

Reversible Syntheses of Cyclopentadienylrhodium–Triruthenium Cluster Complexes; Crystal and Molecular Structure of $(\eta\text{-C}_5\text{Me}_5)\text{RhRu}_3(\mu\text{-H})_4(\text{CO})_9$

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The mixed metal complexes $\text{cpRhRu}_3(\mu\text{-H})_2(\mu\text{-CO})(\text{CO})_9$ ($\text{cp} = \eta\text{-C}_5\text{H}_5$ or $\eta\text{-C}_5\text{Me}_5$) and $(\eta\text{-C}_5\text{Me}_5)\text{RhRu}_3(\mu\text{-H})_4(\text{CO})_9$ (in which the four bridging hydrogen atoms have been located in an X-ray structure determination) are formed when H_2 is bubbled through solutions of $\text{Ru}_3(\text{CO})_{12}$ and the respective $\text{cpRh}(\text{CO})_2$ at 70–90 °C but, under 1 atm CO at 25 °C, are easily disrupted into the starting materials, which are obtained with complete ^{13}C -enrichment under 1 atm ^{13}CO .

We wished to introduce the cpRh ($\text{cp} = \eta\text{-C}_5\text{H}_5$ or $\eta\text{-C}_5\text{Me}_5$) moiety into cluster complexes in order to make use of the nuclear spin of ^{103}Rh in elucidating intramolecular exchange processes. We were successful in synthesising the mixed metal cluster complexes but also found them to be easily disrupted into the starting materials (Scheme 1†).

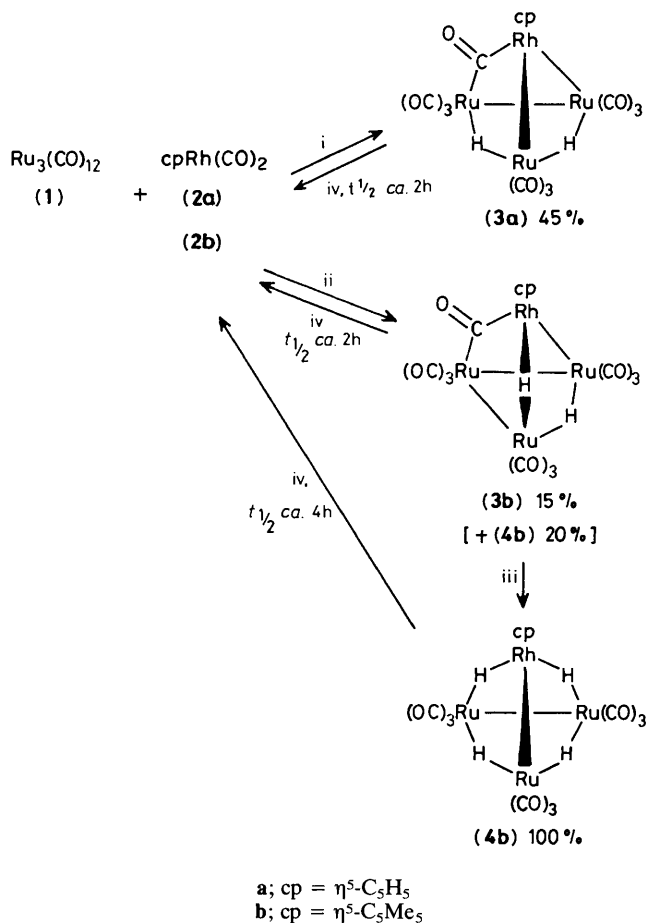
The isomeric structures shown in Scheme 1 for (3a) and (3b) have been confirmed by X-ray studies.¹ These isomeric structures parallel those found for the analogous cobalt- and rhodium–triosmium complexes, $(\eta\text{-C}_5\text{H}_5)\text{M}(\mu\text{-CO})\text{Os}_3(\mu\text{-H})_2(\text{CO})_9$ ($\text{M} = \text{Co}^{2+}$ or Rh^{3+}) and $(\eta\text{-C}_5\text{Me}_5\text{Et})\text{Co}(\mu\text{-CO}, \mu\text{-H})\text{Os}_3(\mu\text{-H})(\text{CO})_9$,⁴ including, in the latter, a mixture of isomers in solution as observed for (3b). We find it significant that the subtle differences between homologous cyclopentadienyl derivatives are maintained despite a complete change in the metal atoms of the cluster.

For (4b), three-dimensional X-ray diffraction data‡ were collected ($3^\circ < 2\theta < 50^\circ$) by the θ - 2θ scan method. The 6756 reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. Each molecule (Figure 1) consists of an $(\eta\text{-C}_5\text{Me}_5)\text{Rh}$ unit linked to an $\text{Ru}_3(\mu\text{-H})_2(\text{CO})_9$ fragment via an Rh–Ru bond and two hydrogen bridges. Within the Ru_3 fragment, hydrogen bridges connect $\text{Ru}(1) \cdots \text{Ru}(2)$ and $\text{Ru}(1) \cdots \text{Ru}(3)$. The $\text{Ru}(2)$ – $\text{Ru}(3)$ distance is comparable to those of other single bonds [2.8512(4), 2.8518(4), and 2.8595(4) Å in $\text{Ru}_3(\text{CO})_{12}$]⁵ and significantly shorter than the bridged $\text{Ru} \cdots \text{Ru}$ distance.

In attempts to enrich products (3a), (3b), or (4b) with ^{13}CO , we discovered that they are disrupted into the starting

materials (Scheme 1) with complete ^{13}CO exchange. While (2) undergoes exchange at 25 °C with ^{13}CO (1 atm) (1) does not, nor does it exchange in the presence of an added amount of (2). Thus, attachment of the cpRh moiety to the Ru_3 skeleton as in (3a), (3b), or (4b), leads on disruption under ^{13}CO to the completely enriched starting materials $\text{Ru}_3(^{13}\text{CO})_{12}$ and $\text{cpRh}(^{13}\text{CO})_2$.

By contrast, the mixed metal cluster $\text{Rh}_2\text{Ru}_2(\mu\text{-H})_2(\text{CO})_{12}$ ⁶ requires 90 h under 1 atm CO at 25 °C to be converted back into $\text{Rh}_4(\text{CO})_{12}$ and mixture of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}(\text{CO})_5$. Disruption of the cyclopentadienylcobalt–triosmium cluster complexes^{2,4} requires 50 bar CO (1 atm = 1.013 bar) and 50 or 150 °C and 2 or 4 h (respectively).⁴ Thus the disruptions observed in the present work proceed with appreciable



† Spectroscopic data. (3a): $\nu(\text{CO})$ (hexane) 2088m, 2066s, 2049s, 2018m, 2009m, 2001w, 1982w, and 1827m cm^{-1} ; ^1H n.m.r. (90 MHz, 26 °C) ($\text{C}_6\text{D}_5\text{CD}_3$) δ 5.16(s, C_5H_5) and -17.2 [s, $(\mu\text{-H})_2$]. (3b): $\nu(\text{CO})$ (KBr) 2072m, 2041s, 2012vs, 2000m, 1983s, 1960w, 1934w, and 1790s cm^{-1} . In solution, for an equilibrium mixture of apparently three isomers: $\nu(\text{CO})$ (light petroleum, b.p. 40–60 °C) 2089m, 2080m, 2060s, 2051m, 2042vs, 2035m, 2013m, 2004w, 1994w, 1831w, 1812w, and 1800w cm^{-1} ; ^1H n.m.r. (90 MHz, 26 °C) ($\text{C}_6\text{D}_5\text{CD}_3$) δ (C_5Me_5), 1.63(s), 1.54(s), δ ($\mu\text{-H}$) -13.0 (s), -17.0 (d, J 8 Hz), and -20.3 (s). (4b): $\nu(\text{CO})$ (hexane) 2079s, 2051vs, 2043vs, 2008s, 2001w, 1994w, and 1989m cm^{-1} ; ^1H n.m.r. (90 MHz, 26 °C) ($\text{C}_6\text{D}_5\text{CD}_3$) δ 1.71(s, C_5Me_5) and -15.93 [d, $(\mu\text{-H})_4$, J 13.5 Hz].

‡ Crystal data: $(\eta\text{-C}_5\text{Me}_5)\text{RhRu}_3(\mu\text{-H})_4(\text{CO})_9$, (4b), $\text{RhRu}_3\text{O}_9\text{C}_{19}\text{H}_9$, $M = 797.5$, crystallizes from hexane (30 °C) as brown prisms; crystal dimensions $0.2 \times 0.14 \times 0.45$ mm, monoclinic, $a = 17.470(1)$, $b = 18.451(1)$, $c = 17.200(1)$ Å, $\beta = 114.684(1)^\circ$, $U = 5037.6(5)$ Å³, $Z = 8$, $D_c = 2.10$ g cm^{-3} , space group $P2_1/a$ (C_2^5 , No. 14), $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 24.09$ cm^{-1} , $F(000) = 3056$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Scheme 1.† Reagents and conditions: i, 1 atm/ H_2 , octane, 90 °C, 2 h; ii, 1 atm/ H_2 , heptane, 70 °C, 1.25 h; iii, 1 atm/ H_2 , octane, 22 °C, 4 days; iv, 1 atm/ CO , 25 °C.

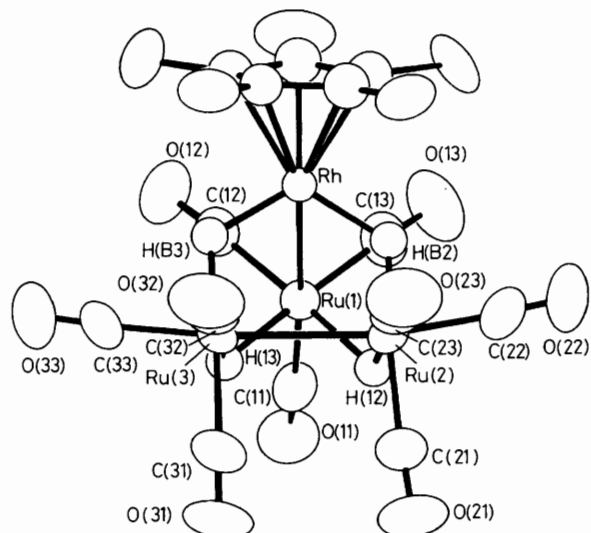


Figure 1. Interatomic distances (Å) and angles (°) for (4b) with estimated standard deviations: Rh–Ru(1) 2.735(1), 2.752(1), Rh ··· Ru(2) 2.912(1), 2.888(1), Rh ··· Ru(3) 2.891(1), 2.871(1), Ru(1) ··· Ru(2) 2.926(1), 2.912(1), Ru(1) ··· Ru(3) 2.938(1), 2.924(1), Ru(2)–Ru(3) 2.809(1), 2.813(1), Rh–H(B2) 1.70(7), 1.73(7), Rh–H(B3) 1.77(7), 1.71(7), Ru(1)–H(12) 1.71(7), 1.81(7), Ru(1)–H(13) 1.86(7), 1.78(7), Ru(2)–H(12) 1.72(7), 1.80(7), Ru(3)–H(13) 1.76(7), 1.82(7); Ru(1)–Rh ··· Ru(2) 62.31(2), 62.11(2), Ru(1)–Rh ··· Ru(3) 62.89(2), 62.63(2), Ru(2) ··· Rh ··· Ru(3) 57.89(2), 58.48(2).

velocity among the mildest conditions thus far observed for cluster disruption by CO,⁷ a fact which would need to be taken into account in postulating or attempting catalysis by these mixed metal species under homogeneous conditions.^{6,8}

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