Phosphaalkyne Tetramerisation: First Structural Characterisation of a Tetraphosphabishomoprismane. Synthesis and Molecular Structure of $[W_2(CO)_{10}(P_4C_4Bu^t{}_4)]$

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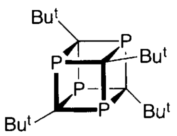
The first structural characterisation of a tetraphosphabishomoprismane resulting from the tetramerisation of a phosphaalkyne is reported.

The cyclo-oligomerisation of phosphaalkynes, RC≡P, is of considerable current interest[1] and the relative energies of a number of oligomers of HCP have been calculated[2–5] by several *ab initio* methods.

There is a special interest in the cyclotetramers of $Bu^tC{\equiv}P$, $P_4C_4Bu^t{}_4$, and following the seminal work of Regitz and coworkers[6] on the thermal formation of the tetraphosphacubane **1** with low selectivity, the subsequent use of the precursor $[Zr(\eta^5\text{-}C_5H_5)_2(P_2C_2Bu^t{}_2)]$ gives **1** in high yield[7–9] and has also enabled syntheses of the new tetraphosphacyclooctadienes **2** and **3** to be achieved.[5] Using biscyclooctatetraene zirconium, Binger *et al.*[10] have recently synthesised the 1,3,5,7-tetraphosphabarrelene **4** in high yield directly from $Bu^tC{\equiv}P$.

Using a stepwise route, the polycyclic phosphaalkyne tetramers **5** and **6** can also be made,[10,12] and they both can be quantitatively thermally transformed into the more thermodynamically stable tetraphosphabishomoprismane compound **7**[12,13] in agreement with theoretical calculations on the relative stabilities $(HCP)_4$ tetramers.[5]

The structures of the yellow oily compounds **5**–**7** have only previously been deduced by multinuclear NMR spectroscopic studies. We now describe the synthesis and first full structural characterisation of the crystalline yellow–orange bis-$[W(CO)_5]$ adduct **8** of the tetraphosphabishomoprismane **7**, which confirms the previous structural assignment.



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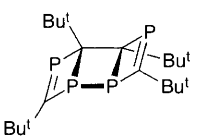

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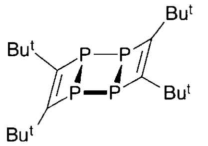

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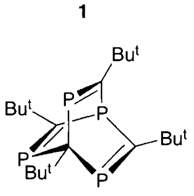

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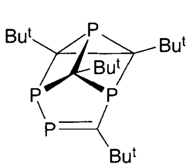

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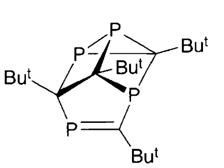

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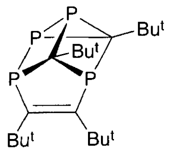

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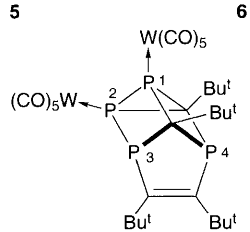

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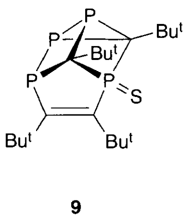

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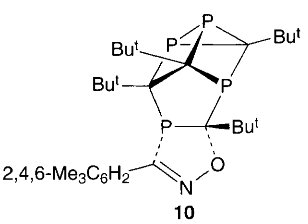

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Treatment of **7** with an excess of $[W(CO)_5(thf)]$ at room temperature affords **8** in *ca.* 32% yield and changes in the $^{31}P\{^1H\}$ NMR spectra of **7** and **8** strongly suggest that the two $[W(CO)_5]$ fragments are ligated at positions P(1) and P(2) of the tetraphosphabishomoprismane.† Interestingly, the ^{31}P resonances of P(3) and P(4) are also significantly affected by the presence of the two $[W(CO)_5]$ fragments.† Significant ^{31}P chemical shift changes of the three unoxidised P centres in $P_4C_4Bu^t{}_4S$ **9** have been previously reported,[14] while coordination of two $[PtCl_2(PR_3)]$ fragments in the tetraphosphacubane **1** also strongly affects the ^{31}P shifts of the uncoordinated centres.[15] The mass spectrum of **8** exhibited the parent ion peak at *m*/*z* 1048 with the expected isotropic distribution pattern, and suitable crystals (mp 166 °C decomp.) for a single-crystal X-ray diffraction study were obtained following chromatography (Kieselgel/hexane).

The molecular structure of **8** determined by a single-crystal X-ray diffraction study, shown in Fig. 1,‡ reveals the tetraphosphabishomoprismane structure and shows that the two $[W(CO)_5]$ fragments are indeed attached to both phosphorus atoms on the three-membered ring. In this respect the structure differs from that proposed on the basis of ^{13}C and ^{31}P NMR

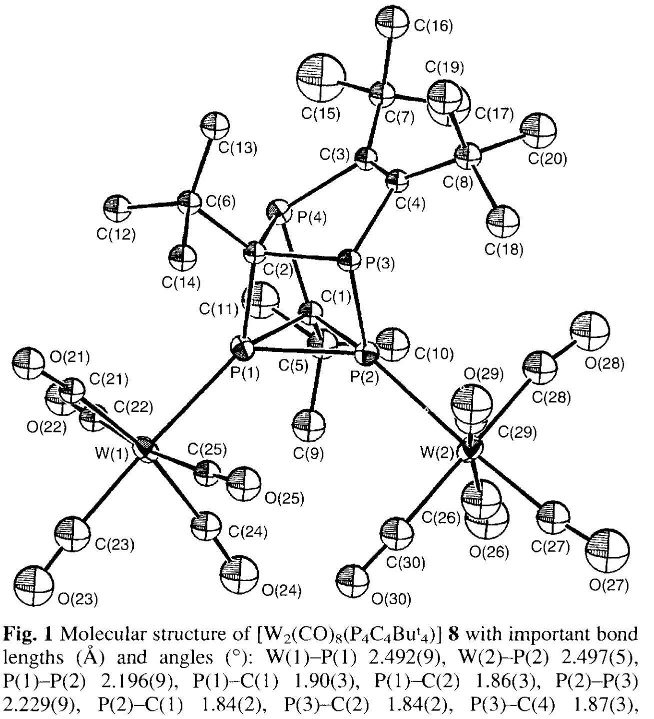

Fig. 1 Molecular structure of $[W_2(CO)_8(P_4C_4Bu^t{}_4)]$ **8** with important bond lengths (Å) and angles (°): W(1)–P(1) 2.492(9), W(2)–P(2) 2.497(5), P(1)–P(2) 2.196(9), P(1)–C(1) 1.90(3), P(1)–C(2) 1.86(3), P(2)–P(3) 2.229(9), P(2)–C(1) 1.84(2), P(3)–C(2) 1.84(2), P(3)–C(4) 1.87(3), P(4)–C(1) 1.91(2), P(4)–C(2) 1.88(2), P(4)–C(3) 1.86(3), C(3)–C(4) 1.29(3); W(1)–P(1)–P(2) 130.0(4), W(1)–P(1)–C(1) 139.3(8), W(1)–P(1)–C(2) 134.1(8), P(2)–P(1)–C(1) 52.9(6), P(2)–P(1)–C(2) 84.7(8), C(1)–P(1)–C(2) 84(1), W(2)–P(2)–P(1) 139.0(5), W(2)–P(2)–P(3) 122.3(3), W(2)–P(2)–C(1) 137.4(7), P(1)–P(2)–P(3) 81.2(3), P(1)–P(2)–C(1) 55.4(9), P(3)–P(2)–C(1) 97.2(8), P(2)–P(3)–C(2) 84.1(9), P(2)–P(3)–C(4) 100.3(7), C(2)–P(3)–C(4) 99(1), C(1)–P(4)–C(2) 83(1), C(1)–P(4)–C(3) 107(1), C(2)–P(4)–C(3) 99(1), P(1)–C(1)–P(2) 71.8(9), P(1)–C(1)–P(4) 89.7(9), P(2)–C(1)–P(4) 112(1), P(1)–C(2)–P(4) 92.0(9), P(3)–C(4)–C(3) 116(2), P(3)–C(2)–P(4) 102(1)

spectroscopic studies[14] on **9**, in which the sulfur has selectively oxidised P(4). Since theoretical calculations[16] at different levels *on the* parent $P_4C_4H_4$ bishomoprismane tetramer all show that P(2) has the lowest charge (because it has only one C neighbour), the differences in the ligating behaviour of **7** towards $[W(CO)_5]$ and S may reflect steric as well as electronic factors.

The presence of a three-membered PPC ring in **8** is noteworthy since in related 'cage' structures which have recently been published, such as the phosphaalkyne pentamer $P_5C_5Bu^t{}_5$,[17] and hexamer $P_6C_6Bu^t{}_6$,[4] the three-membered rings consist of PCC atoms. The PPC 'diphosphirane' ring system has also been established[11] in **10**, which is the cycloadduct of **7** with mesitylnitrile oxide, and the bond lengths and bond angles in **10** are comparable with those observed in **8**.

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Footnotes

† ^{31}P NMR: compound **7**, (ref. 14) $\delta_{P(1)}$ −155.7, $\delta_{P(2)}$ −242.5, $\delta_{P(3)}$ 82.4, $\delta_{P(4)}$ 87.8, $^1J_{P(1)P(2)}$ 105, $^2J_{P(1)P(3)}$ 33, $^2J_{P(1)P(4)}$ 10, $^1J_{P(2)P(3)}$ 168 Hz. Compound **8**, $\delta_{P(1)}$ −96.9, $\delta_{P(2)}$ −189.0, $\delta_{P(3)}$ 132.7, $\delta_{P(4)}$ 119.2; $^1J_{P(1)P(2)}$ 82, $^1J_{P(2)P(3)}$ 196, $^2J_{P(1)P(3)}$ 26, $^2J_{P(1)P(4)}$ 30, $^2J_{P(2)P(4)}$ 8, $^2J_{P(3)P(4)}$ 26, $^1J_{WP(1)}$ 246, $^1J_{WP(2)}$ 230 Hz.

‡ *Crystal data* for **8**. $C_{30}H_{36}O_{10}P_4W_2$, M = 1048.2, triclinic, space group $P\bar{1}$ (no. 2), a = 11.561(3), b = 12.109(3), c = 16.189(5) Å, α = 69.98(2), β = 71.94(2), γ = 67.02(2)°, V = 1909(1) Å^3, Z = 2, D_c 1.82. The data were collected with Mo-Kα radiation (λ = 0.71073 Å, μ = 63.6 cm^{-1}) using an Enraf-Nonius CAD4 diffractometer on a crystal of dimensions 0.2 × 0.15 × 0.1 mm. A total of 6712 reflections were measured and 3548 having $|F^2| > 2\sigma(F^2)$ used on the refinement. Non H-atoms were located by heavy-atom methods SHELXS-86 and refined by full-matrix least squares (W and P atoms anisotropic) using Enraf-MolEN programs. H-atoms were in fixed calculated positions. The final residuals were R = 0.085, R' = 0.090. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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