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Preliminary communication

CONDENSATION PRODUCTS FROM THE REACTION OF TRIRUTHENIUM DODECACARBONYL WITH PHENYLPHOSPHINE

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Summary

The reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of $PPhH_2$ in toluene under reflux leads not only to the formation of trinuclear products such as $[Ru_3(\mu_2\text{-H})(\mu_2\text{-PPhH})(CO)_{10}]$ and $[Ru_3(\mu_2\text{-H})_2(\mu_3\text{-PPh})(CO)_9]$ but to tetranuclear $[Ru_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(CO)_{10}]$ and to pentanuclear $[Ru_5(\mu_4\text{-PPh})(CO)_{15}]$; the X-ray crystal structure of $[Ru_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(CO)_{10}]$ is described.

It has very recently been reported [1] that reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$ in chloroform, hexane or cyclohexane affords a range of trinuclear products and in particular $[Ru_3(\mu_2\text{-H})(\mu_2\text{-PPhH})(CO)_{10}]$, $[Ru_3(\mu_2\text{-H})(\mu_2\text{-PPhH})(CO)_9(PPhH_2)]$, $[Ru_3(\mu_2\text{-H})\{\mu_2\text{-P}(C_6H_4)H\}(CO)_9]$, $[Ru_3(\mu_2\text{-H})_2(\mu_3\text{-PPh})(CO)_9]$ or $[Ru_3(\mu_2\text{-H})_2(\mu_3\text{-PPh})(CO)_8(PPhH_2)]$ depending on the solvent and reaction conditions employed. Similar products were obtained from the reaction of $[Os_3(CO)_{12}]$ with $PPhH_2$ in toluene or di-n-butyl ether under reflux, except that in this case the monosubstituted derivative $[Os_3(CO)_{11}(PPhH_2)]$, the intermediate in the formation of the bridged and capped species, could be isolated [1]. We now wish to report that condensation products are also formed in the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$ under conditions slightly more forcing than those described above.

Treatment of $[Ru_3(CO)_{12}]$ with an equimolar amount of $PPhH_2$ in toluene under reflux has been found to afford a whole host of products five of which could be separated and purified by means of column chromatography. These compounds had the colours, yellow, yellow, green, purple and brown respectively. The two yellow compounds were established as trinuclear and were characterised respectively as $[Ru_3(\mu_2\text{-H})(\mu_2\text{-PPhH})(CO)_{10}]$ (I) and $[Ru_3(\mu_2\text{-H})_2(\mu_3\text{-PPh})(CO)_9]$ (II), the structures of which have been previously established X-ray crystallographically [1].

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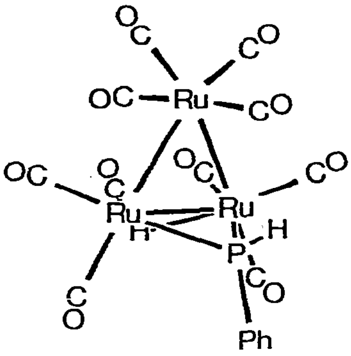
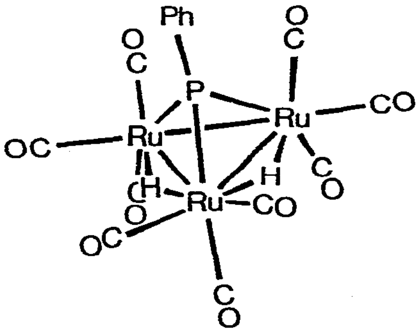
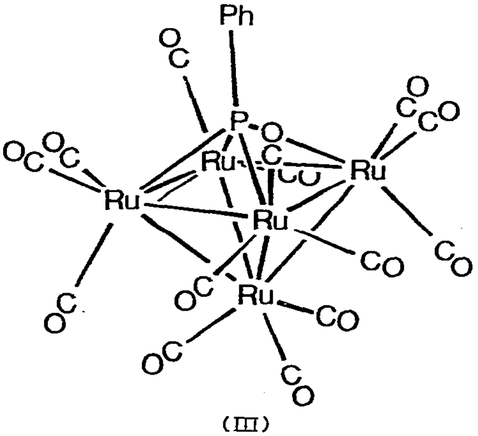


(I)



(II)

The green species on the other hand was found to be a condensation product and in particular to be the pentanuclear compound [$Ru_5(\mu_4$-PPh)-$(CO)_{15}$] (III). This compound has recently been reported as being formed in the reaction of [$Ru_3(CO)_{12}$] with [Mn(η-C_5H_5)($PPhCl_2$)$(CO)_2$] and its structure, which has been determined X-ray crystallographically [2], is depicted diagrammatically. Preliminary X-ray studies confirmed that the green compound isolated in this study was the same as that reported by Huttner et al. [2].



(III)

Elemental analyses and a molecular weight determination on the purple compound were not inconsistent with it being tetranuclear and of stoichiometry [$\{Ru_2(CO)_6(PPhH)_x\}_2$]. The purple colour of this species and the presence of a bridging carbonyl stretching band in its infrared spectrum (ν(C—O): 2075w, 2035s, 2018s, 1980s and 1838m cm^{-1}, measured in C_6H_{12}) indicated that it had an unusual stereochemistry and its crystal structure was thus determined.

Crystal data: Crystals of $C_{23}H_{10}O_{11}P_2Ru_4 \cdot \sim 0.14$ $CHCl_3$ grown by vapour diffusion from $CHCl_3$/petroleum ether are monoclinic, space group *C2/c*, *a* 30.87(4), *b* 17.69(2), *c* 33.87(4) Å, β = 102.8(1)°, *V* 18039.5 Å^3, *Z* = 24.

Data were collected on a Philips PW1100 diffractometer (NPRL, CSIR, Pretoria) with graphite-monochromated Mo-K_α radiation to θ 23°. Of the 13165 reflections measured, 8426 were classed as observed ($I > 4.0\sigma(I)$). The structure was solved by standard direct and Fourier methods and refined by full matrix least squares to $R = 0.140$ for 8426 data, all ruthenium and phosphorus atoms anisotropic*.

The three crystallographically independent molecules in the asymmetric unit are structurally equivalent with the molecular stereochemistry of one of these being illustrated in Fig. 1. The four ruthenium atoms adopt a planar isosceles trapiezoidal configuration with three ruthenium—ruthenium distances being essentially equal and the fourth appreciably shorter (Ru(1)—Ru(2), 2.874; Ru(1)—Ru(4), 2.878; Ru(3)—Ru(4), 2.854; Ru(2)—Ru(3), 2.717(5) Å). Ten of the carbonyl groups bond terminally to the ruthenium atoms while the eleventh bridges the two ruthenium separated by the shortest distance. Two of the terminal carbonyls lie essentially in the tetraruthenium plane, leaning towards adjacent ruthenium atoms Ru(2) and Ru(3) (Ru(2)—Ru(1)—C(0), 66°; Ru(3)—Ru(4)—C(0), 65(2)°). However, the distances (ca. 2.7 Å) between the carbon atoms of these carbonyl groups and the adjacent ruthenium atoms are too long for these carbonyls to be considered as semi-bridging. The two phen-

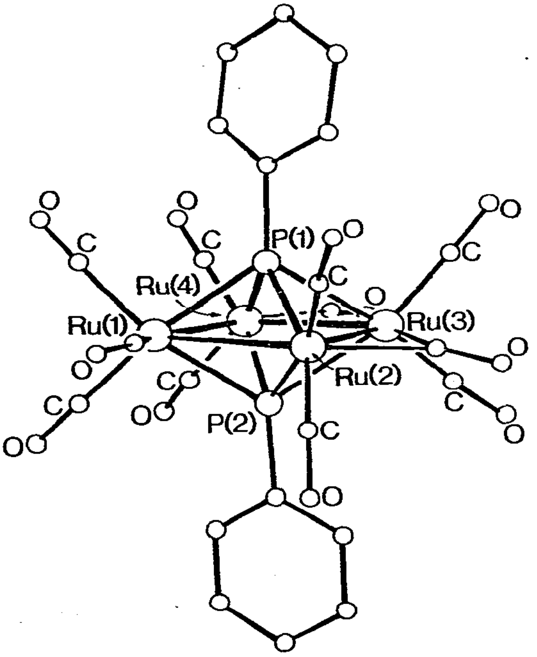


Fig. 1. The molecular structure of $[Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}]$; Bond lengths: Ru(1)—Ru(2), 2.874(5); Ru(1)—Ru(4), 2.878(5); Ru(2)—Ru(3), 2.717(5); Ru(3)—Ru(4), 2.854(5); Ru(1)—P(1), 2.39(1); Ru(2)—P(1), 2.48(1); Ru(3)—P(1), 2.45(1); Ru(4)—P(1), 2.42(1); Ru(1)—P(2), 2.39(1); Ru(2)—P(2), 2.46(1); Ru(3)—P(2), 2.52(1); Ru(4)—P(2); 2.38(1) Å. Bond angles: Ru(1)—Ru(2)—Ru(3), 91.5(2); Ru(2)—Ru(3)—Ru(4), 91.6(1); Ru(3)—Ru(4)—Ru(5), 88.7(1); Ru(4)—Ru(1)—Ru(2), 88.0(1)°.

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*Supplementary material is available from the authors.

ylphosphino groups bridge all four of the ruthenium atoms, above and below the metal atom plane, but asymmetrically such that for each group two of the ruthenium—phosphorus distances are shorter than the other two (see Fig. 1).

On the basis of the stoichiometry and the structure established X-ray crystallographically for $[Co_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})_2(CO)_8]$ [3] it was initially anticipated that $[Ru_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(CO)_{10}]$ would have the stoichiometry $[Ru_4(\mu_4\text{-PPh})_2(CO)_{12}]$ and would contain four bridging and eight terminal carbonyl groups. In terms of the 18-electron rule this undecacarbonyl is coordinatively unsaturated, consistent with its intense purple colour. An alternative interpretation is that it contains two hydridic ligands and, indeed, the presence of a uniquely short Ru—Ru edge and the displacement of the phenylphosphino groups away from the ruthenium atoms defining this edge could be regarded as being consistent with these hydride ligands bridging this edge. However, the insertion of a hydrogen atom across a metal—metal bond leads either to an increase in the metal—metal distance or to no change, and not to a decrease [4]. More important, all attempts to establish the presence of hydride ligands by means of ^1H NMR spectroscopy proved unsuccessful. Significantly, coordination unsaturation in $[Os_3(\mu\text{-H})_2(CO)_{10}]$ [5], $[Os_5(\mu\text{-H})(\mu\text{-PhNC}_6H_4N)(CO)_{13}]$ [6] and $[Os_3Au(\mu\text{-H})(CO)_{10}PPh_3]$ [7] has also been found to be associated with a decrease in one of the metal—metal distances compared with the others.

Although the yield of the fifth compound isolated in crystalline form was insufficient for characterisation purposes, its intense brown colour is indicative of it being a third condensation product. Significantly different products again are isolated from the reaction of $[Ru_3(CO)_{12}]$ with twice and threefold molar amounts of $PPhH_2$ in toluene under reflux. These are currently being investigated.

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