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Preliminary communication

REVERSIBLE REARRANGEMENT OF A TETRARUTHENIUM CLUSTER CONTAINING QUADRUPLY BRIDGING PPh GROUPS TO ONE CONTAINING TRIPLY BRIDGING PPh LIGANDS THROUGH UPTAKE OF CARBON MONOXIDE; CRYSTAL AND MOLECULAR STRUCTURES OF $[Ru_4(\mu_3\text{-}XPh)_2(CO)_{13}]$ (X = P or As)

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Summary

$[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$, in which an essentially square planar array of ruthenium atoms is capped by two phenylphosphinidene groups, readily and reversibly adds carbon monoxide to afford the tridecacarbonyl derivative $[Ru_4(\mu_3\text{-}PPh)_2(CO)_{13}]$; crystal structure determinations on this compound and its arsenic analogue reveal that the CO addition is accompanied by a rearrangement of the cluster framework, and that these compounds can be considered as derivatives of $[Ru_3(\mu_3\text{-}XPh)_2(CO)_9]$ (X = P or As) in which an $Ru(CO)_4$ unit has been inserted into one of the three Ru—P or Ru—As bonds.

We have previously reported that while the reactions of $[Ru_3(CO)_{12}]$ with primary phosphines and arsines XRH_2 (X = P or As, R = aryl group) under mild conditions afford bridged dinuclear and capped trinuclear derivatives of the type $[Ru_2(\mu_2\text{-}AsRH)_2(CO)_6]$ and $[Ru_3(\mu_3\text{-}XR)(\mu_2\text{-}H)_2(CO)_9]$ and $[Ru_3(\mu_3\text{-}XR)_2(CO)_9]$, respectively [1], the corresponding reactions under more rigorous conditions yield condensed as well as trinuclear products including the tetranuclear undecacarbonyl derivative, $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ (I), in which an essentially square planar array of ruthenium atoms* is capped by two phenylphosphinidene ligands [2].

Vahrenkamp et al. reported simultaneously that the corresponding iron

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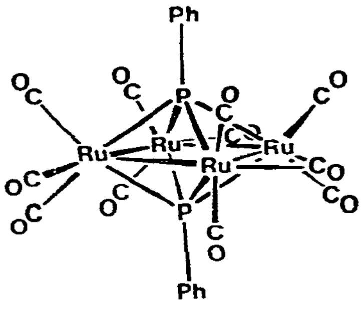
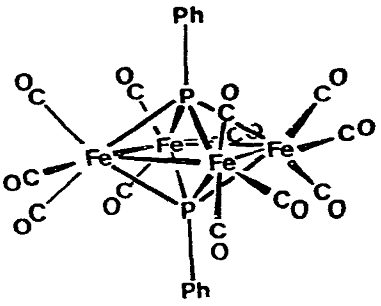
*More precisely the four Ru atoms adopt a planar isosceles trapiezoidal configuration with the distance between the two Ru atoms bridged by a carbonyl group being shorter (2.717(5) Å) than the other three Ru—Ru distances (2.874(5), 2.878(5) and 2.854(5) Å).



(I)



(II)

compound, $[Fe_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$, can be obtained by suitable treatment of $[Fe_2(\mu_2\text{-}PPhH)_2(CO)_6]$ with $[Fe_3(CO)_{12}]$ [3]. These tetranuclear compounds are, in a formal sense, coordinatively unsaturated and thus, not surprisingly, will readily add carbon monoxide. In the case of the carbonylation of $[Fe_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$, the product was found [4] to be $[Fe_4(\mu_4\text{-}PPh)_2(CO)_{12}]$ (II) in which, as confirmed X-ray crystallographically for the trimethylphosphite-substituted derivative $[Fe_4(\mu_4\text{-}PPh)_2(CO)_{11}\{P(OMe)_3\}]$ [4,5], the four iron atoms are perfectly square planar and the carbonyl groups are all terminal.

Similar to that established for $[Fe_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$, the carbonylation of $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$ has been found to be a reversible process but in contrast the product has been established by means of elemental analysis and mass spectrometry to be a tridecacarbonyl derivative of stoichiometry $[Ru_4(PPh)_2(CO)_{13}]$. The corresponding arsenic derivative has also been isolated but as one of the products of the reaction of $[Ru_3(CO)_{12}]$ with $[Cr(CO)_5(AsPhH_2)]$. It is apparent that the carbonylation of $[Ru_4(\mu_4\text{-}PPh)_2\text{-}(\mu_2\text{-}CO)(CO)_{10}]$ must involve the rearrangement of the cluster framework and thus with the object of gaining insight into this rearrangement process and in particular of establishing unequivocally the structures of the tridecacarbonyl compounds single crystal X-ray diffraction studies were carried out on $[Ru_4(PPh)_2(CO)_{13}]$ (IIIa) and $[Ru_4(AsPh)_2(CO)_{13}]$ (IIIb).

Crystal Data: Crystals of $C_{25}H_{10}P_2O_{13}Ru_4$ are monoclinic, space group $P2_1/c$, a 11.490(5), b 16.82(1), c 16.33(1) Å, β 90.61(5)°, V 3155.2 Å^3, D_c 2.07 g/cm^3, μ 19.9 cm^{-1}, $Z = 4$. Data were collected on a Philips PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria) using graphite monochromated Mo-K_α radiation to θ 23°. Of the 4938 reflections measured, 4133 were classed as observed ($I > 3.0\sigma(I)$). The structure was solved by direct and Fourier methods and refined by full matrix least squares to $R = 0.045$ (unit weights) all Ru and P atoms anisotropic*.

Crystals of $C_{25}H_{10}As_2O_{13}Ru_4$ are monoclinic, space group $P2_1/c$, a 9.38(1), b 17.70(6), c 18.18(3) Å, β 92.7(1)°, V 3016.62 Å^3, D_c 2.36 g/cm^3, μ 42.8 cm^{-1}, $Z = 4$. Data were collected on a Nicolet (Syntex) R3 four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.71069 Å). Of the 3887 reflections measured, 2390 were classed as observed ($I > 4.0\sigma(I)$).

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*Supplementary material is available from the authors.

The structure was solved by direct methods and refined by least squares refinement using the SHELXTL program to R = 0.106*.

The molecular stereochemistries of IIIa and IIIb are very similar and are illustrated in Fig. 1. Three of the ruthenium atoms (Ru(2), Ru(3) and Ru(4)), each of which have three terminal carbonyl groups coordinated to them, are capped by either a phenyl-phosphinidene or -arsinidene ligand with two of the Ru—Ru distances corresponding to formal metal—metal bonds (IIIa: Ru(2)—Ru(3), 2.885(1); Ru(3)—Ru(4), 2.926(1); IIIb: Ru(2)—Ru(3), 2.927(8); Ru(3)—Ru(4), 2.969(8) Å) and the third being much longer (IIIa: Ru(2)—Ru(4), 4.214(2); IIIb: Ru(2)—Ru(4), 4.29(1) Å). One of the short Ru—Ru edges (Ru(2)—Ru(3)) is also bridged by a second phenyl-phosphinidene or -arsinidene ligand (on the opposite side of the triruthenium plane) which in turn is coordinated to an $Ru(CO)_4$ unit directly bonded through a Ru—Ru bond to the unbridged Ru atom (Ru(4)). These compounds can thus be considered as derivatives of $[Ru_3(\mu_3\text{-PPh})_2(CO)_9]$ or $[Ru_3(\mu_3\text{-AsPh})_2(CO)_9]$ [1,6—8] in which an $Ru(CO)_4$ moiety has formally inserted into one of the three Ru—P or Ru—As bonds.

On the assumption that $[Ru_4(\mu_4\text{-PPh})_2(CO)_{12}]$ is an intermediate in the formation of $[Ru_4(\mu_3\text{-PPh})_2(CO)_{13}]$ from $[Ru_4(\mu_4\text{-PPh})_2(\mu\text{-CO})(CO)_{10}]$ and that it has a structure very similar to its iron analogue it is apparent that the carbonylation of the dodecacarbonyl species must be accompanied by cleavage

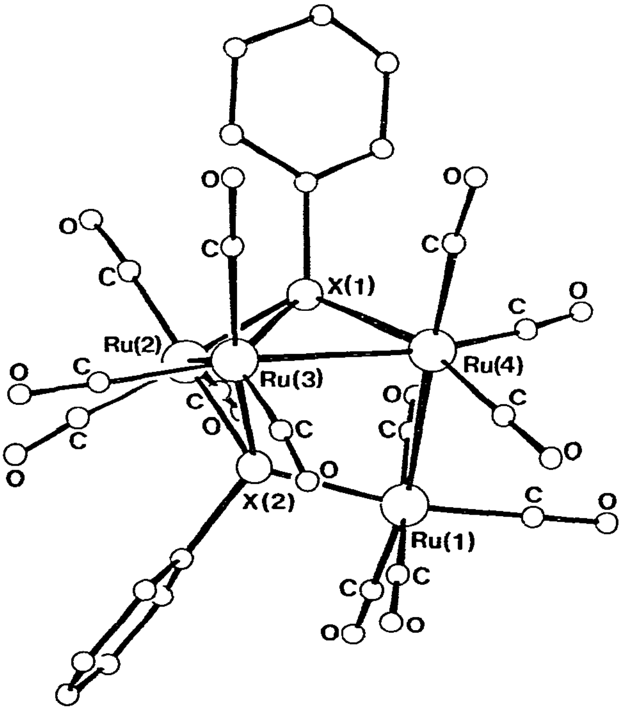
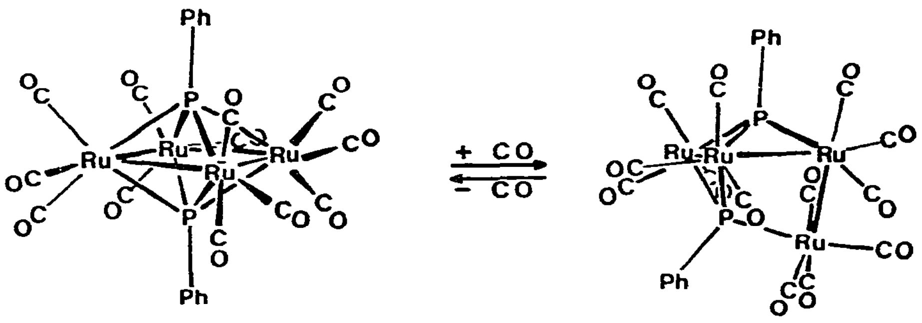


Fig. 1. The molecular stereochemistry of $[Ru_4(\mu_3\text{-XPh})_2(CO)_{13}]$ (X = P or As). Some relevant bond lengths in Å. IIIa (X = P): Ru(1)—Ru(4), 2.903(1); Ru(2)—Ru(3), 2.885(1); Ru(3)—Ru(4), 2.926(1); Ru(1)—P(2), 2.420(1); Ru(2)—P(1), 2.335(1); Ru(2)—P(2), 2.372(1); Ru(3)—P(1), 2.395(1); Ru(3)—P(2), 2.374(1); Ru(4)—P(1), 2.343(1); IIIb (X = As): Ru(1)—Ru(4), 2. 928(9); Ru(2)—Ru(3), 2.927(8); Ru(3)—Ru(4), 2.969(8); Ru(1)—As(2), 2.504(8); Ru(2)—As(1), 2.422(8); Ru(2)—As(2), 2.475(7); Ru(3)—As(1), 2.508(8); Ru(3)—As(2), 2.472(8); Ru(4)—As(1), 2.437(8).



SCHEME 1

of both Ru—Ru and Ru—P bonds and the movement of one of the ruthenium atoms (Ru(1)) out of the tetraruthenium plane of the dodecacarbonyl derivative as illustrated in the scheme; this movement is substantial amounting to 2.58 Å. Interestingly a similar unfolding of a metal cluster framework has been observed on addition of carbon monoxide to the tetrahedral cluster $[\mathrm{FeCo_2M}(\mu_3\text{-S})(\mu_2\text{-AsMe_2})(\eta\text{-C_5H_5})(\mathrm{CO})_8]$ (M = Mo or W) to produce $[\mathrm{FeCo_2M}(\mu_3\text{-S})(\mu_2\text{-AsMe_2})(\eta\text{-C_5H_5})(\mathrm{CO})_{10}]$ [9] but in contrast to the above the carbonylation is accompanied by the effective cleavage of two metal—metal bonds only. The reason why the carbonylation of $[\mathrm{Ru_4}(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\mathrm{CO})_{10}]$ should afford a tridecacarbonyl product when the corresponding reaction involving $[\mathrm{Fe}(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\mathrm{CO})_{10}]$ gives rise to a dodecacarbonyl product [4] is not immediately clear particularly in the light that Ru—Ru bonds are considered to be stronger than corresponding Fe—Fe bonds.

It was anticipated that $[\mathrm{Ru_4}(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\mathrm{CO})_{10}]$ might also be susceptible to attack by hydrogen but no reaction between these two species could be detected even at hydrogen pressures of 10 atmospheres.

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