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Unusual mixed metal cluster reactions: formation of the mixed metal chain $Rh_2Ru_3(CO)_{10}(\mu\text{-SEt})_8$

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Abstract

The tetranuclear mixed metal carbonyl cluster $HRuRh_3(CO)_{12}$ reacts with ethanethiol to give a pentanuclear compound $Rh_2Ru_3(CO)_{10}(\mu\text{-SEt})_8$ as a minor product. An X-ray diffraction study has revealed that five metal atoms form a thiolate-bridged chain structure without direct metal–metal bonds. The rhodium atoms end the chain, and each metal has two terminal carbonyl ligands.

Keywords: Rhodium; Ruthenium; Carbonyl; Clusters; Thiol; Crystal structure

1. Introduction

Transition metal carbonyl clusters are typically based on triangular arrays of metals, but clusters with open framework are also formed as a result of formal bond scission. There is a variety of trinuclear transition metal compounds with a linear arrangement. Homometallic compounds are the commonest, but some mixed metal complexes are also known. Extended chain geometries are significantly rarer. Ruthenium is able to form metal chains such as $Ru_4(\mu\text{-Br})_2\{\mu\text{-C, P;P-}(C_6H_4)PPhCH_2PPh_2\}_2(\mu\text{-CO})(CO)_8$ [1], $Ru_4(CO)_{10}(CH_3C{=}CHCH{=}N_iPr)_2$ [2,3] and $H_2Ru_4(CO)_8(\text{neopent-DAB})_2$ (R-DAB = 1,4-disubstituted 1,4-diaza-1,3-butadiene [4] containing an almost linear Ru_4 moiety with three Ru–Ru bonds. Sulfur-bridged osmium compounds $Os_4(CO)_{12}(\mu_3\text{-S})_2L$ (L = PMe_2Ph, ${}^tBuNC$) [5] and $Os_4(CO)_{11}(\mu_3\text{-S})(\mu_3\text{-MeC}_2NMe_2)(\mu_2\text{-MeC}_2NMe_2)$ [6,7] have also been reported. There are also several multimetallic-tetranuclear complexes with chain-like arrangements of metal atoms and bridging arsenic atoms. The structure of a complex with the chain Fe–As–Co–As–Cr–As–Cr has been determined an X-ray diffraction study [8].

Few longer chain molecules have been structurally characterized. Two isomers of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{15}$ with an open metal chain are formed in reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with CO [9].

There are also mixed platinum–tungsten chain structures with direct metal–metal bonds and stabilizing bridging ligands [10,11]. Further extension of these chains leads to the formation of a cyclic eight-membered metal ring.

In our earlier studies on reactions of transition metal clusters of ruthenium, rhodium and cobalt with organic sulfur ligands, thioethers SR_2 typically replaced carbonyl or hydride ligands in the parent clusters. Thiolate groups SR^- readily bridge metal bonds to form both inorganic and organometallic chain complexes. Under vigorous conditions, thiols, RSH, and organic disulfides, RSSR, react with $Ru_3(CO)_{12}$ to give mononuclear complexes or dinuclear and polymeric products of the type $[Ru(CO)_2(\mu\text{-SR})_2]_n$, which have been characterized spectroscopically and analytically [12].

Dimeric compounds are usual for rhodium. Thus $Rh_2(CO)_4Cl_2$ gives $Rh_2(CO)_4(\mu\text{-SR})_2$ in high yield in reactions with ethanethiol, EtSH, and thiophenol, PhSH [13,14]. Phosphine-substituted derivatives $Rh_2(CO)_{4-n}(\mu\text{-SR})_2L_n$ (L = phosphine, phosphite) have also been characterized, and found to be catalytically

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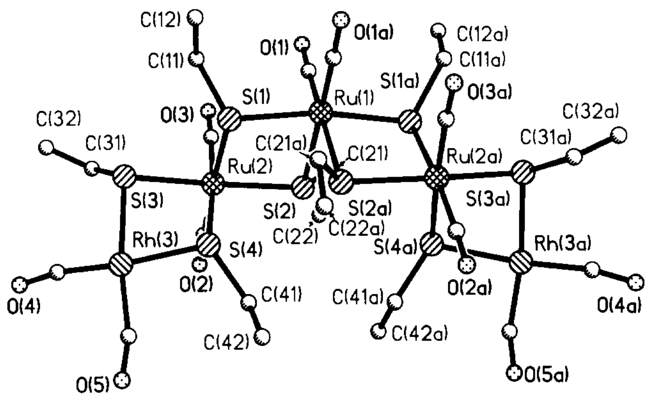

Fig. 1. Structure of $Rh_2Ru_3(CO)_{10}(\mu\text{-}SEt)_8$.

active [15–18]. The trinuclear chain cation $[Rh_3I_2(PhCH_2NC)_{12}]^{3+}$, which was formed in the three-centre oxidative addition from $[(PhCH_2NC)_4Rh]X$ (X = I, Br) and iodine, has a nearly linear linkage I–Rh–Rh–Rh–I, with an Rh–Rh distance of 279.1 pm [19].

We report now the synthesis and structural characterization of a pentanuclear chain species, $Rh_2Ru_3(CO)_{10}(\mu\text{-}SEt)_8$.

2. Results and discussion

The reaction between the tetrahedral cluster $HRuRh_3(CO)_{12}$ and ethanethiol did not give the products of ligand substitution but instead a pentanuclear mixed compound $Rh_2Ru_3(CO)_{10}(\mu\text{-}SEt)_8$, which was formed in small amounts along with $Rh_2(CO)_4(\mu\text{-}SEt)_2$ and a brown solid of low solubility. The title compound was characterized by X-ray crystallography; the molecule lies on a twofold crystallographic axis. The structure and numbering scheme are shown in Fig. 1, the atomic coordinates are presented in Table 1, and the bond lengths and angles in Tables 2 and 3, respectively.

The thiols are sufficiently reactive to cause the rupture of the metal skeleton and to form an open-chain structure with two thiolate bridges between each metal pair. The ruthenium to rhodium ratio 3:2 was determined by atomic absorption spectroscopy, since ruthenium and rhodium are too similar in electron density to be distinguished in Fourier maps. The end metal atoms were judged to be rhodium, and the metal atoms between them to be ruthenium. The planar coordination sphere of the end metals strongly resemble that of the Rh atoms in the compound $Rh_2(CO)_4(SEt)_2$. The C–Rh–C and S–Rh–S bond angles at 94.0° and 81.7° (in the dimer 92.5° and 78.5°), and the Rh–S bond length of 237.6 pm (av.) is close to the Rh–S distance of 233.9 pm (av.) in the dimer. The octahedral symmetry of the inner metal with CO groups in the *cis* positions results in a bent overall structure for the molecule. The coordination is typical for ruthenium, and is seen in several compounds of the type $Ru_2(CO)_6(\mu\text{-}X)_2$ (X = PR_2, AsR_2, SR, SeR, TeR) [20,21] and in the polymeric compounds $[RuX_2(CO)_4]_n$ (X = SR, SeR, TeR) [12,21] with a kinked structure. The S–Ru–S angles are slightly smaller (Av. 84.8°) than the C–Ru–C (av. 94.9°) and S–Ru–C (av. 93.3°) angles. The Ru–Rh distance is 343 pm and the Ru–Ru distance is 365 pm, showing that the chain is connected together mainly by metal–sulfur interactions. The Ru–Ru bond lengths reported for ruthenium chain complexes vary between 270 and 300 pm depending on the ligands attached to the molecules. The mean S–C–C

Table 1
Atomic coordinates (×10^4) for $Rh_2Ru_3(CO)_{10}(\mu\text{-}SEt)_8$

Atom	*x*	*y*	*z*
Ru(1)	0	5683(2)	2500
Ru(2)	2389(2)	6689(1)	3006(1)
Rh(3)	2999(2)	7886(2)	4321(1)
S(1)	1141(6)	5798(4)	3476(3)
S(2)	1069(5)	6747(4)	2114(3)
S(3)	3339(6)	6592(5)	4064(4)
S(4)	1436(6)	7615(4)	3683(3)
O(1)	1374(20)	4507(10)	1892(10)
O(2)	3785(18)	7906(14)	2427(11)
O(3)	3604(17)	5469(12)	2341(11)
O(4)	5101(22)	8163(18)	4933(13)
O(5)	2560(24)	9523(15)	4512(12)
C(1)	882(24)	4991(14)	2108(13)
C(2)	3246(23)	7456(21)	2659(16)
C(3)	3135(22)	5927(18)	2578(15)
C(4)	4318(30)	8005(24)	4675(17)
C(5)	2658(37)	8892(29)	4404(17)
C(11)	1843(27)	4891(18)	3640(16)
C(12)	1227(28)	4374(17)	4036(15)
C(21)	1588(20)	6484(14)	1315(12)
C(22)	2156(21)	7118(16)	1011(13)
C(31)	4705(23)	6426(24)	3896(17)
C(32)	5223(22)	6120(24)	4426(20)
C(41)	1059(19)	8449(13)	3188(12)
C(42)	233(19)	8913(14)	3475(12)

Table 2
Bond lengths (pm) in $Rh_2Ru_3(CO)_{10}(\mu\text{-}SEt)_8$

Ru(1)–S(1)	241.2(7)	Ru(1)–S(2)	246.0(7)
Ru(1)–C(1)	185(3)	Ru(1)–S(1A)	241.2(7)
Ru(1)–S(2A)	246.0(7)	Ru(1)–C(1A)	185(3)
Ru(2)–S(1)	245.1(8)	Ru(2)–S(2)	242.3(7)
Ru(2)–S(3)	241.5(8)	Ru(2)–S(4)	247.0(8)
Ru(2)–C(2)	189(3)	Ru(2)–C(3)	187(3)
Rh(3)–S(3)	237.2(9)	Rh(3)–S(4)	238.0(8)
Rh(3)–C(4)	183(4)	Rh(3)–C(5)	183(5)
S(1)–C(11)	186(3)	S(2)–C(21)	181(3)
S(3)–C(31)	182(3)	S(4)–C(41)	183(3)
O(1)–C(1)	115(3)	o(2)–C(2)	116(4)
O(3)–C(3)	112(4)	O(4)–C(4)	115(5)
O(5)–C(5)	114(6)	C(11)–C(12)	146(5)
C(21)–C(22)	147(4)	C(31)–C(32)	135(5)
C(41)–C(42)	147(4)		

Table 3
Bond angles (°) in $Rh_2Ru_3(CO)_{10}(\mu\text{-SEt})_8$

S(1)–Ru(1)–S(2)	82.0(2)	S(1)–Ru(1)–C(1)	92.1(9)
S(2)–Ru(1)–C(1)	90.6(9)	S(1)–Ru(1)–S(1A)	170.3(4)
S(2)–Ru(1)–S(1A)	90.6(2)	C(1)–Ru(1)–S(1A)	94.2(9)
S(1)–Ru(1)–S(2A)	90.6(2)	S(2)–Ru(1)–S(2A)	81.0(3)
C(1)–Ru(1)–S(2A)	170.7(8)	S(1A)–Ru(1)–S(2A)	82.0(2)
S(1)–Ru(1)–C(1A)	94.2(9)	S(2)–Ru(1)–C(1A)	170.7(8)
C(1)–Ru(1)–C(1A)	98(2)	S(1A)–Ru(1)–C(1A)	92.1(9)
S(2A)–Ru(1)–C(1A)	90.6(9)	S(1)–Ru(2)–S(2)	82.0(2)
S(1)–Ru(2)–S(3)	86.2(3)	S(2)–Ru(2)–S(3)	165.9(3)
S(1)–Ru(2)–S(4)	82.4(2)	S(2)–Ru(2)–S(4)	91.8(2)
S(3)–Ru(2)–S(4)	79.0(3)	S(1)–Ru(2)–C(2)	174.0(10)
S(2)–Ru(2)–C(2)	95.7(10)	S(3)–Ru(2)–C(2)	95.2(10)
S(4)–Ru(2)–C(2)	92.1(11)	S(1)–Ru(2)–C(3)	94.0(10)
S(2)–Ru(2)–C(3)	92.7(9)	S(3)–Ru(2)–C(3)	95.8(9)
S(4)–Ru(2)–C(3)	173.8(9)	C(2)–Ru(2)–C(3)	91.7(14)
S(3)–Rh(3)–S(4)	81.7(3)	S(3)–Rh(3)–C(4)	91.1(13)
S(4)–Rh(3)–C(4)	169.7(13)	S(3)–Rh(3)–C(5)	173.0(12)
S(4)–Rh(3)–C(5)	92.7(14)	C(4)–Rh(3)–C(5)	94.0(2)
Ru(1)–S(1)–Ru(2)	97.4(3)	Ru(1)–S(1)–C(11)	110.4(10)
Ru(2)–S(1)–C(11)	107.3(11)	Ru(1)–S(2)–Ru(2)	96.9(2)
Ru(1)–S(2)–C(21)	108.0(8)	Ru(2)–S(2)–C(21)	111.8(9)
Ru(2)–S(3)–Rh(3)	91.5(3)	Ru(2)–S(3)–C(31)	108.1(11)
Rh(3)–S(3)–C(31)	112.3(14)	Ru(2)–S(4)–Rh(3)	89.9(3)
Ru(2)–S(4)–C(41)	110.9(8)	Rh(3)–S(4)–C(41)	109.3(8)
Ru(1)–C(1)–O(1)	173(2)	Ru(2)–C(2)–O(2)	177(3)
Ru(2)–C(3)–O(3)	178(3)	Rh(3)–C(4)–O(4)	172(4)
Rh(3)–C(5)–O(5)	171(4)	S(1)–C(11)–C(12)	111(2)
S(2)–C(21)–C(22)	112(2)	S(3)–C(31)–C(32)	112(3)
S(4)–C(41)–C(42)	115(2)		

angle of the thiolate groups is 113°, which is not far from that, from the viz. 110.3°, in the dimeric $Rh_2(CO)_4(\mu\text{-SEt})_2$.

The complex $Rh_2Ru_3(CO)_{10}(\mu\text{-SEt})_8$ is not formed (or at least not readily) by reaction of the thiolate-bridged rhodium dimer with ruthenium species, or from carbonyl chlorides of these metals. The mixed metal cluster $HRuRh_3(CO)_{12}$ probably produces during the reaction the reactive fragments needed to form the pentanuclear chain.

3. Experimental details

3.1. Crystallographic data

Data were collected on a Nicolet R3m diffractometer using Mo Kα radiation with $\lambda = 71.073$ pm and a graphite monochromator. The unit cell was determined from 26 reflections of $14 < 2\theta < 26°$. The compound crystallizes in the monoclinic space group $C2/c$ with $a = 1283.2(5)$, $b = 1758.2(6)$, $c = 2003.7(7)$ pm, $\beta = 91.94(3)°$, $V = 4518(3) \times 10^6$ pm^3, $Z = 4$, $\mu = 2.90$ mm^{-1}, MW = 1278.01 g, $D_{calc} = 1.88$ g cm^{-3}. Intensity data were collected in the h, k, l region 0–16, 0–21, -24–$+24$ with $5 < 2\theta < 50°$ and corrected for Lorenz, polarization, background and absorption effects. The structure was determined by direct methods and subsequent Fourier synthesis using the SHELXTL [22] program package. The number of data was 3961 of which 1230 reflections with $I > 2\sigma(I)$ were used in calculations and the number of parameters was 222. The final R values were $R = 7.33\%$ and $R_w = 6.10\%$. Anisotropic refinement was made for all non-hydrogen atoms. The ethyl hydrogens were placed in calculated positions with C–H = 96 pm and $U = 800$ pm^2.

Tables of anisotropic thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

3.2. Synthesis of $Rh_2Ru_3(CO)_{10}(\mu\text{-SEt})_8$

$HRuRh_3(CO)_{12}$ [23] and ethanethiol (Aldrich) were refluxed in CH_2Cl_2 under a dinitrogen atmosphere for 1 h. The mixture was chromatographed on silica column. Elution with hexane gave a small yellow fraction containing some by-products and impurities derived from the starting material [$Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$], and an orange fraction of dimeric $Rh_2(CO)_4(\mu - SEt)_2$ as the main product. A 1:1 hexane/CH_2Cl_2 mixture eluted an orange fraction containing the title compound. The yield varied in the reaction from traces to 34% yield based on ruthenium. The IR spectrum was recorded on a Galaxy 6020 spectrometer and the ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer at 0°C with TMS as reference. IR (CH_2Cl_2) (cm^{-1}): 2064 (vs); 2033 (s); 2001 (ms); 1973 (m). ^1H NMRδ: 2.4–3.5 (br, m, CH_2); 1.2–1.6 (br, m, CH_3) ppm. Anal. Found: C, 24.36; H, 3.13%. Calc.: C, 24.43; H, 3.14%. AAS: Found: Ru/Rh = 1.42 (w:w). Calc.: 1.47. Crystallization from a hexane/dichloromethane mixture gave orange crystals (and one of dimensions $0.4 \times 0.1 \times 0.15$ mm was chosen for structure determination. The reactions also gave less soluble, brown fractions and insoluble products.

References

[1] M.I. Bruce, J.R. Hinchcliffe, R. Surynt, B.W. Skelton and A.H. White, *J. Organomet. Chem., 469* (1994) 89.

[2] W.P. Mul, C.J. Elsevier, M. van Leijen and J. Spaans, *Organometallics, 10* (1991) 251.

[3] L.H. Polm, W.P. Mul, C.J. Elsevier, K. Vrieze, M.J.N. Christophersen and C.H. Stam, *Organometallics, 7* (1988) 423.

[4] J. Keijsper, L.H. Polm, G. van Koten, K. Vieze, E. Nielsen and C.H. Stam, *Organometallics, 4* (1985) 2006.

[5] R.D. Adams, I.T. Horwath and K. Natarajan, *Organometallics, 3* (1984) 1540.

[6] R.D. Adams, G. Chen, S. Sun, J.T. Tanner and T.A. Woplfe, *Organometallics, 9* (1990) 251.

[7] D.F. Schriver, F. Kaesz and R.D. Adams, in D.M.P. Mingos and A.S. May (eds.), *The Chemistry of Metal Cluster Complexes*, VCH Publishers, New York, 1990.

[8] H.J. Langenbach, E. Keller and H. Vahrenkamp, *J. Organomet. Chem., 191* (1980) 95.

[9] M.I. Bruce and M.L. Williams, *J. Organomet. Chem.*, *282* (1985) C11.

[10] M.R. Awang, G.A. Carriedo, J.A.K. Howard, K.A. Mead, I. Moore, C.M. Nunn and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1983) 964.

[11] G.P. Elliot, J.A.K. Howard, C.M. Nunn and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1986) 431.

[12] G. Cetini, O. Gambino, E. Sappa and M. Valle, *J. Organomet. Chem.*, *15* (1968) 4.

[13] W. Hieber and K. Heinicke, *Z. Naturforsch., Teil B, 16* (1961) 554.

[14] J. Pursiainen, T. Teppana, S. Rossi and T.A. Pakkanen, *Acta Chem., Scand.*, *47* (1993) 416.

[15] F. Senocq, C. Randrianalimanana, A. Thorez, P. Kalck, R. Choukroun and D. Gervais, *J. Mol. Catal.*, *35* (1986) 213.

[16] P. Kalck, P. Escaffre, F. Serein-Spirau and A. Thorez, *New J. Chem.*, *12* (1988) 687.

[17] P. Kalck, C. Randrianalimanana, M. Ridmy and A. Thorez, *New J. Chem.*, *12* (1988) 679.

[18] A. Dedieu, P. Escaffre, J.M. Frances, P. Kalck and A. Thorez, *New J. Chem.*, *10* (1986) 631.

[19] A.L. Balch and M.M. Olmstead, *J. Am. Chem. Soc.*, *101* (1979) 3128.

[20] R.E. Dessy, A.L. Rheingold and G.D. Howard, *J. Am. Chem. Soc.*, *94* (1972) 746.

[21] E.D. Schermer and W.H. Baddley, *J. Organomet. Chem.*, *30* (1971) 67.

[22] SHELXTL Plus, Release 3.4, Nicolet Co., Madison, WI, 1988.

[23] T.A. Pakkanen, J. Pursiainen, T. Venäläinen and T.T. Pakkanen, *J. Organomet. Chem.*, *372* (1989) 129.