Synthesis and Structural Characterisation of the First Example of a 3,3′-Diphospha-1,1′-biphospholyl Ring System; Crystal and Molecular Structure of $P_4C_6Bu^t_6$

Salih S. Al-Juaid, Peter B. Hitchcock, Robson M. Matos and John F. Nixon*

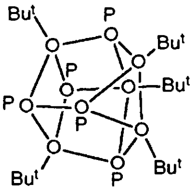
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

The novel 3,3′-diphospha-1,1′-biphospholyl compound $P_4C_6Bu^t_6$, obtained by oxidative coupling of two $P_2C_3Bu^t_3$ anions, has been synthesised and its open structure is contrasted with the cage compounds $P_5C_5Bu^t_5$ and $P_6C_4Bu^t_4$ (two isomers).

Phospholyl anions of the type $[P_n(CR)_{5-n}]^-$, (n = 1–5), are of considerable current interest, since they not only exhibit significant electron delocalisation, but readily form η^5-transition metal complexes of the following types.[1–7]

The organic chemistry of these types of compounds is only just being developed and, to date, reports have appeared on (*i*) oxidative coupling of $P_2C_3Bu^t_3^-$ and $P_3C_2Bu^t_2^-$ anions to afford the $P_5C_5Bu^t_5$ cage **1**,[8] (*ii*) protonation of $P_3C_2Bu^t_2^-$ to afford the cage $P_6C_4Bu^t_4H_2$ **2**,[2] (*iii*) protonation of $P_3C_2Bu^t_2^-$/$P_2C_3Bu^t_3^-$ mixtures to afford the tricyclic compound $P_5C_5Bu^t_5H_2$ **3**[3] and (*iv*) protonation of $P_2CHC_2Ph_2^-$ to generate the transient $P_2CH_2C_2Ph_2$, which can be trapped.[9]

Very recent reports by Mathey *et al.*[10,11] of tetraphosphafulvenes **4** and their dianions **5** and double open-edged coordina-



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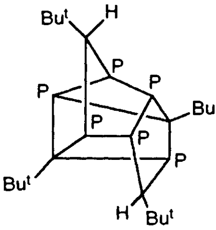

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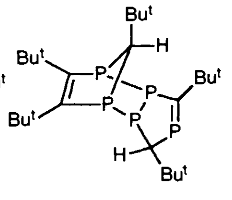

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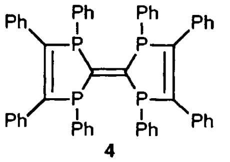

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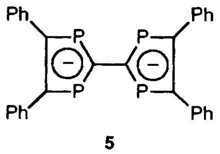

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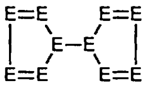

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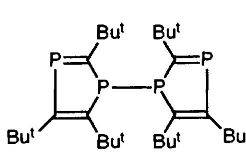
a; E = P

b; E = As



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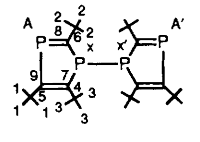

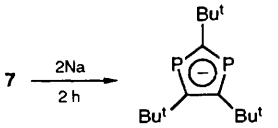

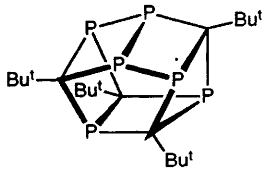

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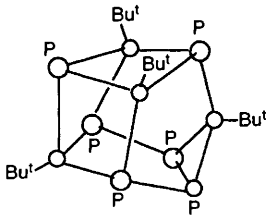

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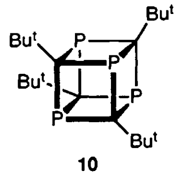

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tion complexes of decaphospha- and decaarsa-analogues of dihydrofulvalene, **6a** and **b** by Scherer *et al.*,[12] prompts us to describe the synthesis and structural characterisation of the first example of a 3,3′-diphospha-1,1′-biphospholyl compound $P_4C_6Bu^t_6$ **7**, which is isoelectronic with tetraphosphafulvenes of type **4**.

Thus, treatment of a solution of the sodium salts of $P_3C_2Bu^t_2{}^-$ and $P_2C_3Bu^t_3{}^-$ anions in dimethoxyethane[13] with $[RuCl_2(cod)]_n$ (cod = cycloocta-1,5-diene) at −30 °C gave a black residue after 4 h which, after column chromatography and recrystallisation from CH_2Cl_2, yielded orange crystals of **7** (m.p. 112 °C) in 37% yield. Careful control of the reaction temperature is necessary, since, at room temperature, the reaction proceeds differently to afford the organometallic ruthenium(II) complex $[Ru(\eta^5\text{-}P_2C_3Bu^t_3)(\eta^5\text{-}C_8H_{11})]$. The mass spectrum of **7** showed a parent ion peak at m/z 538 and the expected fragmentation peaks. Particularly significant were the $^{31}P\{^1H\}$ and ^1H NMR spectroscopic data, the former exhibiting two resonances at δ 303.3 and 24.6 typical for sp^2 and sp^3 hybridised P atoms, respectively, and the latter three different Bu^t resonances.† The ^{13}C NMR data‡ provide further confirmation of the unusual diphosphabiphospholyl structure.

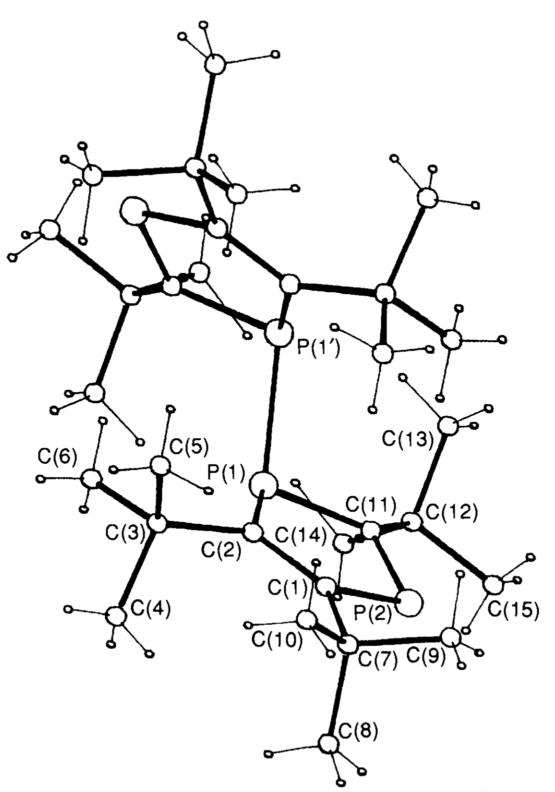

Fig. 1 Molecular structure of **7**. Selected bond lengths (Å) and bond angles (°) are P(1)–C(2) 1.819(4), P(1)–C(11) 1.784(5), P(2)–C(1) 1.816(5), P(2)—C(11) 1.673(5), C(1)–C(2) 1.397(7), C(1)–C(7) 1.543(7), C(2)–C(3) 1.566(6) P(1)–P(1′) 2.244(2); C(2)–P(1)–C(11) 99.7(2), C(1)–P(2)–C(11) 100.5(2), P(2)–C(1)–C(2) 115.4(3), P(2)–C(1)–C(7) 111.1(3), C(2)–C(1)–C(7) 133.2(4) P(1)–C(2)–C(1) 112.1(3) P(1)–C(2)–C(3) 116.2(3), C(1)–C(2)–C(3) 130.2(4) P(1′)–P(1)–C(2) 107.2(2), P(1′)–P(1)–C(11) 113.1(2). The angle between the two rings is 46°.

A single crystal X-ray diffraction study revealed the molecular structure shown in Fig. 1.§ The two $P_2C_3Bu^t_3$ fragments, which are not parallel to each other, are joined by a P–P bond [2.244(2) Å], which is of comparable length to other diphosphanes. The P–C and C–C bond lengths within each ring reflect the expected bond orders.

Treatment of **7** with an excess of Na in monoglyme readily affords $P_2C_3Bu^t_3{}^-$, which was confirmed by its characteristic singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ_P 189. The synthesis of $P_4C_6Bu^t_6$ **7** is interesting since it provides a further example of a framework based on a 10-atom system involving P and C atoms. The structures, which have been established to date by single crystal X-ray diffraction for three other members of this structural type, are shown in **1**, **8** and **9**. The compound $P_6C_4Bu^t_4$, which was recently made independently by Regitz *et al.*[14] and Zenneck *et al.*,[15] using very different synthetic routes, surprisingly exists in two stable forms, **8** and **9**, at room temperature. It appears that the structures of these systems are controlled by the steric effect of the bulky Bu^t groups, and

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† The $^{31}P\{^1H\}$ spectrum can be simulated as an $[AX]_2$ spin system. ^{31}P: δ_{PA} 303.3; δ_{PX} 24.6; $^2J_{PAPX}$ 24.4 Hz; $^1J_{PXPX'}$ 470 Hz; $J_{PA'PX'} \approx 0$ ^1H: δ_H 1.67 s, 2Bu^t; 1.62 s, 2Bu^t; 1.33 s, 2Bu^t.

‡ ^{13}C NMR: C_1 34.76, d, $^3J_{C1P}$ 14.2 Hz; C_2 34.99, t, $^3J_{C2P}$ 11.6 Hz; C_3 35.28, dt, $^3J_{C3P}$ 13.2 Hz, $^4J_{C3P}$ 13.2 Hz, $^4J_{C3P}$ 7.2 Hz; C_4 37.12, t, $^2J_{C4P}$ 24.6 Hz; C_5 36.86, dd, $^2J_{C5P}$ 24.5 Hz; $^3J_{C5P}$ 9.9 Hz; C_6 36.59, m; C_7, C_8, C_9 198.04 m.

§ *Crystal data*: $C_{30}H_{54}P_4$, M = 538.7, monoclinic, space group $C2/c$, (No. 15), a = 19.765(7), b = 19.261(9), c = 8.991(4) Å, β = 109.28(4)°, U = 3230.5, Z = 4, D_c = 1.11 g cm^{-3}. The structure was solved using direct methods using 1751 reflections (from a total of 2934 unique reflections) having $|F^2| > 2\sigma(F)^2$ measured on an Enraf-Nonius CAD4 diffractometer, using monochromated Mo-Kα radiation, λ = 0.71069 Å, μ = 2.44 cm^{-1}. The structure was refined by full-matrix least-squares, R = 0.057, R' = 0.063. P and C atoms were refined with anisotropic thermal parameters and H atoms were refined freely with isotropic thermal parameters, making 262 refined parameters in all. The molecule lies on a twofold rotation axis. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

of special interest is the similar structure established for $P_5C_5Bu^t_5$ and one of the $P_6C_4Bu^t_4$ isomers which can be regarded as arising from the $P_4C_4Bu^t_4$ tetraphosphacubane structure **10** in which one C atom has been replaced by a PCC triangle of atoms in the case of $P_5C_5Bu^t_5$ **1**, and by a PPC triangle of atoms in the case of $P_6C_4Bu^t_4$ **9**. The steric effect of six Bu^t groups in **7** prevents 'cage' formation, but it may be expected that a range of compounds of the general type $P_nC_{10-n}Bu^t_{10-n}$ having cage or open structures, depending on the number of P atoms, may result from appropriate synthetic routes.

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