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Reactions of cyclic thioethers with $Ru_3(CO)_{12}$. Synthesis, reactivity and crystal structures of $HRu_3(CO)_9(\mu_3\text{-}\eta^3(C,S,S)$-1,3-dithiacyclohexane), $Ru_3(CO)_9(\mu_3\text{-}\eta^3$-1,3,5-trithiacyclohexane) and $Ru_3(CO)_9(\mu_2\text{-}\eta^3$-1,4,7-trithiaheptane)

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Abstract

Cyclic polydentate thioether ligands 1,3-dithiacyclohexane, 1,3,5-trithiacyclohexane and 1,4,7-trithiacyclononane react with $Ru_3(CO)_{12}$ to give the carbonyl substitution products $HRu_3(CO)_9(\mu_3\text{-}\eta^3$-1,3-dithiacyclohexane) (**1**), $Ru_3(CO)_9(\mu_3\text{-}\eta^3$-1,3,5-trithiacyclohexane) (**2**) and $Ru_3(CO)_9(\mu_2\text{-}\eta^3$-1,4,7-trithiaheptane) (**3**) in moderate yields. The crystal structures of **1**-**3** have been determined. A different coordination mode is observed in each case. Carbon monoxide was found not to replace the cyclic thioethers in the ruthenium complexes, but complexes **1** and **3** react with H_2. Thus complex **1** under a hydrogen atmosphere in chloroform gives the new cluster complex $(\mu_2\text{-}H)_2Ru_3(CO)_8Cl(\mu_3\text{-}\eta^3\text{-}1,3\text{-}[S_2CH(CH_2)_3])$ (**4**) the crystal structure of which was determined.

Introduction

Interactions between sulphur donor and transition metal compounds are important in biochemistry and various catalytic processes. Sulphur-coordinated transition metals are the active centres in many redox reactions in life processes. Such centres have been modelled with complexes containing cyclic polydentate sulphur ligands [1]. Much studied have been transition metal–1,4,7-trithia-cyclononane complexes, in which the ligand has facial conformation in contrast to the other crown thioethers [2,3]. Mononuclear bis-sandwich complexes of type $[M(1,4,7\text{-trithiacyclononane})_2]^{x+}$, in which the ligands stabilize metal centres in different oxidation states have been reported for a wide range of transition metals (Ru, Os, Rh, Pd, Pt, Ir) [4].

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Transition metal insertions into C–S bonds to give thioether complexes have been studied in the context of desulphurization of cyclic thioethers, which are found as impurities in crude oil [5,6]. Because they are sterically strained small-ring thioethers show a greater tendency to undergo ring opening and desulphurization [7].

Cluster compounds with polydentate sulphur ligands are rare, although 1,3,5-trithiacyclohexane, for example, has been shown to have the appropriate geometry to cap a triangular face of $Rh_4(CO)_{12}$ [8]. However, the tridentate phosphorus ligand $CH(PPh_2)_3$ has been widely used for coordination at tetrahedral clusters (Co_2Rh_2, Rh_4, Co_4 [9], H_4Ru_4 [10], Ir_4, $HFeCo_3$) [11]. Derivatives of trinuclear clusters are less well known; for example, the reaction between $Ru_3(CO)_{12}$ and $CH(PPh_2)_3$ gives a mixture of products, none of them in good yield. This has been attributed to the preference for initial equatorial coordination of the ligand [12,13]. Some compounds, such as $Ni_3(CO)_6(HC(PPh_2)_3)$ have been synthesized from mononuclear fragments [14]. The corresponding Si-containing ligands $MeSi(PR_2)_3$ can coordinate at $Ru_3(CO)_{12}$ to give the derivatives $Ru_3(CO)_9(MeSi(PR_2)_3)$, R = Bu [15], Et, Pr [16], which have been characterized by X-ray crystallography. The $MeSi(PR_2)_3$ derivatives of larger clusters $M_4(CO)_{12}$ (M = Co, Rh, Ir) and $Rh_6(CO)_{16}$ are also known [16].

We previously studied some reactions of aliphatic thioethers with tetrahedral ruthenium-, cobalt- and rhodium-containing cluster compounds [17,18] and with $Rh_6(CO)_{16}$ [19]. Several bonding modes were observed, depending on the metal or metals present in the cluster and the ligand used. We report below reactions of 1,3-dithiacyclohexane, 1,3,5-trithiacyclohexane, and 1,4,7-trithiacyclononane with the ruthenium carbonyl cluster $Ru_3(CO)_{12}$.

Results and discussion

The cyclic polydentate thioethers 1,3-dithiacyclohexane, 1,3,5-trithiacyclohexane and 1,4,7-trithiacyclononane react with $Ru_3(CO)_{12}$ to give complexes involving entirely different coordination modes (Fig. 1). Both 1,3-dithiacyclohexane and 1,3,5-trithiacyclohexane replace axial carbonyl groups of the $Ru_3(CO)_{12}$ parent cluster. $Ru_3(CO)_9(\mu_3\text{-}\eta^3$-1,3-dithiacyclohexane) (**1**) and $Ru_3(CO)_9(\mu_3\text{-}\eta^3$-1,3,5-trithiacyclohexane) (**2**) were obtained in 91 and 43% yields, respectively. The formation of $Ru_3(CO)_9(\mu_2\text{-}\eta^3$-1,4,7-trithiaheptane) (**3**) from $Ru_3(CO)_{12}$ and 1,4,7-trithiacyclononane is more complex involving a ligand modification, and the yield is low, *viz.* 9%.

Structure of $HRu_3(CO)_9(\mu_3\text{-}\eta^3$-1,3-dithiacyclohexane) (1)

The crystal structure of **1** is given with the atomic numbering scheme in Fig. 2. The atomic coordinates, bond lengths and relevant bond angles are given in Tables 1–3.

1,3-Dithiacyclohexane coordinates *via* the sulphur atoms and the carbon atom lying between them. Each ruthenium bears three terminal carbonyl groups. On coordination of 1,3-dithiacyclohexane to the ruthenium cluster the C–H bond of the SCH_2S group is activated and undergoes an intramolecular oxidative addition to a Ru centre; the hydride ligand eventually bridges the Ru(1)–Ru(2) bond, as observed previously in $HRu_3(CO)_9(\mu_3$-1–4-η^4-dihydrotiophene) [20]. The hydro-

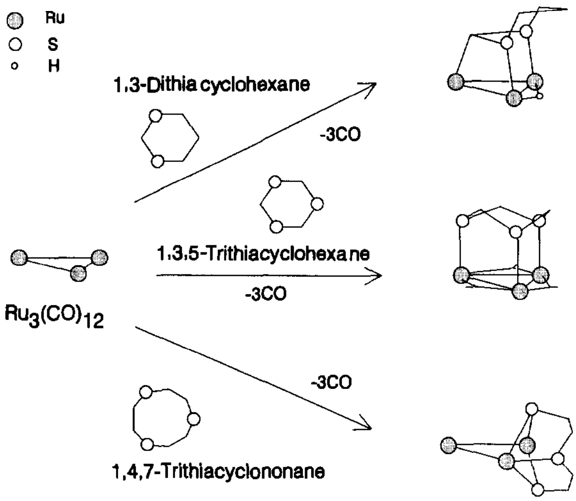

Fig. 1. Reactions of cyclic thioethers with $Ru_3(CO)_{12}$.

gen position was inferred from the cluster geometry. The Ru(1)–Ru(2) bond is significantly longer (305pm) than the other two bonds (282 and 281pm); for comparison, the average metal–metal bond length in the parent cluster $Ru_3(CO)_{12}$ is 285.4 pm [21]. The hydride ligand also causes opening of the Ru(1)–Ru(2)–C bond angles. Space filling models suggest that the hydride is less bent out of the metal plane than in $[HRu_3(CO)_{11}]^-$ [22], which has μ_2-H and μ_2-CO in the shortest bond of the isoceles triangle. The Ru(2)–Ru(1)–C(11) and Ru(1)–Ru(2)–C(22) angles are clearly larger (mean 117.6°) than the corresponding angles for the

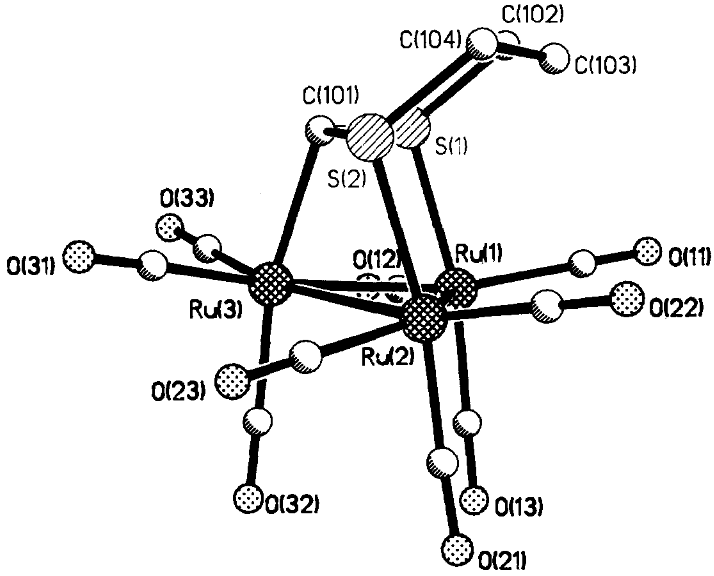

Fig. 2. Structure and numbering scheme for $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ (1).

Table 1

Atomic coordinates (10^4) for $HRu_3(CO)_9(\mu_3\text{-}\eta^3$-1,3-dithiacyclohexane) (**1**)

Atom	*x*	*y*	*z*
Ru(2)	6373(1)	1869(2)	5627(1)
Ru(1)	5455(1)	2903(2)	6551(1)
Ru(3)	6887(1)	2022(2)	6886(1)
S(1)	6217(2)	4877(5)	6721(2)
S(2)	7131(2)	3855(5)	5814(2)
O(11)	4037(7)	4466(16)	6109(8)
O(12)	5322(9)	3054(20)	7904(7)
O(13)	4695(9)	100(17)	6526(10)
O(21)	5555(8)	−840(15)	5541(8)
O(22)	5880(9)	2465(17)	4260(7)
O(23)	7739(8)	170(20)	5580(8)
O(31)	8475(7)	1324(19)	6845(7)
O(32)	6349(8)	−876(14)	7119(7)
O(33)	7149(8)	2783(18)	8242(6)
C(11)	4553(10)	3912(18)	6239(9)
C(12)	5385(9)	2959(19)	7391(10)
C(13)	4990(10)	1129(22)	6519(10)
C(21)	5864(10)	181(21)	5602(9)
C(22)	6063(9)	2248(18)	4772(8)
C(23)	7247(11)	790(23)	5589(10)
C(31)	7900(11)	1602(20)	6859(8)
C(32)	6541(8)	185(21)	7027(8)
C(33)	7042(10)	2490(21)	7723(8)
C(101)	7068(8)	4137(18)	6580(8)
C(102)	5982(10)	6209(17)	6148(8)
C(103)	6015(10)	5815(19)	5500(9)
C(104)	6761(9)	5363(18)	5376(8)
Ru(1B)	416(1)	2311(2)	6393(1)
Ru(2B)	1613(1)	2223(1)	5601(1)
Ru(3B)	1883(1)	1948(1)	6874(1)
S(1B)	893(2)	4445(5)	6818(2)
S(2B)	2067(2)	4364(4)	6033(2)
O(11B)	−1062(7)	3534(21)	5844(8)
O(12B)	75(8)	1623(18)	7663(7)
O(13B)	−49(9)	−580(17)	5966(8)
O(21B)	1213(9)	−749(16)	5282(8)
O(22B)	1232(8)	3191(18)	4274(6)
O(23B)	3194(7)	1483(17)	5542(7)
O(31B)	3538(6)	1993(16)	7064(7)
O(32B)	1688(8)	−1167(15)	6759(8)
O(33B)	1811(7)	2117(20)	8241(6)
C(11B)	−520(10)	3102(22)	6028(9)
C(12B)	201(7)	1849(21)	7186(8)
C(13B)	147(10)	480(22)	6126(9)
C(21B)	1345(10)	374(20)	5406(9)
C(22B)	1357(8)	2836(20)	4768(7)
C(23B)	2605(10)	1760(20)	5565(8)
C(31B)	2930(10)	1971(18)	6979(8)
C(32B)	1754(9)	−8(25)	6805(9)
C(33B)	1840(8)	2048(18)	7721(8)
C(101B)	1842(8)	4204(17)	6768(8)
C(102B)	589(9)	5920(18)	6333(9)
C(103B)	773(10)	5864(19)	5701(9)
C(104B)	1594(9)	5874(18)	5676(9)

Table 2

Bond lengths (pm) for $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ (**1**)

	Molecule A	Molecule B
Ru(1)–Ru(3)	280.7(3)	281.3(3)
Ru(2)–Ru(1)	304.7(4)	305.7(4)
Ru(2)–Ru(3)	281.8(3)	280.7(3)
Ru(1)–S(1)	240.1(5)	241.1(5)
Ru(2)–S(2)	241.0(5)	240.9(5)
Ru(3)–C(101)	223(2)	223(2)
Ru(1)–C(11)	199(2)	198(2)
Ru(1)–C(12)	189(2)	192(2)
Ru(1)–C(13)	194(2)	193(2)
Ru(2)–C(21)	191(2)	191(2)
Ru(2)–C(22)	194(2)	194(2)
Ru(2)–C(23)	196(2)	193(2)
Ru(3)–C(31)	195(2)	194(2)
Ru(3)–C(32)	196(2)	194(3)
Ru(3)–C(33)	189(2)	190(2)
S(1)–C(101)	182(2)	181(2)
S(2)–C(101)	174(2)	175(2)
S(1)–C(102)	183(2)	184(2)
S(2)–C(104)	185(2)	184(2)
C(102)–C(103)	150(3)	150(3)
C(103)–C(104)	153(3)	155(3)
O(11)–C(11)	111(2)	112(2)
O(12)–C(12)	117(3)	114(2)
O(13)–C(13)	115(3)	114(3)
O(21)–C(21)	115(2)	115(3)
O(22)–C(22)	116(2)	114(2)
O(23)–C(23)	111(3)	115(2)
O(31)–C(31)	112(2)	113(2)
O(32)–C(32)	113(3)	115(3)
O(33)–C(33)	118(2)	117(2)

other metal bonds (89.8–100.5°). In $[HRu_3(CO)_{11}]^-$ the axial carbonyls (mean Ru–Ru–C angle 118.7°) are more distorted than the equatorial carbonyls (mean Ru–Ru–C angle 107.5°). The ^1H NMR signal from the Ru(μ-H)Ru proton is at −14.9 ppm, which is not far from the corresponding resonances of $[HRu_3(CO)_{11}]^-$ derivatives.

The formation of the Ru(3)–C(101) bond causes distortion in the ligand coordination geometry at Ru(3). The Ru–Ru–C_{eq} angles are slightly opened (mean 99.3°) and the Ru–Ru–C(101) angle is smaller (78.9°) than the Ru–Ru–C_{ax} angle in the parent cluster (89.54°). Furthermore, the Ru–S bonds are bent towards Ru(3) with a mean Ru(3)–Ru-S angle of 71.5°. The Ru(3)–Ru–C_{ax} bonds of the carbonyls *trans* to the S atoms are slightly opened (mean 99.1°) compared with those in $Ru_3(CO)_{12}$.

Structure of $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3,5\text{-trithiacyclohexane})$ *(2)*

As indicated in Fig. 3, the 1,3,5-trithiacyclohexane ligand in **2** caps the ruthenium triangle as a tridentate six electron donor in eclipsed configuration, with each sulphur bound to one ruthenium atom. Atomic coordinates, bond lengths and selected bond angles are given in Tables 4–6. The structure of **2** closely resembles

Table 3

Selected bond angles (°) for $HRu_3(CO)_9(\mu_3\text{-}\eta^3\text{-1,3-dithiacyclohexane})$ (1)

	Molecule A	Molecule B
Ru(1)-Ru(2)-S(2)	89.6(1)	89.5(1)
Ru(3)-Ru(2)-S(2)	71.5(1)	71.6(1)
Ru(2)-Ru(1)-S(1)	89.5(1)	89.4(1)
Ru(3)-Ru(1)-S(1)	71.7(1)	71.3(1)
Ru(2)-Ru(3)-C(101)	78.0(5)	78.5(4)
Ru(1)-Ru(3)-C(101)	79.4(4)	79.5(4)
Ru(2)-Ru(1)-C(11)	117.9(6)	117.3(6)
Ru(2)-Ru(1)-C(12)	143.7(5)	142.9(4)
Ru(3)-Ru(1)-C(12)	87.5(5)	87.3(4)
Ru(2)-Ru(1)-C(13)	88.5(7)	88.7(6)
Ru(3)-Ru(1)-C(13)	97.9(6)	101.1(5)
Ru(1)-Ru(2)-C(21)	88.7(6)	88.1(6)
Ru(3)-Ru(2)-C(21)	99.7(6)	97.9(6)
Ru(1)-Ru(2)-C(22)	118.8(5)	116.5(5)
Ru(3)-Ru(2)-C(23)	85.0(6)	89.7(5)
Ru(2)-Ru(3)-C(31)	98.2(5)	98.2(5)
Ru(2)-Ru(3)-C(32)	92.2(5)	90.9(6)
Ru(1)-Ru(3)-C(32)	90.0(5)	89.6(5)
Ru(1)-Ru(3)-C(33)	100.5(6)	100.4(4)
S(1)-Ru(1)-C(11)	96.1(5)	94.1(6)
S(1)-Ru(1)-C(12)	87.2(6)	87.9(6)
S(1)-Ru(1)-C(13)	168.8(6)	171.9(5)
S(2)-Ru(2)-C(21)	170.4(5)	168.7(6)
S(2)-Ru(2)-C(22)	95.3(5)	97.4(6)
S(2)-Ru(2)-C(23)	88.3(7)	86.5(6)
Ru(1)-S(1)-C(101)	99.6(6)	99.8(6)
Ru(1)-S(1)-C(102)	113.2(6)	113.0(6)
Ru(2)-S(2)-C(101)	99.8(6)	99.9(6)
Ru(2)-S(2)-C(104)	113.2(5)	114.5(6)
C(31)-Ru(3)-C(101)	89.6(7)	91.1(7)
C(32)-Ru(3)-C(101)	167.8(6)	167.1(7)
C(33)-Ru(3)-C(101)	93.8(8)	92.7(7)
C(101)-S(1)-C(102)	106.7(9)	106.4(8)
C(101)-S(2)-C(104)	108.1(8)	107.7(9)
Ru(1)-C(11)-O(11)	175(2)	177(2)
Ru(1)-C(12)-O(12)	177(2)	178(2)
Ru(1)-C(13)-O(13)	176(2)	176(2)
Ru(2)-C(21)-O(21)	175(2)	177(2)
Ru(2)-C(22)-O(22)	180(2)	178(2)
Ru(2)-C(23)-O(23)	178(2)	180(2)
Ru(3)-C(31)-O(31)	178(2)	177(2)
Ru(3)-C(32)-O(32)	179(2)	179(2)
Ru(3)-C(33)-O(33)	179(2)	180(2)
Ru(3)-C(101)-S(1)	98.0(8)	98.1(7)
Ru(3)-C(101)-S(2)	100.7(8)	100.2(8)
S(1)-C(101)-S(2)	115.0(9)	115.1(9)
S(1)-C(102)-C(103)	116(1)	115(1)
C(102)-C(103)-C(104)	115(2)	114(1)
S(2)-C(104)-C(103)	115(1)	113(1)

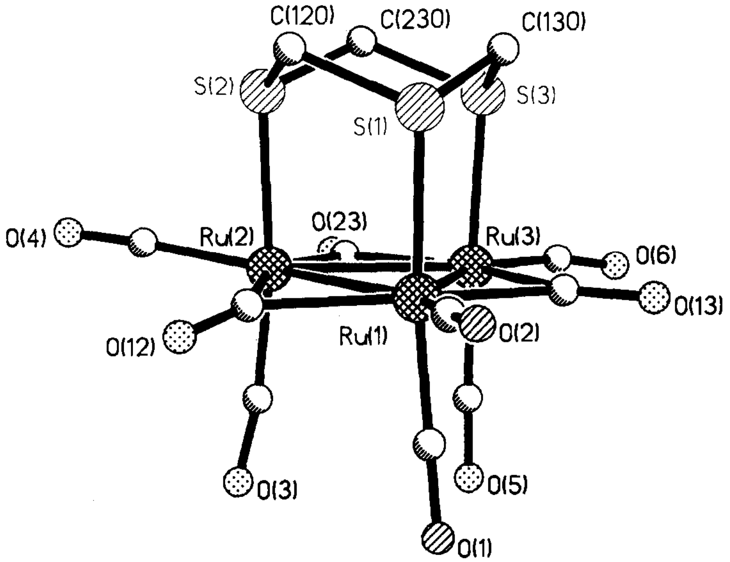

Fig. 3. Structure and numbering scheme for $Ru_3(CO)_9(\mu_3-\eta^3$-1,3,5-trithiacyclohexane) (2).

Table 4

Atomic coordinates ($\times 10^4$) for $Ru_3(CO)_9(\mu_3-\eta^3$-1,3,5-trithiacyclohexane) (2)

Atom	*x*	*y*	*z*
Ru(1)	8014(1)	428(1)	314
Ru(2)	6074(1)	−448(1)	−501(1)
Ru(3)	7715(1)	1(1)	−2124(1)
S(1)	7342(2)	2202(2)	155(3)
S(2)	5296(2)	1273(2)	−746(3)
S(3)	7060(2)	1752(2)	−2494(3)
O(1)	9213(8)	−1570(8)	761(10)
O(2)	9283(12)	1301(11)	2370(11)
O(3)	6648(9)	−2718(7)	−62(12)
O(4)	3800(7)	−1063(8)	−63(10)
O(5)	8567(9)	−2211(8)	−1978(10)
O(6)	8542(11)	−94(9)	−4622(12)
O(12)	6426(8)	−319(8)	2222(9)
O(13)	9845(7)	917(7)	−1390(9)
O(23)	5709(8)	−1065(7)	−3122(10)
C(1)	8724(9)	−823(9)	594(11)
C(2)	8797(10)	974(11)	1621(13)
C(3)	6477(10)	−1855(11)	−240(12)
C(4)	4645(9)	−827(9)	−225(10)
C(5)	8262(9)	−1354(9)	−1998(11)
C(6)	8199(10)	−11(9)	−3687(13)
C(12)	6653(10)	−115(9)	1264(13)
C(13)	9018(9)	633(10)	−1188(13)
C(23)	6194(9)	−678(9)	−2350(11)
C(120)	5928(8)	2189(9)	227(11)
C(130)	7493(9)	2643(9)	−1338(12)
C(230)	5677(8)	1780(8)	−2175(11)

Table 5

Bond lengths (pm) for $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3,5\text{-trithiacyclohexane})$ (2)

Ru(1)–Ru(2)	287.1(2)	Ru(1)–Ru(3)	282.8(2)
Ru(2)–Ru(3)	284.2(2)	Ru(1)–S(1)	242.7(3)
Ru(2)–S(2)	242.4(3)	Ru(3)–S(3)	242.0(3)
Ru(1)–C(12)	216(1)	Ru(1)–C(13)	214(1)
Ru(2)–C(12)	217(1)	Ru(2)–C(23)	211(1)
Ru(3)–C(13)	213(1)	Ru(3)–C(23)	214(1)
Ru(1)–C(1)	186(1)	Ru(1)–C(2)	191(1)
Ru(2)–C(3)	189(1)	Ru(2)–C(4)	191(1)
Ru(3)–C(5)	187(1)	Ru(3)–C(6)	187(1)
S(1)–C(120)	181(1)	S(1)–C(130)	179(1)
S(2)–C(120)	180(1)	S(2)–C(230)	180(1)
S(3)–C(130)	182(1)	S(3)–C(230)	180(1)
O(12)–C(12)	115(2)	O(13)–C(13)	114(2)
O(23)–C(23)	118(2)	O(1)–C(1)	115(2)
O(2)–C(2)	113(2)	O(3)–C(3)	114(2)
O(4)–C(4)	114(2)	O(5)–C(5)	116(2)
O(6)–C(6)	115(2)		

Table 6

Bond angles (°) for $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3,5\text{-trithiacyclohexane})$ (2)

Ru(1)–Ru(3)–S(3)	92.1(1)	Ru(2)–Ru(3)–S(3)	92.4(1)
Ru(1)–Ru(2)–S(2)	92.2(1)	Ru(2)–Ru(1)–S(1)	91.9(1)
Ru(3)–Ru(2)–S(2)	92.7(1)	Ru(3)–Ru(1)–S(1)	93.4(1)
Ru(2)–Ru(3)–C(23)	47.6(3)	Ru(3)–Ru(2)–C(12)	107.5(3)
Ru(2)–Ru(1)–C(12)	48.5(4)	Ru(3)–Ru(1)–C(12)	108.2(4)
Ru(1)–Ru(2)–C(12)	48.3(3)	Ru(2)–Ru(1)–C(13)	108.1(3)
Ru(3)–Ru(1)–C(13)	48.3(3)	Ru(2)–Ru(3)–C(13)	109.6(4)
Ru(1)–Ru(3)–C(13)	48.7(4)	Ru(1)–Ru(2)–C(23)	107.9(3)
Ru(3)–Ru(2)–C(23)	48.6(3)	Ru(2)–Ru(1)–C(1)	98.2(4)
Ru(3)–Ru(1)–C(1)	93.8(4)	Ru(1)–Ru(2)–C(3)	94.8(4)
Ru(3)–Ru(2)–C(3)	95.2(4)	Ru(1)–Ru(3)–C(5)	93.1(4)
Ru(2)–Ru(3)–C(5)	92.4(4)	S(1)–Ru(1)–C(1)	169.6(4)
S(2)–Ru(2)–C(3)	171.4(4)	S(3)–Ru(3)–C(5)	174.2(4)
S(1)–Ru(1)–C(2)	84.4(4)	S(2)–Ru(2)–C(4)	81.7(4)
S(3)–Ru(3)–C(6)	87.7(4)	S(1)–Ru(1)–C(12)	92.9(3)
S(2)–Ru(2)–C(12)	93.8(3)	S(1)–Ru(1)–C(13)	92.2(3)
S(3)–Ru(3)–C(13)	90.4(4)	S(2)–Ru(2)–C(23)	92.5(3)
S(3)–Ru(3)–C(23)	92.2(3)	Ru(1)–S(1)–C(120)	109.9(4)
Ru(1)–S(1)–C(130)	109.0(4)	C(120)–S(1)–C(130)	98.8(5)
Ru(2)–S(2)–C(120)	109.6(4)	Ru(2)–S(2)–C(230)	108.4(4)
C(120)–S(2)–C(230)	101.0(5)	Ru(3)–S(3)–C(130)	110.4(4)
Ru(3)–S(3)–C(230)	108.9(4)	C(130)–S(3)–C(230)	98.2(5)
Ru(1)–C(1)–O(1)	176(1)	Ru(1)–C(2)–O(2)	178(1)
Ru(2)–C(3)–O(3)	175(1)	Ru(2)–C(4)–O(4)	179(1)
Ru(3)–C(5)–O(5)	176(1)	Ru(3)–C(6)–O(6)	174(1)
Ru(1)–C(12)–O(12)	138(1)	Ru(2)–C(12)–O(12)	137(1)
Ru(1)–C(13)–O(13)	139(1)	Ru(3)–C(13)–O(13)	138(1)
Ru(2)–C(23)–O(23)	139(1)	Ru(3)–C(23)–O(23)	137(1)
S(1)–C(120)–S(2)	115.3(6)	S(1)–C(130)–S(3)	116.5(6)
S(2)–C(230)–S(3)	115.8(6)		

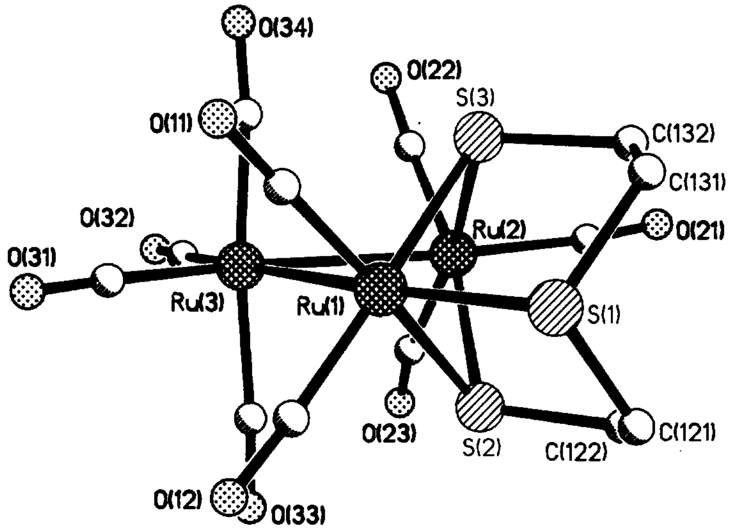

Fig. 4. Structure and numbering scheme for $Ru_3(CO)_9(\mu_2\text{-}\eta^3\text{-}1,4,7\text{-trithiaheptane})$ (3).

those of $Ru_3(CO)_9(MeSi(PR_2)_3)$ (R = Bu, Et, Pr) [15,16] and $Ru_3(CO)_9(HC(PPh_2)(PhPC_6H_4PPh))$ [12]. The ligand is practically parallel with the metal triangle and is bound in an endodental position. The Ru–Ru–S bond angles are 92.5° and the Ru–Ru–C_{ax} bond angles are 94.6°, close to the Ru–Ru–C_{ax} angles in $Ru_3(CO)_{12}$ (mean 89.54°) and the Ru–Ru–P angles in $Ru_3(CO)_9\text{-}(MeSi(PR_2)_3)$ (96.52°) indicating that the ligand geometry fits the Ru_3 triangle very well. The mean Ru–S bond length is 242.4 pm and the mean S–C bond length 180 pm. Typical values for Ru–SR_2 groups where R is a C(sp^3) centred group are 230 pm for Ru–S and 182 pm for S–C bonds [23]. The average Ru–Ru bond length in **2** is 284.7 pm. Symmetric μ_2-CO bridges are formed in the metal plane, the remaining six carbonyls are terminal, one axial and one equatorial on each metal.

Structure of $Ru_3(CO)_9(\mu_2\text{-}\eta^3\text{-}1,4,7\text{-trithiaheptane})$ (3)

The structure of **3** is presented in Fig. 4. Atomic coordinates, bond lengths and relevant bond angles are given in Tables 7–9.

The overall carbonyl geometry of **3** is very similar to that of $[HRu_3(CO)_{11}]^-$. A CH_2CH_2 fragment is lost from the ligand and a 1,4,7-trithiaheptane becomes bound to the cluster. The bridging sulphur atoms occupy the sites corresponding to the μ_2-CO and μ_2-H ligands of $[HRu_3(CO)_{11}]^-$ anion. The Ru(1)–Ru(2) bond is significantly longer (323.8 pm) than a normal Ru–Ru bond. With three electrons from the bridging sulphurs and the two electrons from the terminal sulphur, the total electron number of the cluster is 50, suggesting that the Ru(1)–Ru(2) bond is broken; typically the total valence electron number of a closed trinuclear cluster is 48. The remaining Ru–Ru bonds are shorter (mean 286.4 pm). The lengths of the Ru–S bonds for the bridging sulphurs are 244.9 pm (mean), and those for the terminally-bound sulphur 239 pm. For comparison, in $[Ru(1,4,7\text{-trithiacyclononane})_2]^{2+}$ the average Ru–S bond length is 233.2 pm. The average S–C and C–C bond lengths in **3** (184 and 151 pm, respectively) are very similar to those in

Table 7

Atomic coordinates ($\times 10^3$) for $Ru_3(CO)_9(\mu_2$-η^3-1,4,7-trithiaheptane) (3)

Atom	*x*	*y*	*z*
Ru(1)	156.9(2)	363.6(2)	705.0(1)
Ru(2)	185.9(2)	437.4(2)	551.4(1)
Ru(3)	78.2(2)	232.1(2)	534.6(1)
S(1)	239.4(6)	504.7(5)	834.6(4)
S(2)	322.2(5)	451.9(5)	667.4(4)
S(3)	82.0(6)	458.7(5)	652.5(4)
O(11)	−590(2)	238(2)	728(1)
O(12)	244(2)	232(2)	751(2)
O(21)	280(3)	650(2)	554(1)
O(22)	−16(2)	379(2)	416(1)
O(23)	320(3)	381(3)	440(2)
O(31)	−10(3)	54(2)	586(2)
O(32)	21(3)	130(2)	343(1)
O(33)	306(2)	231(2)	557(2)
O(34)	−140(2)	243(2)	524(2)
C(121)	380(3)	574(2)	836(2)
C(122)	399(2)	576(2)	752(2)
C(131)	178(2)	587(2)	821(2)
C(132)	158(3)	589(2)	738(2)
C(11)	23(2)	286(2)	721(2)
C(12)	214(3)	285(2)	734(2)
C(21)	251(3)	574(3)	559(2)
C(22)	63(2)	400(2)	466(2)
C(23)	265(4)	392(3)	476(2)
C(31)	20(3)	118(2)	569(2)
C(32)	42(3)	166(2)	413(2)
C(33)	223(3)	235(2)	549(1)
C(34)	−56(3)	245(3)	530(2)
Ru(1B)	202.7(2)	388.4(2)	212.5(1)
Ru(2B)	231.5(2)	455.3(2)	56.1(1)
Ru(3B)	115.8(2)	251.6(2)	43.4(1)
S(1B)	287.2(6)	530.9(5)	340.7(4)
S(2B)	367.1(5)	471.2(5)	172.1(4)
S(3B)	131.0(5)	484.4(5)	158.8(4)
O(11B)	−7(2)	272(2)	246(2)
O(12B)	285(3)	253(2)	257(2)
O(21B)	355(2)	662(2)	52(2)
O(22B)	33(2)	408(2)	−79(2)
O(23B)	346(3)	378(2)	−64(2)
O(31B)	1(3)	74(2)	92(1)
O(32B)	48(3)	143(2)	−145(2)
O(33B)	337(2)	245(2)	66(1)
O(34B)	−92(2)	284(2)	34(2)
C(121B)	426(2)	602(2)	336(2)
C(122B)	444(2)	598(2)	253(1)
C(131B)	226(2)	612(2)	327(1)
C(132B)	208(3)	613(2)	240(2)
C(11B)	78(4)	319(2)	231(2)
C(12B)	256(2)	306(2)	242(2)
C(21B)	313(3)	593(2)	61(2)
C(22B)	104(3)	421(3)	−33(2)
C(23B)	304(4)	404(3)	−21(2)

Table 7 (continued)

Atom	x	y	z
C(31B)	49(3)	141(3)	75(2)
C(32B)	77(3)	184(3)	−75(2)
C(33B)	260(2)	251(2)	59(2)
C(34B)	−15(3)	274(2)	40(2)
Ru(1C)	497.1(2)	999.0(2)	152.1(1)
Ru(2C)	515.0(2)	1008.1(2)	343.4(1)
Ru(3C)	342.9(2)	1018.2(2)	238.7(1)
S(1C)	644.7(6)	976.9(6)	108.5(5)
S(2C)	634.0(6)	1120.7(5)	284.8(4)
S(3C)	480.6(5)	875.3(5)	212.4(4)
O(11C)	316(2)	852(2)	−9(1)
O(12C)	517(2)	1174(2)	103(1)
O(21C)	697(2)	987(2)	448(2)
O(22C)	323(2)	862(2)	381(2)
O(23C)	534(2)	1184(2)	487(1)
O(31C)	210(3)	1028(3)	88(2)
O(32C)	213(3)	1044(3)	366(2)
O(33C)	208(2)	788(2)	157(1)
O(34C)	493(2)	1246(2)	317(2)
C(121C)	768(3)	1077(3)	188(2)
C(122C)	755(3)	1106(2)	277(2)
C(131C)	641(3)	869(3)	130(2)
C(132C)	607(4)	857(3)	205(2)
C(11C)	379(3)	901(3)	51(2)
C(12C)	503(3)	1105(2)	121(2)
C(21C)	628(3)	996(2)	410(2)
C(22C)	397(2)	917(2)	366(2)
C(23C)	528(3)	1117(2)	432(2)
C(31C)	257(2)	1026(2)	147(2)
C(32C)	265(4)	1036(4)	324(3)
C(33C)	261(2)	876(3)	188(2)
C(34C)	444(3)	1160(3)	287(2)

[Ru(1,4,7-trithiacyclononane)$_2$]$^{2+}$ (182.4 and 151.3 pm) and in the free ligand (182.2 and 151.0 pm). The conformation of the ligand in **3** is in good agreement with that of the ligands in the stable compounds [RuL$_2$]$^{2+}$ although a CH_2CH_2 fragment is missing. The C–S–C and C–C–S bond angles in the free ligand, 102.8 and 115.0° respectively, are similar to those in **3** (101 and 114°). The Ru–C bond lengths lie in a narrow range; Ru(1), which is bound to all the three sulphurs, has shorter Ru–C bonds (mean 187 pm) than those between the other Ru atoms and the carbonyl groups (194 pm).

Reactions with hydrogen and carbon monoxide

The reaction of **1** with CO was studied at four different temperatures in the range 21–69°C, with CH_2Cl_2, THF and hexane as solvents. The IR spectrum and the absence of any change in the colour of the solutions, indicated that no reaction occurred.

When **1** was exposed to H_2 (1 atm) in chloroform ($CDCl_3$) at 61°C the yellow colour of the solution remained unchanged but two new metal hydride signals

Table 8

Bond lengths (pm) for $Ru_3(CO)_9(\mu_2\text{-}\eta^3\text{-}1,4,7\text{-trithiaheptane})$ (3)

	Molecule A	Molecule B	Molecule C
Ru(1)–Ru(3)	284.4(4)	284.5(4)	283.7(4)
Ru(1)–S(1)	239.4(6)	239.0(6)	239(1)
Ru(1)–S(2)	244.5(8)	243.9(8)	243.9(6)
Ru(1)–S(3)	245(1)	244(1)	243.2(9)
Ru(1)–C(11)	187(3)	177(5)	195(2)
Ru(1)–C(12)	188(4)	189(4)	188(4)
Ru(2)–Ru(3)	288.5(4)	289.2(4)	288.1(5)
Ru(2)–S(2)	245.8(8)	244.2(8)	247.0(8)
Ru(2)–S(3)	245.6(9)	246.5(8)	245.0(7)
Ru(2)–C(21)	194(4)	198(4)	188(3)
Ru(2)–C(22)	186(3)	195(4)	187(3)
Ru(2)–C(23)	198(5)	197(5)	192(4)
Ru(3)–C(31)	196(4)	191(4)	194(4)
Ru(3)–C(32)	197(4)	194(4)	197(6)
Ru(3)–C(33)	196(5)	197(4)	192(4)
Ru(3)–C(34)	194(4)	198(4)	192(3)
S(1)–C(121)	179(3)	182(3)	180(2)
S(1)–C(131)	187(4)	186(4)	184(5)
S(2)–C(122)	184(3)	184(2)	180(4)
S(3)–C(132)	190(3)	186(3)	190(6)
O(11)–C(11)	113(4)	121(5)	108(3)
O(12)–C(12)	116(6)	114(6)	118(5)
O(21)–C(21)	114(5)	110(5)	117(4)
O(22)–C(22)	116(4)	109(5)	117(4)
O(23)–C(23)	110(6)	110(6)	117(6)
O(31)–C(31)	108(5)	116(5)	155(6)
O(32)–C(32)	113(4)	113(4)	111(7)
O(33)–C(33)	116(6)	110(5)	118(4)
O(34)–C(34)	114(5)	113(5)	116(5)
C(121)–C(122)	154(5)	149(4)	156(5)
C(131)–C(132)	146(5)	151(4)	148(6)

appeared at −14.2 and −22.2 ppm in the ^1H NMR spectrum in addition to signal of **1** at −14.9 ppm. Isolation of the products by thin layer or column chromatography gave as the major product the cluster $(\mu_2\text{-H})_2Ru_3(CO)_8Cl(\mu_3\text{-}\eta^3\text{-}1,3\text{-}[S_2CH(CH_2)_3])$ (**4**), which was characterized by its IR and ^1H NMR spectra, elemental analysis, and an X-ray-diffraction study (Tables 10–12.). The structure of **4**, shown in Figure 5, is similar to that of **1** except that one carbonyl has been replaced by a chlorine and the Ru(1)–Ru(3) metal bond is bridged by a hydride ligand. Compound **4** can be formally regarded as a product of an oxidative addition of HCl to **1**. We suggest that the cluster **4** is formed in a reaction between $CHCl_3$ and a cluster hydride derived from **1**. In the presence of H_2, compound **1** presumably forms an unstable hydride, which in the presence of $CHCl_3$ acts as a hydrogen-atom donor to give the corresponding metal chloride **4** and CH_2Cl_2. This mechanism of formation of **4** is supported by the observation that a similar reaction of **1** with H_2 in CCl_4 gives compound **4**. The latter reaction, which is analogous to those of tin hydrides, has been used to confirm the presence of a metal hydride group in unstable metal hydrides [24].

Table 9

Bond angles (°) for $Ru_3(CO)_9(\mu_2\text{-}\eta^3\text{-}1,4,7\text{-trithiaheptane})$ (3)

	Molecule A	Molecule B	Molecule C
Ru(3)–Ru(1)–S(1)	166.1(2)	167.0(2)	165.9(3)
Ru(3)–Ru(1)–S(2)	83.9(2)	84.9(2)	84.0(2)
S(1)–Ru(1)–S(2)	85.6(2)	86.3(2)	87.0(3)
Ru(3)–Ru(1)–S(3)	84.2(2)	84.3(2)	82.0(2)
S(1)–Ru(1)–S(3)	85.9(3)	85.7(3)	86.6(3)
S(2)–Ru(1)–S(3)	86.1(3)	86.0(3)	85.9(3)
Ru(3)–Ru(1)–C(11)	89.3(8)	89.2(8)	92(1)
S(1)–Ru(1)–C(11)	101.0(8)	99.6(8)	97(1)
S(3)–Ru(1)–C(11)	93(1)	94(2)	93(1)
Ru(3)–Ru(1)–C(12)	90.3(8)	89.6(8)	89(1)
S(1)–Ru(1)–C(12)	99.2(8)	100.3(7)	101(1)
S(2)–Ru(1)–C(12)	91(1)	92(1)	88.9(7)
Ru(3)–Ru(2)–S(2)	82.8(2)	83.9(2)	82.5(2)
Ru(3)–Ru(2)–S(3)	83.2(2)	82.9(2)	80.8(2)
S(2)–Ru(2)–S(3)	85.6(3)	85.5(3)	84.8(2)
S(2)–Ru(2)–C(21)	100(1)	96(1)	98(1)
S(3)–Ru(2)–C(21)	96(1)	99(1)	97(1)
Ru(3)–Ru(2)–C(22)	85.0(9)	86(1)	84(1)
S(2)–Ru(2)–C(22)	167(1)	169(1)	166(1)
S(3)–Ru(2)–C(22)	89(1)	90(1)	89.4(9)
Ru(3)–Ru(2)–C(23)	84(1)	85(1)	89(1)
S(2)–Ru(2)–C(23)	88(1)	89(1)	91(1)
S(3)–Ru(2)–C(23)	166(1)	167(1)	170(1)
Ru(1)–Ru(3)–C(31)	89.4(8)	92.1(9)	93(1)
Ru(2)–Ru(3)–C(32)	100(1)	100(1)	95(2)
Ru(1)–Ru(3)–C(33)	87.3(7)	85.8(8)	86(1)
Ru(2)–Ru(3)–C(33)	88(1)	88(1)	91(1)
Ru(1)–Ru(3)–C(34)	87(1)	86.9(7)	86(1)
Ru(2)–Ru(3)–C(34)	87(1)	85(1)	83(1)
Ru(1)–S(1)–C(121)	105.3(9)	104(1)	104(1)
Ru(1)–S(1)–C(131)	105.3(8)	105.2(7)	105(1)
C(121)–S(1)–C(131)	103(2)	100(2)	101(2)
Ru(1)–S(2)–Ru(2)	82.7(2)	82.7(2)	83.7(2)
Ru(1)–S(2)–C(122)	106(1)	105.3(9)	103.5(9)
Ru(2)–S(2)–C(122)	115(1)	113(1)	112(1)
Ru(1)–S(3)–Ru(2)	82.7(3)	82.2(3)	84.3(3)
Ru(1)–S(3)–C(132)	104(1)	105(1)	104(2)
Ru(2)–S(3)–C(132)	111(1)	112(1)	112(1)
S(1)–C(121)–C(122)	117(2)	119(2)	115(2)
S(2)–C(122)–C(121)	112(2)	112(2)	114(3)
S(1)–C(131)–C(132)	115(3)	113(2)	117(3)
S(3)–C(132)–C(131)	112(2)	112(2)	112(4)
Ru(1)–C(11)–O(11)	178(3)	178(4)	175(4)
Ru(1)–C(12)–O(12)	177(2)	178(2)	174(3)
Ru(2)–C(21)–O(21)	171(2)	170(3)	178(3)
Ru(2)–C(22)–O(22)	176(3)	174(4)	178(3)
Ru(2)–C(23)–O(23)	170(3)	178(4)	179(2)
Ru(3)–C(31)–O(31)	177(4)	175(4)	175(4)
Ru(3)–C(32)–O(32)	178(4)	173(4)	173(3)
Ru(3)–C(33)–O(33)	176(3)	176(3)	178(3)
Ru(3)–C(34)–O(34)	173(3)	177(2)	171(4)

Table 10

Atomic coordinates ($\times 10^4$) for $(\mu_2\text{-H})_2\text{Ru}_3(\text{CO})_8\text{Cl}(\mu_3\text{-}\eta^3\text{-1,3-}[\text{S}_2\text{CH}(\text{CH}_2)_3])$ (**4**)

Atom	*x*	*y*	*z*
Ru(1)	2927(2)	5020(1)	8755(1)
Ru(2)	3440(2)	7023(1)	7425(1)
Ru(3)	2210(2)	7197(1)	8888(1)
Cl(1)	3003(7)	3611(5)	8093(4)
S(1)	421(6)	5429(4)	8654(3)
S(2)	917(6)	7336(4)	7332(3)
O(12)	2289(17)	3539(14)	10277(11)
O(13)	6054(19)	4635(13)	9059(11)
O(21)	6471(19)	6785(13)	7910(12)
O(22)	4246(22)	6369(17)	5906(12)
O(23)	3817(20)	9332(13)	6786(12)
O(31)	1414(20)	9494(12)	8278(11)
O(32)	4970(19)	7667(17)	9483(11)
O(33)	498(21)	7035(16)	10483(11)
C(12)	2516(25)	4101(18)	9688(14)
C(13)	4862(27)	4780(16)	8911(15)
C(21)	5324(28)	6835(16)	7741(17)
C(22)	3907(29)	6627(19)	6473(16)
C(23)	3603(26)	8452(19)	7030(15)
C(31)	1678(24)	8649(20)	8484(14)
C(32)	3939(30)	7510(25)	9279(17)
C(33)	1153(29)	7048(18)	9901(14)
C(101)	447(22)	6815(14)	8305(11)
C(102)	−319(25)	4976(17)	7870(13)
C(103)	330(25)	5395(18)	7075(13)
C(104)	127(22)	6592(15)	6748(11)
H(101)	−502	7081	8401
H(10A)	−1307	5192	7863
H(10B)	−210	4232	7992
H(10C)	1331	5232	7095
H(10D)	−42	5059	6718
H(10E)	516	6785	6218
H(10F)	−874	6763	6762
Ru(1B)	2501(2)	9070(1)	4060(1)
Ru(2B)	2865(2)	6866(1)	3689(1)
Ru(3B)	3127(2)	8720(1)	2489(1)
Cl(2)	8722(8)	11201(5)	4616(5)
S(1B)	371(6)	9388(4)	3367(3)
S(2B)	719(6)	7257(4)	3020(3)
O(12B)	5330(22)	8752(15)	4808(13)
O(13B)	2586(22)	11411(14)	3824(15)
O(21B)	5865(21)	6623(19)	4233(13)
O(22B)	1727(30)	5440(20)	5001(17)
O(23B)	3672(22)	5297(19)	2713(15)
O(31B)	3190(23)	7693(20)	1125(13)
O(32B)	6376(18)	8669(13)	2456(11)
O(33B)	2647(29)	10952(16)	1536(16)
C(12B)	4248(30)	8840(16)	4533(17)
C(13B)	2508(26)	10529(20)	3906(17)
C(21B)	4721(31)	6729(21)	4072(19)
C(22B)	2154(43)	5806(27)	4629(22)

Table 10 (continued)

Atom	*x*	*y*	*z*
C(23B)	3411(25)	5931(19)	3059(16)
C(31B)	3177(28)	8055(21)	1635(17)
C(32B)	5171(26)	8639(17)	2457(15)
C(33B)	2853(32)	10099(24)	1881(19)
C(201)	849(22)	8633(14)	2686(11)
C(202)	11185(23)	1148(17)	6002(15)
C(203)	11056(23)	2339(16)	5671(14)
C(204)	10905(22)	2977(15)	6291(13)
H(201)	239	8894	2265
H(20A)	10414	706	6053
H(20B)	12065	739	6013
H(20C)	10231	2502	5373
H(20D)	11882	2535	5333
H(20E)	11675	3318	6418
H(20F)	10024	3285	6459

Table 11

Bond lengths (pm) for $(\mu_2\text{-H})_2Ru_3(CO)_8Cl(\mu_3\text{-}\eta^3\text{-}1,3\text{-}[S_2CH(CH_2)_3])$ (4)

	Molecule A	Molecule B
Ru(1)-Ru(2)	313.3(3)	314.8(3)
Ru(1)-Ru(3)	298.7(3)	293.4(3)
Ru(2)-Ru(3)	280.5(3)	284.6(3)
Ru(1)-Cl(1)	243.6(7)	248.4(8)
Ru(1)-S(1)	241.0(6)	240.4(6)
Ru(2)-S(2)	241.3(6)	239.6(6)
Ru(3)-C(101)	219(2)	217(2)
Ru(1)-C(12)	183(2)	190(3)
Ru(1)-C(13)	187(3)	189(3)
Ru(2)-C(21)	190(3)	192(3)
Ru(2)-C(22)	189(3)	201(3)
Ru(2)-C(23)	188(2)	188(3)
Ru(3)-C(31)	193(2)	192(3)
Ru(3)-C(32)	194(3)	193(3)
Ru(3)-C(33)	195(3)	190(3)
S(1)-C(101)	180(2)	176(2)
S(1)-C(102)	185(3)	186(2)
S(2)-C(101)	172(2)	179(2)
S(2)-C(104)	183(2)	188(2)
O(12)-C(12)	114(3)	116(3)
O(13)-C(13)	117(3)	116(4)
O(21)-C(21)	115(3)	113(4)
O(22)-C(22)	115(4)	82(4)
O(23)-C(23)	117(3)	116(4)
O(31)-C(31)	111(3)	112(4)
O(32)-C(32)	112(4)	115(3)
O(33)-C(33)	116(3)	116(4)
C(102)-C(103)	148(3)	155(3)
C(103)-C(104)	156(3)	153(4)

Table 12

Bond angles (°) for $(\mu_2\text{-H})_2\text{Ru}_3(\text{CO})_8\text{Cl}(\mu_3\text{-}\eta^3\text{-1,3-[S}_2\text{CH(CH}_2)_3])$ (**4**)

	Molecule A	Molecule B
Ru(1)-Ru(2)-S(2)	89.5(1)	89.0(2)
Ru(3)-Ru(2)-S(2)	71.3(2)	70.9(1)
Ru(2)-Ru(1)-S(1)	88.2(1)	88.3(2)
Ru(3)-Ru(1)-S(1)	70.1(2)	70.7(2)
Ru(2)-Ru(3)-C(101)	76.5(5)	77.4(4)
Ru(1)-Ru(3)-C(101)	75.2(5)	75.5(6)
Ru(2)-Ru(1)-C(12)	164.8(8)	159.7(9)
Ru(3)-Ru(1)-C(12)	110.5(8)	104.2(9)
Ru(2)-Ru(1)-C(13)	92.0(6)	90.8(8)
Ru(3)-Ru(1)-C(13)	105.4(7)	105.5(9)
Ru(1)-Ru(2)-C(21)	84.8(7)	87.7(9)
Ru(3)-Ru(2)-C(21)	95.0(9)	99.4(8)
Ru(1)-Ru(2)-C(22)	108.6(7)	109.0(12)
Ru(3)-Ru(2)-C(23)	94.9(8)	96.9(7)
Ru(2)-Ru(3)-C(31)	91.6(7)	95.5(8)
Ru(2)-Ru(3)-C(32)	95.6(9)	94.2(6)
Ru(1)-Ru(3)-C(32)	101.0(10)	99.4(8)
Ru(1)-Ru(3)-C(33)	104.4(7)	99.8(11)
Cl(1)-Ru(1)-S(1)	94.7(2)	95.4(2)
S(1)-Ru(1)-C(12)	88.1(7)	86.6(8)
S(1)-Ru(1)-C(13)	174.2(8)	175.8(9)
S(2)-Ru(2)-C(21)	166.2(9)	169.9(8)
S(2)-Ru(2)-C(22)	99.1(9)	98.5(12)
S(2)-Ru(2)-C(23)	87.9(8)	87.7(8)
Ru(1)-S(1)-C(101)	98.8(7)	98.6(7)
Ru(1)-S(1)-C(102)	113.7(7)	112.1(8)
Ru(2)-S(2)-C(101)	96.8(7)	97.9(7)
Ru(2)-S(2)-C(104)	114.9(7)	112.5(7)
C(31)-Ru(3)-C(101)	88.7(9)	92.0(10)
C(32)-Ru(3)-C(101)	172.0(10)	171.4(8)
C(33)-Ru(3)-C(101)	94.4(10)	89.6(10)
C(101)-S(1)-C(102)	105.4(10)	109.4(11)
C(101)-S(2)-C(104)	108.1(10)	107.7(9)
Ru(1)-C(12)-O(12)	178(3)	177(2)
Ru(1)-C(13)-O(13)	176(2)	176(3)
Ru(2)-C(21)-O(21)	176(2)	173(3)
Ru(2)-C(22)-O(22)	177(2)	169(4)
Ru(2)-C(23)-O(23)	175(2)	174(2)
Ru(3)-C(31)-O(31)	177(3)	178(2)
Ru(3)-C(32)-O(32)	177(2)	174(2)
Ru(3)-C(33)-O(33)	175(2)	172(3)
Ru(3)-C(101)-S(1)	103.2(9)	104.4(11)
Ru(3)-C(101)-S(2)	102.1(10)	100.6(9)
S(1)-C(101)-S(2)	119.1(12)	117.4(10)
S(1)-C(102)-C(103)	115(2)	114(2)
C(102)-C(103)-C(104)	116(2)	115(2)
S(2)-C(104)-C(103)	113(2)	115(2)

The location of the second metal hydride ligand was based on the lengthening of the Ru(1)-Ru(3) distance from 281 pm in **1** to 296 pm in **4**. The bending of the metal carbonyls away from the Ru(1)-Ru(2) bond supports the assignment of the Ru(1)-Ru(3) distance to the hydride-bridged Ru-Ru bond. The Ru-Ru distance

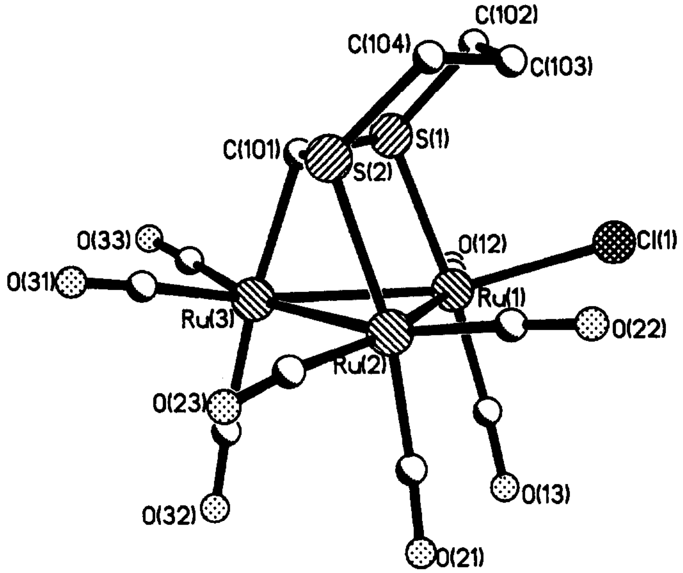

Fig. 5. Structure and numbering scheme for $H_2Ru_3(CO)_8Cl(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})$ (4).

of the other hydride-bridged metal–metal bond (Ru(1)–Ru(2)) is elongated from 305 pm in **1** to 314 pm in **4**.

The chlorine atom in **4** is bonded to one of the sulphur-coordinated ruthenium atoms with a mean ruthenium–chlorine distance of 246 pm. The presence of chlorine in **4** was also inferred from the elemental analysis of **4**. The chloride ligand in **4** distorts the C_s symmetry shown by the starting cluster **1**. This effect is clearly seen in the ^1H NMR spectrum of **4**, in which the $(CH_2)_3$ part of the 1,3-dithiacyclo-hexane ligand shows up as a complex pattern (AA'BB'CC') of resonances. The hydride resonance of the hydride-bridged Ru(1)–Ru(2) is shifted downfield from -14.9 in **1** to -14.2 ppm in **4**. The ^1H signal of the new hydride ligand lies at -22.2 ppm, well upfield from the original hydride resonance.

Prolonged heating of **1** in hexane under H_2 at higher temperatures gave different products from those formed in chloroform. A brownish solution was finally obtained, which is a complex mixture of unchanged **1**, an unsaturated organic compound, and a brown material soluble only in more polar solvents such as acetone.

The reactivity of **1** towards H_2 suggested that **1** might be active in catalysis, and it was, indeed, found to catalyze hydrogenation of 1-hexene [25].

Because of low solubility in nonpolar solvents, the reaction of **2** with CO and H_2 (1 atm) was performed in THF, at three different temperatures: ambient, 40°C, and 67°C. There was no change in colour even during 20 h under reflux, and FT-IR spectroscopic monitoring of the metal–carbonyl stretching frequency region revealed no evidence for reaction. The capping ligands tend to stabilize and, render inactive, the otherwise reactive clusters [25].

Reactions of **3** with CO and H_2 were studied over a temperature range of 21–69°C in the same solvents as used for **1**. There was no reaction with CO even at elevated temperatures as indicated by IR spectroscopy. However under H_2 solutions of **3** at 67°C turned from yellow to brown and new bands, at 2073, 2032, 1991 and 1966 cm^{-1}, appeared in the IR spectrum. The brown component of the product mixture could not be characterized owing to its low solubility in organic solvents.

Conclusions

The reactions of $Ru_3(CO)_{12}$ with the cyclic thioethers resulted in different coordination modes depending on the ligand. 1,3,5-trithiacyclohexane replaces three axial carbonyls to form a symmetrical structure with three bridging carbonyls. The coordination of 1,3-dithiacyclohexane also involves the carbon between the sulphur atoms. The hydrogen of the coordinated CH_2 group is removed and one metal–metal bond of the cluster core is bridged by a hydride. 1,4,7-Trithiacyclononane loses a H_2CCH_2 fragment during the complexation and two sulphur bridges are formed between two ruthenium atoms with breaking of a bond between these atoms.

Carbon monoxide does not displace the cyclic thioethers in the complexes **1**–**3**. This contrasts with the behaviour of the SMe_2-substituted $HRuCo_3(CO)_{12}$ clusters, in which the SMe_2 ligand is readily displaced by CO [26,27].

Experimental

General comments

Except for chromatographic separations, all manipulations were carried out under nitrogen in deoxygenated solvents. THF was distilled from K-benzophenone under nitrogen. $Ru_3(CO)_{12}$ (Johnson-Matthey) and the thioethers (Aldrich) were from commercial sources. IR spectra were recorded on a Nicolet 20SXC or a Galaxy 6020 spectrometer, and ^1H NMR spectra on a Bruker AM-250 spectrometer at 0°C with TMS as reference.

Preparation of $HRu_3(CO)_9(\mu_3$-η^3-1,3-dithiacyclohexane) (1)

A mixture of $Ru_3(CO)_{12}$ (170 mg, 0.27 mmol) and 1,3-dithian (32 mg, 0.27 mmol) in 250 ml of hexane was refluxed for 22 h. After evaporation of the solvent *in vacuo*, the residue was chromatographed on a silica column. Elution with hexane removed the unchanged starting material and elution with 4:1 hexane-dichloromethane mixture then gave the title compound (164 mg, 91%). Orange crystals were obtained from hexane-dichloromethane. IR (CH_2Cl_2): 2083m, 2053s, 2028vs, 2008m, 1996m,sh, 1964w, 1950w. Found: C, 23.8; H, 1.30. $Ru_3S_2C_{13}O_9H_8$ calc.: C, 23.1; H, 1.19%. The proton on C(101) shows a resonance at 3.9 ppm (s) in the ^1H-NMR spectrum. (The corresponding CH_2 resonance of free 1,3-dithiane is at 3.8 ppm (s).) The protons on C(102) and C(104) resonate at 2.8 ppm (m) and those on C(103) at 1.9 ppm (m); the corresponding signals from the free ligand are at 2.8 (m) and 2.0 (m) ppm, respectively [28]. The cluster hydride signal is at -14.9 ppm.

Preparation of $Ru_3(CO)_9(\mu_3$-η^3-1,3,5-trithiacyclohexane) (2)

Treatment of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) with 1,3,5-trithiane (44 mg, 0.31 mmol) in refluxing hexane for 2 h gave a yellow precipitate of **2**. The solid residue was filtered from the hot hexane solution and washed with CH_2Cl_2, and shown to be **2** (93 mg, 43%). Crystals suitable for the structural study were obtained by recrystallization from THF-CCl_4 mixture. The complex is soluble in THF, acetone, and CCl_4. IR (THF): 2052s, 2004s, 1972w, 1950m, 1809s. Found: C, 20.9; H 0.85. $Ru_3S_3C_{12}O_9H_6$ calc.: C, 20.8; H, 0.87%. Both 1,3,5-trithiane and **2** gave a ^{1}H-NMR signal at 3.0 (m) in acetone-d_6.

Preparation of $Ru_3(CO)_9(\mu_2\text{-}\eta^3\text{-}1,4,7\text{-trithiaheptane})$ (3)

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and 1,4,7-trithiacyclononane (56 mg, 0.31 mmol) in THF was refluxed for 2 h; the colour immediately became red-brown. The mixture was dried *in vacuo* and the residue was chromatographed with 1:1 hexane-dichloromethane on silica plates. The second yellow band (after that containing the unchanged $Ru_3(CO)_{12}$) yielded the title compound, which was dried *in vacuo* (19 mg, 9%). Orange crystals for the X-ray structural study were obtained from CH_2Cl_2. IR(CH_2Cl_2): 2089m, 2053s, 2008vs, 1947w. Found: C, 22.0; H, 1.10. $Ru_3S_3C_{13}O_9H_8$ calc.: C, 22.1; H, 1.14%. Compound **3** shows four ^{1}H NMR signals (THF-d_8): 3.45 ppm (1, d of d), 3.33 ppm (2, d of d), 2.46 ppm (3, d of d of d), 1.93 ppm (4, d of d of d). $J_{12} = 0$, $J_{13} = 12$, $J_{14} = 5$, $J_{34} = 12$, $J_{23} = 5$, $J_{24} = 12$ Hz. (The spectrum of the free ligand consists of a singlet at 3.2 ppm in $CDCl_3$. (3.15 in CCl_4 [29].)

Reactions of 1–3 with H_2 or CO

A saturated solution of **1–3** was prepared in an appropriate degassed solvent (CH_2Cl_2, $CHCl_3$, THF or hexane) in a 100 ml flask. The vessel was charged with H_2 or CO to a slightly higher than one atmosphere pressure by use of a mercury bubbler. The mixtures were first kept at ambient temperature for several hours and then at higher temperatures (normally at the reflux temperature of the solvent), samples being taken at intervals for IR monitoring. The products were separated on thin layer or column chromatography and characterized by IR and NMR spectroscopy.

Reaction of 1 with H_2 in $CDCl_3$

Hydrogen was bubbled through a refluxing solution of **1** (0.12 mmol) in $CDCl_3$ (20 ml), and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 5 h the solvent was removed under vacuum and the residue chromatographed on Kieselgel plates with CH_2Cl_2 as eluent. The first, yellow, band contained unchanged **1**. The second, orange, band gave $H_2Ru_3(CO)_8Cl$-1,3-$[S_2CH(CH_2)_3]$ (21.3 mg, 26% yield), which was recrystallized from a hexane/CH_2Cl_2 mixture (1:2). IR (CH_2Cl_2): 2096.5 m, 2062.7 s, 2025.1 m, 2003.9 sh. Anal. Found: C, 22.01; H, 1.52; S, 8.54. $C_{12}H_9ClO_8Ru_3S_2$ calc.: C, 21.07; H, 1.33; S, 9.37%. ^{1}H NMR ($CDCl_3$): δ 4.04 (s, 1 H, CH), 2.9–1.6 (4 m, 6 H, $(CH_2)_3$), −14.17 (s, 1 H, RuHRu), −22.23 (s, 1 H, RuHRu). The third, major, band, which did not move on the plate, gave a brown substance soluble in acetone.

Crystallographic studies

Data were collected on a Nicolet R3m diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Intensities were corrected for background, polarization and Lorenz factors. Table 13 presents further crystallographic data. The metal atom positions were solved by direct methods with the

Table 13

Crystallographic data

	1 (×2)	**2**	**3** (×3)	**4** (×2)
FW	675.52	693.56	707.58	683.96
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1/n$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a, Å	18.73(2)	12.779(5)	13.805(8)	9.500(5)
b, Å	9.814(6)	12.751(4)	15.85(1)	13.318(7)
c, Å	22.21(2)	11.277(3)	17.49(2)	17.665(10)
α, deg	-	-	106.89(6)	75.81(5)
β, deg	98.87(8)	-	97.86(6)	85.42(4)
γ, deg	-	-	113.70(5)	85.48(5)
V, Å^3	4033(6)	1837.6(8)	3209(4)	2156(2)
Z	8	4	6	4
D_{calc}, g cm^{-3}	2.22	2.51	2.20	2.10
Crystal dimensions, mm	0.2×0.2×0.2	0.8×0.6×0.5	0.4×0.2×0.2	0.5×0.3×0.3
Centred reflections	25	26	25	25
Cent2θ	5–21	15–25	15–25	10–20
hkl range	23, 12, ±27	16, 16, 14	17, ±19, ±21	12, ±16, ±22
2θ, deg	4–50	4–50	5–50	5–50
No unique reflections	7036	1704	10856	7426
No. observed data, $I \geq 3\sigma(I)$	3973	1651	4595	4416
μ, mm^{-1}	1.21	2.76	1.19	2.38
No. parameters	495	243	757	469
R	0.0489	0.0325	0.0711	0.0679
R_w	0.0489	0.0312	0.0711	0.0627

Weight $= 1/(\sigma^2(F) + 0.0005F^2)$

SHELXTL package [30]. All remaining non-hydrogen atoms and the hydrogen on the ruthenium bonding carbon of the ligand in **1** were located by the usual combination of full-matrix least-squares refinement and difference electron syntheses. Non-hydrogen atoms were refined anisotropically for all four compounds. The CH_2 hydrogens were placed in calculated positions (C–H = 0.96 Å, $U = 0.08$ Å^2) and not refined.

The cluster hydride ligands in **1** and **4** were not found in the Fourier maps, but their positions could be derived from the geometry of the compounds. For **1** and **4** there were two independent molecules in the unit cell, and for **3**, three independent molecules. Both absolute structures for **2** were refined and gave the same R factor.

Tables of hydrogen atom coordinates, anisotropic thermal parameters and structure factors are available from the authors.

References

1 E.W. Abel, P.D. Beer, I. Moss, K.G. Orrell, V. Šik, P.A. Bates and M.B. Hursthouse, J. Organomet. Chem., 341 (1988) 559 and refs. therein.

2 B. de Groot and S.J. Loeb, J. Chem. Soc., Chem. Commun., (1990) 1755.

3 R.S. Glass, G.S. Wilson and W.N. Setzer, J. Am. Chem. Soc., 102 (1980) 5068.

4 M.N. Bell, A.J. Blake, A.J. Holder, T.I. Hyde and M. Schröder, J. Chem. Soc., Dalton Trans., (1990) 3841.

5 W.D. Jones and L. Dong, J. Am. Chem. Soc., 113 (1991) 559.
6 B.C. Wiegand, C.M. Friend and J.T. Roberts, Langmuir, 5 (1989) 1292.
7 R.D. Adams and M.P. Pompeo, Organometallics, 9 (1990) 1718.
8 R.J. Crowte, J. Evans and M. Webster, J. Chem. Soc., Chem. Commun., (1984) 1344.
9 D.J. Darensbourg, D.J. Zalewski and T. Delord, Organometallics, 3 (1984) 1217.
10 A.A. Bahsoun, J.A. Osborn, J.-P. Kitzinger, P.H. Bird and U. Siriwardane, Nouv. J. Chim., 8 (1984) 125.
11 A.A. Arduini, A.A. Bahsoun, J.A. Osborn and C. Voelker, Angew. Chem. Int. Ed. Engl., 19 (1980) 1024.
12 M.M. Harding, B.S. Nicholls and A.K. Smith, J. Organomet. Chem., 226 (1982) c17.
13 J.A. Clucas, M.M. Harding, B.S. Nicholls and A.K. Smith, J. Chem. Soc., Dalton Trans., (1985) 1835.
14 J.A. Osborn and G.G. Stanley, Angew. Chem. Int. Ed. Engl., 19 (1980) 1025.
15 J.J. deBoer, J.A. van Doorn and C. Masters, J. Chem. Soc., Chem. Commun., (1978) 1005.
16 D.F. Foster, B.S. Nicholls and A.K. Smith, J. Organomet. Chem., 244 (1983) 159.
17 S. Rossi, J. Pursiainen, M. Ahlgren and T.A. Pakkanen, Organometallics, 9 (1990) 475.
18 S. Rossi, J. Pursiainen and T.A. Pakkanen, Organometallics, 10 (1991) 1390.
19 S. Rossi, K. Kallinen, J. Pursiainen, T.T. Pakkanen and T.A. Pakkanen, J. Organomet. Chem., 419 (1991) 219.
20 M.-G. Choi, L.M. Daniels and R.J. Angelici, Inorg. Chem., 30 (1991) 3647.
21 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2655.
22 B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Süss, J. Chem. Soc., Dalton Trans., (1978) 1356.
23 A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard and D.G. Watson, J. Chem. Soc., Dalton Trans., (1989) S1.
24 J.P. Collman, L.S. Hegedeus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Walley, USA, p. 70.
25 Unpublished results.
26 K. Kallinen, T.T. Pakkanen, J. Pursiainen and T.A. Pakkanen, VII International Symposium on Homogenous Catalysis, Lyon, France, 1990.
27 K. Kallinen, A. Härkönen, J. Pursiainen, S. Rossi, T.T. Pakkanen and T.A. Pakkanen, 4th Nordic Symposium on Catalysis, Trondheim, Norway, 1991.
28 The Sadtler Handbook of Proton NMR Spectra, 493.
29 D. Sellmann and L. Zapf, Angew. Chem., Int. Ed. Engl., 23 (1984) 807.
30 SHELXTL PLUS, Release 3.4, Nicolet Co., Madison, WI, 1988.