A Hexaphosphorus Chain as Part of a Dimeric *P,P'*-containing Ligand; 1,3-Phosphozirconation of White Phosphorus; *X*-Ray Structure of $[Zr(\eta\text{-}C_5H_5)_2\{P(PR_2)PP(PR_2)P\}]$ (R = $SiMe_3$)†

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A three-fragment oxidative addition of $[ZrCp_2(PR_2)_2]$ to P_4, in toluene at 25 °C, yields the zircona(tetraphospha)bicyclo[2.1.0]pentane $[ZrCp_2\{P(PR_2)PP(PR_2)P\}]$ (Cp = η-C_5H_5, R = $SiMe_3$) (**1**), which shows a first order $^{31}P\{^1H\}$ n.m.r. spectrum at 145.8 MHz; the *X*-ray structure of the crystalline complex (**1**) reveals it to have retained one of the triangular faces [P(2)P(3)P(4)] of P_4, with Zr–P(1) 2.632(3) and Zr–P(2) 2.607(4) Å.

We report a novel reaction of white phosphorus, namely its facile insertion into both the Zr–P bonds of bis[bis(trimethylsilyl)phosphido]zirconocene(IV) $[ZrCp_2(PR_2)_2]$ (Cp = η-C_5H_5, R = $SiMe_3$)[1] to yield $[ZrCp_2\{P(PR_2)PP(PR_2)P\}]$ (**1**); reaction (i) in Scheme 1.

It is probable that reaction (i) occurs stepwise, with $[ZrCp_2\{PPP(PR_2)P\}PR_2]$ (**2**), a product of 1,3-bis(trimethylsilyl)phosphozirconation of P_4, as an intermediate. It is suggested that final conversion of (**2**) into (**1**) proceeds by ring-expansion of the tetraphosphabicyclobutane and a concomitant 1,2-shift of PR_2 from Zr to P (c in Scheme 1).

White phosphorus is known to behave both as (a) a nucleophile and (b) a substrate for nucleophilic attack. Hence there are plausible alternative pathways to (**2**) from P_4 (a1 and a2, followed by b1 and b2, respectively in Scheme 1), with (**3**) and (**3**)' as further intermediates or transition states. Precedents for such reaction patterns are (a) the behaviour of P_4 as an σ-, η^2-, or η^4-donor, as in $[Ni(\{PPh_2(CH_2)_2\}_3N)(\sigma\text{-}P_4)]$,[2] $[RhCl(\eta^2\text{-}P_4)(PPh_3)_2]$ (at low temperature),[3] or $[Co\{PPh_2CH_2PPh_2P_4PPh_2CH_2PPh_2\}]^+$;[4] and (b) the degradation of P_4 by strong nucleophiles such as hydroxide, phosphinite, or phosphide ions (*cf.*, ref. 5). The reaction of P_4 with PhMgBr or LiPh was also considered to be of type (b), and products included cyclotetraphosphanes.[6] White phosphorus

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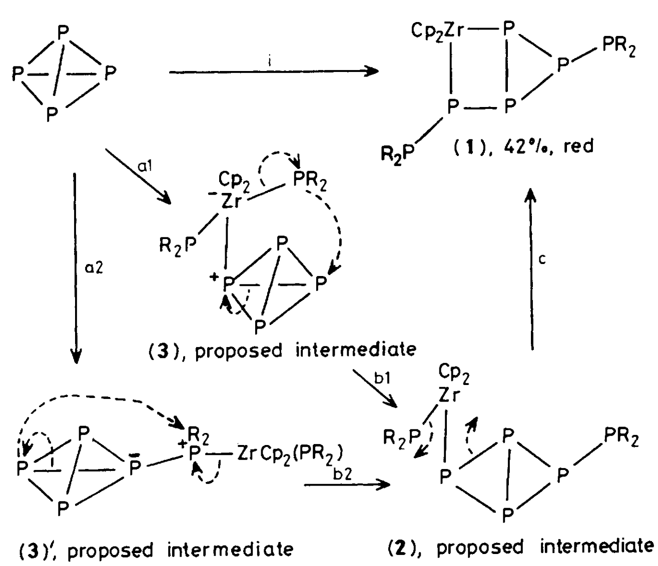
† No reprints available.



Scheme 1. Cp = η-C_5H_5, R = $SiMe_3$. *Reagents and conditions:* i, [$ZrCp_2(PR_2)_2$] (1 mol), PhMe, 25 °C, 1 day. *Proposed reaction pathway: via* intermediates (**3**) [or (**3**)'] and (**2**), involving successive steps a, b, and c; either (a2) nucleophilic attack at P_4, or (a1) nucleophilic attack of P_4; b, 1,3-phosphozirconation of P_4; and c, a Wagner–Meerwein-type rearrangement of intermediate (**2**).

can also function as a reducing agent, as in the conversion of [$\{ZrCp_2H_2\}_n$] into [$\{ZrCp_2\}_4$].[7]

Complex (**1**) may be regarded as derived from Zr^{IV} and a 1,1,6,6-tetrakis(trimethylsilyl)(P^2-P^4)hexaphosphane-3,5-di-ido ligand. Other examples of compounds having P_6-ligands include α- and β-K_4P_6 (**4**)[8] and [$\{Mo(\eta\text{-}C_5Me_5)\}_2(\mu,\eta\text{-}P_6)$] (**5**),[9] in each of which the P_6 moiety is planar. Compounds (**4**) and (**5**) were made from P_4 and K or [$\{Mo(\eta\text{-}C_5Me_5)(CO)_2\}_2$], respectively. In the latter reaction, dimolybdenum products other than (**5**) contained P_2-, P_3-, and P_4-fragments.[9]

The high field $^{31}P\{^1H\}$ n.m.r. spectrum of complex (**1**) was first order and showed extensive coupling between the six phosphorus atoms, Figure 1. Assignments were checked by PANIC simulation. Of the 15 possible coupling constants, 3 had zero magnitudes. The highest field chemical shift was for P(3), which is attached only to P atoms derived from P_4; this atom was also associated with the largest ^1J and ^2J values.

The *X*-ray structure of complex (**1**)‡ is illustrated in Figure 2. It is evident that the P(2)P(3)P(4) fragment is effectively an intact triangular face of the original P_4 tetrahedron. The PP bond lengths in P_4 are 2.21(2) Å.[10] The ZrP(1)P(2)P(3) ring is essentially planar. The environment at P(5) and P(6), the phosphorus atoms bearing the $SiMe_3$ substitutents, is pyramidal with the sum of the bond angles at P(5) and P(6) 299.9 and 303.5°, respectively.

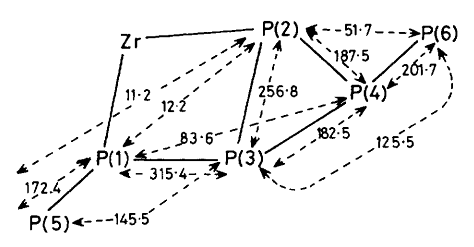


Figure 1. N.m.r. coupling constants (hatched lines) (Hz) for [$ZrCp_2\{P(PR_2)PP(PR_2)P\}$] (**1**), obtained from the ^{31}P n.m.r. spectrum at 145.8 MHz at 308 K, using the numbering system of Figure 2. Chemical shifts (δ in p.p.m. rel. to external 85% aq. H_3PO_4): P(1) 88.7, P(2) 62.9, P(3) −236.4, P(4) −110.6, P(5) −163.5, and P(6) −139.

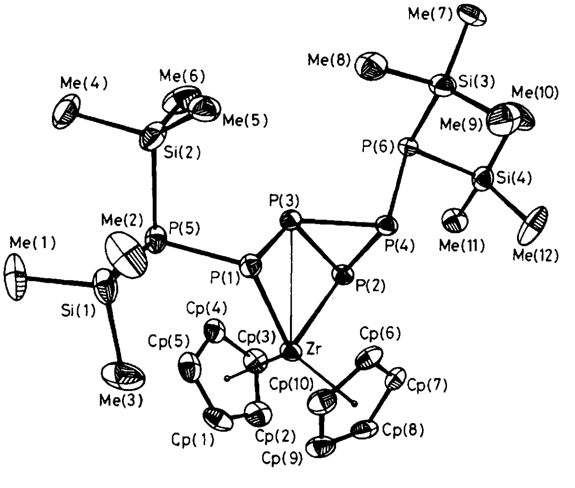


Figure 2. *X*-Ray structure and atom numbering scheme for complex (**1**). Selected bond distances and angles are as follows: Zr–P(1) 2.632(3), Zr–P(2) 2.607(4), P(1)–P(3) 2.241(4), P(1)–P(5) 2.219(4), P(4)–P(6) 2.210(5), Zr · · · P(3) 3.010(4), P(1) · · · P(2) 3.74, P(1) · · · P(4) 3.52, av. P–Si 2.266(4) Å, P(1)–Zr–P(2) 91.0(1), Zr–P(2)–P(3) 76.8(1), P(1)–P(3)–P(2) 114.1(2), Zr–P(1)–P(3) 75.8(1)°, P(2)P(3)P(4) equilateral triangle: av. P–P 2.213(5) Å.

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‡ *Crystal data* for (**1**), $C_{22}H_{46}P_6Si_4Zr$, triclinic, space group $P\bar{1}$, a = 10.745(9), b = 12.882(9), c = 15.641(6) Å, α = 68.81(7), β = 80.25(9), γ = 65.95(8)°, U = 1843 Å^3, Z = 2, D_c = 1.27 g cm^{-3}, μ = 16.72 cm^{-1}, 3949 reflections were recorded, out of which 2127 were considered as 'observed' reflections [$I > 3\sigma(I)$], $2\theta_{max.}$ = 42°, R = 0.045, R' = 0.044 [Mo-K_α radiation, λ = 0.71069 Å, T = 295 K]. 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.