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Structural characterisation and properties of heteronuclear cluster $[(\eta^5\text{-}C_5Me_5)_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$

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Abstract

One of the three products of the reaction, earlier reported, between $[Cp^\star Rh(CO)_2]$ ($Cp^\star = \eta^5\text{-}C_5Me_5$) and $[Ru_3(CO)_{12}]$ in toluene at 70 °C in the presence of gaseous H_2 has now been fully characterised as $[Cp^\star_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$. A single crystal X-ray diffraction study {space group *Ccca*, *a* 16.019(3), *b* 19.168(3), *c* 20.743(3) Å; 2697 independent reflections with $I > 3\sigma(I)$; final $R = 0.037$, $R_w = 0.050$} has revealed a tetrahedral metal core with triply-bridging CO ligands on the two Rh_2Ru faces. This structure is consistent with IR and $^{13}C\{^1H\}$ and ^1H NMR spectra, although the ion of highest mass in the FAB-mass spectrum is $[M-28]^+$, formed by loss of CO from the parent cluster. The cluster is readily cleaved at ambient temperatures by reaction with CO or H_2.

Introduction

In a recent paper on heteronuclear clusters containing rhodium, the reaction of $[Cp^\star Rh(CO)_2]$ ($Cp^\star = \eta^5\text{-}C_5Me_5$) with $[Ru_3(CO)_{12}]$ under an atmosphere of hydrogen at 70 °C was reported to yield three new products, separable by column chromatography [1]. Two of these products, namely $[Cp^\star RhRu_3(\mu\text{-}H)_4(CO)_9]$ and $[Cp^\star RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9]$, were structurally characterised in the solid state. Spectroscopic studies on the latter cluster indicated the existence of isomers in solution. The third product, for which crystals suitable for X-ray analysis had not been obtained, was formulated on the basis of mass spectral and analytical data as $[Cp^\star_2Rh_2Ru_2(CO)_7]$, a 58-electron tetranuclear cluster. Since such a cluster would be electronically unsaturated its structure appeared to be of particular interest. We have now subjected this product to further investigation, in particular by X-ray crystallographic analysis, and have established its composition to be $[Cp^\star_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$. This cluster, however, shows some interesting structural features and chemical properties.

While the present investigation was in progress, Shore and coworkers [2] reported reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $[Cp^\star Rh(CO)_2]$ or $[Cp^\star_2Rh_2(\mu\text{-}CO)_2]$ from

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which the interconvertible clusters $[Cp^{\star}_2Rh_2Os_2(\mu_3\text{-}CO)_2(CO)_6]$ and $[Cp^{\star}_2Rh_2Os_2(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_6]$ were isolated. Other recently structurally characterised tetranuclear $Rh_{4\text{-}n}Ru_n$ clusters include $[Cp^{\star}_3Rh_3Ru(\mu_3\text{-}CO)_2(CO)_3]$ [3] and $[Rh_2Ru_2(\mu\text{-}H)_2(\mu\text{-}CO)_3(CO)_8L]$ (L = CO [4] or PPh_3 [5]).

Experimental

Cluster $[Cp^{\star}_2Rh_2Ru_2(CO)_n]$ ($n = 8$) was prepared as previously described (formulated as $n = 7$) [1] and ^{13}CO labelled product for ^{13}C NMR analysis was produced from $[Ru_3(^{13}CO)_{12}]$ (30–40% ^{13}CO enriched) [6]. Fast atom bombardment mass spectra (FAB-MS) were also recorded previously [1]. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured with a Bruker WP 200 SY spectrometer and IR spectra on a Perkin–Elmer 580 instrument. The carbonyl absorptions in the IR spectrum of $[Cp^{\star}_2Rh_2Ru_2(CO)_8]$ in hexane, are as earlier reported [1] ν(CO): 2042s, 2015vs, 1982m, 1974m, 1959w, 1709w, 1684w cm^{-1}.

Reactions of $[Cp^{\star}_2Rh_2Ru_2(CO)_8]$

(i) With CO. The title cluster (5 mg) in hexane (5 cm^3) was stirred under CO (20 cm^3, 1 atm) at 19 °C and the reaction was monitored by IR spectroscopy. After 22.5 h complete conversion into $[Cp^{\star}Rh(CO)_2]$ (ν(CO): 2025, 1963 cm^{-1}) and $[Ru(CO)_5]$ (ν(CO): 2035, 1999 cm^{-1}) with a small amount $[Ru_3(CO)_{12}]$ (ν(CO): 2060, ca. 2030, 2010 cm^{-1}) was observed. IR bands at 2086, 2049 and ca. 1982 cm^{-1}, observed during the course of the reaction, are associated with intermediate species.

(ii) With H_2. Hydrogen was bubbled slowly through a solution of the title cluster (5 mg) in 60–80 °C petroleum ether (3 cm^3) at 22 °C. The reaction was monitored by IR spectroscopy over a period of 20 h. The parent cluster decomposes to form $[Cp^{\star}Rh(CO)_2]$ and insoluble products.

Crystal structure determination of $[Cp^{\star}_2Rh_2Ru_2(\eta_3\text{-}CO)_2(CO)_6]$

A single crystal of the cluster, grown from dichloromethane/hexane at −20 °C, of approximate size 0.5 × 0.25 × 0.1 mm, was mounted in a Lindemann tube and used for X-ray data collection.

Crystal data. $C_{28}H_{30}O_8Rh_2Ru_2$, $M = 902.49$, brown plates, orthorhombic, space group *Ccca* (No. 68), a 16.019(3), b 19.168(3), c 20.743(3) Å, U 6369.2 Å, $Z = 8$, D_c 1.882 g cm^{-3}, $F(000)$ 3520, $\mu(\text{Mo-}K_\alpha)$ 19.59 cm^{-1}.

Data collection. The intensity data were collected on an Enraf–Nonius CAD4 diffractometer over the octant ($+h$: 0–21, $+k$: 0–25, $+l$: 0–27; $1 < \theta \leqslant 28$) using graphite monochromated Mo-K_α radiation (λ 0.710693 Å) and ω–2θ scanning. Of the 3850 unique data measured, 2697, having $I > 3\sigma(I)$, were used in subsequent structural solution and refinement. The data were corrected for Lorentz and polarisation effects and absorption (DIFABS [7]).

Structure solution. The positions of the Rh and Ru atoms were determined by direct methods (SHELXS-86 [7]) and those of the remaining non-hydrogen atoms from a subsequent difference Fourier map. The structure was refined by full-maxtrix least squares methods (SHELX-76 [7]) using anisotropic temperature factors for all the non-hydrogen atoms. The methyl groups were treated as idealised, rigid groups (d(C–H) 0.95 Å) with a fixed isotropic temperature factor for the hydrogen atoms (U_{iso} 0.10 $Å^2$). At convergence, the discrepancy factors were $R = 0.037$ and

$R_w = 0.050$, where the weighting scheme $w = [\sigma^2(F) + 0.00034(F^2)]^{-1}$ gave satisfactory analyses of variance. The final difference Fourier map was featureless (general noise level below ± 0.4 e Å^{-3}) apart from a peak ca. 1.4 e Å^{-3} of no apparent chemical significance. The computer programme CALC [7] was used for incidental calculations and in the compilation of Table 2. A list of structure factors and lists of thermal parameters are available from the authors.

Results and discussion

One of the products from the reaction of $[Cp^{\star}Rh(CO)_2]$ and $[Ru_3(CO)_{12}]$ in toluene in the presence of gaseous hydrogen, isolated after chromatography using a 5/1 mixture of petroleum ether/dichloromethane on a silica gel column, has now been identified as $[Cp^{\star}_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$. The original [1] formulation of this species as $[Cp^{\star}_2Rh_2Ru_2(CO)_7]$ was primarily based on the FAB-mass spectrum which gave an ion of maximum *m/e* corresponding to this latter composition, accompanied by ions arising from loss of 2–7 CO groups (See Fig. 1). Since FAB-MS of related tetranuclear $RhRu_3$ clusters provided molecular-ion peaks [1], this was also assumed to be the case with the title cluster. Analytical results were not of sufficient precision to indicate the true formula: found: C 37.00; H, 3.05. $C_{27}H_{30}O_7Rh_2Ru_2$ calcd.: C, 37.08; H, 3.46% and for $C_{28}H_{30}O_8Rh_2Ru_2$ calcd.: C, 37.26; H, 3.35%. The absence of resonances attributable to hydrido ligands in the ^{1}H NMR spectrum was consistent with the unsaturated formula. It now appears that loss of one CO ligand occurs in the FAB-MS, so that the fragment of highest *m/e* is actually $[M - CO]^+$; note that the electron impact mass spectrum gave $[Rh_2(CO)_2Cp^{\star}_2]^+$ as the ion of highest observable *m/e* value.

Structural studies

The molecular structure of $[Cp^{\star}_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$ determined by X-ray diffraction on a small brown crystal grown from dichloromethane/hexane at −20 °C, is depicted in Fig. 2. Tables 1 and 2, respectively, list atomic fractional coordinates and a selection of the more important derived geometrical parameters. The cluster contains a tetrahedral arrangement of Rh_2Ru_2 atoms with a *penta-hapto*-C_5Me_5 ring bonded to each Rh atom and with three terminal CO groups bonded to each Ru atom. Two CO groups triply bridge the two Rh_2Ru faces.

The point symmetry of the molecule approaches C_{2v} although some asymmetry in the distribution of ligands reduces this to C_2 with the two-fold axis bisecting the

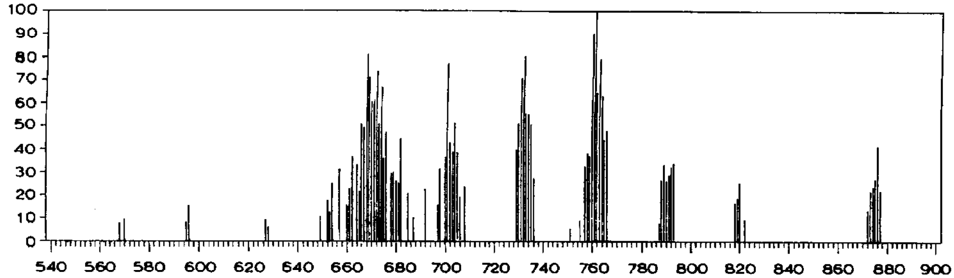


Fig. 1. FAB-mass spectrum of $[Cp^{\star}_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$.

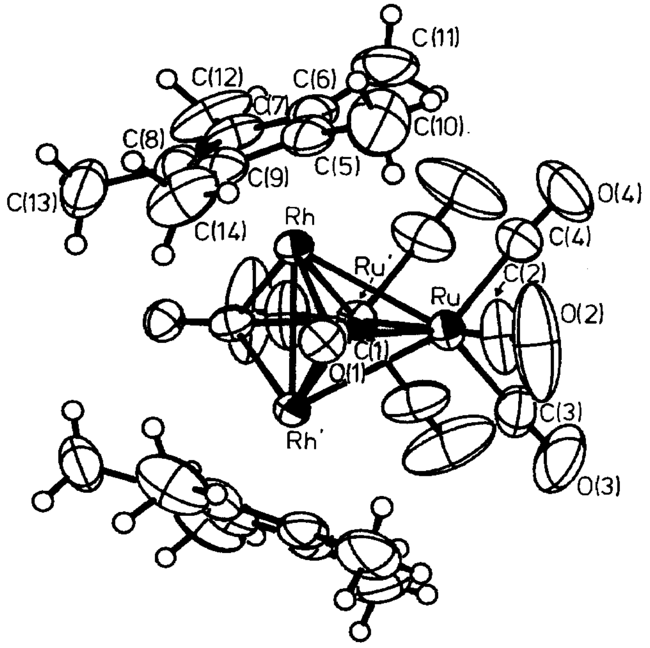


Fig. 2. The molecular structure of the title cluster (ORTEP [7], 50% probability ellipsoids).

Rh–Rh and Ru–Ru bonds. Thus, in the solid state, the clusters are located at special positions such that the crystallographic and point group two-fold symmetry axes are coincident. The Rh–ring and Ru–C bonding distances are typical. The

Table 1

Fractional coordinates of atoms with standard deviations

	x	*y*	*z*
Rh	0.72577(3)	0.06707(2)	0.09336(2)
Ru	0.83108(3)	0.02008(3)	0.18820(2)
C(1)	0.8432(4)	0.0230(3)	0.0821(3)
O(1)	0.89944(25)	0.03741(22)	0.04810(19)
C(2)	0.9440(5)	0.0470(5)	0.1776(3)
O(2)	1.0103(4)	0.0641(5)	0.1728(3)
C(3)	0.6347(6)	0.0510(4)	0.2469(4)
O(3)	0.6128(6)	0.0882(4)	0.2834(4)
C(4)	0.8090(6)	0.0903(4)	0.2490(4)
O(4)	0.8001(5)	0.1326(4)	0.2868(4)
C(5)	0.7622(4)	0.1761(3)	0.0714(4)
C(6)	0.6888(5)	0.1767(3)	0.1090(3)
C(7)	0.6253(4)	0.1428(4)	0.0721(3)
C(8)	0.6606(4)	0.1238(3)	0.0124(3)
C(9)	0.7436(4)	0.1433(4)	0.0112(3)
C(10)	0.8398(6)	0.2100(4)	0.0884(5)
C(11)	0.6758(7)	0.2160(4)	0.1711(4)
C(12)	0.5340(5)	0.1352(6)	0.0899(5)
C(13)	0.6126(6)	0.0889(5)	−0.0430(4)
C(14)	0.7984(6)	0.1354(5)	−0.0452(4)

Table 2

Derived geometrical data for $[(\eta^5\text{-}C_5Me_5)_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$

(a) Bond lengths (Å) with standard deviations

Rh(1)–Ru(1)	2.7436(7)	C(1)–O(1)	1.177(7)
Rh(1)–Rh(1′)	2.6858(6)	C(2)–O(2)	1.115(12)
Rh(1)–Ru(1′)	2.7368(7)	C(3)–O(3)	1.099(12)
Ru(1)–Ru(1′)	2.7093(7)	C(4)–O(4)	1.138(12)
Rh(1)–C(1)	2.075(6)	C(5)–C(6)	1.412(10)
Rh(1′)–C(1)	2.063(6)	C(5)–C(9)	1.429(10)
Ru(1)–C(1)	2.210(6)	C(5)–C(10)	1.446(12)
Ru(1)–C(2)	1.894(9)	C(6)–C(7)	1.429(10)
Ru(1)–C(3)	1.908(9)	C(6)–C(11)	1.507(12)
Ru(1)–C(4)	1.877(8)	C(7)–C(8)	1.409(10)
Rh(1)–C(5)	2.218(7)	C(7)–C(12)	1.516(12)
Rh(1)–C(6)	2.207(7)	C(8)–C(9)	1.380(9)
Rh(1)–C(7)	2.211(7)	C(8)–C(13)	1.536(11)
Rh(1)–C(8)	2.257(6)	C(9)–C(14)	1.472(11)
Rh(1)–C(9)	2.262(7)		

(b) Angles (degrees) with standard deviations

Ru(1)–Rh(1)–Rh(1′)	60.528(17)	Ru(1′)–Ru(1)–C(3)	94.2(3)
Ru(1)–Rh(1)–Ru(1′)	59.256(17)	Ru(1′)–Ru(1)–C(4)	91.3(3)
Ru(1)–Rh(1)–C(1)	52.39(16)	C(1)–Ru(1)–C(2)	78.1(3)
Rh(1′)–Rh(1)–Ru(1′)	60.780(17)	C(1)–Ru(1)–C(3)	129.0(3)
Rh(1′)–Rh(1)–C(1)	49.35(16)	C(1)–Ru(1)–C(4)	131.8(3)
Ru(1′)–Rh(1)–C(1)	97.71(16)	C(2)–Ru(1)–C(3)	89.7(4)
Rh(1)–Ru(1)–Rh(1′)	58.692(16)	C(2)–Ru(1)–C(4)	93.6(4)
Rh(1)–Ru(1)–Ru(1′)	60.247(17)	C(3)–Ru(1)–C(4)	97.9(4)
Rh(1)–Ru(1)–C(1)	48.05(15)	Rh(1)–Rh(1′)–C(1)	49.72(16)
Rh(1)–Ru(1)–C(2)	114.5(3)	Ru(1′)–Rh(1′)–C(1)	97.79(16)
Rh(1)–Ru(1)–C(3)	150.3(3)	Rh(1)–C(1)–Ru(1)	79.56(20)
Rh(1)–Ru(1)–C(4)	97.5(3)	Rh(1)–C(1)–Rh(1′)	80.93(21)
Rh(1′)–Ru(1)–Ru(1′)	60.497(17)	Rh(1)–C(1)–O(1)	131.8(5)
Rh(1′)–Ru(1)–C(1)	47.86(15)	Ru(1)–C(1)–Rh(1′)	79.57(20)
Rh(1′)–Ru(1)–C(2)	113.6(3)	Ru(1)–C(1)–O(1)	132.1(4)
Rh(1′)–Ru(1)–C(3)	96.8(3)	Ru(1′)–C(1)–O(1)	132.3(5)
Rh(1′)–Ru(1)–C(4)	194.0(3)	Ru(1)–C(2)–O(2)	178.0(8)
Ru(1′)–Ru(1)–C(1)	95.25(15)	Ru(1)–C(3)–O(3)	174.9(8)
Ru(1′)–Ru(1)–C(2)	173.3(3)	Ru(1)–C(4)–O(4)	176.3(8)

Rh–Rh separation (2.6858(6) Å) is slightly smaller than in $[Cp^{\star}_2Rh_2Os_2(\mu_3\text{-}CO)_2(CO)_6]$ (2.694(1) Å) [2] and as might be expected, the Ru–Ru bond (2.7093(7) Å) is shorter than Os–Os in the Rh_2Os_2 cluster: this Ru–Ru separation is relatively short when compared with the range of similar bonds in other ruthenium carbonyl clusters. The Rh–Ru distances are longer than corresponding bonds in $[Cp^{\star}_3Rh_3Ru(\mu_3\text{-}CO)_2(CO)_3]$ (2.705–2.715(1) Å) [3] but comparable to unbridged Rh–Ru distances in clusters $[Cp^{\star}RhRu_3(\mu\text{-}H)_{2m}(CO)_{11-m}]$ ($m = 1,2$) [1].

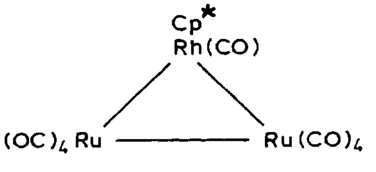
The closely related structures of $[Cp^{\star}_2Rh_2M_2(\mu_3\text{-}CO)_2(CO)_6]$ (M = Ru, Os [2]) contrast with that of the isoelectronic $[Cp_2Rh_2Fe_2(\mu\text{-}CO)_3(CO)_5]$ ($Cp = \eta^5\text{-}C_5H_5$) [8], which contains CO ligands bridging the Rh–Rh and two Rh–Fe edges. In the series of tetranuclear derivatives $[Cp^{\star}_{4-n}Rh_{4-n}Ru_n(CO)_{3n+2}]$ the heteroclusters with

$n = 1$ and 2 have now been structurally characterised, whereas the species with $n = 3$ in unknown and only $[Cp^\star RhRu_3H_{2m}(CO)_{11-m}]$ ($m = 1,2$) have been characterised.

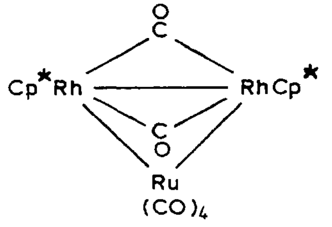
Two bands in the carbonyl region of the IR spectrum of $[Cp^\star_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$, those at 1709 and 1684 cm^{-1} (hexane), are assignable to $\nu(\mu_3\text{-}CO)$ vibrations. A singlet assignable to hydrogens of equivalent $\eta^5\text{-}C_5Me_5$ rings is the only resonance in the ^1H NMR spectrum, observable between −110 and +17 °C $\{CD_2Cl_2/CFCl_3$: −110 °C δ 1.79 ppm; +17 °C δ 1.90 ppm$\}$. The $^{13}C\{^1H\}$ spectrum at ambient temperature shows resonances attributable to terminal and bridging CO ligands $\{CD_2Cl_2/CFCl_3$, 20 °C: δ 200.9 (broad, $\Delta\nu$ ~ 70 Hz: terminal CO) δ 242.3 (poorly defined triplet; $J(Rh\text{-}C)$ ~ 47 Hz; $\mu_3\text{-}CO)\}$: the broad, single resonance for the inequivalent terminal CO ligands indicates structural non-rigidity but the poor signal/noise ratio of the sample prevented useful low temperature studies.

Reactions

$[Cp^\star_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$ is cleaved in hexane solution by CO at ambient temperature and pressure with a half-life for decomposition of ca. 4–5 h. The final products are $[Cp^\star Rh(CO)_2]$ and $[Ru(CO)_5]$, accompanied by a little $[Ru_3(CO)_{12}]$ which is probably a secondary product. In this process three new IR bands (2086, 2049, ~ 1982 cm^{-1}) assignable to intermediate(s) are observed (other bands may be obscured by absorptions of products or reactant). The nature of this(these) intermediate(s) has(have) not been determined, but trinuclear species such as **A** and **B** are possible, with subsequent cleavage to mononuclear species. **A** is isostructural with $[CpRhOs_2(CO)_9]$ [9] and its IR spectrum could well include the observed intermediate bands, whereas **B**, related to $[Cp_2Rh_2Fe(CO)_6]$ [10], should exhibit IR bands of bridging CO groups, which were not detected, and so is less likely.



(**A**)



(**B**)

Reaction of $[Cp^\star_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$ with hydrogen at ambient temperature and pressure also causes cluster cleavage to give $[Cp^\star Rh(CO)_2]$ and products insoluble in petroleum ether. No evidence was found by using IR spectroscopy for the formation of a cluster $[Cp^\star_2Rh_2Ru_2H_2(CO)_7]$ under these conditions. It has been reported [9] that for the related Rh_2Os_2 system conversion of $[Cp^\star_2Rh_2Os_2(\mu_3\text{-}CO)_2(CO)_6]$ into $[Cp^\star_2Rh_2Os_2(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_6]$ occurs under H_2 with minimal fragmentation and this must reflect the greater stability of osmium–rhodium relative to ruthenium–rhodium clusters. It may also be noted that $[Cp^\star_2Rh_2Ru_2(\mu_3\text{-}CO)_2(CO)_6]$ reacts with PPh_3 under mild conditions primarily to give fragmentation products.

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