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Reactions of 1,3,5-trithiacyclohexane with tetrahedral ruthenium–cobalt clusters

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Abstract

The cyclic polydentate thioether 1,3,5-trithiane reacts with the tetrahedral Ru–Co clusters $[H_4Ru_4(CO)_{12}]$, $[H_3Ru_3Co(CO)_{12}]$, $[HRuCo_3(CO)_{12}]$ and $[Co_4(CO)_{12}]$ by displaying either carbonyl or hydride ligands. The ligand can adopt various coordination modes, the choice of which can be affected by the reaction conditions. In refluxing THF a butterfly cluster $[H_2Ru_4(CO)_{12}(\eta^1\text{-}\mu_2\text{-trithiane})]$ (**1**) and a disubstituted $[H_4Ru_4(CO)_{10}(\eta^2\text{-trithiane})]$ (**2**) are the main products from the parent cluster $[H_4Ru_4(CO)_{12}]$. In refluxing hexane or heptane the trisubstituted derivatives $[H_2Ru_4(CO)_{10}(\eta^3\text{-(trithiane)}]$ (**3**), $[HRu_3Co(CO)_{10}(\eta^3\text{-trithiane})]$ (**4**), $[HRuCo_3(CO)_9(\eta^3\text{-trithiane})]$ (**5**) and $[Co_4(CO)_9(\eta^3\text{-trithiane})]$ (**6**) are formed from the corresponding parent clusters $[H_xRu_xCo_{4-x}(CO)_{12}]$ ($x = 0, 1, 3, 4$). The crystal structures of **1**, **2**, **3**, **4** and **5** have been established. Trithiane prefers coordination at cobalt in the mixed metal clusters.

Introduction

Di- and tri-dentate ligands have been used in cluster chemistry to stabilize metal frameworks. The tridentate phosphorus ligand $CH(Ph_2P)_3$ has been observed to fit to triangular metal faces of clusters, and tetrahedral derivatives with a Rh_4, Co_4, Ru_4, Ir_4, $FeCo_3$ or Co_2Rh_2 metal core have been prepared [1,2]. Polydentate sulphur ligands are widely used in mononuclear metal complexes, but they are less well known in metal cluster compounds. However, 1,3,5-trithiane has the right dimensions to permit coordination on a triangular metal face of a cluster, and such coordination has been demonstrated in the case of the tetranuclear cluster $[Rh_4(CO)_9(\text{trithiane})]$ [3].

In trinuclear clusters capping a face by a tridentate ligand has been found not to be especially favoured, and this has been attributed to a preference for equatorial coordination by the phosphine ligands, or to stepwise attachment of the ligand, so that reactions tend to give mixtures of products [4]. However, such compounds can

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have very stable frameworks. For example, $[Ru_3(CO)_9(MeSi(PBu_2)_3]$ is stable under 100 bar hydrogen-carbon monoxide at 300°C [5].

We previously studied the reactions of the tetranuclear clusters $[H_xRu_xCo_yRh_z(CO)_{12}]$ $(x+y+z=4)$ with SMe_2; several carbonyl substitution derivatives with varying geometry depending on the metal composition of the cluster were obtained [6,7]. In the present work we have studied reactions of tetranuclear Ru-Co clusters with 1,3,5-trithiane in order to gain an insight into its behaviour as a capping ligand in metal clusters.

Results and discussion

Syntheses

1,3,5-Trithiane reacts readily with tetrahedral ruthenium and cobalt metal clusters. The tridentate cyclic thioether evidently can show various coordination geometries depending on the reaction conditions (Fig. 1). It reacts with $H_4Ru_4(CO)_{12}$ in refluxing tetrahydrofuran (THF) to give the butterfly cluster $[H_2Ru_4(CO)_{12}$(trithiane)] (**1**) and the disubstituted $[H_4Ru_4(CO)_{10}$(trithiane)] (**2**) as the main products along with some trisubstituted $[H_2Ru_4(CO)_{10}$(trithiane)] (**3**). In refluxing hexane $[HRuCo_3(CO)_{12}]$ gives a mixture containing monosubstituted $[HRuCo_3(CO)_{11}$(trithiane)] and $[HRuCo_3(CO)_9$ (μ_3-η^3-trithiane)] (**5**).

The formation and stability of these di- and tri-substituted compounds differs from the behaviour of the corresponding derivatives of SMe_2. In the case of SMe_2 no trisubstituted compounds have been observed and even $[HRuCo_3(CO)_{10}(SMe_2)_2]$ loses the second sulphide ligand readily. On the other hand there is close structural similarity between the monosubstituted derivatives. Complex $[H_2Ru_4(CO)_{12}(SMe_2)]$ and **1** are both butterfly clusters with one broken Ru–Ru bond, and in both $[HRuCo_3(CO)_{11}(SMe_2)]$ and $[HRuCo_3(CO)_{11}$(trithiane)] the sulphur ligand is coordinated axially to cobalt.

In refluxing heptane or hexane the reactions proceed almost exclusively to the trisubstituted stage. With $[H_4Ru_4(CO)_{12}]$ and $[H_3Ru_3Co(CO)_{12}]$ the derivatives **3** and **4** are the main products in refluxing hexane; formation of $[HRuCo_3(CO)_9$(trithiane)] (**5**) and $[Co_4(CO)_9$(trithiane)] (**6**) in good yields requires use of refluxing heptane as solvent. Under these conditions almost pure trisubstituted products separate out from the solution during the reaction.

Structures of the substituted clusters

$[H_2Ru_4(CO)_{12}$(1,3,5-trithiane)] (1). The four ruthenium atoms of $[H_2Ru_4(CO)_{12}$(trithiane)] (**1**) define a butterfly core, with one of the sulphur atoms bridging the wing tip positions of the cluster (Fig. 2). The twelve terminal carbonyl ligands of the parent cluster have been maintained, three on each metal, but only two of the hydrides are present in the trithiane derivative. The atomic coordinates are given in Table 1. The geometry of **1** is very similar to that of the SMe_2 derivative $[H_2Ru_4(CO)_{12}(SMe_2)]$, for which consideration of the bond length and bond angle data with the aid of space-filling models and analysis of the ^{1}H-NMR spectrum provide satisfactory information on the hydride positions [7]. In the case of **1** it is also reasonable to locate the two cluster hydrides in the Ru(2)–Ru(3) and Ru(2)–Ru(4) bonds on the basis of the bond lengths (Table 2) and bond angles (Table 3). The hydrogen-bridged wing bond Ru(2)–Ru(4) is clearly longer (302.8

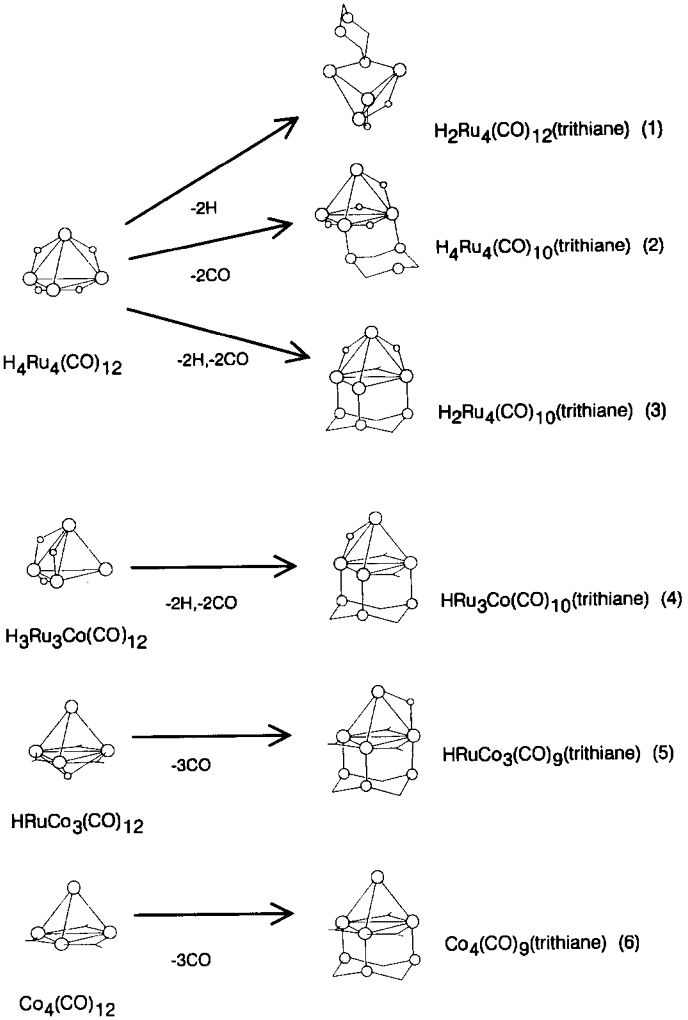

Fig. 1. Formation of trithiane derivatives of tetrahedral ruthenium-cobalt clusters.

pm) than the remaining Ru–Ru bonds (average 284.7 pm). Also the hinge bond Ru(2)–Ru(3) (289.5 pm) is longer than the corresponding nonhydrogen bridged distance in $[Ru_4(CO)_{13}(SMe_2)]$ (280.4 pm), which is a carbonyl-bridged bond. The repulsion by the hydrogens can also be seen from the Ru–Ru–C bond angle data. The ^1H NMR signals from **1** (−15.9 and −17.2 ppm) are close to those from $[H_2Ru_4(CO)_{12}(SMe_2)]$ (−15.6 and −16.7 ppm).

$[H_4Ru_4(CO)_{10}$(trithiane)$]$ (2). $[H_4Ru_4(CO)_{10}$(trithiane)$]$ (**2**) has a conformation in which the ligand has replaced two carbonyls in the parent cluster (Fig. 3a) and the third sulphur atom is bent out away from the ligand.

Final atomic positional parameters for **2** are listed in Table 4. For compounds **2**–**5**, the intramolecular bond lengths and values of selected bond angles are given in Tables 8 and 9 respectively.

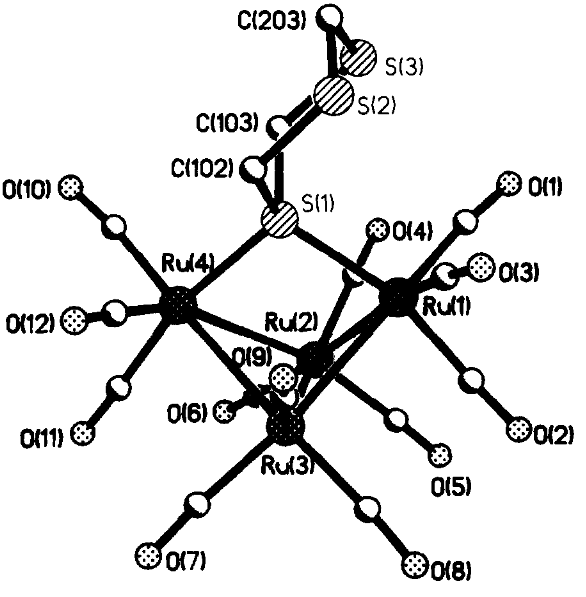

Fig. 2. Structure and numbering scheme for $[H_2Ru_4(CO)_{12}(\text{trithiane})]$ (1).

All the carbonyls are terminal in **2**. The hydride ligand positions were deduced from the lengthening of Ru–Ru bonds and opening of Ru–Ru–C bond angles caused by the hydrides. Three of them are bridging the edges in the Ru(2)–Ru(3)–Ru(4) triangle and the fourth bridges the Ru(1)–Ru(3) bond. The parent cluster and the derivatives with monodentate phosphines and phosphites have the hydrides arranged to give two hydride bonds on each metal- [8–10]. In $[H_4Ru_4(CO)_{10}(\text{dppe})]$ and $[H_4Ru_4(CO)_{10}(\text{dppm})]$ the hydride arrangement is similar to that in **2**, and with respect to the sulphur or phosphorus atoms also [11,12]. The $[H_4Ru_4(CO)_{10}(\text{dppe})]$ isomer with the phosphorus atoms on the same ruthenium also has a similar hydride geometry [13,14].

In $[H_4Ru_4(CO)_{12}]$ phosphine and phosphite ligands favour the positions *trans* to each other along the short unbridged Ru–Ru bonds. In $[H_4Ru_4(CO)_{10}(\text{dppe})]$, $[H_4Ru_4(CO)_{10}(\text{dppm})]$ and in **2** such coordination is sterically prevented, allowing a different coordination geometry. In $[H_4Ru_4(CO)_{12}]$ the Ru–C bonds *trans* to the unbridged Ru–Ru bonds were reported to be longer (193.8 pm) than those *trans* to the bridged Ru–Ru bonds (190.2 pm), and this was attributed to competition with the back-bonding electrons. A similar feature was observed in the phosphine derivative $[H_4Ru_4(CO)_{10}(PPh_3)_2]$, in which Ru–C bond lengths are 185 and 183 pm, respectively. The phosphorus donor ligands have affected the electron distribution over the whole cluster and shortened the Ru–C bonds. In **2** the Ru–C bonds *trans* to the short Ru–Ru bonds average 193 pm and those *trans* to the long Ru–Ru bonds average 190 pm. Thus the trend is similar in each case, but the sulphur ligand affects the bond length more like a carbonyl than a phosphine ligand.

$[H_2Ru_4(CO)_{10}(\text{trithiane})]$ (3) and $[HRu_3Co(CO)_{10}(\text{trithiane})]$ (4). The compounds $[H_2Ru_4(CO)_{10}(\text{trithiane})]$ (**3**) and $[HRu_3Co(CO)_{10}(\text{trithiane})]$ (**4**) are formed

Table 1

Atomic coordinates ($\times 10^4$) for $[H_2Ru_4(CO)_{12}(1,3,5\text{-trithiane})]$ (**1**)

Atom	x	y	z
Ru(1)	4246(1)	8421(1)	1106(1)
Ru(2)	3783(1)	7562(1)	−475(1)
Ru(3)	4685(1)	6698(1)	1115(1)
Ru(4)	1745(1)	6703(1)	419(1)
S(1)	1946(2)	7987(1)	1092(1)
S(2)	1547(3)	8859(2)	2709(2)
S(3)	628(3)	9694(2)	998(2)
O(1)	3834(11)	10212(5)	541(8)
O(2)	7258(7)	8549(6)	931(6)
O(3)	5129(9)	8841(7)	2992(6)
O(4)	2481(10)	9161(6)	−1243(7)
O(5)	6539(8)	8022(6)	−927(6)
O(6)	3032(10)	6566(7)	−2113(6)
O(7)	4826(11)	4837(5)	949(6)
O(8)	7885(10)	6774(7)	1575(7)
O(9)	4475(10)	6784(6)	2953(6)
O(10)	−1369(9)	6699(7)	−415(7)
O(11)	2103(11)	5135(6)	−559(7)
O(12)	1439(12)	5716(6)	1980(7)
C(1)	3906(11)	9538(7)	743(8)
C(2)	6099(11)	8485(7)	972(7)
C(3)	4733(10)	8680(8)	2274(7)
C(4)	2931(12)	8565(8)	−935(8)
C(5)	5537(12)	7867(7)	−722(8)
C(6)	3347(10)	6911(8)	−1493(7)
C(7)	4711(12)	5528(7)	992(7)
C(8)	6661(13)	6782(7)	1377(8)
C(9)	4544(13)	6766(7)	2249(8)
C(10)	−217(12)	6757(7)	−119(8)
C(11)	2013(13)	5718(7)	−170(8)
C(12)	1531(13)	6088(7)	1398(9)
C(102)	1418(10)	7925(6)	2119(5)
C(103)	538(9)	8674(6)	575(6)
C(203)	247(12)	9465(7)	2009(6)

from the parent clusters $[H_4Ru_4(CO)_{12}]$ and $[H_3Ru_3Co(CO)_{12}]$ by replacement of two hydrides and two carbonyls by the trithiane ligand (Figs. 3b and 3c). The trithiane ligand is bound in η^3-fashion to the Ru_3-face in **3** and to the Ru_2Co-face in **4**.

Final atomic positional parameters for **3** and for **4** are listed in Tables 5 and 6. Both derivatives have carbonyl arrangements different from those in the solid parent clusters, in which all the carbonyl groups are terminal. Both compounds have bridging carbonyls on the Ru(3)–M(4) bond and the Ru(2)–Co(4) is also bridged in **4**. In **3** the corresponding carbonyl C(6)–O(6) is slightly semi-bridging with Ru(3)–C(6)–O(6) angle 164° and the Ru(2)–C(6) distance 281 pm. For bridging groups the Ru–C distances are near 210 pm and for terminal groups the corresponding nonbonded distances are > 300 pm. The parent cluster has Ru(μ-CO)Co carbonyl bridges in solution, and two such bridges are present also in the crystal structure of $[H_3Ru_3Co(CO)_{10}(dppe)]$ [15].

Table 2

Bond lengths (pm) for $[H_2Ru_4(CO)_{12}(1,3,5\text{-trithiane})]$ (**1**)

Ru(4)–Ru(3)	285.0(3)	Ru(4)–Ru(2)	302.8(4)
Ru(3)–Ru(2)	289.5(3)	Ru(3)–Ru(1)	283.3(3)
Ru(2)–Ru(1)	285.9(3)	Ru(1)–S(1)	234.5(4)
Ru(4)–S(1)	234.2(4)	Ru(1)–C(1)	191(1)
Ru(1)–C(2)	187(1)	Ru(1)–C(3)	189(1)
Ru(2)–C(4)	191(1)	Ru(2)–C(5)	190(1)
Ru(2)–C(6)	193(1)	Ru(3)–C(7)	191(1)
Ru(3)–C(8)	189(1)	Ru(3)–C(9)	187(1)
Ru(4)–C(10)	193(1)	Ru(4)–C(11)	191(1)
Ru(4)–C(12)	192(1)	S(1)–C(102)	184(1)
S(1)–C(103)	183.0(9)	S(2)–C(102)	178(1)
S(2)–C(203)	180(1)	S(3)–C(103)	179(1)
S(3)–C(203)	179(1)	O(1)–C(1)	114(1)
O(2)–C(2)	115(1)	O(3)–C(3)	117(1)
O(4)–C(4)	114(2)	O(5)–C(5)	112(2)
O(6)–C(6)	113(2)	O(7)–C(7)	113(2)
O(8)–C(8)	117(2)	O(9)–C(9)	115(2)
O(10)–C(10)	113(1)	O(11)–C(11)	115(2)
O(12)–C(12)	114(2)		

The ^{1}H-NMR spectrum of **3** shows a singlet at −19.0 ppm and that for **4** a broadened signal at −18.8 ppm in the cluster hydride region. It is deduced that the hydrides bridge the two equivalent Ru(1)–Ru(3) bonds in **3** and the Ru(1)–Ru(3) bond in **4**.

Table 3

Selected bond angles (°) for $[H_2Ru_4(CO)_{12}(1,3,5\text{-trithiane})]$ (**1**)

Ru(3)–Ru(4)–S(1)	80.8(1)	Ru(2)–Ru(4)–S(1)	79.1(1)
Ru(3)–Ru(4)–C(12)	87.0(4)	Ru(3)–Ru(4)–C(11)	87.9(4)
Ru(2)–Ru(4)–C(11)	88.8(4)	Ru(2)–Ru(4)–C(10)	116.9(4)
Ru(4)–Ru(3)–C(9)	96.4(4)	Ru(1)–Ru(3)–C(9)	84.5(4)
Ru(4)–Ru(3)–C(7)	89.8(3)	Ru(2)–Ru(3)–C(7)	113.5(3)
Ru(2)–Ru(3)–C(8)	105.6(4)	Ru(1)–Ru(3)–C(8)	94.3(4)
Ru(3)–Ru(2)–C(5)	101.1(3)	Ru(1)–Ru(2)–C(5)	94.5(3)
Ru(4)–Ru(2)–C(6)	95.9(4)	Ru(3)–Ru(2)–C(6)	117.4(4)
Ru(4)–Ru(2)–C(4)	107.7(4)	Ru(1)–Ru(2)–C(4)	84.5(4)
Ru(3)–Ru(1)–S(1)	81.1(1)	Ru(2)–Ru(1)–S(1)	82.7(1)
Ru(3)–Ru(1)–C(3)	102.0(4)	Ru(3)–Ru(1)–C(2)	84.6(3)
Ru(2)–Ru(1)–C(2)	84.2(3)	Ru(2)–Ru(1)–C(1)	101.9(4)
Ru(4)–S(1)–Ru(1)	105.0(1)	Ru(4)–S(1)–C(102)	110.9(3)
Ru(1)–S(1)–C(102)	117.1(3)	Ru(4)–S(1)–C(103)	110.5(3)
Ru(1)–S(1)–C(103)	116.4(3)	C(102)–S(1)–C(103)	96.9(4)
C(102)–S(2)–C(203)	99.7(4)	C(103)–S(3)–C(203)	98.8(5)
Ru(1)–C(1)–O(1)	174(1)	Ru(1)–C(2)–O(2)	176(1)
Ru(1)–C(3)–O(3)	175(1)	Ru(2)–C(4)–O(4)	176(1)
Ru(2)–C(5)–O(5)	175(1)	Ru(2)–C(6)–O(6)	176(1)
Ru(3)–C(7)–O(7)	175(1)	Ru(3)–C(8)–O(8)	174(1)
Ru(3)–C(9)–O(9)	178(1)	Ru(4)–C(10)–O(10)	172(1)
Ru(4)–C(11)–O(11)	176(1)	Ru(4)–C(12)–O(12)	178(1)
S(1)–C(102)–S(2)	115.7(6)	S(1)–C(103)–S(3)	114.8(5)
S(2)–C(203)–S(3)	115.6(6)		

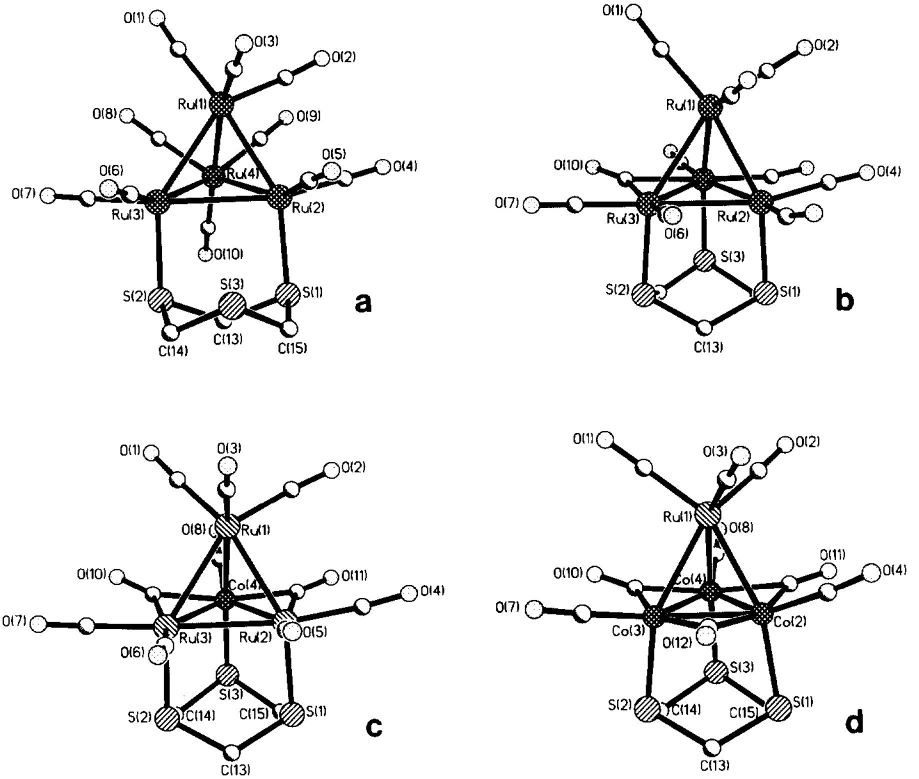

Fig. 3. Crystal structures and numbering schemes of [$H_4Ru_4(CO)_{10}$(trithiane)] (**2**) (a), [$H_2Ru_4(CO)_{10}$-(trithiane) (**3**) (b), [$HRu_3Co(CO)_{10}$(trithiane) (**4**) (c) and [$HRuCo_3(CO)_9$(trithiane)] (**5**) (d).

In **3** the bridged metal–metal bonds are longer (289.1 pm) than the remaining such bonds (av. 277.1 pm). Opening of the M–M–CO bond angles by the hydrides can also be seen from the bond angle data. The repulsion by the hydrides is most marked in the case of carbonyl 7, the angle Ru(1)–Ru(3)–C(7) being 121.3°.

In **4** the Ru(1)–Ru(3) bond is longer (288.0 pm) than the Ru(1)–Ru(2) bond (273.5 pm). Although the Ru(2)–Ru(3) bond is also long (286.3 pm), the space filling models [16] show space for the hydride ligand only at the Ru(1)–Ru(3) bond. The bond angle data also support this. The repulsion by the hydride has opened the Ru–Ru–C angles only along the Ru(1)–Ru(3) bond.

There is significant asymmetry in the bonding of the sulphur ligand in **4**. The Ru(1)–Co(4)–S(3) angle is larger (160.6°) than the Ru(1)–Ru–S angles (143.5° and 147.6°). Those values, however, are very close to those of the corresponding Ru–Co–C and Ru–Ru–C angles in [$H_3Ru_3Co(CO)_{12}$] (157.9° and 148.0°), indicating that the sulphur ligand does not cause strain in the cluster relative to the parent cluster. In **3** the Ru(1)–Ru–S angles are 147.6° and 151.7°.

[$HRuCo_3(CO)_9$(trithiane)] (5) and [$Co_4(CO)_9$(trithiane)] (6). In [$HRuCo_3$ $(CO)_9$(trithiane)] (**5**) the sulphur ligand is bound to the Co_3-face, leaving coordination of the other carbonyls unchanged (Fig. 3d). The atomic coordinates are given in Table 7.

Table 4

Atomic coordinates (10^4) for [$H_4Ru_4(CO)_{10}$(1,3,5-trithiane)] (**2**)

Atom	*x*	*y*	*z*
Ru(1)	2419(1)	3741(1)	2867(1)
Ru(2)	756(1)	1121(1)	2151(1)
Ru(3)	−1013(1)	2912(1)	3313(1)
Ru(4)	−30(2)	3400(1)	1285(1)
S(1)	−1728(5)	−696(4)	1722(3)
S(2)	−3546(4)	1180(4)	2932(3)
S(3)	−1966(5)	−765(4)	3983(3)
O(1)	3773(16)	6784(14)	3517(12)
O(2)	5025(15)	3263(15)	1532(10)
O(3)	4477(17)	3227(13)	4661(9)
O(4)	2888(15)	279(14)	619(9)
O(5)	2501(14)	−106(13)	3649(10)
O(6)	−620(17)	2713(13)	5530(9)
O(7)	−2634(16)	5247(11)	3653(11)
O(9)	2625(15)	3795(13)	−148(9)
O(8)	308(16)	6418(11)	1864(10)
O(10)	−2976(16)	2782(13)	−359(10)
C(1)	3252(22)	5665(17)	3115(14)
C(2)	3985(20)	3389(17)	2024(12)
C(3)	3653(19)	3406(18)	4011(12)
C(4)	2070(20)	588(15)	1194(11)
C(5)	1842(19)	397(16)	3105(13)
C(6)	−747(19)	2746(15)	4699(12)
C(7)	−2038(18)	4356(14)	3542(12)
C(8)	167(20)	5286(17)	1644(12)
C(9)	1657(21)	3647(15)	396(12)
C(10)	−1913(19)	2997(17)	261(12)
C(13)	−3466(17)	57(13)	1777(12)
C(14)	−3672(17)	−29(14)	3818(11)
C(15)	−2120(22)	−1683(14)	2731(13)

The ^1H NMR spectrum shows a relatively sharp cluster hydride resonance at −23.7 ppm, which is unusual for $RuCo_3$ cluster derivatives. This is attributed to the extraordinary Ru(μ_2-H)Co position of the hydride. In the crystal structure this hydride position is revealed by the significant asymmetry of the structure. The hydride is deduced to bridge the Ru(1)–Co(3) bond, which is longer (269.7 pm) than the two other Ru–Co bonds (av. 262.0 pm). Further, the Ru(1)–Co(3)–C(7) angle (113.0°) is larger than the other two Ru–Co–C_{eq} angles (av. 100.7°), and is similar to the corresponding angles involving Ru(μ-H)Rh bridges. The Co–Ru–C_{ap} angles should also indicate the positions of the hydride, and the angle Co(3)–Ru(1)–C(1) (110.2°) is typical of the presence of the hydride but the Co(3)–Ru(1)–C(3) angle is not. There are also two other large angles, Co(4)–Ru(1)–C(2) (105.4°) and Co(2)–Ru(1)–C(3) (108.2°). The apical carbonyls have rotated around the pseudo C_{3v} axis of the cluster. This rotation is expressed in terms of the torsion angles between the apical and the bridging carbonyls below them (*e.g.* carbonyls 1 and 10), and these are 14.5°, 14.3° and 7.6° for carbonyls 1, 2 and 3, respectively. These findings, together with a study of the space filling models of the cluster,

Table 5

Atomic coordinates ($\times 10^4$) for $[H_2Ru_4(CO)_{10}(\text{trithiane})]$ (3)

Atom	*x*	*y*	*z*
Ru(1)	7187(1)	1001(2)	2500
Ru(2)	5704(1)	398(2)	2500
Ru(3)	6173(1)	2975(1)	3534(1)
S(1)	4435(3)	1185(5)	2500
S(2)	4957(2)	3977(5)	3645(3)
O(1)	8765(8)	2231(19)	2500
O(2)	7440(8)	−1497(15)	1012(9)
O(4)	5574(7)	−2133(14)	1032(8)
O(6)	5931(7)	684(13)	5165(9)
O(7)	6697(6)	4991(17)	5216(10)
O(10)	6875(10)	5829(18)	2500
C(1)	8171(13)	1808(28)	2500
C(2)	7326(8)	−490(16)	1537(11)
C(4)	5610(8)	−1126(19)	1567(10)
C(6)	5973(9)	1395(18)	4462(14)
C(7)	6500(7)	4258(17)	4578(12)
C(10)	6569(11)	4652(26)	2500
C(13A)	4275(6)	2485(15)	1494(10)
C(14)	4740(11)	4939(23)	2500

suggested that the hydride ligand is not on the top of the Ru(1)–Co(3) bond but is slightly bent toward Co(4).

There seems to be no room for a hydride in the $Co_3(\mu_3\text{-H})$ position. With a Co–H distance of 170 pm the hydride would be on average only 221 pm from the S atoms, which is significantly below the sum of the van der Waals radii of H and S atoms (305 pm). In $[HRuCo_3(CO)_{11}(SEt_2)]$, $[HRuCo_3(CO)_{11}(SMe_2)]$ and $[HRuCo_3(CO)_{10}(SMe_2)_2]$, which have a $Co_3(\mu\text{-H})$ hydride, the corresponding values fall in the range 270–290 pm for both experimental and calculated (Co–H = 170 pm) hydride positions.

The average Co–Co–S (96.9°) and Ru–Co–S (155.4°) angles are smaller than the Co–Co–C_{ax} (117.7°) and Ru–Co–C_{ax} (175.0°) angles in the parent cluster [17]. These values also indicate that a metal triangle with a $M_3(\mu_3\text{-H})$ hydride does not have a good geometry for the trithiane ligand.

As judged from IR data the structure of **6** is analogous to that of **5**. A similar IR spectrum was also found for $[Co_4(CO)_9(HC(PPh_2))]$.

Conclusion

1,3,5-Trithiane coordinates readily on the tetrahedral Ru, Co and Rh clusters as a tridentate ligand. The homonuclear members of the group $[H_xRu_xCo_yRh_z(CO)_{12}]$ ($x = 0$–4, $x + y + z = 4$) as well as the Ru–Co mixed metal compounds have been investigated. It seems likely that analogous products would also be formed with other members of this group.

Under milder conditions butterfly compounds or mono- or di-substituted products were also isolated from reactions with $[H_4Ru_4(CO)_{12}]$ and $[HRuCo_3(CO)_{12}]$.

Table 6

Atomic coordinates ($\times 10^4$) for [$HRu_3Co(CO)_{10}$(1,3,5-trithiane)] (**4**)

Atom	*x*	*y*	*z*
Ru(1)	1422(1)	3825(1)	4514(1)
Ru(2)	666(1)	2442(1)	4675(1)
Ru(3)	1677(1)	1380(1)	5730(1)
Co(4)	1359(1)	4012(2)	5957(1)
S(1)	390(1)	1382(4)	5625(2)
S(2)	1476(1)	246(4)	6748(2)
S(3)	1188(1)	3398(4)	7045(2)
O(1)	2400(5)	5681(17)	5202(10)
O(2)	691(5)	6302(13)	3447(8)
O(3)	1382(5)	2438(16)	2906(8)
O(4)	−323(4)	3694(13)	3268(7)
O(5)	481(6)	−29(20)	3381(10)
O(6)	1460(5)	−1361(13)	4582(8)
O(7)	2750(4)	188(16)	6663(7)
O(8)	1775(6)	7010(14)	6381(8)
O(11)	2462(5)	3800(16)	6952(9)
O(10)	459(3)	5788(10)	4999(6)
C(1)	2045(6)	4947(19)	4946(10)
C(2)	985(6)	5401(18)	3857(9)
C(2)	1406(6)	2949(18)	3506(11)
C(4)	42(5)	3185(16)	3814(9)
C(5)	572(6)	832(22)	3906(11)
C(6)	1508(6)	−317(17)	5012(10)
C(7)	2353(5)	662(16)	6349(8)
C(8)	1610(6)	5813(20)	6262(9)
C(10)	2030(7)	3327(20)	6489(11)
C(11)	717(5)	4693(16)	5175(8)
C(13)	802(5)	−131(15)	6238(9)
C(14)	1522(5)	1660(16)	7527(8)
C(15)	556(5)	2666(15)	6536(8)

1,3,5-Trithiane is a valuable member of the small group of ligands, that can hold together the metal atoms of a triangular face.

Experimental

General comments

All manipulations except the chromatographic separations were carried out under dinitrogen and with deoxygenated solvents. THF was distilled from potassium-benzophenoneketyl. A silica gel column was used for chromatographic separations [$H_4Ru_4(CO)_{12}$], [$H_3Ru_3Co(CO)_{12}$] and [$HRuCo_3(CO)_{12}$] were prepared by literature methods (refs. [18,19,20] respectively). [$Co_4(CO)_{12}$] (Johnson Matthey) and 1,3,5-trithiane (Aldrich) were of commercial origin.

FT-IR spectra were recorded on a Nicolet 20SXC spectrometer in appropriate solvents. The ^{1}H-NMR spectra were recorded on a Bruker AM-250 spectrometer at 0°C in $CDCl_3$ or in acetone-d_6 with Me_4Si as reference.

Preparation of compounds 1 and 2. A mixture of [$H_4Ru_4(CO)_{12}$] (58 mg, 0.078 mmol) and 1,3,5-trithiane (18 mg, 0.078 mmol) in THF was refluxed for 5 h. The

Table 7

Atomic coordinates ($\times 10^4$) for [$HRuCo_3(CO)_9$(1,3,5-trithiane)] (**5**)

Atom	x	y	z
Ru(1)	2008	9164(1)	48889
Co(2)	1305(1)	6866(1)	5600(1)
Co(3)	1700(1)	8922(1)	6554(1)
Co(4)	3127(1)	7573(2)	5940(1)
S(1)	1214(2)	5181(3)	6616(2)
S(2)	1751(2)	7715(3)	7772(2)
S(3)	3474(2)	6029(4)	7013(2)
O(1)	2912(10)	2121(11)	4884(8)
O(2)	3166(9)	8146(13)	3388(7)
O(3)	−7(8)	9954(12)	3884(8)
O(4)	−33(10)	5888(13)	4166(8)
O(6)	1071(8)	11603(9)	7276(7)
O(8)	5111(8)	7658(13)	5181(8)
O(10)	3776(7)	10225(11)	6792(7)
O(11)	2795(7)	5388(9)	4601(6)
O(12)	−507(7)	8477(11)	6067(7)
C(1)	2612(10)	11005(14)	4884(8)
C(2)	2712(11)	8508(13)	3949(8)
C(3)	747(11)	9680(14)	4265(8)
C(4)	480(11)	6240(15)	4752(9)
C(6)	1305(10)	10548(13)	7015(8)
C(8)	4331(9)	7600(13)	5492(8)
C(10)	3225(9)	9286(13)	6548(7)
C(11)	2543(9)	6168(11)	5097(8)
C(12)	356(10)	8175(12)	6075(7)
C(13)	992(10)	6128(13)	7595(8)
C(14)	3008(10)	6897(13)	7933(8)
C(15)	2526(10)	4601(12)	6890(9)

solvent was evaporated in vacuum and the residue was chromatographed on silica. Elution with hexane gave a yellow fraction of unchanged starting material, and further elution with 2:1 hexane–CH_2Cl_2 gave an orange fraction containing **1** (28 mg, 46%). With a 1:1 hexane–CH_2Cl_2 mixture a dark orange fraction of **2** (18 mg, 28%) was eluted. Some **3** (eluted with 5:1 solvent mixture) was also formed. IR (CH_2Cl_2); **1**: 2077m, 2054s, 2034vs, 2010vs, 1966w; **2**: 2077m, 2054s, 2035vs, 2009vs, 1966w. ^{1}H-NMR ($CDCl_3$); **1**: −15.9 and −17.2 ppm (br); **2**: −16.2 (br) ppm. Anal. Found: C, 20.8; H, 1.1. $Ru_4S_3C_{15}O_{12}H_8$ (**1**) calcd.: C, 20.5; H, 0.9%.

Preparation of compound 3. A mixture of [$H_4Ru_4(CO)_{12}$] (150 mg, 0.20 mmol) and trithiane (28 mg, 0.20 mmol) in hexane (200 ml) was refluxed for 22 h. The red-brown precipitate of **3** was filtered off from the hot solution (to prevent separation of uncharged trithiane) and dried in vacuum. Yield 125 mg, 78%. IR (CH_2Cl_2): 2076m, 2054w, 2009s, 1981m, 1792 w cm^{-1}. ^{1}H NMR ($CDCl_3$): −19.0 ppm. Anal. Found: C, 20.3; H, 1.3. $Ru_4S_3C_{13}O_{10}H_8$ calcd.: C, 18.9; H, 1.0%.

Preparation of compound 4. To a solution of [$H_3Ru_3Co(CO)_{12}$] (120 mg, 0.171 mmol) in hexane was added 1,3,5-trithiane (23 mg, 0.171 mmol). The mixture was refluxed for 3.5 h. The less soluble **3** separated out and the unchanged starting materials remained in solution. Chromatographic separation of the solution on

Table 8

Bond lengths (pm) for $[H_4Ru_4(CO)_{10}(\text{trithiane})]$ (**2**), $[H_2Ru_4(CO)_{10}(\text{trithiane})]$ (**3**), $[HRu_3Co(CO)_{10}(\text{trithiane})]$ (**4**) and $[HRuCo_3(CO)_{10}(\text{trithiane})]$ (**5**) [a]

	2	**3**	**4**	**5**
Ru(1)–M(2)	273.4(2)	273.3(3)	273.5(2)	260.9(3)
Ru(1)–M(3)	*295.4(2)*	*289.1(3)*	*288.0(2)*	*269.7(3)*
Ru(1)–M(4)	278.3(2)		263.1(3)	263.0(3)
M(2)–M(3)	*299.5(2)*	280.9(3)	286.3(2)	249.8(4)
M(2)–M(4)	*295.8(3)*	–	261.4(2)	248.7(4)
M(3)–M(4)	*300.2(3)*	276.7(3)	264.1(2)	248.7(3)
M(2)–S(1)	242.7(4)	240.0(5)	239.1(5)	225.8(4)
M(3)–S(2)	240.6(4)	237.7(4)	237.2(5)	223.3(4)
M(4)–S(3)	–	–	227.0(5)	226.7(4)
S(2)–C(14)	184(2)	180(1)	181(2)	180(1)
S(3)–C(14)	180(2)	–	182(1)	182(1)
S(3)–C(15)	180(2)	–	180(1)	182(1)
S(1)–C(15)	182(2)	–	182(1)	183(1)
S(2)–C(13)	183(2)	182(1)	182(1)	181(1)
S(1)–C(13)	182(2)	180(1)	180(1)	181(1)
Ru(1)–C(1)	191(2)	192(2)	194(2)	192(1)
Ru(1)–C(2)	188(2)	187(2)	189(2)	190(1)
Ru(1)–C(3)	192(2)	–	191(2)	190(1)
M(2)–C(4)	188(2)	185(2)	188(1)	176(1)
M(2)–C(5)	187(2)	–	189(2)	–
M(3)–C(6)	191(2)	191(2)	187(2)	–
M(3)–C(7)	190(2)	190(2)	190(1)	179(1)
M(4)–C(8)	190(2)	–	175(2)	176(1)
M(4)–C(9)	193(2)	–	188(2)	–
M(3)–C(10)	–	216(2)	213(2)	199(1)
M(4)–C(10)	195(2)	–	188(2)	193(1)
M(2)–C(11)	–	–	217(1)	199(1)
M(4)–C(11)	–	–	186(1)	196(1)
M(2)–C(12)	–	–	–	188(1)
M(3)–C(12)	–	–	–	202(1)
C(1)–O(1)	113(2)	114(3)	115(2)	115(2)
C(2)–O(2)	116(2)	116(2)	116(2)	115(2)
C(3)–O(3)	112(2)	–	112(3)	112(2)
C(4)–O(4)	114(2)	115(2)	115(2)	116(2)
C(5)–O(5)	114(2)	–	112(3)	–
C(6)–O(6)	113(2)	114(2)	116(2)	–
C(7)–O(7)	115(2)	113(2)	114(2)	113(2)
C(8)–O(8)	114(2)	–	116(2)	115(2)
C(9)–O(9)	114(2)	–	–	–
C(10)–O(10)	114(2)	118(3)	123(2)	116(2)
C(11)–O(11)	–	–	119(2)	114(2)
C(12)–O(12)	–	–	–	119(2)

[a] The hydride bridged bonds are in italics.

silica first gave the yellow fraction of the parent cluster, and elution with CH_2Cl_2 then gave the brown compound **4** (50 mg, 39%). IR (CH_2Cl_2): 2086s, 2019vs, 1998s, 1969m, 1788w cm^{-1}. ^1H-NMR (acetone-d_6): -18.8 ppm (br). Anal. Found: C, 21.2; H, 1.5. $Ru_3CoS_3O_{10}C_{13}H_7$ calcd.: C, 20.0; H, 0.90%.

Reactions of $[HRuCo_3(CO)_{12}]$ with trithiane. A suspension of $[HRuCo_3(CO)_{12}]$ (300 mg, 0.49 mmol) in 150 ml of heptane was added to a refluxing heptane

Table 9

Selected bond angles (°) for [$H_4Ru_4(CO)_{10}$(trithiane)] (**2**), [$H_2Ru_4(CO)_{10}$(trithiane)] (**3**), [$HRu_3Co(CO)_{10}$(trithiane)] (**4**) and [$HRuCo_3(CO)_{10}$(trithiane)] (**5**)

	2	**3**	**4**	**5**
M(3)–Ru(1)–C(1)	112.0(6)	111.1(6)	104.0(5)	110.2(4)
M(4)–Ru(1)–C(1)	101.4(6)	–	95.9(6)	96.8(4)
M(2)–Ru(1)–C(2)	85.0(5)	89.6(4)	91.3(6)	91.9(4)
M(4)–Ru(1)–C(2)	94.0(5)	–	100.4(6)	105.4(4)
M(2)–Ru(1)–C(3)	97.5(5)	–	105.3(5)	108.2(4)
M(3)–Ru(1)–C(3)	103.3(5)	100.8(5)	104.5(5)	99.7(4)
Ru(1)–M(2)–C(4)	102.3(4)	103.6(5)	109.1(5)	102.1(4)
M(4)–M(2)–C(4)	98.8(5)	107.1(5)	125.2(4)	141.1(4)
Ru(1)–M(2)–C(5)	94.7(4)	–	96.5(7)	–
M(3)–M(2)–C(5)	105.8(5)	–	87.2(5)	–
Ru(1)–M(3)–C(6)	102.3(5)	89.1(5)	103.2(5)	–
M(2)–M(3)–C(6)	109.1(5)	70.3(5)	88.6(4)	–
Ru(1)–M(3)–C(7)	114.1(4)	121.3(4)	120.3(5)	113.0(4)
M(4)–M(3)–C(7)	95.6(5)	137.4(5)	125.7(4)	149.5(4)
M(3)–M(4)–C(8)	91.0(5)	–	136.8(7)	144.3(5)
Ru(1)–M(4)–C(8)	85.8(5)	–	97.3(7)	99.3(5)
Ru(1)–M(4)–C(9)	88.3(5)	–	–	–
M(2)–M(4)–C(9)	98.2(5)	–	–	–
Ru(1)–M(3)–C(10)	–	8.4(5)	73.5(5)	80.9(3)
M(2)–M(3)–C(10)	117.9(5)	110.4(4)	110.8(5)	109.3(4)
M(4)–M(3)–C(10)	112.5(5)	50.1(4)	44.8(5)	49.6(3)
M(1)–M(4)–C(10)	–	–	83.7(7)	83.7(4)
M(2)–M(4)–C(10)	–	–	118.4(5)	111.7(4)
M(3)–M(4)–C(10)	–	–	53.1(5)	51.6(4)
Ru(1)–M(4)–C(11)	–	–	81.5(5)	77.6(3)
M(2)–M(4)–C(11)	–	–	54.9(4)	51.6(3)
M(3)–M(4)–C(11)	–	–	120.6(4)	111.4(3)
Ru(1)–M(2)–C(11)	–	–	74.0(4)	77.5(3)
M(3)–M(2)–C(11)	–	–	101.7(3)	109.6(4)
M(4)–M(2)–C(11)	–	–	44.5(3)	50.3(4)
Ru(1)–M(2)–C(12)	–	–	–	81.3(4)
M(3)–M(2)–C(12)	–	–	–	52.5(4)
M(4)–M(2)–C(12)	–	–	–	111.9(4)
Ru(1)–M(3)–C(12)	–	–	–	76.8(3)
M(2)–M(3)–C(12)	–	–	–	47.7(3)
M(4)–M(3)–C(12)	–	–	–	107.1(3)
M(3)–C(10)–M(4)	–	79.8(8)	82.1(6)	78.7(5)
M(2)–C(11)–M(4)	–	–	80.6(5)	78.1(4)
M(2)–C(12)–M(3)	–	–	–	79.8(4)
Ru(1)–C(1)–O(1)	173(2)	177(2)	176(2)	178(1)
Ru(1)–C(2)–O(2)	175(1)	174(1)	175(2)	178(1)
Ru(1)–C(3)–O(3)	176(2)	–	178(1)	176(1)
M(2)–C(4)–O(4)	179(1)	175(1)	175(2)	178(1)
M(2)–C(5)–O(5)	176(1)	–	173(2)	–
M(3)–C(6)–O(6)	176(1)	164(2)	172(2)	–
M(3)–C(7)–O(7)	178(1)	178(2)	175(1)	177(1)
M(4)–C(8)–O(8)	179(2)	–	173(2)	176(1)
M(4)–C(9)–O(9)	178(2)	–	–	–
M(3)–C10)–O(10)	–	140.1(4)	138(2)	138(1)
M(4)–C(10)–O(10)	–	–	140(2)	143(1)
M(2)–C(11)–O(11)	–	–	138.2(8)	141(1)

Table 9 (continued)

	2	3	4	5
M(4)-C(11)-O(11)	-	-	141(1)	141(1)
M(2)-C(12)-O(12)	-	-	-	146(1)
M(3)-C(12)-O(12)	-	-	-	134(1)
Ru(1)-M(2)-S(1)	153.0(1)	151.7(1)	147.6(1)	157.5(1)
M(3)-M(2)-S(1)	91.9(1)	92.9(1)	92.7(1)	98.8(1)
M(4)-M(2)-S(1)	104.5(1)	-	91.2(1)	97.5(1)
Ru(1)-M(3)-S(2)	145.0(1)	147.6(1)	143.5(1)	152.4(1)
M(2)-M(3)-S(2)	90.9(1)	93.4(1)	92.4(1)	95.5(1)
M(4)-M(3)-S(2)	103.8(1)	93.6(1)	91.2(1)	96.9(1)
Ru(1)-M(4)-S(3)	-	-	160.6(1)	156.2(1)
M(2)-M(4)-S(3)	-	-	100.1(1)	97.3(1)
M(3)-M(4)-S(3)	-	-	99.3(1)	97.7(1)
M(2)-S(1)-C(13)	107.7(4)	110.0(4)	109.6(6)	104.6(4)
M(2)-S(1)-C(15)	111.8(5)	-	108.6(5)	107.1(5)
M(3)-S(2)-C(13)	109.2(5)	110.2(4)	110.3(5)	108.3(4)
M(3)-S(2)-C(14)	110.7(4)	109.1(6)	108.3(5)	107.6(4)
M(4)-S(3)-C(14)	-	-	107.0(6)	106.1(4)
M(4)-S(3)-C(15)	-	-	107.3(5)	106.7(5)
C(13)-S(1)-C(15)	98.4(8)	96.9(9)	97.7(6)	99.2(6)
C(15)-S(3)-C(14)	98.8(8)	96.4(8)	98.0(6)	98.2(6)
C(13)-S(2)-C(14)	99.2(7)	-	98.9(7)	98.6(6)
S(1)-C(13)-S(2)	117.3(8)	115.9(7)	116.3(8)	115.3(7)
S(1)-C(15)-S(3)	117.2(8)	-	115.9(9)	114.9(6)
S(3)-C(14)-S(2)	117.2(8)	117(1)	115.0(7)	115.0(7)
S(1)-M(2)-C(4)	101.0(4)	97.2(5)	98.1(6)	99.9(4)
S(1)-M(2)-C(5)	99.0(5)	-	102.2(7)	-
S(2)-M(3)-C(6)	94.5(4)	93.5(5)	94.1(6)	-
S(2)-M(3)-C(7)	94.8(4)	90.9(4)	91.5(5)	94.5(4)
S(3)-M(4)-C(8)	-	-	102.0(7)	104.3(5)
S(2)-M(3)-C(10)	-	95.0(6)	96.5(6)	97.1(3)
S(3)-M(4)-C(10)	-	-	98.0(7)	96.1(4)
S(3)-M(4)-C(11)	-	-	96.4(5)	97.7(4)
S(1)-M(2)-C(11)	-	-	93.8(4)	97.0(3)
S(1)-M(2)-C(12)	-	-	-	99.5(4)
S(2)-M(3)-C(12)	-	-	-	96.7(3)

solution (70 ml) of trithiane (68 mg, 0.49 mmol). After 1 h under reflux the solid **5** was filtered from hot solution and purified on a silica column. A minor yellow fraction of impurity was eluted with 1:1 hexane-CH_2Cl_2 solution and then complex **5** with CH_2Cl_2. The yield was 235 mg, 72%. IR (CH_2Cl_2): 2071m, 2001s, 1818w, 1784w cm^{-1}. ^{1}H NMR ($CDCl_3$): −23.7 ppm. Found: H, 1.12; C, 21.3. Calcd.: H, 1.05; C, 21.5%.

This reaction was also attempted in refluxing hexane. After 4 h only about half of each of the starting materials had reacted. During chromatographic separation a 1/1 CH_2Cl_2/hexane eluted first the unchanged parent cluster and then a minor reddish brown fraction of [$HRuCo_3(CO)_{11}$(trithiane)] (IR (CH_2Cl_2): 2086w, 2048vs, 2013vs, 1867w, 1843w cm^{-1}; ^{1}H NMR ($CDCl_3$): −19.6 ppm, br). These were followed by a brown fraction of **5** (CH_2Cl_2), which was identified by the close similarity of its spectra to those of the corresponding monosubstituted derivatives of $HRuCo_3(CO)_{12}$. On one occasion the brown band was preceded by a violet

Table 10

Crystallographic data

	1	2	3	4	5
Formula	$C_{15}H_8Ru_4O_{12}S_3$	$C_{13}H_{10}Ru_4O_{10}S_3$	$C_{13}H_8O_{10}Ru_4S_3$	$O_{12}H_7Ru_3CoO_9S_3$	$C_{12}H_7Co_3RuO_9S_3$
Formula weight	880.67	826.67	824.65	753.50	669.2
Cryst. syst.	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	*Pcam*	$C2/c$	*Cc*
a (Å)	9.75(1)	8.444(5)	18.08(1)	30.309(9)	13.01(1)
b (Å)	16.26(2)	10.322(5)	8.899(7)	8.924(4)	9.420(8)
c (Å)	16.13(2)	13.529(7)	13.38(1)	17.504(5)	15.80(2)
α (deg)	90	98.09(4)	90	90	90
β (deg)	102.10(9)	94.37(5)	90	119.06(2)	93.74(8)
γ (deg)	90	103.75(4)	90	90	90
V (Å^3)	2499(5)	1127(1)	2152	4138(3)	1933(3)
Z	4	2	4	8	4
No. cent. refl.	25	25	25	26	25
Cent. 2θ	14–25	12–25	14–25	14–25	11–23
Cyst. dim. (mm)	0.7×0.5×0.4	0.3×0.3×0.2	0.2×0.2×0.4	0.4×0.2×0.1	0.4×0.3×0.1
$D_{calcd.}$ (g cm^{-3})	2.34	2.44	2.54	2.51	2.30
2θ-limits	5–50	5–55	5–50	5–50	5–50
h, *k*, *l* range	12, 20, ±20	11, ±14, ±18	11, 16, 22	37, 11, ±21	15, 11, ±18
No. uniq. refl.	4368	5154	1978	3654	1780
Obsd. data	3407	2320	1208	2136	1517
μ (mm^{-1})	2.62	2.90	3.03	3.24	3.64
No. param.	307	271	148	271	251
R%	4.88	4.71	4.99	4.65	3.17
R_w%	6.51	4.43	4.81	4.52	3.16

fraction; CH_2Cl_2 spectroscopic characterization of the violet compound was complicated by the presence of **5**, but in its colour, ^1H NMR ($CDCl_3$) spectrum (-19.4 ppm) and IR spectrum (CH_2Cl_2, main peaks: 2070m, 2001vs, 1843m) it resembles $[HRuCo_3(CO)_{10}(SMe_2)_2]$, and it is thus probably $[HRuCo_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-trithiane})]$.

Preparation of compound 6. A solution of $[Co_4(CO)_{12}]$ (200 mg, 0.35 mmol in 25 ml heptane) was added to a refluxing heptane solution (50 ml) of trithiane (48 mg, 0.35 mmol), and the mixture refluxed for a further 20 min. The black solid **6** was filtered off and dried. The product is insoluble in CH_2Cl_2, but soluble in THF. Yield 194 mg, 89%. IR (THF): 2060m, 2009s, 1980m, 1797s. Found: H, 1.02; C, 22.9. Calcd.: H, 0.97; C, 23.0%.

Crystallographic studies

Crystals for structure determination were grown by slow evaporation of saturated CH_2Cl_2 or CH_2Cl_2/hexane solutions.

Intensity data were collected on a Nicolet R3m diffractometer. Mo-K_α radiation with $\lambda = 0.71073$ Å. Intensities were corrected for Lorenz, polarization, and background effects.

Empirical absorption correction was made from Ψ data for **2** and **5**. Table 10 presents further crystallographic data. The structures were determined by direct methods and subsequent Fourier synthesis using the SHELXTL program package [21]. Anisotropic refinement was carried out for all non-hydrogen atoms. Methylene protons were placed in calculated positions (C–H 96 pm, U 0.08 Å^2) and not refined. The cluster hydrides were not found in Fourier maps. The structure of **3** was solved in space group *Pcam*, a non-standard setting of *Pbcm*. The two alternative absolute structures for **5** were refined and the one with better *R* factors was chosen.

Steric studies

The nonbonded H–S distances of **5** were calculated by using the CHEM-X molecular modelling program. Crystal structure coordinates were used in the studies, except the hydride ligands, which were placed in calculated positions with a Co–H distance of 170 pm, the average of the Co–H distances observed in $[HRuCo_3(CO)_{11}(SMe_2)]$ and $[HRuCo_3(CO)_{10}(SMe_2)_2]$. For these two compounds both observed and theoretical hydride positions were used in the calculations.

Tables, temperature factors, full lists of bond distances and angles, and lists of structure factors are available from the authors.

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