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Preliminary communication

REACTIVITY OF BIS(DIPHENYLPHOSPHINOMETHYL)PHENYLPHOSPHINE-BRIDGED TRINUCLEAR RHODIUM COMPLEXES: CLUSTER FAMILIES RELATED BY REVERSIBLE CARBON MONOXIDE BINDING AND OXIDATIVE ADDITION

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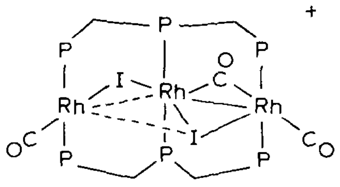
Summary

The preparation and interconversion of the following clusters bridged by bis(diphenylphosphinomethyl)phenylphosphine (dpmp) are reported: $[Rh_3(\mu\text{-dpmp})_2(CO)_aX_b][BPh_4]$; X = I, a = 2, 3, 4, b = 2; X = I, a = 3, 2, 1, b = 4; X = I, a = 1, b = 6. The structure of one of these, $[Rh_3(\mu\text{-dpmp})_2(CO)I_4][BPh_4]$, has been determined by X-ray diffraction.

While transition metal clusters, particularly carbonyl clusters, continue to attract interest as catalyst precursors [1], the low chemical reactivity of many clusters has hampered their development. This has led to cluster modification and activation via the incorporation of heteroatoms [2] or weakly bound ligands [3]. An alternate approach involves constructing clusters by combining several reactive d^8 metal clusters, like rhodium(I), which are well known for their ability to undergo ligand exchange and oxidative-addition reactions. Here we report on observations of some trinuclear clusters bridged by bis(diphenylphosphinomethyl)phenylphosphine (dpmp) which demonstrate two potentially useful properties: evidence for multiple degrees of coordination unsaturation and the ability to exist in several, non-classical oxidation states.

The preparations and structures of the trinuclear monocations, $[Rh_3(\mu\text{-dpmp})_2(CO)_3X_2]^+$ (X = Cl, Br, I), have been reported earlier [4,5]. While each has a unique structure, all have a basic arrangement of two *trans*-triphosphine ligands connected by the three rhodium atoms as found in the structure of iodide complex I. Treatment of brown $[Rh_3(\mu\text{-dpmp})_2(CO)_3I_2][BPh_4]$ in dichloromethane solution with carbon monoxide (1 atm) yields red $[Rh_3(\mu\text{-dpmp})_2(CO)_4I_2][BPh_4]$ which readily precipitates from solution. Under mild heating (boiling in dichloromethane solution) this red tetracarbonyl reverts back to the brown tricarbonyl. Under more vigorous conditions, heating in boiling acetone for 18 h, brown $[Rh_3(\mu\text{-dpmp})_2(CO)_3I_2][BPh_4]$ is



(I)

converted to red $[Rh_3(\mu\text{-dpmp})_2(CO)_2I_2][BPh_4]$. This reaction also is reversible. All of the clusters have been isolated in pure crystalline form. The infrared and $^{31}P\{^1H\}$ NMR spectral data which serve to characterize them are given in Table 1.

TABLE 1

SPECTROSCOPIC PROPERTIES FOR RHODIUM CLUSTERS

Compound	ν(CO (cm^{-1})^a		$^{31}P\{^1H\}$NMR ^{b} (δ, ppm; J, Hz)					
	Terminal	Bridging	δ_1	δ_2	δ_3	$J(Rh,P_1)$	$J(Rh,P_2)$	$J(Rh,P_3)$
$[Rh_3(\mu\text{-dpmp})_2(CO)_2I_2][BPh_4]$	1975	1783	19.9	11.0	14.6	112	100	108
$[Rh_3(\mu\text{-dpmp})_2(CO)_3I_2][BPh_4]$	1988, 1974	1832	24.3	14.0	17.8	98	100	106
$[Rh_3(\mu\text{-dpmp})_2(CO)_4I_2][BPh_4]$	1980	1845, 1825 1760	21.4	15.8	21.4	88	106	88
$[Rh_3(\mu\text{-dpmp})_2(CO)_3I_4][BPh_4]$	2037, 2025 1989	1815	24.3	14.0	17.8	96	100	107
$[Rh_3(\mu\text{-dpmp})_2(CO)_2I_4][BPh_4]$	2046, 2003 1996		15.1	0.4	3.0	103	95	88
$[Rh_3(\mu\text{-dpmp})_2(CO)I_4][BPh_4]$	2047w, 1994		18.7	16.1	11.3	88	97	94
$[Rh_3(\mu\text{-dpmp})_2(CO)I_6][BPh_4]$	1994		14.2	2.1	−12.5	83	91	86

[a] Nujol mull. [b] In dichloromethane solution, phosphorus—phosphorus coupling is present but is not reported. Spectra recorded at 81 MHz.

Oxidative-addition to $[Rh_3(\mu\text{-dpmp})_2(CO)_3I_2][BPh_4]$ is achieved by treating one mole of iodine with one mole of the complex salt in dichloromethane solution. This yields a grey solution from which black crystals of $[Rh_3(\mu\text{-dpmp})_2(CO)_3I_4][BPh_4]$ may be obtained by precipitation with ether. As a solid or in solution this complex is unstable toward carbon monoxide loss and is gradually converted into green $[Rh_3(\mu\text{-dpmp})_2(CO)_2I_4][BPh_4]$ and finally to violet $[Rh_3(\mu\text{-dpmp})_2(CO)I_4][BPh_4]$. The latter reaction is reversible and the green dicarbonyl is best obtained in pure form by the addition of carbon monoxide (1 atm) to a dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(CO)I_4][BPh_4]$. Under these conditions, the grey tricarbonyl does not form. Treatment of $[Rh_3(\mu\text{-dpmp})_2(CO)I_4][BPh_4]$ with one mole of iodine in acetonitrile yields brown crystals of $[Rh_3(\mu\text{-dpmp})_2(CO)I_6][BPh_4]$. However, $Rh_3(\mu\text{-dpmp})_2(CO)I_9$, which forms when an excess of iodine is used in this reaction, is simply the triiodide salt, $[Rh_3(\mu\text{-dpmp})_2(CO)I_6]I_3$. Carbon monoxide does not add to $[Rh_3(\mu\text{-dpmp})_2(CO)I_6][BPh_4]$ under mild conditions. These reactions are summarized in Scheme 1.

$$\begin{tikzcd}
\mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)_2I_2^+} \arrow[r, shift left, "+\mathrm{CO}"] & \mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)_3I_2^+} \arrow[l, shift left, "-\mathrm{CO}"] \arrow[r, shift left, "+\mathrm{CO}"] \arrow[d, "\mathrm{I_2}"] & \mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)_4I_2^+} \arrow[l, shift left, "-\mathrm{CO}"] \\
\mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)_2I_4^+} \arrow[d, shift left, "-\mathrm{CO}"] & \mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)_3I_4^+} \arrow[l, "-\mathrm{CO}"'] & \\
\mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)I_4^+} \arrow[u, shift left, "+\mathrm{CO}"] \arrow[r, "+\mathrm{I_2}"] & \mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)I_6^+} &
\end{tikzcd}$$

SCHEME 1

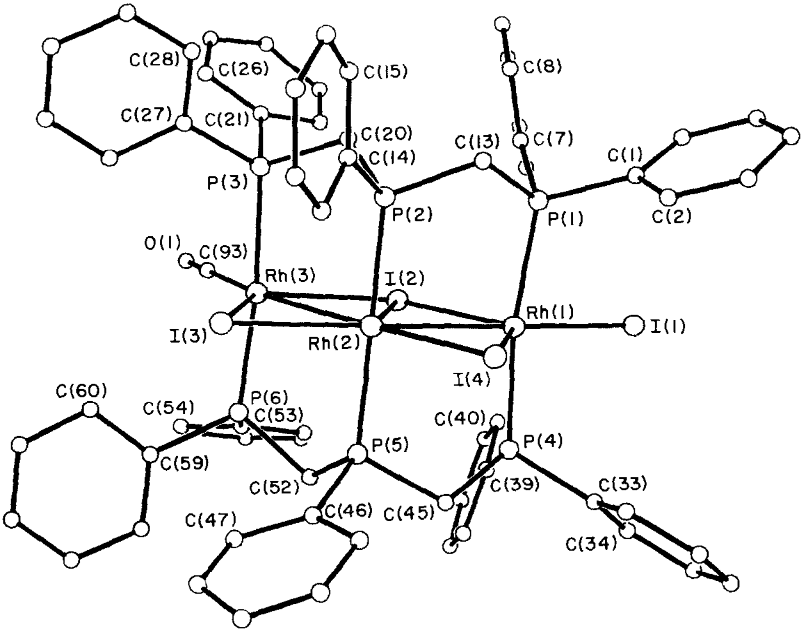


Fig. 1. A perspective drawing of the cation $[\mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)I_4}]^+$.

The ligand addition/removal from these clusters undoubtedly involves features such as the opening and closing of metal—metal bonds and metal—halide bridges which have been previously demonstrated for their binuclear counterparts [6]. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR data indicate that the six Rh—P bonds remain intact. However, structural determinations by X-ray diffraction will be necessary to establish the geometric details of these materials particularly since we have already shown that the isostoichiometric group of compounds $[\mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)_3X_2}]^+$ have three distinct structures for X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$ or $\mathrm{I^-}$.

The results of an X-ray diffraction study on one of these clusters, $[\mathrm{Rh_3(\mu\text{-}dpmp)_2(CO)I_4}][\mathrm{BPh_4}]$, which has been obtained as suitable crystals, are shown in Fig. 1*. Figure 2 compares corresponding planar sections of $[Rh_3(\mu\text{-dpmp})_2(CO)_3I_2]^+$ and $[Rh_3(\mu\text{-dpmp})_2(CO)I_4]^+$. Both cations are built around similar $Rh_3(\mu\text{-dpmp})_2$ units, but in $[Rh_3(\mu\text{-dpmp})_2(CO)I_4]^+$ two iodine atoms have replaced two of the carbonyl ligands in I and the core of the complex has, in general, contracted upon oxidation. $[Rh_3(\mu\text{-dpmp})_2(CO)I_4]^+$ is related to the electron-precise, linear cation $[Rh_3(CNR)_{12}I_2]^{3+}$ [7]. Both have a fractional average oxidation state of 5/3. While electron counting must be an oversimplification in this cluster (particularly with the unusual

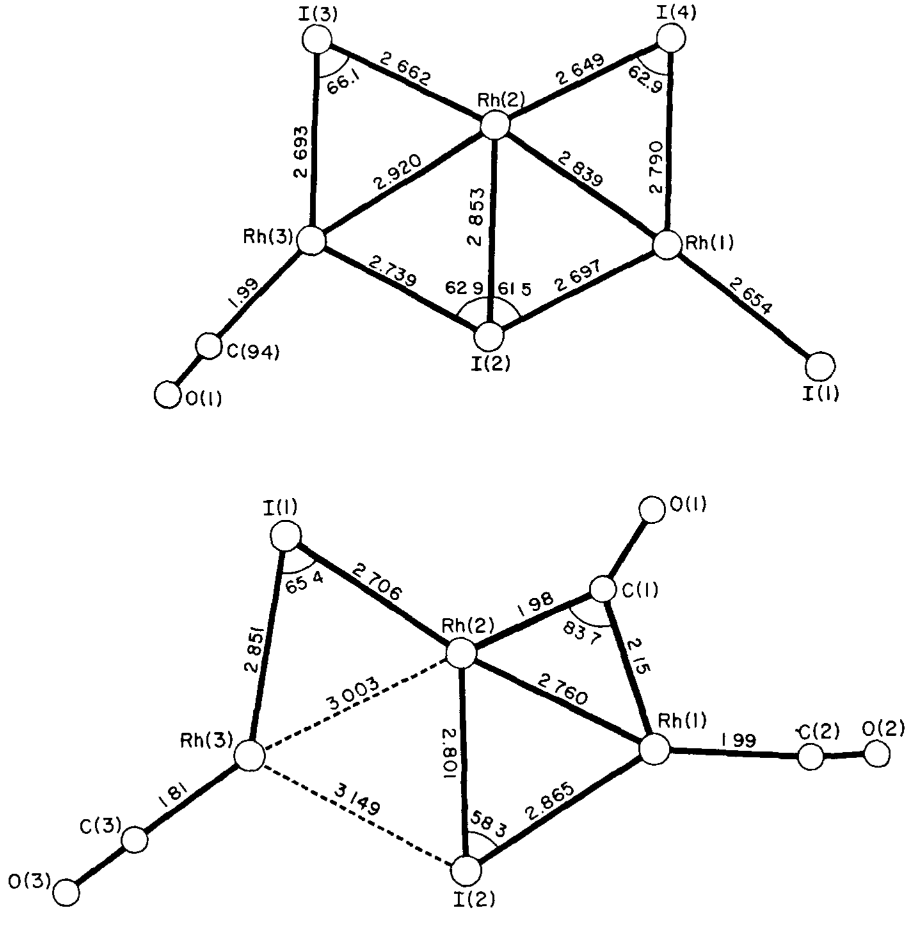


Fig. 2. Comparison of corresponding planar sections of: $[Rh_3(\mu\text{-dpmp})_2(CO)I_4]^+$, top, and $[Rh_3(\mu\text{-dpmp})_2(CO)_3I_2]^+$, bottom.

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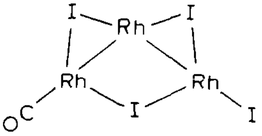
*Crystal data: Dark violet plates of $[Rh_3(\mu\text{-dpmp})_2(CO)I_4][BPh_4]\cdot 2.2CDCl_3\cdot 1.4CH_2Cl_2$ were grown by slow evaporation of a solution of the complex in a 1/1 mixture of chloroform-d_1 and dichloromethane. It crystallizes in the space group $P2_1/n$ with a 11.517(3), b 23.301(7), c 36.815(10) Å, β 97.48(2)°, $Z = 4$ at 140 K, $R = 0.076$ for 8877 reflections with $I > 2.5\sigma(I)$ and 610 parameters. The terminal iodo and carbonyl ligands at opposite ends of the molecule show a 80/20 disorder.

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.

three coordinate I(2)), nevertheless it is interesting to note that using the electron pair bonds in the planar section shown in II and remembering that each phosphine above and below that plane is a two electron donor, the cluster achieves an 18-electron count for each rhodium. This rudimentary bonding scheme accounts for the shortening of the Rh(2)—Rh(3) and Rh(3)—I(2) distances and the slight lengthening of the Rh(2)—I(2) distance (all other Rh—I distances contract) which accompany oxidation.

Structural and reactivity studies of these cluster families are in progress.



(II)

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