

Notes

Preparation and X-Ray Crystal Structure of $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]^*$

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The synthesis and X-ray crystal structure determination of a new ruthenium–rhodium mixed-metal cluster $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]$ have been performed. The complex crystallises in the space group $P\bar{1}$ with $a = 8.356(8)$, $b = 9.261(8)$, $c = 13.83(1)$ Å, $\alpha = 82.56(7)$, $\beta = 80.12(7)$, $\gamma = 68.83(7)^\circ$, and $Z = 2$. Its ^1H n.m.r. properties are also discussed.

Tetranuclear mixed-metal carbonyls of ruthenium, cobalt, and rhodium form an exceptionally well defined group of cluster compounds. Of the dodecacarbonyl clusters of the type $[\text{Ru}_x\text{Co}_y\text{Rh}_z\text{H}_3(\text{CO})_{12}]$ ($x + y + z = 4$) only $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]$ is entirely unknown.¹ The compound $[\text{CoRh}_3(\text{CO})_{12}]$ has been reported to be unstable.² The metal combination Ru_3Rh , however, is known from several clusters containing C_5H_5 or C_5Me_5 ligands.^{3–6}

In this work the new parent cluster $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]$ has been prepared and characterised by X-ray crystallography and ^1H n.m.r. spectroscopy.

Results and Discussion

The crystal structure of $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]$, (1), is shown in the Figure. The structure is isomorphous with the cobalt and osmium analogues $[\text{Ru}_3\text{CoH}_3(\text{CO})_{12}]$,⁷ $[\text{Os}_3\text{CoH}_3(\text{CO})_{12}]$,⁸ and $[\text{Os}_3\text{RhH}_3(\text{CO})_{12}]$.⁹ The atomic co-ordinates are presented in Table 1, bond lengths and selected bond angles in Table 2.

The hydrogen atoms were placed and refined isotropically in $\text{Ru}(\mu\text{-H})\text{Ru}$ positions, which were indirectly evidenced as the hydride sites. These positions correspond to those observed in the cobalt and osmium analogues mentioned above. The metal–metal distances corresponding to the bridging hydrides (av. 293.0 pm) are clearly longer than the three others (av. 275.9 pm) and are of the size of hydride-bridged Ru–Ru bond lengths.¹

The carbonyls also bend away from these bridged Ru–Ru edges as a result of the steric demands of the hydrides. The *cis* Ru–Ru–C angles of the carbonyls 6, 7, and 11 are significantly larger (111.0–116.5, av. 113.9°) than for 4, 5, 8, 9, 10, and 12 (95.8–98.0, av. 96.9°). This supports the positions of the hydrides being opposite the metal assigned as rhodium in the Figure. Corresponding Rh–Ru–C and Ru–Rh–C angles of carbonyls *cis* to the Ru–Rh bonds are 89.7–93.4 (av. 91.4) and 95.0–99.2 (av. 97.1°), respectively.

Computer-simulated space filling models of the cluster were also used to locate the hydrides.¹⁰ The models showed 'holes' in the carbonyl coverage only in the three directions where the hydride ligands in the Figure are located.

The assignment of the metals is based on ^1H n.m.r. results. The only signal observed between 0 and -50°C (at $\delta = 17.3$) contains no evidence of couplings to the rhodium atom. This

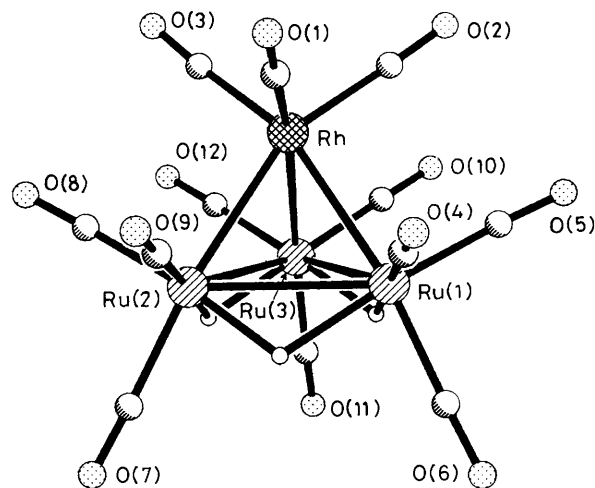


Figure. The schematic representation and numbering scheme of $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]$. Hydrides H(12), H(13), and H(23) are numbered according to the ruthenium atoms they bridge

can be explained by three equivalent $\text{Ru}(\mu\text{-H})\text{Ru}$ hydrides. The chemical shift is nearly the same as for the C_{3v} isomer of $[\text{Ru}_3\text{CoH}_3(\text{CO})_{12}]$.⁷ No evidence of isomerism was observed at these temperatures for compound (1). At 0°C the signal, however, is broader than we have observed for the $\text{Ru}(\mu\text{-H})\text{Ru}$ hydride in, for example, $[\text{Ru}_2\text{Rh}_2\text{H}_2(\text{CO})_{12}]$.¹¹ This might be due to a rapid hydride exchange between the different edges. The signal became slightly narrower at lower temperatures.

Experimental

The literature method was used to prepare $[\text{Rh}(\text{CO})_4]^-$.¹² Other reagents were obtained from commercial sources. Reactions and manipulations were carried out under a dinitrogen atmosphere using standard Schlenk-tube techniques.

Infrared spectra were recorded on a Nicolet 20SXC FT-IR spectrometer.

Crystallography.—Crystal data. $\text{C}_{12}\text{H}_3\text{O}_{12}\text{RhRu}_3$, $M = 745.26$, triclinic, space group $P\bar{1}$, $a = 8.356(8)$, $b = 9.261(8)$, $c = 13.83(1)$ Å, $\alpha = 82.56(7)$, $\beta = 80.12(7)$, $\gamma = 68.83(7)^\circ$, $U = 980.75$ Å³ (by least-squares refinement on diffractometer angles for 13 automatically centred reflections, $\lambda = 0.71073$ Å), $Z = 2$, $D_c = 2.52$ g cm⁻³, $F(000) = 696$, $\mu(\text{Mo-K}\alpha) = 3.10$ mm⁻¹.

Data collection and processing. Nicolet R3m diffractometer,

* 1,1,1,2,2,2,3,3,3,4,4,4-Dodecacarbonyl-2,3,2;4;3,4-tri- μ -hydrido-tetrahedro-1-rhodium-2,3,4-triruthenium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

Table 1. Atomic co-ordinates ($\times 10^4$) of compound (1)

Atom	x	y	z	Atom	x	y	z
Rh	2 210(1)	2 112(1)	8 538(1)	C(1)	1 921(12)	113(10)	8 873(6)
Ru(1)	5 135(1)	1 210(1)	7 173(1)	C(2)	3 454(12)	2 066(10)	9 626(7)
Ru(2)	1 640(1)	2 433(1)	6 600(1)	C(3)	-67(12)	3 430(11)	9 110(6)
Ru(3)	2 989(1)	4 488(1)	7 374(1)	C(4)	5 276(12)	-912(10)	7 388(6)
O(1)	1 739(12)	-1 061(9)	9 092(5)	C(5)	6 610(12)	1 003(10)	8 137(7)
O(2)	4 141(10)	2 019(9)	10 268(5)	C(6)	6 967(12)	913(10)	6 085(7)
O(3)	-1 344(10)	4 179(10)	9 489(6)	C(7)	1 491(12)	2 775(10)	5 204(7)
O(4)	5 375(11)	-2 181(8)	7 502(6)	C(8)	-747(12)	3 591(10)	6 981(7)
O(5)	7 539(10)	877(10)	8 678(5)	C(9)	1 275(11)	488(9)	6 768(6)
O(6)	8 090(10)	724(10)	5 450(5)	C(10)	4 087(13)	4 845(11)	8 373(6)
O(7)	1 354(13)	2 988(10)	4 393(5)	C(11)	3 797(12)	5 825(10)	6 362(7)
O(8)	-2 178(9)	4 288(9)	7 186(6)	C(12)	830(12)	6 019(10)	7 810(7)
O(9)	1 042(10)	-659(8)	6 859(5)	H(12)	3 790(121)	1 439(103)	6 125(63)
O(10)	4 760(10)	5 083(9)	8 963(5)	H(23)	1 941(107)	4 130(93)	6 389(57)
O(11)	4 324(11)	6 549(9)	5 767(5)	H(13)	5 009(139)	3 182(116)	6 917(73)
O(12)	-473(10)	6 947(9)	8 052(6)				

Table 2. Bond lengths (pm) and angles ($^\circ$)

Rh-Ru(1)	275.7(3)	Rh-Ru(2)	276.2(3)
Rh-Ru(3)	275.9(3)	Ru(1)-Ru(2)	293.4(3)
Ru(1)-Ru(3)	293.7(3)	Ru(2)-Ru(3)	292.1(3)
Rh-C(1)	194.0(10)	Rh-C(2)	195.9(11)
Rh-C(3)	194.5(8)	Ru(1)-C(4)	191.2(10)
Ru(1)-C(5)	191.3(11)	Ru(1)-C(6)	192.4(9)
Ru(2)-C(7)	193.4(9)	Ru(2)-C(8)	191.0(8)
Ru(2)-C(9)	191.1(10)	Ru(3)-C(10)	190.5(11)
Ru(3)-C(11)	194.4(10)	Ru(3)-C(12)	190.6(8)
O(1)-C(1)	114.7(14)	O(2)-C(2)	112.5(13)
O(3)-C(3)	112.7(11)	O(4)-C(4)	114.0(12)
O(5)-C(5)	113.5(13)	O(6)-C(6)	115.0(11)
O(7)-C(7)	113.1(12)	O(8)-C(8)	114.1(10)
O(9)-C(9)	113.6(13)	O(10)-C(10)	115.0(14)
O(11)-C(11)	112.6(12)	O(12)-C(12)	114.4(10)
Ru(1)-H(12)	192.7(103)	Ru(1)-H(13)	178.2(109)
Ru(2)-H(12)	175.1(83)	Ru(2)-H(23)	166.1(93)
Ru(3)-H(23)	186.2(97)	Ru(3)-H(13)	175.3(91)
Ru(1)-Rh-C(1)	98.7(2)	Ru(2)-Rh-C(1)	97.0(3)
Ru(3)-Rh-C(1)	158.1(3)	Ru(1)-Rh-C(2)	95.1(3)
Ru(2)-Rh-C(2)	156.2(3)	Ru(3)-Rh-C(2)	97.5(3)
Ru(1)-Rh-C(3)	157.3(3)	Ru(2)-Rh-C(3)	99.2(3)
Ru(3)-Rh-C(3)	95.0(3)	Rh-Ru(1)-C(4)	91.4(3)
Ru(2)-Ru(1)-C(4)	96.2(3)	Ru(3)-Ru(1)-C(4)	147.4(3)
Rh-Ru(1)-C(5)	91.9(3)	Ru(2)-Ru(1)-C(5)	148.4(2)
Ru(3)-Ru(1)-C(5)	97.9(3)	Rh-Ru(1)-C(6)	169.7(2)
Ru(2)-Ru(1)-C(6)	114.3(3)	Ru(3)-Ru(1)-C(6)	113.0(3)
Rh-Ru(2)-C(7)	172.2(3)	Ru(1)-Ru(2)-C(7)	116.5(3)
Ru(3)-Ru(2)-C(7)	115.0(3)	Rh-Ru(2)-C(8)	89.7(3)
Ru(1)-Ru(2)-C(8)	146.0(3)	Ru(3)-Ru(2)-C(8)	95.8(3)
Rh-Ru(1)-C(9)	90.2(3)	Ru(1)-Ru(2)-C(9)	96.0(3)
Ru(3)-Ru(2)-C(9)	146.8(3)	Rh-Ru(3)-C(10)	91.5(3)
Ru(1)-Ru(3)-C(10)	97.3(3)	Ru(2)-Ru(3)-C(10)	148.2(3)
Rh-Ru(3)-C(11)	167.9(3)	Ru(1)-Ru(3)-C(11)	111.0(2)
Ru(2)-Ru(3)-C(11)	113.5(3)	Rh-Ru(3)-C(12)	93.4(3)
Ru(1)-Ru(3)-C(12)	149.6(3)	Ru(2)-Ru(3)-C(12)	98.0(4)

graphite-monochromated Mo- K_α radiation, 4 494 unique reflections measured ($5 < 2\theta < 55^\circ$, merging $R = 0.0052$ after absorption correction), giving 3 034 with $I > 3\sigma(I)$.

Structure analysis and refinement. The positions of the metal atoms were solved by the direct methods of the SHELXTL PLUS program package.¹³ These were anisotropically refined to $R = 0.0390$ and $R' = 0.0390$, $\sigma(w) = 0.0005$, together with isotropically refined hydrogen atoms. From the n.m.r. data the rhodium atom was deduced to occupy the same metal site as cobalt in the isomorphous crystal structure of $[\text{Ru}_3\text{CoH}_3(\text{CO})_{12}]$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond angles.

Proton N.M.R. Spectroscopy.—The ^1H n.m.r. spectra were recorded on a Bruker AM-250 spectrometer using CDCl_3 as solvent. The chemical shifts are relative to SiMe_4 .

Preparation of $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]$.—The ion $[\text{Rh}(\text{CO})_4]^-$ prepared from $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ (150 mg) {50% conversion into $[\text{Rh}(\text{CO})_4]^-$ was assumed} in tetrahydrofuran (thf) (25 cm^3) was added dropwise to a hexane solution of $[\text{Ru}_3(\text{CO})_{12}]$ {246 mg in ca. 150 cm^3 hexane, which was warmed to 50 $^\circ\text{C}$ to dissolve all the $[\text{Ru}_3(\text{CO})_{12}]$. A dark red solid precipitated during the addition. Hexane-thf solution (cooled to room temperature), which contained unreacted $[\text{Ru}_3(\text{CO})_{12}]$, was removed by a syringe needle and the residue was treated with 85% H_3PO_4 (5 cm^3). The crude product was then extracted by hexane- CH_2Cl_2 (3:1) and chromatographed on silica. The compound $[\text{Ru}_3\text{RhH}_3(\text{CO})_{12}]$ was obtained as the first (yellow) band using hexane as eluant. Some $[\text{Ru}_2\text{Rh}_2\text{H}_2(\text{CO})_{12}]$ was eluted as a reddish band. The product (ca. 100 mg) contained unidentified clusters which decomposed during the chromatographic separation. Compound (1) is relatively stable towards aerial oxidation. After separation, the ^1H n.m.r. spectrum of the product still showed a small singlet due to $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$. Yield of (1) 9% (26 mg) with respect to $[\text{Ru}_3(\text{CO})_{12}]$ (Found: C, 19.5; H, 0.4. Calc. for $\text{C}_{12}\text{H}_3\text{O}_{12}\text{RhRu}_3$: C, 19.3; H, 0.4%). I.r. (CH_2Cl_2): 2 075s, 2 060s, 2 052(sh), and 2 028s cm^{-1} .

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