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Preliminary communication

Unusual oxidative coupling of 1,2,4-triphosphacyclopentadienyl and 1,3-diphosphacyclopentadienyl anions. Synthesis and molecular structure of the novel pentaphosphorus cage compound $P_5C_5Bu_5^+$

Rainer Bartsch, Peter B. Hitchcock, and John F. Nixon *

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (U.K.)

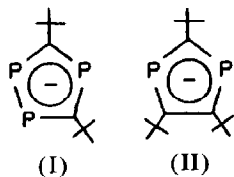
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Abstract

The novel pentaphosphorus cage compound $P_5C_5Bu_5^+$ has been prepared and its structure determined.

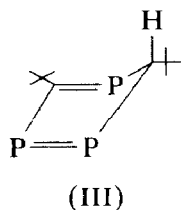
An extensive coordination chemistry of novel unsaturated organophosphorus compounds has recently been developed which parallels that of better known organotransition metal compounds. A wide variety of metal complexes of phosphaaalkynes, $RC\equiv P$, phosphaaalkenes $R_2C=PR$, 1,3-diphosphacyclobutadiene, 1-phosphaallyl, 1,3-diphosphaallyl and mono- and di-phosphaallenes have recently been reported [1,2].

Of special interest in view of the ubiquitous role that the cyclopentadienyl ligand has played in the development of organometallic chemistry of transition metals is the use of the 1,2,4-triphosphacyclopentadienyl, $P_3C_2Bu_2^+$ (I), and 1,3-diphosphacyclopentadienyl, $P_2C_3Bu_3^+$ (II), rings in the synthesis of sandwich compounds of



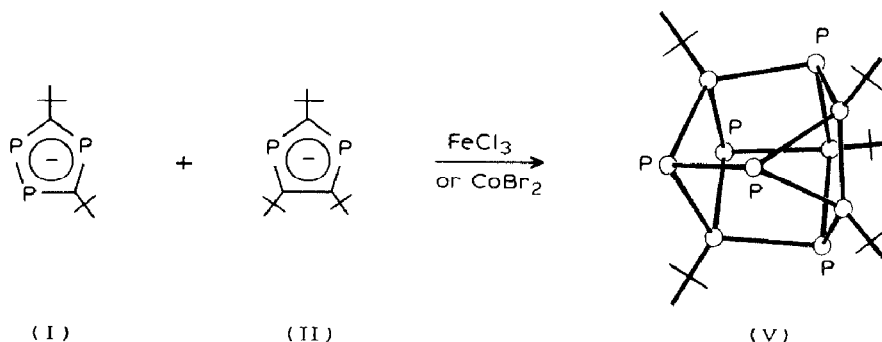
the types $[M(\eta^5-P_3C_2Bu_2^+)_2]$ ($M = Cr, Fe$) [3,4], $[Fe(\eta^5-P_3C_2Bu_2^+)(\eta^5-P_2C_3Bu_3^+)]$ [3], $[Ni(\eta^5-P_3C_2Bu_2^+)(\eta^3-P_2C_3Bu_3^+)]$ [5] and $[Co(\eta^5-P_3C_2Bu_2^+)(\eta^4-P_3C_2Bu_2^+H)]$ [6].

Recently we showed [7] that careful protonation of the lithium salt of I in monoglyme with $EtOH/CH_3CO_2H$ affords $P_6C_4Bu_4H_2$ (IV), which is the dimer of III. The structure of IV, which has been established by a single crystal X-ray

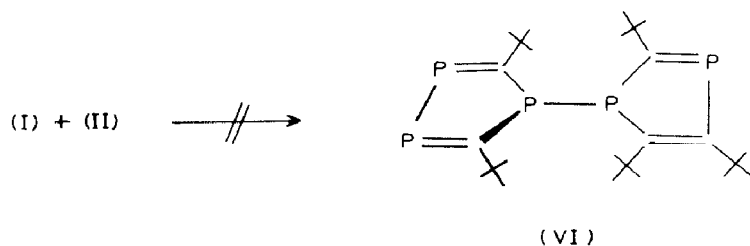


diffraction study, consists of a cage containing five directly bonded phosphorus atoms and no C–C bonds.

We now report that treatment of a 3/2 mixture of the lithium salts of I and II [8] with FeCl_3 or CoBr_2 gives rise to an oxidative coupling reaction of the two ring systems to afford the novel pentaphosphorus cage compound $\text{P}_5\text{C}_5\text{Bu}_5^+$ (V).



One possible structure considered for V was the diphosphane (VI) in view of the recent report by Mathey and Nief [9] of a 3,4,3',4'-tetramethylphospholyll formed by treating lithium 3,4-dimethylphospholide with TiCl_4 . This was, however, considered unlikely in view of the ^{31}P NMR spectrum (vide infra), which although giving the expected pattern of lines exhibited much larger long range $J(\text{PP}')$ coupling constants than expected.



A single crystal X-ray structural determination revealed the cage molecular structure of V shown in Fig. 1, in which the five phosphorus atoms are part of two five-membered rings, three four-membered rings, and one three-membered ring, respectively. The formation of a three-membered ring that could only result from P–P or P–C bond cleavage of the original ring systems I and II is remarkable *. Unlike the hexaphosphorus cage compound VI, in which five phosphorus atoms are joined together, no new P–P bond has been formed in V, the only direct P–P bond

* The structure is derived from that of a tetraphosphorus cubane by replacement of a corner with the three-membered ring.

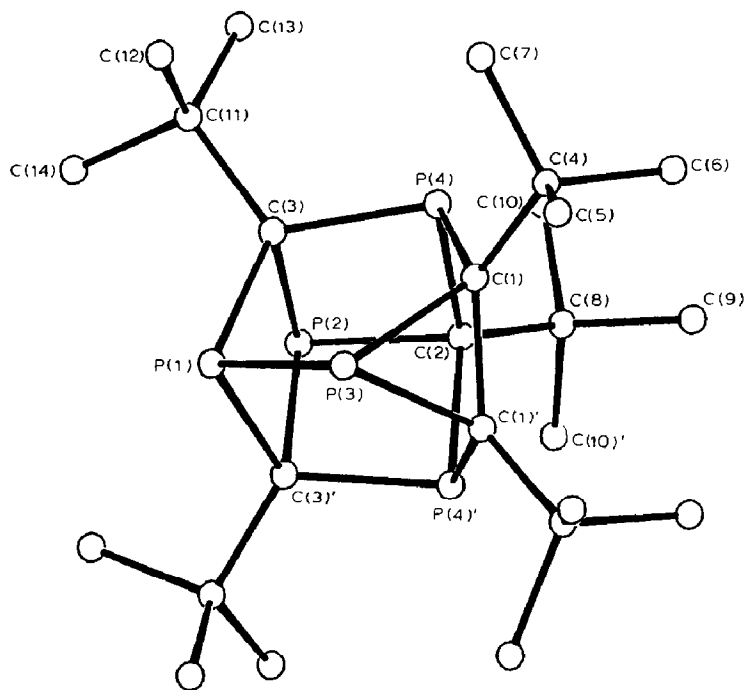


Fig. 1*.

obviously stemming from that of the original $P_3C_2Bu_2$ ring. All bond distances in V are similar to those found in IV, lying in the range typical of phosphorus–phosphorus, phosphorus–carbon and carbon–carbon single bonds.

The ^{31}P NMR spectrum of V is almost first order, and has been fully analysed and simulated as an A_2MNX spin system in which the A part represents the two equivalent phosphorus atoms 4 and 4'. The spectrum shows only one large $^1J(PP)$ coupling ($J(MN)$), which is consistent with the structure established by the X-ray diffraction study. The 1H NMR spectrum exhibits three singlets for the three inequivalent Bu^i groups, as expected (Table 1). The mass spectrum of V shows the parent ion at $m/e = 500$, and ions corresponding to the stepwise loss of Bu^i , Bu^iCP and P_2 fragments (Table 1).

The results show that an extensive chemistry of cage compounds containing carbon and phosphorus is to be expected, and studies are currently underway to develop this new area of cluster chemistry [10].

* *Crystal data:* $C_{25}H_{45}P_5$, $M = 500.5$, orthorhombic, space group $Pnma$ a 9.903(3), b 16.453(13), c 17.123(4) Å, U 2789.8 Å³, $Z = 4$, D_c 1.19 g cm⁻³ $F(000) = 1050$. Monochromated Mo- K_α radiation, (λ 0.71069 Å, μ 3.3 cm⁻¹). A total of 1971 unique reflections were measured on an Enraf–Nonius CAD4 diffractometer and 994 reflections with $|F^2| > \sigma(F^2)^2$ were used in the refinement. The structure was solved by direct methods using MULTAN and non-H atoms refined anisotropically. The final residuals were $R = 0.054$, $R' = 0.088$.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

Table 1

Spectroscopic data for the compound V

¹H NMR (CDCl₃, TMS ext. standard): δ 1.01(s), 1.07(s), 1.44(s);
Intensity 1/1/1

³¹P NMR (CDCl₃, H₃PO₄ ext. standard): δ(4,4') 218.5, δ(1) 179.1, δ(3) 82.5, δ(2) 58.7, *J*_{4,1} 20.2 Hz, *J*_{3,4} 14.0 Hz, *J*_{2,4} 6.4 Hz, *J*_{1,3} 262.4 Hz, *J*_{1,2} 6.6 Hz, *J*_{2,3} 7.7 Hz.

MS: 500 (*M*⁺), 443 [(Bu^tCP)₄PC]⁺, 262 [(Bu^tCP)₂P₂]⁺, 231 [(Bu^tCP)₂P]⁺, 169 [(Bu^tCP)(Bu^tC)], 131 [(Bu^tCP)(P)], 41 [C₃H₅]⁺.

Experimental

FeCl₃ (161 mg, 1 mmol) or CoBr₂ (218 mg, 1 mmol) was added to a solution containing Li[P₃C₂Bu^t]/Li[P₂C₃Bu^t]₃ (0.5 mmol) in monoglyme and the mixture stirred at room temperature for 16 h. After removal of the solvent in vacuo the residue was extracted with hexane and separated by column chromatography (silica gel/hexane). The yellow main fraction was collected, and the solvent removed in vacuo. The oily residue was washed with ethanol and recrystallized from hexane. Cooling to -40 °C afforded colourless needles of V. Yield: 60 mg (24%).

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References

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- 10 *Note added in proof.* After completion of this work a report of V (among other cages) is referred to in Nachr. Chem. Techn., 37 (1989) 582, made in low yield in an unexpected reaction of [Fe(η⁴-1-methylnaphthalene)(η⁶-toluene)] with Bu^tCP (U. Zenneck et al., Angew. Chem., to be published).