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Preliminary communication

Penta- and hexaphospha ferrocenes as ligands: crystal and molecular structures of $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2W(CO)_5]$, $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)W(CO)_5]$ and the novel triruthenium carbonyl cluster complex $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2Ru_3(CO)_{10}]$ containing two interlinked $\eta^5\text{-}P_3C_2{}^tBu_2$ ring systems

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Abstract

The lone-pair electrons of one of the two directly bonded phosphorus atoms of the $P_3C_2{}^tBu_2$ ring in the penta- or hexaphosphaferrocene complexes $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)(\eta^5\text{-}P_2C_3{}^tBu_3)]$ and $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ can ligate to other metal centres to afford novel bi- and tetrametallic complexes, whose structures have been elucidated by NMR and single crystal X-ray crystallographic studies.

Previously [1–6], we have described synthesis and structures of penta- and hexaphosphorus analogues of ferrocene, hexaphosphorus analogues of chromocene and η^3-transition metal complexes of the $P_2C_3{}^tBu_3$ ring system. Unlike their simple metallocene analogues, however, these complexes have the possibility of further ligating potential towards other transition metal centres by virtue of the availability of the ring phosphorus lone-pair electrons not already utilised in their η^3- or η^5-metal ligation. We now describe syntheses and structural characterisation of four such compounds: $[Fe(\eta^5\text{-}P_3C_2{}^tBu)_2Fe(CO)_4]$ (I), $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2W(CO)_5]$ (II), $[Fe(\eta^5\text{-}P_2C_3{}^tBu_3)(\eta^5\text{-}P_3C_2{}^tBu_2)W(CO)_5]$ (III), and $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2Ru_3(CO)_{10}]$ (IV). The latter is of special interest since it represents the first example of (i) attachment of a transition metal carbonyl cluster to another $\eta^5\text{-}P_3C_2{}^tBu_2$ metal complex and (ii) interlinking of both $\eta^5\text{-}(P_3C_2{}^tBu_2)$ ligated ring systems in hexaphospha-ferrocene complexes.

The brown tetracarbonyl iron complex I, which was obtained in 89% yield by treatment of $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ with $[Fe_2(CO)_9]$ in dimethoxyethane, exhibited

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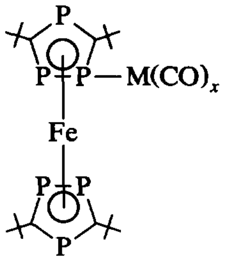
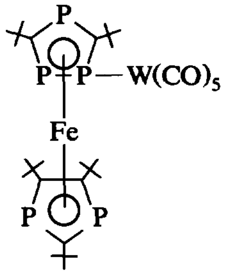
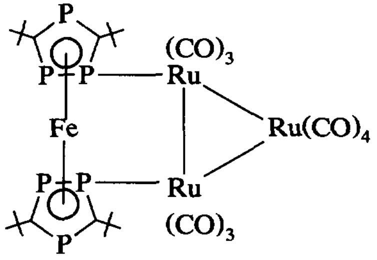


(I) (M = Fe, $x = 4$)
(II) (M = W, $x = 5$)



(III)



(IV)

ν(CO) stretching bands at 2066, 1994, 1986 and 1964 cm^{-1}. The brown pentacarbonyl complexes II, (ν(CO) 2073, 1950, 1942 cm^{-1}), and III, (ν(CO) 2074, 1951, 1941 cm^{-1}), were obtained by treatment of [W(CO)$_5$THF] with [Fe(η^5-$P_3C_2{}^tBu_2)_2$] and [Fe(η^5-$P_3C_2{}^tBu_2$)(η^5-$P_2C_3{}^tBu_3$)] respectively. Since compounds I and II exhibit typical [AMX] and [A_2B] ^{31}P{^{1}H} NMR spectra, (A, M, X = P, I = 1/2 100% abundance) *, and complex III exhibits an [AMX] and [A_2] pattern, it follows that in I–III *one* of the directly bonded phosphorus atoms of a η^5-$P_3C_2{}^tBu_2$ ring acts as the further η^1-ligating centre. Furthermore, neither phosphorus atom of the η^5-$P_2C_3{}^tBu_3$ ring is involved in any further bonding, presumably because of the steric protection of the two flanking ^{t}Bu groups.

Confirmation of the NMR based structural assignments comes from single crystal X-ray crystallographic studies on both II and III, whose molecular structures are shown in Figs. 1 and 2. In III there is a significant displacement of the [W(CO)$_5$] fragment from the molecular plane of the η^5-$P_3C_2{}^tBu_2$ ring system, which may result from steric demands of the nearby η^5-$P_2C_3{}^tBu_3$ ring.

Likewise, [Fe(η^5-$P_3C_2{}^tBu_2)_2$] reacts with [$Ru_3(CO)_{12}$] in refluxing dimethoxyethane for 5 h to afford the novel triruthenium decacarbonyl complex [Fe(η^5-$P_3C_2{}^tBu_2)_2Ru_3(CO)_{10}$] (IV), in 18% yield. The observation of only terminal metal

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* I: $\delta_{P(1)}$ 98.3, $\delta_{P(2)}$ 69.3, $\delta_{P(3)}$ 68.3, $\delta_{P(4)}$ 54.4, $\delta_{P(5)}$ 51.5, $\delta_{P(6)}$ 24.4 ppm; $J_{1,2}$ 0, $J_{1,5}$ 49.9, $J_{2,4}$ 406.7, $J_{3,4}$ 41.5, $J_{4,5}$ 0, $J_{1,3}$ 0, $J_{1,6}$ 437.0, $J_{2,5}$ 0, $J_{3,5}$ 0, $J_{4,6}$ 0, $J_{1,4}$ 14.6, $J_{2,3}$ 37.9, $J_{2,6}$ 0, $J_{3,6}$ 0, $J_{5,6}$ 36.1 Hz.
II: $\delta_{P(1)}$ 23.7, $\delta_{P(2)}$ 48.5, $\delta_{P(3)}$ 49.2, $\delta_{P(4)}$ 47.3, $\delta_{P(5)}$ 71.2, $\delta_{P(6)}$ 72.3 ppm; $J_{1,2}$ 418.6, $J_{1,3}$ 35.8, $J_{2,3}$ 49.6, $J_{2,4}$ 16.0, $J_{4,5}$ 406.8, $J_{4,6}$ 42.4, $J_{5,6}$ 40.4 Hz.
III: $\delta_{P(1)}$ 32.1, $\delta_{P(2)}$ 22.7, $\delta_{P(3)}$ 26.0, $\delta_{P(4)}$ 37.0, $\delta_{P(5)}$ 38.5 ppm; $J_{1,2}$ 401.8, $J_{1,3}$ 47.2, $J_{2,3}$ 32.2, $J_{2,4}$ 12.0, $J_{4,5}$ 32.9, J(PW) 226 Hz.
IV: $\delta_{P(1)}$ 74.7, $\delta_{P(2)}$ 54.1, $\delta_{P(3)}$ 14.1 ppm; $J_{1,3}$ 57.7, $J_{2,3}$ 33.0, $J_{1,2}$ 442.8 Hz.

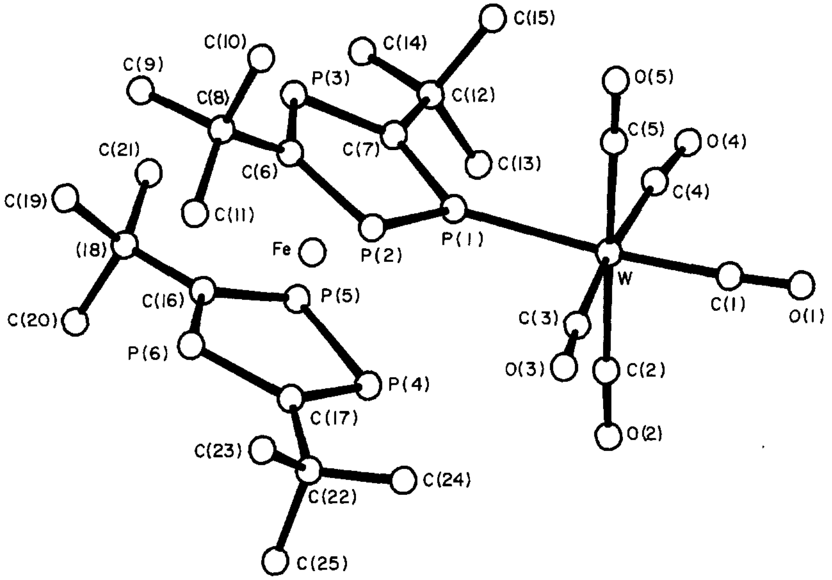

Fig. 1. The molecular structure of II showing the atom numbering scheme. Selected bond lengths are: W–P(1) 2.532(1), Fe–P(1) 2.354(1), Fe–P(2) 2.367(1), Fe–P(3) 2.327(1), Fe–P(4) 2.346(1), Fe–P(5) 2.372(1), Fe–P(6) 2.341(1), Fe–C(6) 2.216(4), Fe–C(7) 2.189(4), Fe–C(16) 2.231(5), Fe–C(17) 2.184(4) Å.

carbonyl bands, (ν(CO) 2093, 2031, 2021, 1995, 1975, 1968 cm^{-1}) in complex IV, and a simple [AMX] pattern in its ^{31}P{^{1}H} NMR spectrum *, indicates that *both* the η^5-$P_3C_2{}^tBu_2$ rings of the original hexaphospha-ferrocene, $[Fe(P_3C_2{}^tBu_2)_2]$,

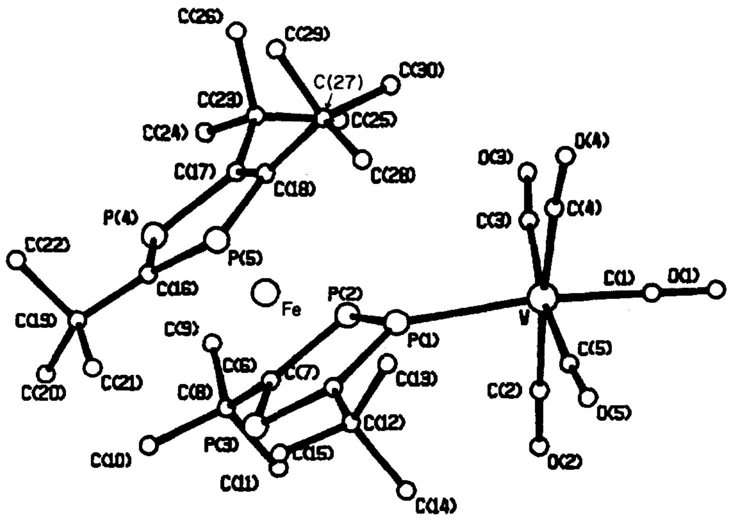

Fig. 2. The molecular structure of III showing the atom numbering scheme. Selected bond lengths are: W–P(1) 2.561(2), Fe–P(1) 2.355(2), Fe–P(2) 2.366(2), Fe–P(3) 2.334(2), Fe–P(4) 2.321(2), Fe–P(5) 2.319(2), Fe–C(6) 2.205(7), Fe–C(7) 2.234(7), Fe–C(16) 2.229(6), Fe–C(17) 2.187(7), Fe–C(18) 2.196(7) Å.

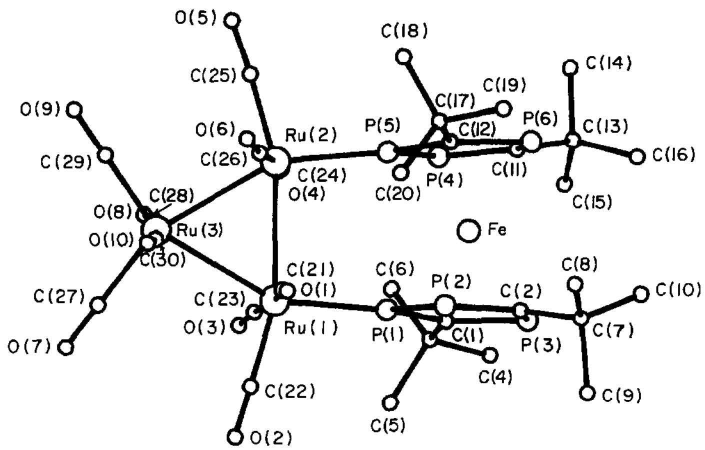

Fig. 3. The molecular structure of IV showing the atom numbering scheme. Selected bond lengths are: Ru(1)–P(1) 2.341(4), Ru(2)–P(5) 2.336(4), Fe–P(1) 2.344(4), Fe–P(2) 2.369(4), Fe–P(3) 2.351(3), Fe–P(4) 2.359(4), Fe–P(5) 2.351(3), Fe–P(6) 2.347(5), Fe–C(1) 2.276 (13), Fe–C(2) 2.170(12), Fe–C(11) 2.207(12), Fe–C(12) 2.272(12) Å.

must have become linked by η^1-ligating to two of the ruthenium atoms of the cluster carbonyl. This was subsequently confirmed by a single crystal X-ray diffraction study, (see Fig. 3), which reveals that the triangle of ruthenium atoms in IV lies in a plane which is perpendicular to those of the two η^5-ligated $P_3C_2{}^tBu_2$ rings of the original $[Fe(\eta^5\text{-}P_3C_2{}^tBu_2)_2]$ complex.

All three crystal structure determinations were carried out using an Enraf–Nonius CAD4 diffractometer with monochromated Mo-K_α radiation (λ = 0.71069 Å). The structures were solved by heavy atom methods (II and III) or direct methods (IV) and refined by full matrix least squares. Hydrogen atoms were found at calculated positions.

II: Crystal data. $C_{25}H_{36}FeO_5P_6W$, $M = 842.1$, triclinic, $P\bar{1}$ (No. 2), $a = 10.362(2)$, $b = 12.901(2)$, $c = 12.930(4)$ Å, $\alpha = 103.53(2)$, $\beta = 93.90(2)$, $\gamma = 98.96(2)°$, $U = 1653.2$ Å^3, $Z = 2$, $D_{calc} = 1.69$ g cm^{-3}, $F(000) = 832$, $R = 0.025$ for 3560 unique reflections with $I > 3\sigma(I)$.

III: Crystal data. $C_{30}H_{45}FeO_5P_5W$, $M = 880.3$, monoclinic, $P2_1/c$ (No. 14), $a = 10.278(7)$, $b = 16.896(7)$, $c = 21.370(11)$ Å, $\beta = 103.47(6)°$, $Z = 4$, $D_{calc} = 1.62$ g cm^{-3}, $F(000) = 1760$, $R = 0.038$ for 3772 unique reflections with $I > 3\sigma(I)$.

IV: Crystal data. $C_{32}H_{40}FeO_{10}P_6Ru_3$, $M = 1129.6$, rhombohedral, (on hexagonal axes), $R\bar{3}$ (No. 148), $a = b = 24.540(7)$, $c = 39.937(8)$ Å, $U = 20827$ Å^3, $Z = 18$, $D_{calc} = 1.62$ g cm^{-3}, $F(000) = 10080$. The crystal structure contains cyclohexane solvate molecules. $R = 0.046$ for 3067 unique reflections with $I > 3\sigma(I)$.

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References

1 R. Bartsch, P.B. Hitchcock and J.F. Nixon, J. Chem. Soc., Chem. Commun., (1987) 1946.
2 R. Bartsch, P.B. Hitchcock and J.F. Nixon, J. Chem. Soc., Chem. Commun., (1988) 819.

3 R. Bartsch, P.B. Hitchcock and J.F. Nixon, J. Organomet. Chem., 356 (1988) C1.
4 R. Bartsch, D. Carmichael, P.B. Hitchcock, M.F. Meidine, J.F. Nixon and G.J.D. Sillett, J. Chem. Soc., Chem. Commun., (1988) 1615.
5 R. Bartsch, P.B. Hitchcock and J.F. Nixon, J. Organomet. Chem., 373 (1989) C17.
6 R. Bartsch, P.B. Hitchcock and J.F. Nixon, J. Chem. Soc., Chem. Commun., (1990) 472.