

Preliminary communication

**THE INSERTION OF ACETYLENE INTO THE FORMAL
 RUTHENIUM–PHOSPHORUS BONDS
 OF *closo*-[Ru₄(μ₄-PPh)₂(μ₂-CO)(CO)₁₀]. CRYSTAL STRUCTURE
 OF [Ru₄(μ₄-PPh){μ₄-η³-P(Ph)CHCH}(μ₂-CO)(CO)₁₀]**

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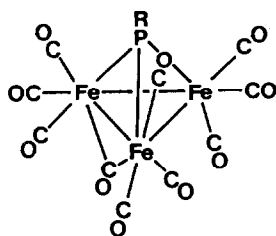
(Received March 7th, 1986)

Summary

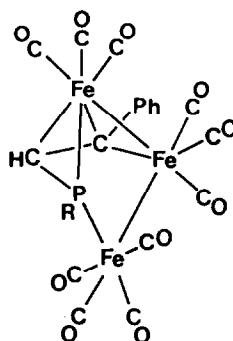
Treatment of *closo*-[Ru₄(μ₄-PPh)₂(μ₂-CO)(CO)₁₀] with acetylene under ambient conditions leads to the insertion of the acetylene into the skeletal framework of the cluster and the formation of [Ru₄(μ₄-PPh){μ₄-η³-P(Ph)CHCH}(μ₂-CO)(CO)₁₀], the structure of which has been determined X-ray crystallographically.

Considerable attention has been focused of late on the design and synthesis of metal cluster compounds containing bridging and/or capping monodentate ligands such as the diphenylphosphido, PPh₂, and phenylphosphinidene, PPh, groups respectively, the function of these ligands being to stabilise the metal cluster compounds to fragmentation during chemical reaction. Their use is based on the premise that the bonding between phosphorus and transition metals is considerably stronger than that between the metals themselves and that as a consequence the formal metal–phosphorus bonds will not be cleaved during reaction.

More recently, however, a number of researchers have established that unsaturated hydrocarbons such as alkynes, dienes, the vinyl group and carbenes can be inserted into the formal metal–phosphorus bond of bridging diphenylphosphido groups [1–6]. Similar insertions into capping phenylphosphinidene groups are not as well documented although Huttner et al. [7] have recently shown that treatment of [Fe₃(μ₃-PC₆H₄-*p*-OCH₃)(μ₂-CO)(CO)₉] (I; R = C₆H₄-*p*-OCH₃) [8] with phenylacetylene at ambient temperature readily gives [Fe₃{μ₃-η³-P(C₆H₄-*p*-OCH₃)-CHCC₆H₅}(CO)₁₀] (II; R = C₆H₄-*p*-OCH₃), and

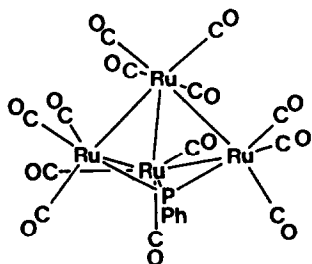


(I)

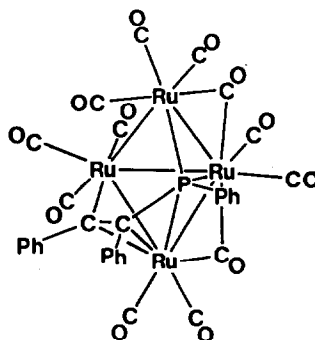


(II)

Carty et al. [9] have observed that reaction of $[\text{Ru}_4(\mu_3\text{-PPh})(\text{CO})_{13}]$ (III) [10] with diphenylacetylene in benzene at 60°C produces $[\text{Ru}_4\{\mu_4\text{-}\eta^3\text{-P}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{Ph})\}(\mu_2\text{-CO})_2(\text{CO})_{10}]$ (IV) as well as $[\text{Ru}_4(\mu_4\text{-PPh})\{\mu_4\text{-C}(\text{Ph})\text{C}(\text{Ph})\}(\mu_2\text{-CO})_2(\text{CO})_9]$. In terms of the polyhedral skeletal electron pair (PSEP) theory, compounds I and III are *nido* species while compounds II and IV are *arachno* and *nido* systems,



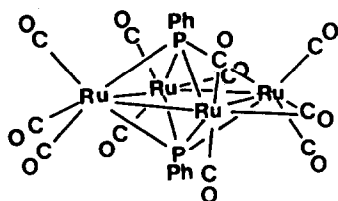
(III)



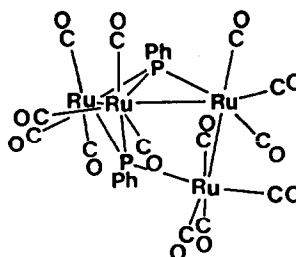
(IV)

respectively [11]. The insertion of acetylene into the formal ruthenium-phosphorus bonds of a *closo* metal cluster, viz. $[\text{Ru}_4(\mu_4\text{-PPh})(\mu_2\text{-CO})(\text{CO})_{10}]$ is now described*.

Previous studies in our laboratories have shown that treatment of a solution of $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ (V) with carbon monoxide leads to the rapid formation of $[\text{Ru}_4(\mu_3\text{-PPh})_2(\text{CO})_{13}]$ (VI) [13] with the expected product, $[\text{Ru}_4(\mu_4\text{-$



(V)



(VI)

* The insertion of acetylene into the formal osmium-sulphur bonds of *closo*- $[\text{Os}_4(\mu_3\text{-S})(\text{CO})_{12}]$ has very recently been reported [12].

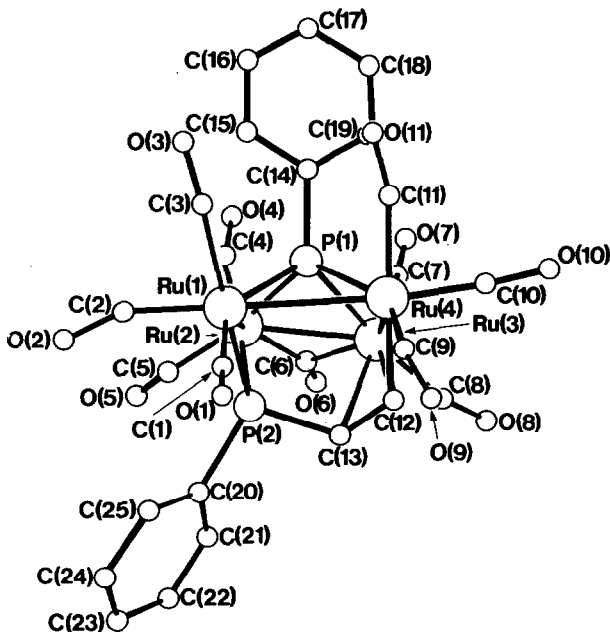


Fig. 1: The molecular stereochemistry of $[\text{Ru}_4(\mu_4\text{-PPh})\{\mu_4\text{-}\eta^3\text{-P(Ph)CHCH}\}(\mu_2\text{-CO})(\text{CO})_{10}]$. Relevant interatomic distances Ru(1)–Ru(2), 3.024(1); Ru(1)–Ru(4), 2.971(1); Ru(2)–Ru(3), 2.853(1); Ru(3)–Ru(4), 2.957(1); Ru(1)–P(1), 2.371(2); Ru(2)–P(1), 2.381(2); Ru(3)–P(1), 2.427(2); Ru(4)–P(1), 2.372(2); Ru(1)–P(2), 2.356(2); Ru(2)–P(2), 2.313(2) Å. Distances of the ruthenium atoms from a least squares plane through the Ru_4 unit: Ru(1), -0.116 ; Ru(2), 0.121 ; Ru(3), -0.124 ; Ru(4), 0.119 Å.

$\text{PPh})_2(\text{CO})_{12}]$, not being detected. With the object of establishing whether alkynes also afford addition products of compound V and, if so, whether on coordination they function as either two- or four-electron donors, the reaction of $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ with acetylene has been investigated. Passage of the alkyne through a purple solution of the undecacarbonyl was found to lead to rapid decolourisation of the solution and the formation of a product characterised by routine methods as well as by X-ray crystallography * as $[\text{Ru}_4(\mu_4\text{-PPh})\{\mu_4\text{-}\eta^3\text{-P(Ph)CHCH}\}(\mu_2\text{-CO})(\text{CO})_{10}]$ (VII). Although other products were also formed in this reaction their yields were very low and as a consequence did not receive further attention.

* *Crystal data:* $\text{C}_{25}\text{H}_{12}\text{O}_{11}\text{P}_2\text{Ru}_4$, $M = 752.43$, triclinic, space group $P\bar{1}$, a 9.568(1), b 9.846(1), c 17.267(2) Å, α 96.18(1), β 95.77(1), γ 113.33(1)°, U 1466.6 Å³. D_c 1.70 g cm⁻³ for $Z = 2$. $F(000) = 1112$. $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 23.41 cm⁻¹. 4344 reflections were measured and empirically corrected for absorption on a CAD-4 diffractometer (N.C.R.L., C.S.I.R., Pretoria), 3576 of which were classed as observed [$I > 3\sigma(I)$]. Full-matrix least-squares refinement gave $R = 0.046$ with the Ru and P atoms being assigned anisotropic temperature factors, and the O and C atoms isotropic temperature factors.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

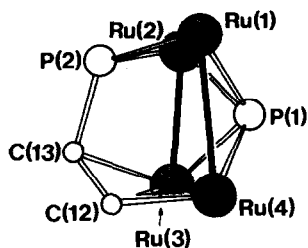


Fig. 2: The geometry of the $\text{Ru}_4\text{P}_2\text{C}_2$ framework in $[\text{Ru}_4(\mu_4\text{-PPh})(\mu_4\text{-}\eta^3\text{-P(Ph)CHCH})(\mu_2\text{-CO})(\text{CO})_{10}]$.

The molecular structure of VII is illustrated in Fig. 1. The four ruthenium atoms define a puckered four-membered ring formally capped on the one side by a phenylphosphinidene ligand and on the other by a PhPCHCH group; the distances of each ruthenium atom from their mean plane are summarised in the caption. While the terminal carbon of the PhPCHCH group is essentially equidistant from Ru(3) and Ru(4) (Ru(3)–C(12) 2.26(1) Å, Ru(4)–C(12) 2.12(1) Å) the internal carbon is much closer to Ru(3) than Ru(4) (Ru(3)–C(13) 2.39(1) Å, Ru(4)–C(13) 3.18(1) Å). The coordination at each ruthenium is completed by the eleven carbonyl groups, three terminal carbonyls each for Ru(1) and Ru(4) and two terminal carbonyls each for Ru(2) and Ru(3) with the eleventh carbonyl bridging the latter rutheniums.

Consideration of the $\text{Ru}_4\text{P}_2\text{C}_2$ fragment of the molecule reveals that ten electron pairs are available for skeletal bonding and, on the basis of the PSEP theory, the skeletal framework should adopt a *nido*-tricapped trigonal prismatic geometry. Figure 2 illustrates that the ternary $\text{Ru}_4\text{P}_2\text{C}_2$ framework does indeed adopt this configuration albeit somewhat distorted.

The inability of $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ to give a stable dodecarbonyl product, $[\text{Ru}_4(\mu_4\text{-PPh})_2(\text{CO})_{12}]$, on reaction with CO, in contrast to $[\text{Fe}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$, is paralleled by its reaction with $\text{HC}\equiv\text{CH}$. On the assumption that $[\text{Ru}_4(\mu_4\text{-PPh})_2(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$, in which the acetylene functions as a two-electron donor, is an intermediate in this reaction it must rearrange with the product actually isolated, resulting from the formal insertion of the acetylene into one of the capping phosphinidene ligands.

It is apparent from this investigation that even for *closo* systems, capping ligands may participate in transformation reactions under mild reaction conditions. Significantly, reaction of V with diphenylacetylene affords four reaction products of almost equal yield, none of which appears to correspond with VII.

Acknowledgements. The authors express their sincere thanks to the South African Council for Scientific and Industrial Research and the University of Natal for financial support, Johnson Matthey Limited for the loan of ruthenium salts and Dr. P.H. van Rooyen of the N.C.R.L., C.S.I.R., Pretoria, for the intensity data collection.

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