Cycloaddition Reactions of a 1,2,4-Triphosphacyclopenta-1,3-diene. Synthesis, Crystal, and Molecular Structure of the Novel Hexaphosphorus Cage Compound $P_6C_4Bu^t{}_4H_2$ containing Five Directly Bonded Phosphorus Atoms

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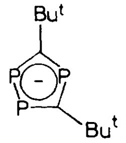
Protonation of the $P_3C_2Bu^t{}_2$ anion affords $P_3C_2Bu^t{}_2H$ which dimerises by [4 + 2] and [2 + 2] cycloaddition reactions to the novel cage compound $P_6C_4Bu^t{}_4H_2$, the structure of which has been elucidated by ^{31}P n.m.r. spectroscopy and a single crystal *X*-ray diffraction study.

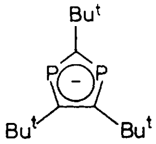
The chemistry and ligating behaviour of organophosphorus compounds containing phosphorus–carbon multiple bonds is of considerable current interest.[1—3] In previous publications[4—7] we have shown how the $(P_3C_2Bu^t{}_2)^-$ and $(P_2C_3Bu^t{}_3)^-$ ring systems (**1**) and (**2**) can be utilised in the synthesis of 'sandwich' compounds of the type (**3**)—(**6**) analogous to their better known η-cyclopentadienyl analogues. Recently[8] we showed that when $CoCl_2$ was treated with the lithium salt of (**1**) in monoglyme the resulting metal complex (**7**) contained an η^4-ligated 1,2,4-triphospha-3,5-di-t-butylcyclopenta-1,3-

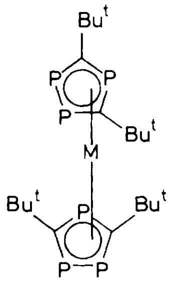
diene, (**8**), which was thought to result from hydrogen abstraction from the solvent.

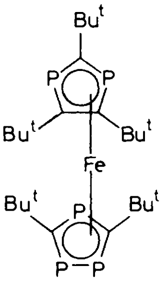
We now report that careful protonation of (**1**) with an EtOH/MeCO$_2$H mixture at room temperature affords a colourless crystalline product (**9**) which was established as the dimer of (**8**) on the basis of, firstly, the observation of the parent ion m/z = 464, $(M)^+$, in the mass spectrum and peaks at 364, $[(\mathrm{Bu^tC})(\mathrm{Bu^tCH})\mathrm{P_3}(\mathrm{Bu^tCHP_2})]^+$; 263, $[(\mathrm{Bu^tCHP})(\mathrm{Bu^tCP})(\mathrm{Bu^tCP})\mathrm{P_2}]^+$; 193, $[(\mathrm{Bu^tCP})\mathrm{P_3}]^+$; 131, $[(\mathrm{Bu^tCP})\mathrm{P}]^+$; 69, $[(\mathrm{Bu^tC})]^+$; and 41, $[\mathrm{C_3H_5}]^+$, secondly, the presence of six different phosphorus resonances in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**9**), and thirdly the observation of four separate Bu^t resonances in the ^{1}H n.m.r. spectrum of (**9**).†

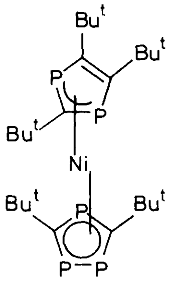
The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. spectrum shown in Figure 1 is almost first-order and has been fully simulated using the chemical shift and coupling constant data shown below.‡ Of particular structural significance is the simplicity of the resonance of P(5) compared with the multiplets of the other phosphorus resonances, suggesting it is attached only to carbon atoms, whereas the remaining five phosphorus atoms are linked together in a chain.

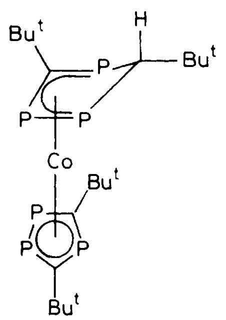

(**1**)

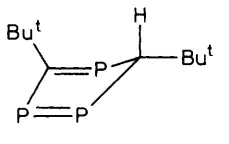

(**2**)


(**3**) M = Fe
(**4**) M = Cr

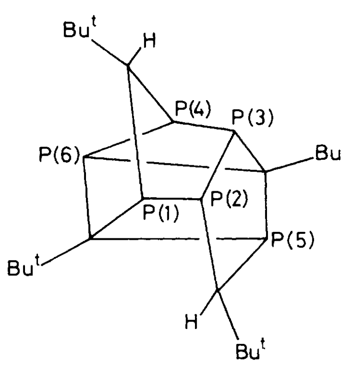

(**5**)


(**6**)

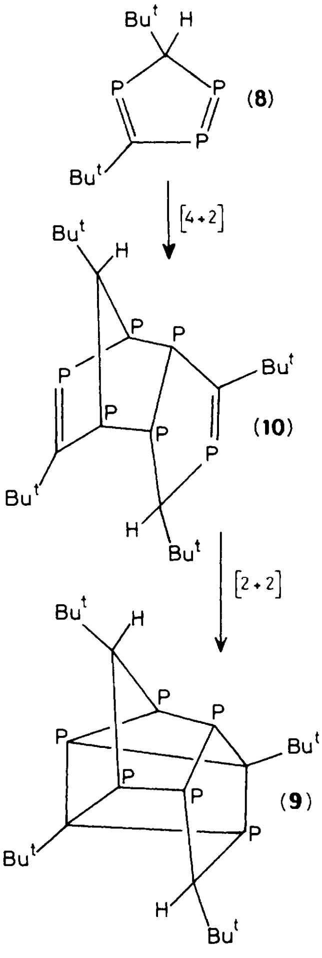

(**7**)


(**8**)

The molecular structure of (**9**) was established by a single crystal X-ray diffraction study§ and is shown in Figure 2. The



(**9**)
(showing P numbering scheme)



Scheme 1

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† δ_H = 1.01, 1.05, 1.11, 1.28 (Bu^t); 3.67, 1.69 (CH).

‡ δ 103.6 [P(1)], 73.9 [P(2)], 43.2 [P(3)], −27.0 [P(4)], 112.4 [P(5)], 163.3 [P(6)] (rel. H$_3$PO$_4$). J_{PP} Values: $J_{1,2}$ 263.7; $J_{1,3}$ 41.4; $J_{1,4}$ 13.3; $J_{1,5}$ 10.0; $J_{1,6}$ 15.0; $J_{2,3}$ 254.4; $J_{2,5}$ 0; $J_{2,6}$ 17.0; $J_{3,4}$ 143.9; $J_{3,5}$ 10.0; $J_{3,6}$ 6.0; $J_{4,5}$ 10.4; $J_{4,6}$ 119.2; $J_{5,6}$ 10.0 Hz. The spectrum can also be simulated if the assignments of both P(1) and P(6), and P(2) and P(4) are interchanged.

§ *Crystal data*: C$_{20}$H$_{38}$P$_6$, M = 464.4, monoclinic, space group $P2_1/c$, a = 22.491(17), b = 12.413(4), c = 19.634(9) Å, β = 112.90(5)°, U = 5049.4 Å^3, Z = 8, D_c = 1.22 g cm^{-3}. The structure was solved by direct methods using 1923 reflections (from a total of 3692 unique reflections), having $|F^2| > 3\sigma(F^2)$ collected on an Enraf-Nonius CAD4 diffractometer using Mo-K_α radiation λ = 0.71069 Å, μ = 4.2 cm^{-1}. The final residuals were R = 0.123, R_w = 0.172. There are two independent molecules in the unit cell which have essentially the same geometry. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

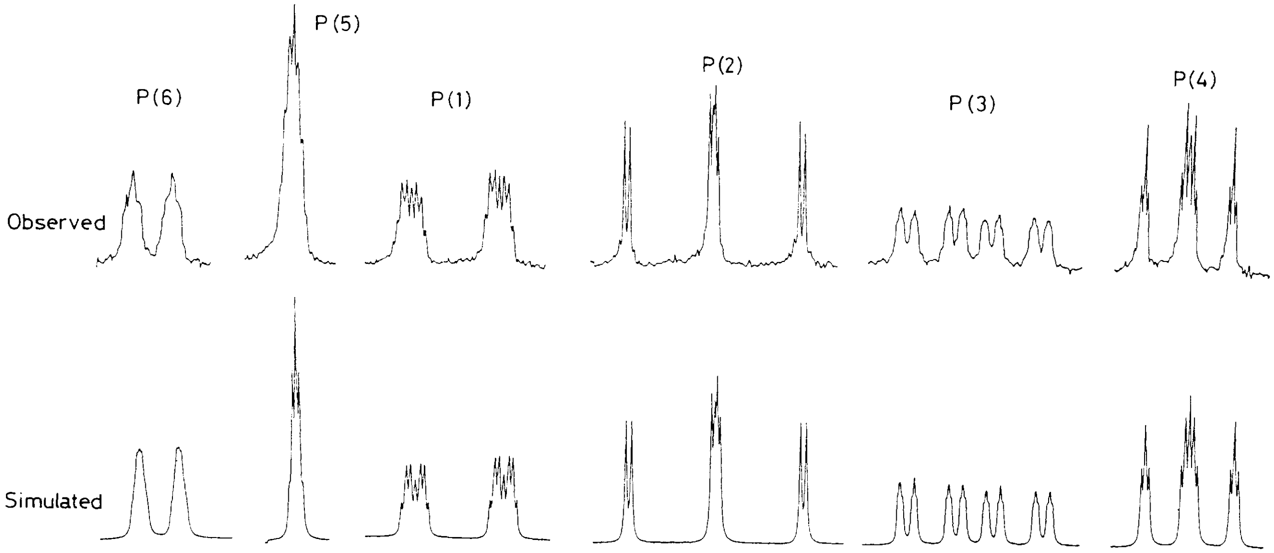

Figure 1. Observed and simulated $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ n.m.r. spectrum of (**9**).

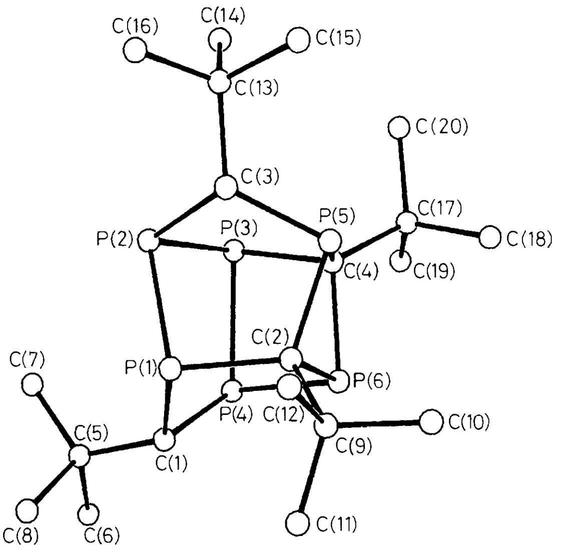

Figure 2. Molecular structure of (**9**). Selected bond lengths for molecule (**1**) are: P(1)–P(2) 2.171(11); P(1)–C(1) 1.89(3); P(1)–C(2) 1.90(3); P(2)–P(3) 2.233(12); P(2)–C(3) 1.92(3); P(3)–P(4) 2.266(11); P(3)–C(4) 1.89(3); P(4)–P(6) 2.206(14), P(4)–C(1) 1.92(3); P(5)–C(2) 1.86(2); P(5)–C(3) 1.84(3), P(5)–C(4) 1.80(3); P(6)–C(2) 1.87(3); P(6)–C(4) 1.87(3) Å.

novel structure which contains no carbon–carbon bonds within the cage consists of three five-membered rings containing 3, 3, and 4 phosphorus atoms respectively, linked together by two four-membered rings containing 2 and 3 phosphorus atoms respectively. The P–C and P–P bond lengths within the cage structure are typical for single bonds.

The mechanism of formation of (**9**) from the intermediate (**8**), summarised in Scheme 1, can be considered to involve an initial [4 + 2] cycloaddition reaction to form the tricyclic compound (**10**), (analogous to the known behaviour of cyclopentadiene itself), and an intramolecular [2 + 2] cycloaddition involving the two P=C bonds of (**10**) which are in close proximity.

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