First Example of a Phosphino-phosphinidene Complex. Crystal and Molecular Structure of the Novel Triruthenium Carbonyl Cluster Complex $[Ru_3(CO)_9(P_5C_5Bu^t_5)]$ Containing a Phosphino-phosphinidene, acting as a Six-electron Donor

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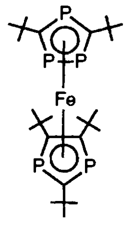
The pentaphospha-ferrocene $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$, **1**, reacts with $[Ru_3(CO)_{12}]$, with extrusion of iron, to afford the novel phosphino-phosphinidene triruthenium nonacarbonyl cluster, $[Ru_3(CO)_9(P_5C_5Bu^t_5)]$, whose structure, elucidated by a single crystal X-ray crystallographic study, is related to that of the $P_5C_5Bu^t_5$ cage.

Previously,[1–6] we described syntheses and structures of penta- and hexa-phosphorus analogues of ferrocene, hexaphosphorus analogues of chromocene, and η^3-transition metal complexes containing the $P_2C_3Bu^t_3$ ring system. Unlike their simple metallocene analogues, these compounds have the possibility of further ligating potential towards other transition metal centres, by virtue of the availability of the ring phosphorus lone-pair electrons. We have already established that one of the two directly bonded phosphorus atoms of $P_3C_3Bu^t_2$ ring acts as an η^1-ligating centre, *e.g.* in $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2W(CO)_5]$ and $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)\text{-}W(CO)_5]$, however, the $P_2C_3Bu^t_3$ ring does not undergo further coordination, presumably for steric reasons.[7]

Recently,[8] we described the novel triruthenium decacar-



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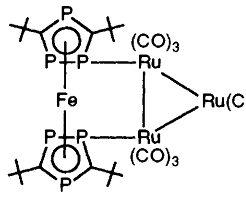

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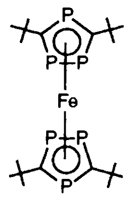

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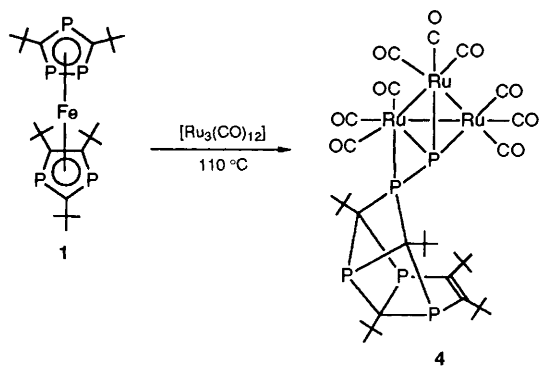


1 **4**

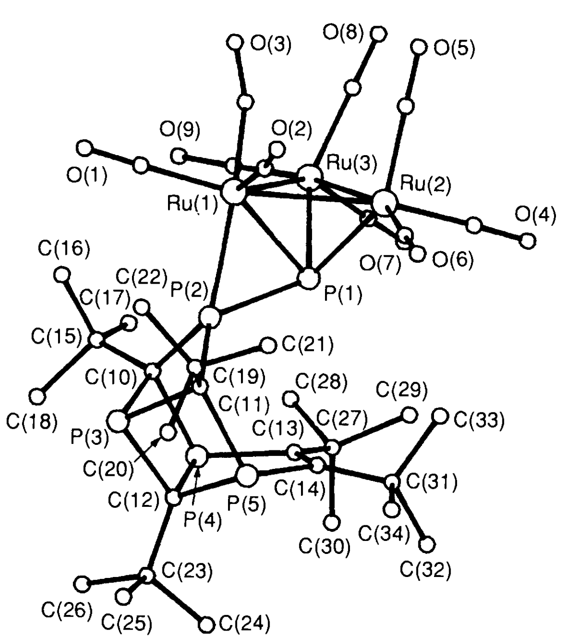
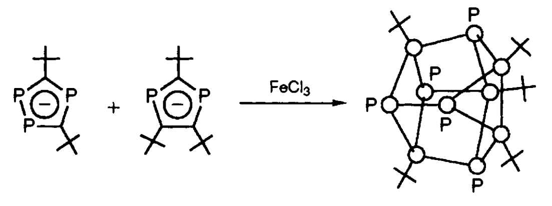


Fig. 1 The molecular structure of **4** showing the numbering scheme. Selected bond lengths (Å): Ru(1)–P(1) 2.425(1), Ru(1)–P(2) 2.447(1), Ru(2)–P(1) 2.285(1), Ru(3)–P(1) 2.350(1), P(1)–P(2) 2.164(1), C(13)–C(14) 1.354(6).



bonyl cluster $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2Ru_3(CO)_{10}]$, **2**, made from $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$, **3**, and $[Ru_3(CO)_{12}]$, which contains two interlinked $\eta^5\text{-}P_3C_2Bu^t_2$ ring systems.

As outlined above, the pentaphospha-ferrocene $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$, **1**, cannot give an analogous compound to **2**, and with triruthenium dodecacarbonyl, in boiling toluene, a surprising reaction occurs, involving extrusion of iron and coupling of the two rings, to afford the novel phosphino-phosphinidene triruthenium nonacarbonyl cluster compound $[Ru_3(CO)_9(P_5C_5Bu^t_5)]$, **4**, albeit in low yield, (*ca.* 4%).

A single crystal X-ray determination on **4** revealed the molecular structure (Fig. 1), in which four phosphorus atoms are contained within one five-membered ring and two four-membered rings, with the remaining phosphinidene-phosphorus atom P(1) lying outside the opened 'cage'.† The formation of the four-membered ring containing P(3), C(10), P(2) and C(11) presumably results from a [2 + 2] cycloaddition of the two original $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ ring systems, accompanied by simultaneous P–C bond cleavage of P(1) and C(11) of the original $P_3C_2Bu^t_2$ ring.

P(1) acts as a four-electron donor towards the triruthenium carbonyl cluster, while P(2) forms a coordinate bond to Ru(1), similar to that of a tertiary phosphane. The P(1)–P(2) system thus represents the first example of a phosphino-phosphinidene ligand, which can be regarded as a six-electron donor. The two carbonyl groups lying between Ru(1) and Ru(3) in the triruthenium cluster are semi-bridging, whereas all the other carbonyl groups are terminal. All bond distances in the opened 'cage' in **4** lie in the range typical of phosphorus–carbon single bonds. The C(13)–C(14) bond distance is typical of a carbon–carbon double bond, as found previously by us in the 'slipped' nickel sandwich complex $[Ni(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^3\text{-}P_2C_3Bu^t_3)]$.[5] The P(1)–P(2) bond distance, 2.164 Å in **4**, is shorter than expected for a P–P single bond, and the Ru(2)–P(1) and Ru(3)–P(2) bonds lying on one side of the metal triangle are shorter than Ru(1)–P(1) and the Ru(1)–P(2) bonds on the other side.

Of special interest is the disposition of the P(2) and P(1) atoms in the structure of **4**, since decomplexation of the $[Ru_3(CO)_9]$ fragment would generate a free phosphino-phosphinidene of just the right geometry to facilitate phosphinidene-phosphorus, P(1), interaction with the unsaturated C(13)–C(14) bond, thereby, generating a three-membered P(1)C(13)(C14) ring system leading to a structure, which is identical to our previously reported oxidative coupling reaction of the $P_3C_2Bu^t_2$ and $P_3C_3Bu^t_3$ anionic rings, and would also provide confirmation of our original proposal that the single P–P bond in $P_5C_5Bu^t_5$ stems from the original $P_3C_2Bu^t_2$ ring.[9]

Phosphido-phosphines, in which the phosphido-phosphorus is attached to an organo group and to two metal centres are the only related compounds to **4**, which have been previously described in the literature.[10] Interestingly, Scherer *et al.*[11] have very recently independently discovered the first example of a phosphido-phosphinidene complex, $[(TaC_5H_3Bu^t_2)_3(P_4)(P_2)]$, during studies on the interaction between $[TaC_5H_3Bu^t_2(CO)_4]$ and P_4.

The extrusion of iron from **1** with formation of an opened 'cage' compound is remarkable, in view of the known thermal stability of the pentaphosphaferrocenes, and reactions of **1**

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† *Crystal data*: $C_{34}H_{45}O_9P_5Ru_3$, $M = 1055.8$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.422(2)$, $b = 12.573(1)$, $c = 16.867(3)$ Å, $\alpha = 91.09(1)$, $\beta = 96.50(1)$, $\gamma = 106.33(1)°$, $U = 2104.3$ Å^3, $Z = 2$, $D_c = 1.67$ g cm^{-3}. The structure was solved by direct methods, using 5600 reflections (from a total of 7389 unique reflections for $2 < \theta < 25°$, having $|F^2| > 2\sigma(F^2)$ collected on an Enraf-Nonius CAD4 diffractometer, using Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 12.70$ cm^{-1}. The final residuals were $R = 0.032$, $R_W = 0.040$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

with other metal carbonyls at high temperatures are expected to show further interesting chemistry.

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