

# Preparation and Ligating Properties of the First Example of a 1,2,4-Triphosphole, $P_3C_2Bu^t_2R$ [ $R = CH(SiMe_3)_2$ ]: Crystal and Molecular Structures of $P_3C_2Bu^t_2CH(SiMe_3)_2$ , $trans-[PtCl_2(PEt_3)\{P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ and $[Fe_2(CO)_6\{\mu-P_3C_2Bu^t_2CH(SiMe_3)_2\}]$

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The first known triphosphole exhibits different modes of ligation to transition-metal centres.

The chemistry of unsaturated five-membered ring systems containing phosphorus is of considerable current interest.<sup>1,2</sup> Both anionic and neutral compounds are known, but to date no examples of phospholes  $P_nC_{5-n}R_{5-n}R'$  are known containing three phosphorus atoms. The recent report of the sterically controlled metal-induced syntheses of the isoelectronic 1-thia-2,4-diphospholes<sup>3,4</sup> **1** from the phosphalkyne  $Bu^tC\equiv P$  and  $\eta^2$ -thiophosphinito complexes prompts us to describe the first synthesis of a 1,2,4-triphosphole **2** and some of its interesting ligating behaviour.

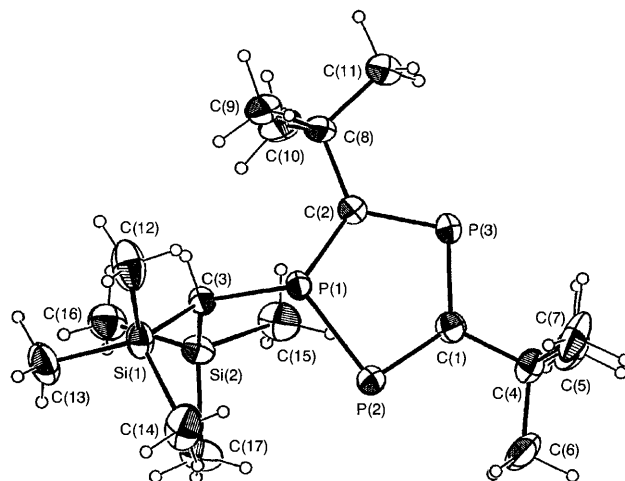
Previously<sup>5</sup> we have described the ready formation of the aromatic di- and tri-phosphacyclopentadienyl ring systems **3** and **4** by treatment of  $Bu^tC\equiv P$  with alkali metals in an ether solvent at room temperature. Treatment of a solution of the lithium salt of **4** with  $(Me_3Si)_2CHBr$  in 1,2-dimethoxyethane (dme) afforded a yellow oil (40%) which was purified by column chromatography to afford orange crystals (mp 79–80 °C) of the 1,2,4-triphosphacyclopentadiene  $P_3C_2Bu^t_2CH(SiMe_3)_2$  **5**. The mass spectrum showed a parent ion at  $m/z$  390 and the  $^{31}P\{^1H\}$  NMR spectrum showed three resonances<sup>†</sup> at  $\delta$  244.4, 180.0 and 112.0, each occurring as a doublet of doublets. The chemical shifts of the first two are typical for  $sp^2$ -hybridised P, while the latter corresponds to that expected of an  $sp^3$ -hybridised P. The  $^1H$  NMR spectrum provided supporting data,<sup>‡</sup> consisting of two different resonances for the  $Bu^t$  groups (9 H, 9 H), a singlet for the  $(Me_3Si)_2$  resonance (18 H), and a doublet of doublets (1 H) for the CH proton.  $^{29}Si\{^1H\}$  and  $^{13}C\{^1H\}$  NMR data fully confirmed the 1,2,4-triphosphole structure.<sup>§</sup>

A single-crystal X-ray diffraction study<sup>¶</sup> on **5** revealed the molecular structure shown in Fig. 1. As expected, the P(2)C(1)P(3)C(2) fragment is planar with the P(2)–C(1), P(3)–C(1) and P(3)–C(2) bond lengths being significantly shorter than P(1)–C(3) and the P(1) atom attached to the  $-CH(SiMe_3)_2$  group exhibiting typical bond angles for an  $sp^3$ -hybridised atom.

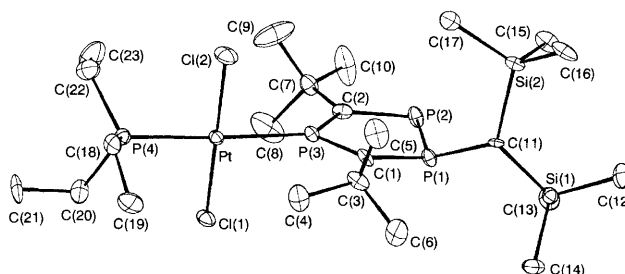
Treatment of **5** with  $[Pt_2Cl_4(PEt_3)_2]$  readily gave the yellow crystalline complex  $trans-[PtCl_2(PEt_3)\{P_3C_2Bu^t_2CH(SiMe_3)_2\}]$  **6** in which the mode of attachment of the 1,2,4-triphosphole ring to platinum was established by NMR spectroscopic studies as *via* the P(3) centre which is unusual for this type of ring system<sup>6,7</sup> but no doubt reflects the steric effect of the large  $-CH(SiMe_3)_2$  group on the P(1) and P(2) positions. Thus the  $^{31}P\{^1H\}$  NMR spectrum of **6**<sup>||</sup> exhibited three

resonances for the ring framework with the resonance of P(3) ( $\delta$  194.9) exhibiting  $^{195}Pt$  satellites [ $^1J_{PtP(3)} = 2369$  Hz] further split by the *trans*- $PEt_3$  ligand [ $^2J_{P(3)P(4)} = 503.1$  Hz]. The  $^{195}Pt\{^1H\}$  NMR spectrum<sup>||</sup> exhibited the expected eight-line pattern and the FAB mass spectrum of **6** showed a parent ion at  $m/z$  774 and the expected fragmentation pattern. Confirmation of the molecular structure was obtained by a single-crystal X-ray diffraction study (Fig. 2).<sup>\*\*</sup> The Pt–ring distance is 2.326(3) Å and the angles at Pt are very close to the ideal square-planar geometry.

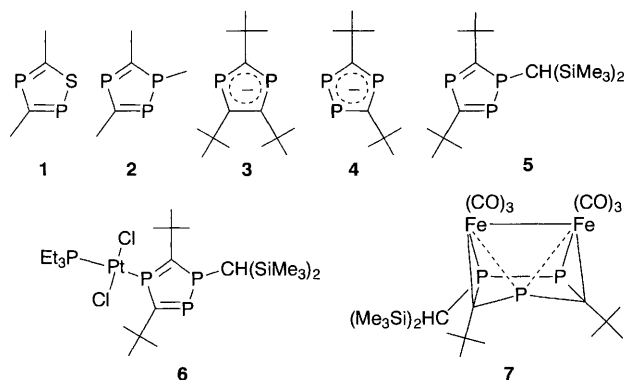
A different type of ligation of the triphosphole ring system occurs in the red crystalline product **7** obtained in 72% yield when  $[Fe_2(CO)_9]$  was refluxed in thf with **5**. Complex **7** was identified as  $[Fe_2(CO)_6\{\mu-P_3C_2Bu^t_2CH(SiMe_3)_2\}]$  by elemen-

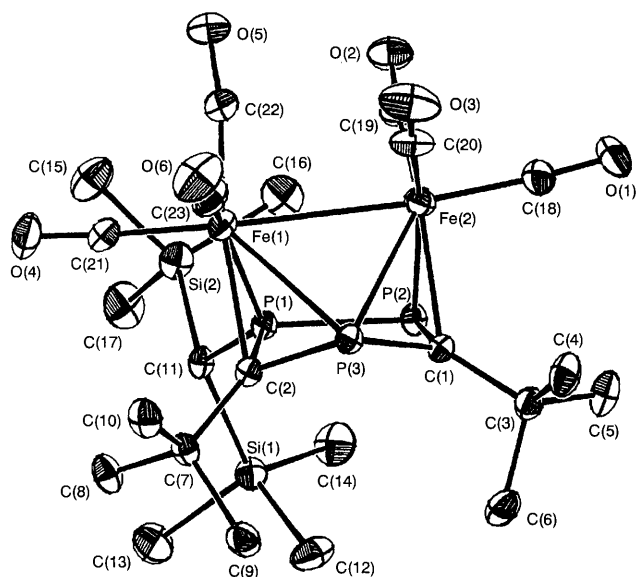


**Fig. 1** Molecular structure of **5**: Selected bond lengths (Å) and angles (°); P(1)–P(2) 2.098(1), P(1)–C(2) 1.734(4), P(1)–C(3) 1.826(4), P(2)–C(1) 1.718(4), P(3)–C(1) 1.763(4), P(3)–C(2) 1.720(3); P(2)–P(1)–C(2) 105.8(1), P(2)–P(1)–C(3) 115.3(1), C(2)–P(1)–C(3) 121.2(2), P(1)–P(2)–C(1) 94.0(1), C(1)–P(3)–C(2) 101.8(2)



**Fig. 2** Molecular structure of **6**: selected bond lengths (Å) and angles (°); Pt–P(4) 2.283(3), Pt–Cl(1) 2.305(3), Pt–Cl(2) 2.315(3), Pt–P(3) 2.326(3), P(4)–C(18) 1.823(13), P(3)–C(2) 1.737(12); P(3)–C(1) 1.721(11), P(1)–C(1) 1.738(11), P(2)–C(2) 1.758(13), P(1)–P(2) 2.086(4), P(4)–Pt–Cl(1) 92.56(11), P(4)–Pt–Cl(2) 87.26(12), Cl(1)–Pt–Cl(2) 179.42(14); P(4)–Pt–P(3) 176.33(12), Cl(1)–Pt–P(3) 90.95(11), Cl(2)–Pt–P(3) 89.22(13), C(2)–P(3)–Pt 126.2(4), C(1)–P(3)–Pt 126.0(4), P(3)–C(1)–P(1) 110.4(6), P(3)–C(2)–P(2) 118.1(7), C(1)–P(1)–P(2) 107.4(4), C(2)–P(2)–P(1) 95.7(4)





**Fig. 3** Molecular structure of **7**: selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.910(1), Fe(1)–P(1) 2.225(2), Fe(1)–P(3) 2.605(2), Fe(2)–P(2) 2.342(2), Fe(1)–C(2) 2.091(6), Fe(2)–P(3) 2.497(1), Fe(2)–C(1) 2.072(6), P(1)–P(2) 2.205(2), P(1)–C(2) 1.775(4), P(2)–C(1) 1.778(5), P(3)–C(1) 1.788(5); P(3)–C(2) 1.804(4), Fe(2)–Fe(1)–P(1) 75.06(4), Fe(2)–Fe(1)–P(3) 53.51(3), Fe(2)–Fe(1)–C(2) 86.6(1), P(1)–Fe(1)–P(3) 72.00(5), P(1)–Fe(1)–C(2) 48.5(1), P(3)–Fe(1)–C(2) 43.5(1), Fe(1)–Fe(2)–P(3) 57.00(4), Fe(1)–Fe(2)–C(1) 91.4(1), P(2)–Fe(2)–P(3) 77.53(5)

tal analyses,  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectroscopy $\dagger\dagger$  and IR spectroscopy ( $\nu_{\text{CO}}$  2049, 2010, 1985, 1966, 1949  $\text{cm}^{-1}$ ). The three  $^{31}\text{P}$  resonances of the ring in **7** were all significantly changed from those in **5**, indicating that unlike **6** the whole of the ring system is strongly interacting with the  $\text{Fe}_2(\text{CO})_6$  dinuclear fragment.

The molecular structure of **7**, elucidated by a single-crystal X-ray diffraction study $\ddagger\ddagger$  is shown in Fig. 3 confirming that the ring system acts as a bridging ligand to the two  $\text{Fe}(\text{CO})_3$  units which are linked by an Fe–Fe bond (2.910 Å). The 1,2,4-triphosphole ring thus may be considered to act as a 6e donor, and its geometry is considerably distorted from that of the parent compound **5**. Interestingly the Fe(1)–P(3) and Fe(2)–P(3) bond distances are significantly longer than the Fe(1)–P(1) and Fe(2)–P(2) bond lengths.

An unusual reaction of **5** with  $[\text{M}(\text{CO})_5(\text{thf})]$  ( $\text{M} = \text{W}$ ) and  $[\text{M}(\text{CO})_4(\text{C}_7\text{H}_8)]$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) to afford the interesting systems  $[\text{M}(\text{CO})_3\{\text{P}_3\text{C}_2\text{Bu}^t\text{CH}(\text{SiMe}_3)_2\}]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) which will be the subject of a separate publication.

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## Footnotes

$\dagger$   $^{31}\text{P}\{^1\text{H}\}$  NMR data for **5** ( $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$  ext. standard, 25 °C):  $\delta$  244.4 [P(3)], 180.0 [P(2)], 112.0 [P(1)];  $^1\text{J}_{\text{P}(1)\text{P}(2)}$  509.5 Hz,  $^2\text{J}_{\text{P}(1)\text{P}(3)}$  8.0 Hz,  $^2\text{J}_{\text{P}(2)\text{P}(3)}$  44.1 Hz.

$\ddagger$   $^1\text{H}$  NMR data for **5** ( $\text{CDCl}_3$ , 25 °C):  $\delta$  0.15 (s, 18H,  $\text{SiMe}_3$ ), 1.57 (d, 9H,  $\text{Bu}^t$ ,  $^4\text{J}_{\text{HP}}$  1.23 Hz), 1.59 (d, 9H,  $\text{Bu}^t$ ,  $^4\text{J}_{\text{HP}}$  1.73 Hz), 2.06 (dd, 1H,  $\text{CH}$ ,  $^2\text{J}_{\text{HP}}$  15.0,  $^3\text{J}_{\text{HP}}$  12.1 Hz).

$\S$   $^{29}\text{Si}\{^1\text{H}\}$  NMR data for **5** ( $\text{CDCl}_3$ ,  $\text{SiMe}_4$  ext. standard, 25 °C):  $\delta$  4.12 (ddd, 2Si,  $^2\text{J}_{\text{SiP}(1)}$  6.56,  $^3\text{J}_{\text{SiP}(2)}$  2.10,  $^4\text{J}_{\text{SiP}(3)}$  0.71 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR data for **5** ( $\text{CDCl}_3$ , 25 °C):  $\delta$  204.7 (ddd,  $\text{C}^{\text{Bu}^t}$ ,  $^1\text{J}_{\text{CP}}$  72.8,  $^1\text{J}_{\text{CP}}$  66.9,  $^2\text{J}_{\text{CP}}$  21.7 Hz), 188.8 (ddd,  $\text{C}^{\text{Bu}^t}$ ,  $^1\text{J}_{\text{CP}}$  69.9,  $^1\text{J}_{\text{CP}}$  39.4,  $^2\text{J}_{\text{CP}}$  8.7 Hz), 41.6 (ddd,  $\text{CMe}_3$ ,  $^2\text{J}_{\text{CP}}$  21.7,  $^2\text{J}_{\text{CP}}$  19.7,  $^3\text{J}_{\text{CP}}$  6.9 Hz), 40.2 (d,  $\text{CMe}_3$ ,  $^2\text{J}_{\text{CP}}$  17.7 Hz), 35.7 (m,  $\text{CCH}_3$ ), 20.9 (dd,  $\text{CH}$ ,  $^1\text{J}_{\text{CP}}$  40.4,  $^2\text{J}_{\text{CP}}$  4.9 Hz), 0.7 (s,  $\text{SiCH}_3$ ,  $^1\text{J}_{\text{CSi}}$  52.9 Hz).

$\P$  *Crystal data* for **5**.  $\text{C}_{17}\text{H}_{37}\text{P}_3\text{Si}_2$ ,  $M = 390.6$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 12.845(6)$ ,  $b = 10.158(2)$ ,  $c = 18.670(5)$  Å,  $\beta = 102.65(3)^\circ$ ,  $V = 2377(1)$  Å $^3$ ,  $Z = 4$ . The data were obtained with an Enraf-Nonius CAD4 diffractometer using monochromated Mo-K $\alpha$  radiation.  $\lambda = 0.71073$  Å,  $\mu = 3.4$   $\text{cm}^{-1}$  on a crystal  $0.4 \times 0.3 \times 0.3$  mm. 4622 reflections were measured and 3069 having  $|F^2| > 2\sigma(F^2)$  were used in the calculation. The structure was solved using direct methods SHELXS-86 and refined using a full-matrix least-squares MOIEN program, non-H atoms anisotropic, H atoms isotropic,  $R = 0.050$ ,  $R' = 0.055$ .

$\parallel$   $^{31}\text{P}\{^1\text{H}\}$  NMR data for **6** ( $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$  ext. standard, 25 °C):  $\delta$  201.5 [P(2)], 194.9 [P(3)], 112.9 [P(1)], 12.0 [P(4)];  $^1\text{J}_{\text{PP}(1)}$  2914 Hz,  $^1\text{J}_{\text{PP}(3)}$  2369 Hz,  $^3\text{J}_{\text{PP}(1)}$  111 Hz,  $^1\text{J}_{\text{P}(1)\text{P}(2)}$  492.2 Hz,  $^2\text{J}_{\text{P}(3)\text{P}(1)}$  53.5 Hz,  $^4\text{J}_{\text{P}(4)\text{P}(1)}$  23.4 Hz,  $^2\text{J}_{\text{P}(3)\text{P}(2)}$  49.0 Hz,  $^2\text{J}_{\text{P}(4)\text{P}(3)}$  503.1 Hz.  $^{195}\text{Pt}\{^1\text{H}\}$  NMR data for **6** ( $\text{CDCl}_3$ ,  $\text{Na}_2[\text{PtCl}_6]$  ext. standard, 25 °C):  $\delta$  -3676,  $^1\text{J}_{\text{PP}(4)}$  2914 Hz,  $^1\text{J}_{\text{PP}(3)}$  2369 Hz,  $^3\text{J}_{\text{PP}(1)}$  111 Hz.

\*\* *Crystal data* for **6**.  $\text{C}_{23}\text{H}_{52}\text{Cl}_2\text{P}_4\text{PtSi}_2$ ,  $M = 774.7$ , orthorhombic, space group  $P2_12_12_1$  (no. 19),  $a = 11.712(3)$ ,  $b = 11.834(2)$ ,  $c = 25.073(5)$  Å,  $V = 3475.1$  Å $^3$ ,  $Z = 4$ . The data were obtained using monochromated Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å as in **5**. 3431 reflections were measured and 3102 having  $|F^2| > 2\sigma(F^2)$  used in the refinement. The final  $R$  values were  $R = 0.043$ ,  $R' = 0.051$ .

$\dagger\dagger$   $^{31}\text{P}\{^1\text{H}\}$  NMR data for **7** ( $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$  ext. standard, 25 °C):  $\delta$  37.3 [P(2)], -62.9 [P(3)], -91.5 [P(1)];  $^1\text{J}_{\text{P}(1)\text{P}(2)}$  388.3 Hz,  $^2\text{J}_{\text{P}(1)\text{P}(3)}$  7.0 Hz,  $^2\text{J}_{\text{P}(2)\text{P}(3)}$  9.3 Hz.  $^1\text{H}$  NMR data for **7** ( $\text{CDCl}_3$ , 25 °C):  $\delta$  0.05 (s, 18H,  $\text{SiMe}_3$ ), 0.63 (dd, 1H,  $\text{CH}$ ,  $^2\text{J}_{\text{HP}}$  15.3,  $^3\text{J}_{\text{HP}}$  13.0 Hz); 1.33 (s, 9H,  $\text{Bu}^t$ ); 1.45 (s, 9H,  $\text{Bu}^t$ ).

$\ddagger\ddagger$  *Crystal data* for **7**.  $\text{C}_{23}\text{H}_{37}\text{Fe}_2\text{O}_6\text{P}_3\text{Si}_2$ ,  $M = 670.3$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 11.493(6)$ ,  $b = 11.494(5)$ ,  $c = 13.751(6)$  Å,  $\alpha = 74.00(3)$ ,  $\beta = 84.70(4)$ ,  $\gamma = 66.74(4)^\circ$ ,  $V = 1603.9$  Å $^3$ ,  $Z = 2$ . The data were obtained with an Enraf-Nonius CAD4 diffractometer using Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 11.6$   $\text{cm}^{-1}$  on a crystal  $0.25 \times 0.2 \times 0.05$  mm. 5625 reflections were measured and 3534 having  $|F^2| > 2\sigma(F^2)$  were used in the calculation, refinement by MOIEN program, non-H atoms were located by direct methods using the SHELXS-86 full-matrix least squares, non-H atoms anisotropic.  $R = 0.047$ ,  $R' = 0.055$ .

Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **5**, **6** and **7** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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