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Preliminary Communication

Triphospha-ferrocenes as ligands. Crystal structures of [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)-$Ru_3(CO)_{11}$] and the novel cluster complex [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)$Ru_3(CO)_9$] involving side-on and end-on coordination of three ruthenium atoms

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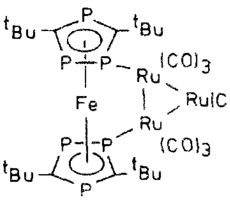
Abstract

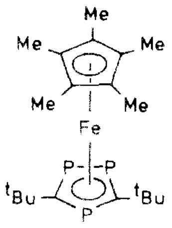
The lone-pair electrons of one or two directly bonded phosphorus atoms of the $C_2{}^tBu_2P_3$ ring in the triphospha-ferrocene complex [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)] can coordinate to one or three ruthenium atoms to afford the novel triruthenium carbonyl cluster complexes [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)$Ru_3(CO)_{11}$] and [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)$Ru_3(CO)_9$], respectively. The structures of the triruthenium carbonyl cluster fragments were determined by single crystal X-ray diffraction studies.

Syntheses and structures of penta- and hexaphosphorus analogues of ferrocene, hexaphosphorus analogues of chromocene and η^3-transition metal complexes of the $C_3{}^tBu_3P_2$ ring system have been described previously [1–7]. Unlike their simple metallocene analogues, these complexes have further coordinating potential towards other transition metal centres by virtue of the availability of the ring phosphorus lone-pair electrons that are not involved in the η^3- or η^5-metal coordination. The recently [8] described complex [Fe($C_2{}^tBu_2P_3$)$_2$$Ru_3(CO)_{10}$], **I**, is of special interest since it represents the first example of attachment of a transition metal carbonyl cluster to another η^5-$C_2{}^tBu_2P_3$ metal complex and interlinkage of both η^5-$C_2{}^tBu_2P_3$-coordinated ring systems in a hexaphosphaferrocene complex.

We now describe the first example of a phosphorus sandwich compound in which the two adjacent phosphorus atoms of a η^5-$C_2{}^tBu_2P_3$ ring are interlinked by a ruthenium carbonyl cluster. In this case the mixed cyclopentadienyl-phosphacyclopentadienyl complex [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)], **II**, was used as starting material; interlinkage via the two phospha-cyclopentadienyl rings as described for **I** can thus be ruled out.



(I)



(II)

Complex **II**, which is easily accessible from [Li(dme)$_3$]$^+$[$C_2{}^tBu_2P_3$]$^-$ [9], LiC_5Me_5 and $FeCl_2$ (DME = 1,2-dimethoxyethane), reacted with $Ru_3(CO)_{12}$ at 65°C in DME during 4 h to afford the novel brown trirutheniumn nonacarbonyl complex [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)$Ru_3(CO)_9$], **IV**, in 75% yield.

Only traces of the red by-product [Fe(η^5-C_5Me_5)(η^5-$C_2{}^tBu_2P_3$)$Ru_3(CO)_{11}$], **III**, were obtained *, and so this could not be characterized by NMR spectroscopy. Under milder conditions (45°C for 2 h) the yield of **III** was higher, but at 90°C no **III** was detected. Obviously complex **IV** is more thermodynamically stable than complex **III**, and this leads to exclusive formation of **IV** from **III** under vigorous conditions.

The molecular structure of **III** is shown in Fig. 1. The Ru1–P2 bond [2.391(1) Å] is somewhat longer than the corresponding phosphorus–ruthenium bond in **I** [2.341(4) and 2.336(4) Å] [8].

The simplicity of the $^{31}P\{^1H\}$ NMR spectrum of complex **IV**, which shows an AX_2 pattern, indicates

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* Preparations of **II**, **III** and **IV**. $FeCl_2$ (150 mg, 1.18 mmol) was added to 6 ml of a solution of $Li(C_5Me_5)$ (157 mg, 1.10 mmol) and [Li(dme)$_3$]$^+$[$C_2{}^tBu_2P_3$]$^-$ (505 mg, 0.99 mmol) in monoglyme. The mixture was stirred at room temperature for 16 h, the solvent was removed, and the residue was extracted with n-hexane. The extract was subjected to column chromatography (kieselgel/n-hexane) to give red crystals of **II** (yield 32%).

A solution containing **II** (328 mg, 0.78 mmol) and $Ru_3(CO)_{12}$ (576 mg, 0.90 mmol) in 2 ml monoglyme was heated to 65°C with stirring for 4 h. Work-up as above gave traces of **III** as red crystals (yield not determined) and brown crystals of **IV** (yield 75%).

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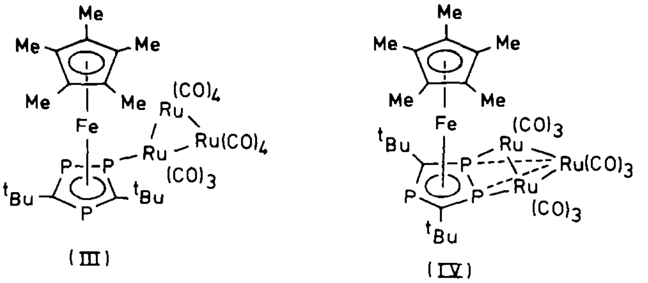

(III) (IV)

Scheme 1.

that the two adjacent phosphorus atoms of the original triphospha-ferrocene **II** must have become linked by η^1-coordination to two or three of the ruthenium atoms of the cluster carbonyl **. This was subsequently confirmed by a single crystal X-ray diffraction study (see Fig. 2) which reveals, in addition to the η^1-coordination of the ruthenium atoms Ru1 and Ru3, a direct interaction between Ru2 and the two phosphorus atoms P1 and P2.

This mode of attachment can be regarded as μ_3-η^2-ligation of a PP and PC multiple-bonded system to three metal centres. A similar side-on and end-on coordination was observed by Huttner [10] in $[Cr_3(CO)_{10}({}^tBuP)({}^tBu_2P_2)]$, in which a *Z*-diphosphene unit RP=PR is incorporated into a cluster and two metal centres are more strongly bonded than the third. A similar pattern is observed in **IV**; the weaker interactions Ru2–P1 and Ru2–P2 are indicated by dotted lines in Scheme 1. The bonds of the $C_2{}^tBu_2P_3$ ring in **IV** are, as expected, longer than the corresponding bonds in **III**. The PP bond length in **IV** [2.131(2) Å] is in good agreement with the corresponding bond length [2.112(3) Å] in $[Cr_3(CO)_{10}({}^tBuP)({}^tBu_2P_2)]$ [10].

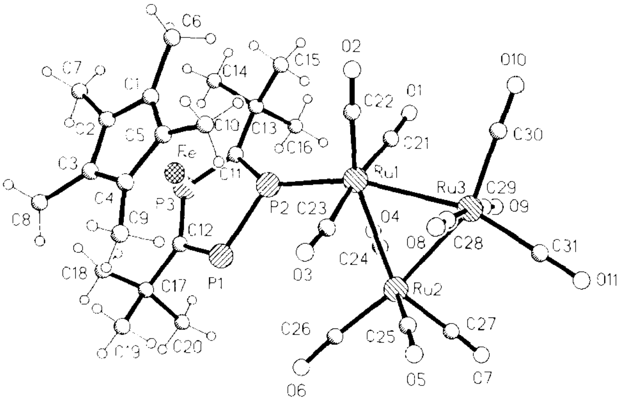

Fig. 1. The molecular structure of **III** showing the atom numbering scheme. Selected bond lengths are: P1–P2 2.107(2), P1–C12 1.763(4), P3–C12 1.756(4), P3–C11 1.764(4), P2–C11 1.761(4), Ru1–P2 2.391(1), Ru1–Ru2 2.882(1), Ru1–Ru3 2.836(1), Ru2–Ru3 2.835(1), Fe–P1 2.338(1), Fe–P2 2.330(1), Fe–P3 2.319(2), Fe–C11 2.189(4), Fe–C12 2.205(4) Å.

The coordination of two adjacent phosphorus atoms to three transition metal centres involving side-on and end-on coordination represents an unusual bonding mode for phosphorus sandwich compounds. The synthesis of related polymetallic compounds is the subject of present studies.

Diffraction data were determined with a Siemens-Nicolet R3 diffractometer fitted with a LT-2 low temperature unit using monochromated Mo-Kα radiation. The structure was solved by direct methods and refined anisotropically on *F* with rigid methyl groups.

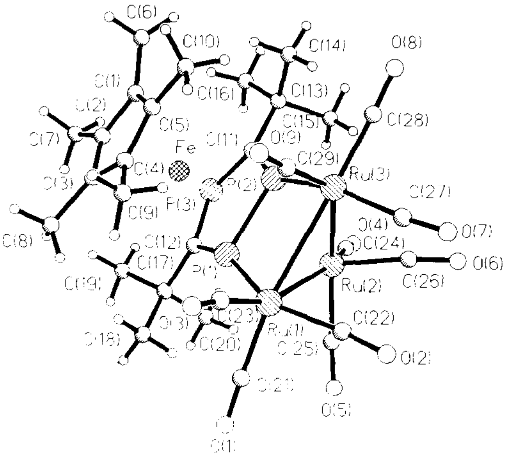

Fig. 2. The molecular structure of **IV** showing the atom numbering scheme. The weak interactions Ru2–P1 and Ru2–P2 are indicated by dotted lines. Selected bond lengths are: P1–P2 2.131(2), P1–C12 1.772(5), P3–C12 1.775(5), P3–C11 1.772(6), P2–C11 1.776(6), Fe–P1 2.358(2), Fe–P2 2.336(2), Fe–P3 2.305(2), Fe–C11 2.142(5), Fe–C12 2.163(6), Ru1–P1 2.377(2), Ru3–P2 2.333(2), Ru2–P1 2.541(2), Ru2–P2 2.508(2) Å.

** **II**: NMR spectra: ^1H ($CDCl_3$): δ 1.39 (s, 18H, ${}^tBu$); 1.85 (s, 15H, C_5Me_5). ^{13}C ($CDCl_3$): δ 12.79 (s, $C_5\mathit{Me}_5$); 36.71 (m, $C\mathit{Me}_3$); 38.87 (m, $\mathit{C}Me_3$); 86.59 (s, C_5Me_5). $^{31}P\{^1H\}$ ($CDCl_3$): (AB_2), δ 38.10 (P^A), 48.24 (P^B), $^2J(PP)$ 44.9 Hz. MS (70 eV, EI): *m/z* 422 (M^+, 100%), 365 ($M^+ - {}^tBu$, 4), 284 ($M^+ - {}^tBu_2C_2$, 73), 253 ($M^+ - {}^tBu_2C_2P$, 11).

III: MS (FAB, *m*-nitrobenzene as matrix): *m/z* 980 ($M^+ - 2$ CO, 3%), 952 ($M^+ - 3$ CO, 2), 924 ($M^+ - 4$ CO, 2), 868 ($M^+ - 6$ CO, 5), 136 ($C_5Me_5 + H^+$, 100). IR (n-hexane): ν(CO) 2095 (m), 2060 (vs), 2035 (s), 2028 (vs), 2012 (s) cm^{-1}.

IV: NMR spectra: ^1H ($CDCl_3$): δ 1.50 (s, 18H, ${}^tBu$); 1.79 (s, 15H, C_5Me_5). ^{13}C ($CDCl_3$): 12.15 (s, $C_5\mathit{Me}_5$); 35.63 (m, $C\mathit{Me}_3$); 39.91 (m, $\mathit{C}Me_3$); 91.48 (s, C_5Me_5); 199.44 (m, CO). $^{31}P\{^1H\}$ ($CDCl_3$): (AB_2), δ 14.74 (P^A), 9.77 (P^B), $^2J(PP)$ 43.2 Hz. MS (FAB, *m*-nitrobenzene as matrix): *m/z* 980 (M^+, 1%), 136 ($C_5Me_5 + H^+$, 83) and fragments caused by subsequent loss of CO; IR (n-hexane): ν(CO) 2066 (vs), 2025 (vs), 2016 (vs), 1998 (s), 1981 (s), 1977 (s) cm^{-1}.

III: Crystal data: $C_{31}H_{33}FeO_{11}P_3Ru_3$, M = 1033.5, triclinic, space group $P\bar{1}$, $a = 9.035(3)$, $b = 12.609(5)$, $c = 17.173(6)$ Å, $\alpha = 98.82(3)$, $\beta = 94.56(3)$, $\gamma = 97.24(3)°$, $U = 1908.0(9)$ Å^3, $Z = 2$, $D_{calc} = 1.799$ g cm^{-3}, $F(000) = 1020$, $R = 0.029$ for 5379 unique reflections with $F > 4\sigma(F)$.

IV: Crystal data: $C_{29}H_{33}FeO_9P_3Ru_3$, M = 977.5, monoclinic, space group $P2_1/n$, $a = 10.419(2)$, $b = 29.821(7)$, $c = 11.738(3)$ Å, $\beta = 108.93(2)°$, $U = 3450.0(11)$ Å^3, $Z = 4$, $D_{calc} = 1.882$ g cm^{-3}, $F(000) = 1928$, $R = 0.034$ for 4182 unique reflections with $F > 4\sigma(F)$ [***].

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[***] The program system "Siemens SHELXTL PLUS" was employed. Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 57041.