald sphere
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.302$, $T_{\max} = 0.658$
 50 118 measured reflections

6923 independent reflections
 6141 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.132$
 $\theta_{\max} = 27.5$ °
 $h = -15 \rightarrow 15$
 $k = -22 \rightarrow 22$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.081$
 $S = 1.04$
 6923 reflections
 279 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 7.857P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.12$ e Å⁻³
 $\Delta\rho_{\min} = -1.48$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00049 (10)

Table 2
Selected geometric parameters (Å, °) for (II).

I1—Ga1	2.5305 (7)	P2—P3	2.2171 (14)
I2—Ga1	2.5050 (7)	P3—C4	1.835 (4)
I3—Ga1	2.5152 (7)	P3—C3	1.851 (4)
Ga1—O1	1.903 (3)	P4—C3	1.823 (4)
P1—O1	1.523 (3)	P4—C4	1.842 (4)
P1—C1	1.795 (4)	P4—C2	1.895 (4)
P1—C2	1.819 (4)	C2—C9	1.575 (5)
P2—C2	1.899 (3)	C3—C13	1.531 (5)
P2—C1	1.911 (4)	C3—C4	1.534 (5)
O1—Ga1—I2	104.97 (8)	P1—C1—P2	88.42 (16)
O1—Ga1—I3	103.46 (8)	C9—C2—P1	117.2 (2)
I2—Ga1—I3	115.81 (2)	C9—C2—P2	114.7 (2)
O1—Ga1—I1	103.02 (8)	P1—C2—P2	88.09 (15)
I2—Ga1—I1	113.68 (3)	C9—C2—P4	110.6 (2)
I3—Ga1—I1	113.96 (2)	P1—C2—P4	114.46 (18)
O1—P1—C1	117.21 (16)	P2—C2—P4	109.96 (17)
O1—P1—C2	120.11 (15)	C13—C3—C4	136.9 (3)
C1—P1—C2	92.83 (16)	C13—C3—P4	128.1 (3)
C2—P2—C1	86.80 (15)	C4—C3—P4	65.94 (19)
C2—P2—P3	96.46 (11)	C13—C3—P3	127.0 (3)
C1—P2—P3	110.13 (12)	C4—C3—P3	64.87 (19)
C4—P3—C3	49.18 (16)	P4—C3—P3	104.66 (19)
C4—P3—P2	95.39 (12)	C17—C4—C3	139.7 (3)
C3—P3—P2	106.12 (12)	C17—C4—P3	126.6 (3)
C3—P4—C4	49.47 (16)	C3—C4—P3	65.95 (19)
C3—P4—C2	105.11 (16)	C17—C4—P4	128.3 (3)
C4—P4—C2	104.02 (16)	C3—C4—P4	64.59 (19)
P1—O1—Ga1	134.87 (17)	P3—C4—P4	104.50 (18)
C5—C1—P1	124.3 (3)	C7—C5—C6	109.2 (4)
C5—C1—P2	123.8 (2)		

In both compounds, methyl H atoms were placed in idealized positions (C—H = 0.96 Å) and refined as riding, with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{C})$. In (II), atom H4 attached to atom P4 was located from a difference Fourier map and refined isotropically, with the P—H distance restrained to 1.33 (2) Å. In (II), methine atom H1 was placed

in an idealized position (C—H = 1.00 Å) and refined as riding, with a $U_{\text{iso}}(\text{H})$ value of $1.2U_{\text{eq}}(\text{C})$, while atom H21 attached to P1 was treated in the same way as atom H4 in (I).

For both compounds, data collection: *COLLECT* (Hooft, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1533). Services for accessing these data are described at the back of the journal.

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