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Tetrahydrothiophene derivatives of metal carbonyl clusters

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Abstract

The cyclic thioether ligand tetrahydrothiophene, SC_4H_8, reacts with transition metal carbonyl clusters $HRuCo_3(CO)_{12}$, $HRuRh_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$ and $Ru_3(CO)_{12}$ to give $HRuCo_3(CO)_{11}(SC_4H_8)$ (**1**), $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (**2**), $H_2Ru_4(CO)_{12}(SC_4H_8)$ (**3**) and $Ru_4(CO)_{13}(SC_4H_8)$ (**4**), respectively. The crystal structures of the products fall into three different structural types. In **1** the tetrahydrotriophene displaces a terminal carbonyl ligand at cobalt; whereas in **2** it acts as a bridging four-electron donor to give a dimerized cluster. Both Ru-clusters have butterfly structures with tetrahydrothiophene ligand coordinated between the wingtips.

Keywords: Ruthenium; Rhodium; Cobalt; Hydride; Tetrahydrothiophene; Cluster

1. Introduction

Sulphur compounds such as hydrogen disulphide, thiols, thiophenes and aliphatic thioethers appear in fossil fuels. They are undesirable since they tend to poison the catalysts used in fuel processing and must therefore be removed. The desulphurization of thioethers by use of a metal catalyst, has been widely studied. The thioether typically acts as a sulphur donor and forms a complex with the metal, and this is followed by a S–C bond breaking and hydrogenation of the hydrocarbon chain. Metals such as Mo, Co, Ru, Fe and Ni can be used as catalysts. The cyclic thioether thiophene is especially difficult to deal with owing to its aromatic character, and the mechanisms of the reactions between thiophene and the metal compounds have been studied with the aim of increasing reactivity. Its bonding to the metal is analogous to that of η^1- and η^5-cyclopentadienyls [1]. An important question is whether the hydrogenation of the ring of tetrahydrothiophene occurs before the cleavage of C–S bond or whether direct elimination of sulphur is possible [2,3]. If hydrogenation occurs first it is important to study the reactions of tetrahydrothiophene with metals that are usually used in hydrodesulphurization. Cluster and complex compounds can be profitably be used as models for metal surfaces because of the relative ease of their characterization. For example, the reaction of thiophene with $Fe_2(CO)_9$ yields $Fe_2(CO)_6(C_4H_4)$ as a result of desulphurization by the iron. In contrast tetrahydrothiophene reacts like many aliphatic thioethers; thus in the reaction with $Fe_2(CO)_9$ tetrahydrothiophene yields $Fe_3(CO)_8(SC_4H_8)_2$, in which the organosulphur ligands remain intact [4].

We have previously studied the relative reactivities of ruthenium, rodium and cobalt towards a series of tetrahedral cluster compounds $H_xRu_xCo_yRh_z(CO)_{12}$ (x, y, $z = 0$–4, $x + y + z = 4$) [5]. Systematic trends in reactivity and spectroscopic properties have been observed. In ligand substitutions by thioethers the reactivities of these metals decrease in series Rh > Co > Ru [5]. In the present work the clusters $HRuRh_3(CO)_{12}$, $HRuCo_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ have been chosen as representive of the series of tetrahedral clusters, and $Ru_3(CO)_{12}$ was used for comparison.

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Earlier studies of aliphatic thioethers SR_2 (R = alkyl, aryl) have shown that the ligands can bond in various ways to the metal core. They can form single bonds to metals, taking terminal positions or they can bridge between two metal atoms [6]. They can also form bridges between two metals causing cleavage of the metal–metal bonds [7].

2. Results and discussion

Compounds $HRuCo_3(CO)_{11}(SC_4H_8)$ (**1**), $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (**2**), $H_2Ru_4(CO)_{12}(SC_4H_8)$ (**3**) and $Ru_4(CO)_{13}(SC_4H_8)$ (**4**) were prepared by reactions between clusters $HRuCo_3(CO)_{12}$, $HRuRh_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$ and $Ru_3(CO)_{12}$ and tetrahydrothiophene. Compounds **1** and **2** were formed in the substitution of carbonyl ligands by tetrahydrothiophene in CH_2Cl_2 or THF. The formation of **3** involved substitution of two hydride ligands, and that of **4** involves fragmentation and rearrangement of the parent cluster. In all these cases refluxing of the solution was necessary to raise the rate of the reaction. The reactions were carried under nitrogen although the products were only slighly unstable in air, and were monitored by IR spectroscopy. The structures were determined by X-ray crystallography. In the crystals of all four complexes studied the asymmetric unit contains two molecules, which differ in the ligand orientation. Further information was obtained from ^1H NMR spectra.

2.1. $HRuCo_3(CO)_{11}(SC_4H_8)$ (1)

Compound **1** was prepared by treatment of $HRuCo_3(CO)_{12}$ with tetrahydrothiophene in CH_2Cl_2. A reasonable yield was obtained when an excess of the ligand and a long (46 h) reaction time were used. Tetrahydrothiophene acts as a two electron donor and displaces one axial carbonyl ligand from cobalt leaving the cluster otherwise unchanged. In the parent cluster each Co–Co bond is bridged by a carbonyl ligand. Three other terminal carbonyl groups are attached at the apical ruthenium and two at each cobalt, one in an axial and the other in an equatorial position. The crystal structure of **1** is shown in Fig. 1, the atomic coordinates in Table 1, and selected bond lengths and angles in Tables 2 and 3. The basal $Co_3(\mu_3\text{-}H)$ cluster hydride is unchanged during the displacement reaction, as shown by comprison of the bond angles and distances with those for structures containing a similar hydride. Furthermore the chemical shift in ^1H-NMR [−19.6 ppm (s, br)] is typical of a $Co_3(\mu_3\text{-}H)$ hydride. The presence of a hydride bridging the metal–metal bond would lengthen the bond, in **1** all the Co–Co (250.9–251.5 pm) and Ru–Co (261.8–264.4 pm) bond distances are approximately equal. In contrast, for example, $HRuCo_3(CO)_9$ (trithiane) has a hydride bridged Ru-μ_2–H–Co bond of length 269.7 pm and two other Ru–Co bonds of length 262.0 pm. An edge-bridging hydride would also need more space along the bridged bond, whereas in this structure there is no distortion of the geometry of the carbonyl ligands. The Co–Ru–C bond angles lie in the narrow range of 100.7–105.3°. The Ru–Co–C_{eq} angles lie between 77.2–80.6°, except for that involving Co(4) (85.0° and 87.1°). However the latter bond angle is not large enough for a Ru-μ_2–H–Co system; e.g. $HRuCo_3(CO)_9$(trithiane) has a Ru–Co–C_{eq} angle of 113.0° for the bridged bond.

Similar structures have been observed previously for products of the reactions of SMe_2 [6], $SeMe_2$ [8] and $TePh_2$ [9] with $HRuCo_3(CO)_{12}$; SMe_2 and $SeMe_2$ can also form disubstituted products with axial ligands at adjacent cobalt atoms [6,8].

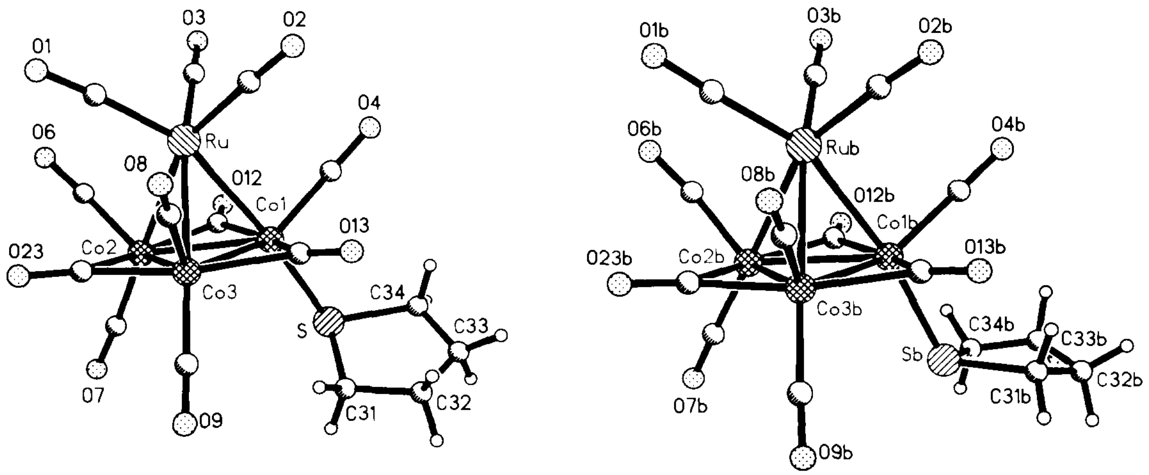

Fig. 1. Structure and numbering scheme of $HRuCo_3(CO)_{11}SC_4H_8)$ (**1**).

Table 1
Atomic coordinates ($\times 10^4$) for $HRuCo_3(CO)_{11}(SC_4H_8)$ (1)

Atom	x	y	z
Ru	2500	652(1)	2500
Co(1)	1924(2)	-1382(2)	1903(1)
Co(2)	288(2)	-72(2)	2313(1)
Co(3)	1624(2)	-1037(2)	3337(1)
S	1182(7)	-3026(5)	1336(5)
O(1)	2363(14)	2742(13)	3596(10)
O(2)	5150(12)	335(14)	2775(10)
O(3)	2807(17)	2080(14)	1022(11)
O(4)	3995(17)	-1074(16)	976(8)
O(6)	-94(13)	2380(11)	1989(10)
O(7)	-2175(11)	-904(12)	2128(10)
O(8)	3355(15)	-97(15)	4483(8)
O(9)	800(13)	-2817(15)	4407(9)
O(12)	652(14)	-117(15)	598(7)
O(13)	3649(10)	-2537(12)	2959(8)
O(23)	-86(13)	673(13)	3945(8)
C(1)	2442(15)	1973(14)	3167(12)
C(2)	4144(16)	471(13)	2669(12)
C(3)	2738(20)	1565(18)	1554(15)
C(4)	3166(19)	-1175(18)	1312(10)
C(6)	98(15)	1414(16)	2109(11)
C(7)	-1200(18)	-622(14)	2192(9)
C(8)	2691(16)	-380(15)	4014(10)
C(9)	1094(14)	-2151(16)	3971(12)
C(12)	839(18)	-413(18)	1233(12)
C(13)	2831(14)	-1981(14)	2777(10)
C(23)	354(15)	133(17)	3481(10)
C(31)	1056(29)	-4050(35)	1971(17)
C(32)	1930(31)	-4922(30)	1831(17)
C(33)	2382(31)	-4884(29)	1122(25)
C(34)	2230(42)	-3843(21)	824(16)
RuB	7530(1)	3935(1)	3911(1)
Co(1B)	6926(2)	6069(2)	4280(1)
Co(2B)	5309(2)	4628(2)	3943(1)
Co(3B)	6552(2)	5413(2)	2886(1)
S(b)	6165(5)	7908(4)	4441(3)
O(1B)	7453(12)	1599(12)	3046(10)
O(2B)	10175(12)	4273(14)	3699(10)
O(3B)	7940(16)	2864(15)	5520(9)
O(4B)	8994(12)	6088(14)	5328(7)
O(6B)	5038(11)	2236(10)	4466(9)
O(7B)	2834(10)	5393(11)	4034(9)
O(8B)	8090(14)	4221(14)	1847(8)
O(9B)	5614(13)	7088(13)	1721(8)
O(12B)	5718(12)	5226(13)	5638(7)
O(13B)	8640(10)	6955(11)	3179(7)
O(23B)	4867(12)	3565(12)	2369(7)
C(1B)	7476(14)	2494(15)	3344(11)
C(2B)	9176(15)	4111(14)	3779(9)
C(3B)	7812(17)	3254(15)	4923(11)
C(4B)	8192(15)	6086(14)	4937(9)
C(6B)	5223(14)	3195(17)	4276(10)
C(7B)	3800(14)	5083(14)	3993(8)
C(8B)	7510(16)	4690(16)	2274(10)
C(9B)	5912(14)	6458(13)	2170(9)
C(12B)	5920(15)	5303(13)	4975(9)
C(13B)	7788(14)	6443(15)	3392(9)
C(23B)	5289(15)	4228(15)	2827(10)
C(31B)	7270(28)	8954(20)	4381(16)
C(32B)	7327(38)	9631(32)	5053(33)
C(33B)	6764(39)	8934(34)	5693(17)
C(34B)	5900(23)	8278(22)	5451(15)

2.2. $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (2)

Owing to the higher reactivity of rhodium the reaction of tetrahydrothiophene with $HRuRh_3(CO)_{12}$ is much faster than that with $HRuCo_3(CO)_{12}$, giving **2** in 86% yield after 30 min refluxing. In the dimeric product two tetrahedral $RuRh_3$ units are bridged by three tetrahydrothiophene ligands. The tetrahydrothiophene acts as bidentate four-electron donor occupying all the axial sites at rhodium atoms. (Similar dimeric structures have been found for $[HRuRh_3(CO)_9]_2[SMe_2]_3$ and $[HRuRh_3(CO)_9]_2[SeMe_2]_3$ [8]). The molecular structure is shown in Fig. 2, atomic coordinates are listed in Table 4 and selected bond lengths and angles in Tables 5 and 6. The basic tetrahedral units have remained unchanged and the overall geometry is symmetrical, as shown in the bond length and bond angle data.

The presence of the $Rh_3(\mu_3\text{-H})$ hydride was evident

Table 2
Bond lengths (pm) for $HRuCo_3(CO)_{11}(SC_4H_8)$ (1)

	A	B
Ru-Co(1)	261.8(2)	263.1(2)
Ru-Co(2)	264.4(2)	264.2(3)
Ru-Co(3)	263.2(2)	264.0(3)
Co(1)-Co(2)	251.4(3)	251.4(3)
Co(1)-Co(3)	251.5(3)	250.9(3)
Co(2)-Co(3)	251.0(3)	250.9(3)
Co(1)-S	226.4(7)	230.4(5)
Ru-C(1)	190(2)	192(2)
Ru-C(2)	188(2)	190(2)
Ru-C(3)	195(2)	191(2)
Co(1)-C(4)	179(2)	178(2)
Co(2)-C(6)	176(2)	175(2)
Co(2)-C(7)	180(2)	179(2)
Co(3)-C(8)	180(2)	175(2)
Co(3)-C(9)	180(2)	184(2)
Co(1)-C(12)	198(2)	190(2)
Co(2)-C(12)	201(2)	201(2)
Co(1)-C(13)	190(2)	189(2)
Co(3)-C(13)	202(2)	200(2)
Co(2)-C(23)	200(2)	196(2)
Co(3)-C(23)	199(2)	197(2)
S-C(31)	161(4)	174(3)
S-C(34)	178(4)	181(3)
C(31)-C(32)	144(5)	138(6)
C(32)-C(33)	134(5)	152(6)
C(33)-C(34)	131(4)	129(5)
O(1)-C(1)	115(2)	115(2)
O(2)-C(2)	116(2)	116(2)
O(3)-C(3)	109(3)	111(2)
O(4)-C(4)	113(3)	110(2)
O(6)-C(6)	115(2)	117(2)
O(7)-C(7)	115(2)	116(2)
O(8)-C(8)	112(2)	114(2)
O(9)-C(9)	113(3)	109(2)
O(12)-C(12)	114(2)	117(2)
O(13)-C(13)	115(2)	120(2)
O(23)-C(23)	114(2)	118(2)

from the [1]H-NMR spectrum. The position of the hydride reconance at −16.8 ppm (q, $^{1}J_{(Rh-H)}$ = 11.4 Hz) is similar to those found for other dimeric clusters containing thio-, seleno- or tellurobridges [6,8,10]. The distance between the two hydrides can be estimated by assuming a Rh–H bond length of 185 pm, as observed crystallographically for $[HRuRh_3(CO)_{10}(PPh_3)_2]$, showing that the H–H distance in **2** is ca. 250 pm, which is same as that in $[HRuRh_3(CO)_9]_2[SMe_2]_3$ [8].

2.3. $H_2Ru_4(CO)_{12}(SC_4H_8)$ (3)

Reactions between $H_4Ru_4(CO)_{12}$ and tetrahydrothiophene for 22 h in refluxing THF gave **3** in which the tetrahedral cluster has opened to a butterfly structure with the tetrahydrothiophene ligand coordinated between the wingtips (Fig. 3). This structure is similar to that of the products formed in the reactions between $H_4Ru_4(CO)_{12}$ and SMe_2 or 1,3,5-trithiacyclohexane. All twelve terminal carbonyl ligands of the parent cluster have been maintained, three terminal groups in each metal, but only two of the hydrides are present in **3**. The [1]H-NMR spectrum shows the presence of two different hydride ligand types (singlets at −16.7 and −15.7 ppm); these are very close to those observed for of $H_2Ru_4(CO)_{12}(SMe_2)$ (−16.7 ppm and −15.6 ppm) [7] and $H_2Ru_4(CO)_{12}$(1,3,5-trithiacyclohexane) (−17.2 ppm and −15.9 ppm) [11]. The hydride ligands can be located on the Ru(2)–Ru(3) and Ru(2)–Ru(4) bonds on basis of the bond lengths and angles. Thus the hydrogen bonded Ru(2)–Ru(4) bond is clearly longer (302.8 pm) than the other wing Ru–Ru bonds (average 284.9 pm), and the hinge bond Ru(2)–Ru(3) is longer (292.3 pm) than corresponding carbonyl bridged bond in **4** (279.9 pm). Atomic coordinates for **3** are listed in Table 7 and selected bond lenghts and bond angles in Tables 8 and 9.

2.4. $Ru_4(CO)_{13}(SC_4H_8)$ (4)

Reaction of tetrahydrothiophene with $Ru_3(CO)_{12}$ for 5 h in refluxing THF gave **4** in 6% yield. The parent cluster structure breaks up during the reaction and a new structure containing the ligand is formed. This structure is shown in Fig. 4. The atom coordinates are listed in Table 10, bond lengths in Table 8, and selected bond angles in Table 9. There are four ruthenium atoms in a butterfly shape with tetrahydrothiophene between the wingtips. One of the carbonyl ligands is μ_2-CO coordinated to the hinge bond Ru(2)–Ru(3), and the others are in terminal positions, three on every metal.

3. Experimental section

3.1. General comments

Reactions were carried out under nitrogen in deoxygenated solvents. Chromatographic separations were carried out in the air except in the case of $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (**2**). THF was distilled from Na-ben-

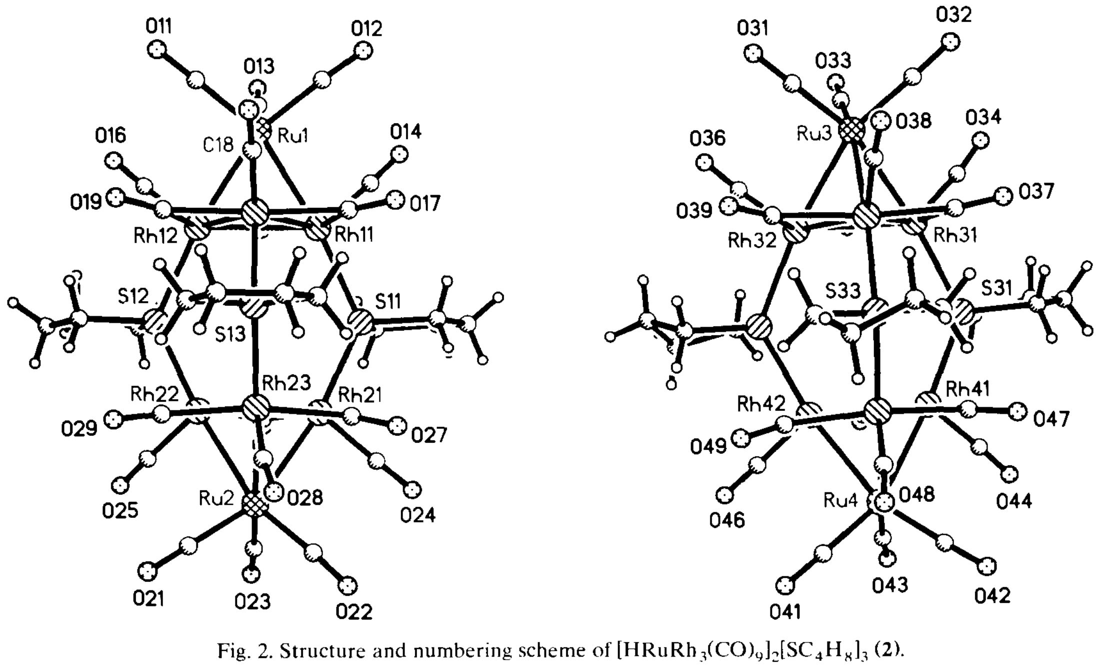

Fig. 2. Structure and numbering scheme of $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (2).

Table 3
Selected bond angles (°) for $HRuCo_3(CO)_{11}(SC_4H_8)$ (**1**)

	A	B
Co(2)-Ru-C(1)	105.2(5)	105.3(5)
Co(3)-Ru-C(1)	103.9(6)	102.8(5)
Co(1)-Ru-C(2)	100.7(5)	101.4(5)
Co(3)-Ru-C(2)	103.5(5)	103.6(5)
Co(1)-Ru-C(3)	101.6(7)	101.5(5)
Co(2)-Ru-C(3)	103.8(7)	102.8(6)
Ru-Co(1)-S	172.0(2)	170.7(2)
Co(2)-Co(1)-S	110.8(2)	111.0(2)
Co(3)-Co(1)-S	118.7(2)	110.0(2)
Ru-Co(1)-C(4)	85.0(6)	87.1(5)
Co(2)-Co(1)-C(4)	133.6(7)	135.1(5)
Co(3)-Co(1)-C(4)	132.5(6)	133.9(5)
Ru-Co(1)-C(12)	81.8(6)	83.6(5)
Co(2)-Co(1)-C(12)	51.6(6)	52.0(5)
Co(3)-Co(1)-C(12)	111.2(6)	111.9(5)
Ru-Co(1)-C(13)	84.5(5)	82.5(5)
Co(2)-Co(1)-C(13)	112.2(5)	111.5(5)
Co(3)-Co(1)-C(13)	52.3(5)	51.7(5)
Ru-Co(2)-C(6)	79.8(5)	77.9(5)
Co(1)-Co(2)-C(6)	127.8(6)	126.8(5)
Co(3)-Co(2)-C(6)	129.2(6)	128.0(6)
Co(1)-Co(2)-C(7)	117.2(5)	118.8(5)
Co(3)-Co(2)-C(7)	116.9(5)	120.0(5)
Ru-Co(2)-C(12)	80.5(6)	81.3(5)
Co(1)-Co(2)-C(12)	50.4(6)	48.1(5)
Co(3)-Co(2)-C(12)	110.2(6)	107.9(5)
Ru-Co(2)-C(23)	81.7(5)	82.7(5)
Co(1)-Co(2)-C(23)	110.8(5)	110.5(5)
Co(3)-Co(2)-C(23)	50.9(5)	50.6(5)
Ru-Co(3)-C(8)	77.2(6)	80.6(6)
Co(1)-Co(3)-C(8)	124.8(6)	128.8(6)
Co(2)-Co(3)-C(9)	128.6(6)	130.0(6)
Co(1)-Co(3)-C(9)	122.5(6)	118.4(5)
Co(2)-Co(3)-C(8)	121.6(5)	119.7(5)
Ru-Co(3)-C(13)	81.8(5)	80.4(5)
Co(1)-Co(3)-C(13)	47.9(5)	48.0(5)
Co(2)-Co(3)-C(13)	107.9(5)	108.0(5)
Ru-Co(3)-C(23)	82.1(5)	82.4(5)
Co(1)-Co(3)-C(23)	111.0(5)	110.0(5)
Co(2)-Co(3)-C(23)	51.2(5)	50.0(5)
Co(1)-S-C(31)	111.5(13)	110.6(10)
Co(1)-S-C(34)	114.1(13)	114.1(8)
C(31)-S-C(34)	92(2)	92.7(12)
Ru-C(1)-O(1)	176(2)	176(2)
Ru-C(2)-O(2)	179(2)	177(2)
Ru-C(3)-O(3)	176(2)	178(2)
Co(1)-C(4)-O(4)	176(2)	178(2)
Co(2)-C(6)-O(6)	176(2)	172.5(14)
Co(2)-C(7)-O(7)	176(2)	179(2)
Co(3)-C(8)-O(8)	172(2)	177(2)
Co(3)-C(9)-O(9)	176(2)	175(2)
Co(1)-C(12)-O(12)	143(2)	142.4(14)
Co(2)-C(12)-O(12)	139(2)	137.7(14)
Co(1)-C(13)-O(13)	143.8(14)	143.9(13)
Co(3)-C(13)-O(13)	136.3(13)	135.7(13)
Co(2)-C(23)-O(23)	139(2)	141.5(14)
Co(3)-C(23)-O(23)	143(2)	138.7(14)
C(31)-C(32)-C(33)	115(3)	107(3)
C(32)-C(33)-C(34)	109(3)	115(3)

Table 4
Atomic coordinates ($\times 10^4$) for $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (**2**)

Atom	*x*	*y*	*z*
Ru(1)	1920(1)	2873(1)	4449(1)
Rh(11)	3033(1)	2632(1)	4301(1)
Rh(12)	1943(1)	1617(1)	3839(1)
Rh(13)	2486(1)	834(1)	4580(1)
Ru(2)	4223(1)	−1838(1)	3606(1)
Rh(21)	4217(1)	285(1)	3885(1)
Rh(22)	3119(1)	−714(1)	3425(1)
Rh(23)	3667(1)	−1508(1)	4162(1)
S(11)	4007(1)	2141(2)	4137(1)
S(12)	2135(1)	367(2)	3345(1)
S(13)	3069(1)	−954(2)	4611(1)
O(11)	642(3)	2161(10)	4524(3)
O(12)	2410(4)	4075(8)	5214(2)
O(13)	1473(5)	5069(9)	4036(3)
O(14)	3281(5)	5001(8)	4584(4)
O(15)	2403(3)	3805(7)	3538(2)
O(16)	651(3)	2460(8)	3410(2)
O(17)	3613(3)	2003(8)	5153(2)
O(18)	1974(4)	474(8)	5253(2)
O(19)	1219(2)	−201(7)	4138(2)
O(21)	3720(4)	−4222(7)	3377(2)
O(22)	5495(3)	−2793(8)	4064(2)
O(23)	4625(5)	−1441(10)	2875(2)
O(24)	5553(3)	640(7)	3867(2)
O(25)	3748(4)	1132(7)	3059(2)
O(26)	2839(4)	−1587(8)	2628(2)
O(27)	4967(3)	−689(6)	4660(2)
O(28)	4332(4)	−3611(6)	4541(2)
O(29)	2540(3)	−2872(7)	3654(2)
C(11)	1118(5)	2456(12)	4486(4)
C(12)	2213(5)	3591(9)	4929(3)
C(13)	1651(6)	4234(11)	4192(4)
C(14)	3212(6)	4107(11)	4481(4)
C(15)	2455(5)	3067(10)	3759(3)
C(16)	1145(5)	2119(10)	3575(3)
C(17)	3256(5)	1869(9)	4855(3)
C(18)	2173(5)	606(11)	5009(3)
C(19)	1648(4)	384(8)	4162(3)
C(21)	3906(5)	−3324(10)	3458(3)
C(22)	5016(5)	−2399(9)	3894(3)
C(23)	4480(5)	−1553(11)	3140(3)
C(24)	5030(5)	511(9)	3861(3)
C(25)	3713(5)	583(9)	3322(3)
C(26)	2935(5)	−1297(10)	2934(3)
C(27)	4520(4)	−609(9)	4394(3)
C(28)	4045(5)	−2859(9)	4388(3)
C(29)	2886(5)	−2104(9)	3712(3)
C(111)	4678(5)	2525(9)	4542(3)
C(112)	4997(7)	3450(15)	4423(5)
C(113)	4729(7)	3917(12)	4068(4)
C(114)	4170(5)	3257(9)	3824(3)
C(121)	1923(5)	1107(10)	2887(3)
C(122)	1256(6)	763(14)	2684(3)
C(123)	1121(7)	−344(15)	2795(4)
C(124)	1459(4)	−578(9)	3191(3)
C(131)	2545(5)	−2138(9)	4652(3)
C(132)	2812(8)	−2579(13)	5048(4)
C(133)	3351(8)	−2080(19)	5260(5)
C(134)	3583(5)	−1116(10)	5109(3)

Table 4 (continued)

Atom	x	y	z
Ru(3)	286(1)	7865(1)	1118(1)
Rh(31)	930(1)	6670(1)	1734(1)
Rh(32)	1545(1)	7694(1)	1256(1)
Rh(33)	768(1)	5836(1)	1000(1)
Ru(4)	3509(1)	3396(1)	1996(1)
Rh(41)	2535(1)	4417(1)	2165(1)
Rh(42)	3182(1)	5483(1)	1709(1)
Rh(43)	2423(1)	3624(1)	1434(1)
S(31)	1603(1)	5438(2)	2234(1)
S(32)	2684(1)	7271(2)	1427(1)
S(33)	1395(1)	4104(2)	978(1)
O(31)	−85(5)	8904(8)	326(2)
O(32)	−1061(4)	7324(8)	1104(3)
O(33)	217(4)	10114(7)	1494(3)
O(34)	−19(3)	7617(8)	2098(2)
O(35)	1653(3)	8888(6)	2015(2)
O(36)	1522(4)	10086(6)	987(3)
O(37)	−19(3)	4730(7)	1472(2)
O(38)	−382(4)	5340(8)	357(2)
O(39)	1261(4)	7071(7)	409(2)
O(41)	4440(4)	2857(8)	1550(2)
O(42)	3323(4)	951(7)	2190(2)
O(43)	4515(3)	3905(8)	2750(2)
O(44)	3019(3)	3376(7)	2948(2)
O(45)	3484(3)	6298(7)	2540(2)
O(46)	4554(3)	6026(8)	1806(3)
O(47)	1785(4)	2218(7)	1927(2)
O(48)	2745(3)	1459(7)	1111(2)
O(49)	3222(3)	4526(7)	932(2)
C(31)	61(5)	8498(10)	621(3)
C(32)	−546(5)	7490(9)	1109(4)
C(33)	242(5)	9250(10)	1347(3)
C(34)	355(5)	7246(10)	1981(3)
C(35)	1503(4)	8155(9)	1807(3)
C(36)	1547(5)	9175(10)	1089(3)
C(37)	356(4)	5331(9)	1427(3)
C(38)	57(5)	5565(10)	600(3)
C(39)	1237(5)	6937(8)	715(3)
C(41)	4088(5)	3042(10)	1719(3)
C(42)	3412(5)	1895(9)	2124(3)
C(43)	4141(4)	3724(9)	2456(3)
C(44)	2827(4)	3791(9)	2656(3)
C(45)	3209(4)	5762(9)	2281(3)
C(46)	4035(5)	5822(9)	1772(3)
C(47)	2062(4)	2997(8)	1870(3)
C(48)	2609(4)	2294(9)	1237(3)
C(49)	3024(5)	4590(9)	1196(3)
C(311)	1083(5)	4438(10)	2381(3)
C(312)	1048(9)	4777(20)	2749(5)
C(313)	1375(7)	5753(17)	2900(4)
C(314)	1819(5)	6192(11)	2700(3)
C(321)	3110(5)	8447(9)	1708(3)
C(322)	3569(5)	8893(10)	1496(3)
C(323)	3236(5)	8775(9)	1069(3)
C(324)	2957(4)	7606(8)	1004(3)
C(331)	1489(5)	3974(9)	498(3)
C(332)	1283(6)	2778(12)	368(3)
C(333)	753(5)	2479(11)	506(3)
C(334)	897(5)	2858(8)	921(3)

zophenoneketyl. The $Ru_3(CO)_{12}$ (Johnson-Matthey) and tetrahydrothiophene (Aldrich) were from commercial sources. $HRuCo_3(CO)_{12}$ [12], $HRuRh_3(CO)_{12}$ [13] and $H_4Ru_4(CO)_{12}$ [14] were prepared by published methods.

FT-IR spectra were recorded on a Galaxy 6020

Table 5
Bond lengths (pm) for $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (**2**)

Ru(1)–Rh(11)	268.1(2)	Ru(3)–Rh(31)	268.8(2)
Ru(1)–Rh(12)	268.6(2)	Ru(3)–Rh(32)	268.8(2)
Ru(1)–Rh(13)	269.0(2)	Ru(3)–Rh(33)	270.5(2)
Ru(1)–C(11)	188.3(12)	Ru(3)–C(31)	189.2(11)
Ru(1)–C(12)	188.6(11)	Ru(3)–C(32)	188.3(11)
Ru(1)–C(13)	186.8(12)	Ru(3)–C(33)	185.2(12)
Rh(11)–Rh(12)	278.3(2)	Rh(31)–Rh(32)	277.9(2)
Rh(11)–Rh(13)	277.7(2)	Rh(31)–Rh(33)	278.0(2)
Rh(11)–S(11)	246.4(3)	Rh(31)–S(31)	246.9(3)
Rh(11)–C(14)	186.3(13)	Rh(31)–C(34)	188.3(12)
Rh(11)–C(15)	208.8(9)	Rh(31)–C(35)	213.3(10)
Rh(11)–C(17)	214.0(10)	Rh(31)–C(37)	213.1(10)
Rh(12)–Rh(13)	278.2(2)	Rh(32)–Rh(33)	277.5(2)
Rh(12)–S(12)	245.9(3)	Rh(32)–S(32)	246.3(3)
Rh(12)–C(15)	211.8(11)	Rh(32)–C(35)	211.2(11)
Rh(12)–C(16)	184.7(10)	Rh(32)–C(36)	185.1(11)
Rh(12)–C(19)	209.1(11)	Rh(32)–C(39)	209.4(9)
Rh(13)–S(13)	245.8(3)	Rh(33)–S(33)	248.3(3)
Rh(13)–C(17)	210.1(10)	Rh(33)–C(37)	210.4(11)
Rh(13)–C(18)	190.8(13)	Rh(33)–C(38)	184.0(9)
Rh(13)–C(19)	210.1(9)	Rh(33)–C(39)	211.2(11)
Ru(2)–Rh(21)	270.5(2)	Ru(4)–Rh(41)	268.7(2)
Ru(2)–Rh(22)	268.7(2)	Ru(4)–Rh(42)	269.3(2)
Ru(2)–Rh(23)	268.8(2)	Ru(4)–Rh(43)	268.7(1)
Ru(2)–C(21)	190.9(11)	Ru(4)–C(41)	189.3(12)
Ru(2)–C(22)	188.4(9)	Ru(4)–C(42)	185.9(11)
Ru(2)–C(23)	197.0(13)	Ru(4)–C(43)	188.8(9)
Rh(21)–Rh(22)	278.3(2)	Rh(41)–Rh(42)	278.6(2)
Rh(21)–Rh(23)	277.3(2)	Rh(41)–Rh(43)	277.1(2)
Rh(21)–S(11)	247.0(3)	Rh(41)–S(31)	246.3(3)
Rh(21)–C(24)	184.3(11)	Rh(41)–C(44)	187.5(9)
Rh(21)–C(25)	206.5(9)	Rh(41)–C(45)	213.4(10)
Rh(21)–C(27)	207.4(9)	Rh(41)–C(47)	209.9(9)
Rh(22)–Rh(23)	277.7(2)	Rh(42)–Rh(43)	277.0(2)
Rh(22)–S(12)	246.6(3)	Rh(42)–S(32)	246.5(3)
Rh(22)–C(25)	211.9(11)	Rh(42)–C(45)	209.7(10)
Rh(22)–C(26)	185.3(10)	Rh(42)–C(46)	187.5(10)
Rh(22)–C(29)	208.9(11)	Rh(42)–C(49)	209.0(10)
Rh(23)–S(13)	247.1(3)	Rh(43)–S(33)	246.3(2)
Rh(23)–C(27)	211.6(9)	Rh(43)–C(47)	211.1(11)
Rh(23)–C(28)	187.7(10)	Rh(43)–C(48)	182.2(11)
Rh(23)–C(29)	213.0(9)	Rh(43)–C(49)	211.8(11)
S(11)–C(111)	182.6(9)	S(31)–C(311)	183.1(13)
S(11)–C(114)	184.5(12)	S(31)–C(314)	185.7(11)
S(12)–C(121)	182.6(11)	S(32)–C(321)	181.9(10)
S(12)–C(124)	181.8(10)	S(32)–C(324)	185.5(11)
S(13)–C(131)	184.8(12)	S(33)–C(331)	183.1(10)
S(13)–C(134)	185.6(9)	S(33)–C(334)	181.3(10)
O(11)–C(11)	115.2(2)	O(31)–C(31)	113.8(14)
O(12)–C(12)	115.8(13)	O(32)–C(32)	114.9(14)
O(13)–C(13)	115.1(2)	O(33)–C(33)	116.0(2)
O(14)–C(14)	111.6(2)	O(34)–C(34)	112.2(14)
O(15)–C(15)	117.0(14)	O(35)–C(35)	113.5(12)
O(16)–C(16)	115.7(12)	O(36)–C(36)	113.4(14)
O(17)–C(17)	115.4(11)	O(37)–C(37)	114.0(13)
O(18)–C(18)	111.0(2)	O(38)–C(38)	114.2(11)
O(19)–C(19)	115.7(12)	O(39)–C(39)	114.6(12)
O(21)–C(21)	114.4(14)	O(41)–C(41)	114.3(2)
O(22)–C(22)	115.9(12)	O(42)–C(42)	116.8(13)

Table 5 (continued)

O(23)–C(23)	111.2(2)	O(43)–C(43)	117.0(11)
O(24)–C(24)	116.1(13)	O(44)–C(44)	113.7(12)
O(25)–C(25)	117.9(13)	O(45)–C(45)	115.7(11)
O(26)–C(26)	113.1(13)	O(46)–C(46)	114.2(13)
O(27)–C(27)	117.3(10)	O(47)–C(47)	115.7(13)
O(28)–C(28)	114.0(12)	O(48)–C(48)	116.2(14)
O(29)–C(29)	116.5(13)	O(49)–C(49)	117.0(14)
C(111)–C(112)	143.3(2)	C(311)–C(312)	142.4(2)
C(112)–C(113)	137.4(2)	C(312)–C(313)	138.8(2)
C(113)–C(114)	151.6(2)	C(313)–C(314)	147.3(2)
C(121)–C(122)	150.2(2)	C(321)–C(322)	153.6(2)
C(122)–C(123)	142.5(2)	C(322)–C(323)	152.7(2)
C(123)–C(124)	145.1(2)	C(323)–C(324)	150.1(2)
C(131)–C(132)	148.7(2)	C(331)–C(332)	151.7(2)
C(132)–C(133)	135.3(2)	C(332)–C(333)	144.7(2)
C(133)–C(134)	142.2(2)	C(333)–C(334)	152.2(2)

spectrometer in appropriate solvents. The ^{1}H-NMR spectra were recorded on a Bruker AM-250 spectrometer at 0°C in $CDCl_3$ with TMS as reference.

3.2. Preparation of $HRuCo_3(CO)_{11}(SC_4H_8)$ (1)

A mixture of $HRuCo_3(CO)_{12}$ (300 mg, 0.49 mmol) and tetrahydrothiophene (172 μl, 1.96 mmol) in 40 ml of CH_2Cl_2 was refluxed for 46 h. The solvent was evaporated in vacuum and the residue was chromatographed on a silica column. Elution with hexane gave three yellow fractions containing by-products. Elution with 4:1 hexane-CH_2Cl_2-mixture then gave a reddish brown band of **1** (150 mg, 45%). Black crystals were obtained from hexane-dichloromethane at −40°C. IR (CH_2Cl_2): 2084m, 2046s, 2011s, 1864m, 1844m cm^{-1}. ^{1}H-NMR ($CDCl_3$): −19.6 ppm (br). Found: C, 26.83;H, 1.33%$RuCo_3SC_{15}O_{11}H_9$ calc.: C, 26.68; H, 1.34%.

3.3. Preparation of $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (2)

A mixture of $HRuRh_3(CO)_{12}$ (150 mg, 0.20 mmol) and tetrahydrothiophene (27 μl, 0.31 mmol) in CH_2Cl_2 (40 ml) was refluxed for 30 min. The mixture was dried in vacuo and the residue was chromatographed on a silica column under nitrogen. Elution with CH_2Cl_2 gave a red fraction containing **2** (137 mg, 86%). Dark red crystals for the X-ray study were obtained from CH_2Cl_2. IR (CH_2Cl_2): 2051s, 2009s, 1971w, 1844m, 1842m cm^{-1}. ^{1}H-NMR ($CDCl_3$): −16.8 ppm (μ_3-H at Rh_3, q, $^1J_{(Rh-H)}$ = 11.4 Hz), 2.6 ppm (C–CH_2–C, m), 3.85 ppm (S–CH_2–C, m). Found: C, 22.54;H, 1.58% $Ru_2Rh_6S_3C_{30}O_{18}H_{26}$ calc.: C, 22.66; H, 1.65%.

3.4. Preparation of $H_2Ru_4(CO)_{12}(SC_4H_8)$ (3)

To a solution of $H_4Ru_4(CO)_{12}$ (150 mg, 0.20 mmol) in THF (40 ml) was added tetrahydrothiophene (25 μl,

Table 6
Bond angles (°) for $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (2)

Rh(12)–Ru(1)–C(11)	99.2(4)	Rh(32)–Ru(3)–C(31)	100.5(4)
Rh(13)–Ru(1)–C(11)	98.8(4)	Rh(33)–Ru(3)–C(31)	101.8(4)
Rh(11)–Ru(1)–C(12)	98.4(3)	Rh(31)–Ru(3)–C(32)	99.8(4)
Rh(13)–Ru(1)–C(12)	102.6(3)	Rh(33)–Ru(3)–C(32)	102.5(3)
Rh(11)–Ru(1)–C(13)	99.7(4)	Rh(31)–Ru(3)–C(33)	99.7(3)
Rh(12)–Ru(1)–C(13)	97.9(4)	Rh(32)–Ru(3)–C(33)	99.7(3)
Ru(1)–Rh(11)–S(11)	172.0(1)	Ru(3)–Rh(31)–S(31)	171.3(1)
Rh(12)–Rh(11)–S(11)	114.6(1)	Rh(32)–Rh(31)–S(31)	114.9(1)
Rh(13)–Rh(11)–S(11)	114.4(1)	Rh(33)–Rh(31)–S(31)	112.8(1)
Ru(1)–Rh(11)–C(14)	86.8(4)	Ru(3)–Rh(31)–C(34)	86.8(3)
Rh(12)–Rh(11)–C(14)	132.5(4)	Rh(32)–Rh(31)–C(34)	131.6(3)
Rh(13)–Rh(11)–C(14)	131.0(5)	Rh(33)–Rh(31)–C(34)	132.2(3)
Ru(1)–Rh(11)–C(15)	79.5(3)	Ru(3)–Rh(31)–C(35)	80.0(2)
Rh(12)–Rh(11)–C(15)	49.0(3)	Rh(32)–Rh(31)–C(35)	48.8(3)
Rh(13)–Rh(11)–C(15)	108.9(3)	Rh(33)–Rh(31)–C(35)	108.5(3)
Ru(1)–Rh(11)–C(17)	80.1(3)	Ru(3)–Rh(31)–C(37)	81.8(3)
Rh(12)–Rh(11)–C(17)	108.4(3)	Rh(32)–Rh(31)–C(37)	108.4(3)
Rh(13)–Rh(11)–C(17)	48.5(3)	Rh(33)–Rh(31)–C(37)	48.6(3)
Ru(1)–Rh(12)–S(12)	170.7(1)	Ru(3)–Rh(32)–S(32)	171.6(1)
Rh(11)–Rh(12)–S(12)	113.6(1)	Rh(31)–Rh(32)–S(32)	113.7(1)
Rh(13)–Rh(12)–S(12)	113.3(1)	Rh(33)–Rh(32)–S(32)	114.4(1)
Ru(1)–Rh(12)–C(15)	78.9(3)	Ru(3)–Rh(32)–C(35)	80.3(2)
Rh(11)–Rh(12)–C(15)	48.1(2)	Rh(31)–Rh(32)–C(35)	49.4(3)
Rh(13)–Rh(12)–C(15)	107.8(3)	Rh(33)–Rh(32)–C(35)	109.4(3)
Ru(1)–Rh(12)–C(16)	90.8(4)	Ru(3)–Rh(32)–C(36)	88.1(3)
Rh(11)–Rh(12)–C(16)	135.1(4)	Rh(31)–Rh(32)–C(36)	131.7(4)
Rh(13)–Rh(12)–C(16)	134.0(4)	Rh(33)–Rh(32)–C(36)	134.0(3)
Ru(1)–Rh(12)–C(19)	80.5(3)	Ru(3)–Rh(32)–C(39)	79.5(3)
Rh(11)–Rh(12)–C(19)	108.3(2)	Rh(31)–Rh(32)–C(39)	108.8(3)
Rh(13)–Rh(12)–C(19)	48.6(2)	Rh(33)–Rh(32)–C(39)	49.0(3)
Ru(1)–Rh(13)–S(13)	170.7(1)	Ru(3)–Rh(33)–S(33)	169.3(1)
Rh(11)–Rh(13)–S(13)	113.3(1)	Rh(31)–Rh(33)–S(33)	113.9(1)
Rh(12)–Rh(13)–S(13)	113.8(1)	Rh(32)–Rh(33)–S(33)	111.4(1)
Ru(1)–Rh(13)–C(17)	80.6(3)	Ru(3)–Rh(33)–C(37)	81.9(3)
Rh(11)–Rh(13)–C(17)	49.7(3)	Rh(31)–Rh(33)–C(37)	49.4(3)
Rh(12)–Rh(13)–C(17)	109.6(3)	Rh(32)–Rh(33)–C(37)	109.4(3)
Ru(1)–Rh(13)–C(18)	90.7(4)	Ru(3)–Rh(33)–C(38)	89.7(4)
Rh(11)–Rh(13)–C(18)	135.1(4)	Rh(31)–Rh(33)–C(38)	132.1(4)
Rh(12)–Rh(13)–C(18)	133.6(3)	Rh(32)–Rh(33)–C(38)	135.1(4)
Ru(1)–Rh(13)–C(19)	80.2(3)	Ru(3)–Rh(33)–C(39)	78.8(3)
Rh(11)–Rh(13)–C(19)	108.2(3)	Rh(31)–Rh(33)–C(39)	108.2(3)
Rh(12)–Rh(13)–C(19)	48.3(3)	Rh(32)–Rh(33)–C(39)	48.4(2)
Rh(22)–Ru(2)–C(21)	98.6(3)	Rh(42)–Ru(4)–C(41)	98.0(3)
Rh(23)–Ru(2)–C(21)	97.8(4)	Rh(43)–Ru(4)–C(41)	101.8(3)
Rh(21)–Ru(2)–C(22)	102.8(3)	Rh(41)–Ru(4)–C(42)	102.2(4)
Rh(23)–Ru(2)–C(22)	100.6(3)	Rh(43)–Ru(4)–C(42)	98.4(3)
Rh(21)–Ru(2)–C(23)	101.6(4)	Rh(41)–Ru(4)–C(43)	98.1(3)
Rh(22)–Ru(2)–C(23)	99.8(3)	Rh(42)–Ru(4)–C(43)	101.8(3)
Rh(22)–Rh(21)–S(11)	112.1(1)	Rh(42)–Rh(41)–S(31)	115.4(1)
Rh(23)–Rh(21)–S(11)	113.1(1)	Rh(43)–Rh(41)–S(31)	114.8(1)
Ru(2)–Rh(21)–C(24)	90.3(3)	Ru(4)–Rh(41)–C(44)	88.0(3)
Rh(22)–Rh(21)–C(24)	136.5(3)	Rh(42)–Rh(41)–C(44)	130.9(3)
Rh(23)–Rh(21)–C(24)	131.5(3)	Rh(43)–Rh(41)–C(44)	134.4(3)
Ru(2)–Rh(21)–C(25)	81.0(3)	Ru(4)–Rh(41)–C(45)	79.6(3)
Rh(22)–Rh(21)–C(25)	49.1(3)	Rh(42)–Rh(41)–C(45)	48.2(3)
Rh(23)–Rh(21)–C(25)	109.0(3)	Rh(43)–Rh(41)–C(45)	107.9(3)
Ru(2)–Rh(21)–C(27)	80.3(3)	Ru(4)–Rh(41)–C(47)	80.7(3)
Rh(22)–Rh(21)–C(27)	109.0(3)	Rh(42)–Rh(41)–C(47)	108.7(3)
Rh(23)–Rh(21)–C(27)	49.2(3)	Rh(43)–Rh(41)–C(47)	49.0(3)
Rh(21)–Rh(22)–S(12)	116.0(1)	Rh(41)–Rh(42)–S(32)	113.1(1)
Rh(23)–Rh(22)–S(12)	114.3(1)	Rh(43)–Rh(42)–S(32)	112.0(1)
Ru(2)–Rh(22)–C(25)	80.5(3)	Ru(4)–Rh(42)–C(45)	80.1(3)
Rh(21)–Rh(22)–C(25)	47.5(2)	Rh(41)–Rh(42)–C(45)	49.4(3)
Rh(23)–Rh(22)–C(25)	107.2(2)	Rh(43)–Rh(42)–C(45)	109.1(3)

Table 6 (continued)

Ru(2)–Rh(22)–C(26)	89.2(3)	Ru(4)–Rh(42)–C(46)	90.0(3)
Rh(21)–Rh(22)–C(26)	130.7(3)	Rh(41)–Rh(42)–C(46)	134.0(3)
Rh(23)–Rh(22)–C(26)	136.5(3)	Rh(43)–Rh(42)–C(46)	134.1(3)
Ru(2)–Rh(22)–C(29)	80.0(3)	Ru(4)–Rh(42)–C(49)	81.1(3)
Rh(21)–Rh(22)–C(29)	109.1(2)	Rh(41)–Rh(42)–C(49)	109.0(3)
Rh(23)–Rh(22)–C(29)	49.5(2)	Rh(43)–Rh(42)–C(49)	49.3(3)
Rh(21)–Rh(23)–S(13)	114.5(1)	Rh(41)–Rh(43)–S(33)	112.5(1)
Rh(22)–Rh(23)–S(13)	112.8(1)	Rh(42)–Rh(43)–S(33)	114.0(1)
Ru(2)–Rh(23)–C(27)	80.0(3)	Ru(4)–Rh(43)–C(47)	80.5(2)
Rh(21)–Rh(23)–C(27)	47.9(3)	Rh(41)–Rh(43)–C(47)	48.7(3)
Rh(22)–Rh(23)–C(27)	107.9(3)	Rh(42)–Rh(43)–C(47)	108.9(3)
Ru(2)–Rh(23)–C(28)	88.0(4)	Ru(4)–Rh(43)–C(48)	87.8(3)
Rh(21)–Rh(23)–C(28)	128.5(3)	Rh(41)–Rh(43)–C(48)	134.6(3)
Rh(22)–Rh(23)–C(28)	136.6(3)	Rh(42)–Rh(43)–C(48)	130.0(3)
Ru(2)–Rh(23)–C(29)	79.3(3)	Ru(4)–Rh(43)–C(49)	80.8(2)
Rh(21)–Rh(23)–C(29)	108.2(3)	Rh(41)–Rh(43)–C(49)	108.7(3)
Rh(22)–Rh(23)–C(29)	48.2(3)	Rh(42)–Rh(43)–C(49)	48.4(3)
Rh(11)–S(11)–Rh(21)	124.7(1)	Rh(31)–S(31)–Rh(41)	123.7(1)
Rh(11)–S(11)–C(111)	107.8(4)	Rh(31)–S(31)–C(311)	107.6(3)
Rh(21)–S(11)–C(111)	109.1(3)	Rh(41)–S(31)–C(311)	109.2(4)
Rh(11)–S(11)–C(114)	108.9(4)	Rh(31)–S(31)–C(314)	109.7(4)
Rh(21)–S(11)–C(114)	108.2(4)	Rh(41)–S(31)–C(314)	109.1(4)
C(111)–S(11)–C(114)	93.9(5)	C(311)–S(31)–C(314)	93.3(5)
Rh(12)–S(12)–Rh(22)	123.8(1)	Rh(32)–S(32)–Rh(42)	125.5(1)
Rh(12)–S(12)–C(121)	109.5(4)	Rh(32)–S(32)–C(321)	108.2(3)
Rh(22)–S(12)–C(121)	109.8(4)	Rh(42)–S(32)–C(321)	108.7(3)
Rh(12)–S(12)–C(124)	107.2(4)	Rh(32)–S(32)–C(324)	107.4(3)
Rh(22)–S(12)–C(124)	109.7(4)	Rh(42)–S(32)–C(324)	108.5(3)
C(121)–S(12)–C(124)	92.2(5)	C(321)–S(32)–C(324)	93.9(5)
Rh(13)–S(13)–Rh(23)	124.7(1)	Rh(33)–S(33)–Rh(43)	125.6(1)
Rh(13)–S(13)–C(131)	108.7(4)	Rh(33)–S(33)–C(331)	108.5(3)
Rh(23)–S(13)–C(131)	108.7(4)	Rh(43)–S(33)–C(331)	106.9(3)
Rh(13)–S(13)–C(134)	107.4(4)	Rh(33)–S(33)–C(334)	110.2(3)
Rh(23)–S(13)–C(134)	109.2(4)	Rh(43)–S(33)–C(334)	107.6(3)
C(131)–S(13)–C(134)	93.7(5)	C(331)–S(33)–C(334)	93.1(5)
Ru(1)–C(11)–O(11)	176.4(11)	Ru(3)–C(31)–O(31)	177.9(11)
Ru(1)–C(12)–O(12)	176.2(11)	Ru(3)–C(32)–O(32)	176.2(10)
Ru(1)–C(13)–O(13)	178.5(13)	Ru(3)–C(33)–O(33)	179.4(10)
Rh(11)–C(14)–O(14)	175.8(12)	Rh(31)–C(34)–O(34)	174.1(9)
Rh(11)–C(15)–O(15)	138.4(8)	Rh(31)–C(35)–O(35)	139.3(9)
Rh(12)–C(15)–O(15)	138.3(7)	Rh(32)–C(35)–O(35)	138.4(9)
Rh(12)–C(16)–O(16)	178.4(11)	Rh(32)–C(36)–O(36)	177.1(11)
Rh(11)–C(17)–O(17)	137.7(9)	Rh(31)–C(37)–O(37)	137.0(8)
Rh(13)–C(17)–O(17)	140.4(9)	Rh(33)–C(37)–O(37)	140.6(8)
Rh(13)–C(18)–O(18)	178.1(9)	Rh(33)–C(38)–O(38)	176.5(10)
Rh(12)–C(19)–O(19)	139.1(7)	Rh(32)–C(39)–O(39)	140.1(8)
Rh(13)–C(19)–O(19)	137.5(8)	Rh(33)–C(39)–O(39)	137.2(8)
Ru(2)–C(21)–O(21)	178.5(9)	Ru(4)–C(41)–O(41)	178.3(11)
Ru(2)–C(22)–O(22)	176.9(9)	Ru(4)–C(42)–O(42)	176.6(7)
Ru(2)–C(23)–O(23)	177.0(12)	Ru(4)–C(43)–O(43)	176.8(10)
Rh(21)–C(24)–O(24)	176.4(9)	Rh(41)–C(44)–O(44)	176.9(10)
Rh(21)–C(25)–O(25)	139.6(8)	Rh(41)–C(45)–O(45)	137.9(8)
Rh(22)–C(25)–O(25)	136.8(7)	Rh(42)–C(45)–O(45)	139.4(9)
Rh(22)–C(26)–O(26)	175.3(11)	Rh(42)–C(46)–O(46)	179.4(7)
Rh(21)–C(27)–O(27)	139.5(8)	Rh(41)–C(47)–O(47)	139.0(8)
Rh(23)–C(27)–O(27)	137.1(8)	Rh(43)–C(47)–O(47)	138.5(8)
Rh(23)–C(28)–O(28)	172.6(9)	Rh(43)–C(48)–O(48)	178.0(9)
Rh(22)–C(29)–O(29)	139.7(8)	Rh(42)–C(49)–O(49)	140.0(8)
Rh(23)–C(29)–O(29)	137.7(8)	Rh(43)–C(49)–O(49)	136.9(8)
C(111)–C(112)–C(113)	118.4(12)	C(311)–C(312)–C(313)	116.3(2)
C(112)–C(113)–C(114)	114.0(13)	C(312)–C(313)–C(314)	116.2(2)
C(121)–C(122)–C(123)	111.3(11)	C(321)–C(322)–C(323)	106.8(8)
C(122)–C(123)–C(124)	111.6(12)	C(322)–C(323)–C(324)	107.5(9)
C(131)–C(132)–C(133)	116.1(2)	C(331)–C(332)–C(333)	108.4(11)
C(132)–C(133)–C(134)	118.9(14)	C(332)–C(333)–C(334)	108.6(9)

Table 7
Atomic coordinates ($\times 10^4$) for $H_2Ru_4(CO)_{12}(SC_4H_8)$ (**3**)

Atom	x	y	z
Ru(1)	2425(1)	409(1)	2054(1)
Ru(2)	1404(1)	279(1)	3032(1)
Ru(3)	3298(1)	−39(1)	3851(1)
Ru(4)	2115(1)	−1181(1)	3119(1)
S(1)	2132(1)	−802(1)	1793(1)
O(1)	1086(3)	986(3)	260(4)
O(2)	2853(4)	1874(3)	2776(4)
O(3)	4010(3)	413(3)	1615(4)
O(4)	−222(3)	402(3)	1243(3)
O(5)	1335(5)	1831(3)	3288(5)
O(6)	385(4)	−42(3)	4123(4)
O(7)	4154(3)	−752(3)	5661(3)
O(8)	4220(4)	1351(3)	4627(4)
O(9)	4682(3)	−627(3)	3335(3)
O(10)	645(3)	−2298(3)	2294(4)
O(11)	2119(3)	−1223(2)	4925(3)
O(12)	3748(3)	−2134(3)	3675(3)
C(1)	1544(4)	741(3)	915(5)
C(2)	2689(5)	1303(4)	2543(5)
C(3)	3424(4)	400(4)	1790(4)
C(4)	408(4)	353(3)	1909(4)
C(5)	1390(5)	1252(4)	3188(5)
C(6)	773(4)	73(3)	3733(4)
C(7)	3796(4)	−488(3)	4983(4)
C(8)	3873(4)	830(4)	4316(5)
C(9)	4149(4)	−397(3)	3513(4)
C(10)	1186(4)	−1890(3)	2573(4)
C(11)	2140(4)	−1212(3)	4258(4)
C(12)	3145(4)	−1773(3)	3483(4)
C(41)	2842(5)	−1315(4)	1426(5)
C(42)	2229(7)	1673(5)	602(7)
C(43)	1312(6)	−1690(4)	456(6)
C(44)	1095(5)	−1040(4)	814(4)
Ru(1B)	3253(1)	1280(1)	−854(1)
Ru(2B)	1863(1)	2228(1)	−1883(1)
Ru(3B)	3741(1)	2554(1)	−1367(1)
Ru(4B)	2721(1)	1998(1)	−3099(1)
S(1B)	3100(1)	951(1)	−2266(1)
O(2B)	3305(4)	2023(3)	756(3)
O(1B)	2341(4)	9(3)	−523(4)
O(3B)	5171(4)	763(3)	248(4)
O(4B)	680(3)	954(3)	−2197(4)
O(5B)	1421(4)	2613(3)	−383(4)
O(6B)	418(4)	3247(3)	−3097(4)
O(7B)	4117(4)	3887(3)	−2121(5)
O(8B)	4680(4)	3101(3)	528(4)
O(9B)	5465(3)	1854(3)	−1115(5)
O(10B)	1455(6)	1375(4)	−4907(5)
O(11B)	2163(4)	3488(3)	−3726(4)
O(12B)	4399(5)	2141(4)	−3377(5)
C(1B)	2666(5)	478(4)	−673(5)
C(2B)	3281(4)	1767(3)	130(5)
C(3B)	4451(5)	950(3)	−186(5)
C(4B)	1143(4)	1421(3)	−2067(5)
C(5B)	1630(4)	2471(3)	−919(5)
C(6B)	970(4)	2888(3)	−2653(5)
C(7B)	3950(5)	3389(4)	−1856(5)
C(8B)	4294(4)	2879(4)	−168(5)
C(9B)	4802(5)	2109(4)	−1223(5)
C(10B)	1934(7)	1584(5)	−4236(6)
C(11B)	2401(5)	2939(4)	−3471(5)
C(12B)	3776(6)	2073(4)	−3264(6)
C(41B)	4039(5)	453(4)	−2283(5)

Table 7 (continued)

Atom	x	y	z
C(42B)	3658(7)	−171(6)	−2761(10)
C(43B)	2730(7)	−229(5)	−3195(8)
C(44B)	2298(5)	249(3)	−2811(5)

0.28 mmol). The solution was refluxed for 22 h. Chromatographic separation on silica with hexane as eluent gave a yellow fraction containing unchanged starting material. Further elution with 4:1 hexane–CH_2Cl_2 mixture gave an orange fraction of **3** (120 mg, 75%). Dark red crystals were obtained from CH_2Cl_2 at −40°C. IR (CH_2Cl_2): 2085m, 2058s, 2038s, 2019s, 2001m, 1972m cm^{-1}. ^1H-NMR ($CDCl_3$): −16.7 ppm (s), −15.7 ppm (s), 2.3 ppm (C–CH_2–C, m), 3.2 ppm (S–CH_2–C, m). Found: C, 23.45; H, 1.24% $Ru_4SC_{16}O_{12}H_{10}$ calc.: C, 23.14; H, 1.21%.

3.5. Preparation of $Ru_4(CO)_{13}(SC_4H_8)$ (4)

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and tetrahydrothiophene (30 μl, 0.34 mmol) in THF (40 ml) was refluxed for 5 h. The solvent was evaporated in vacuum and the residue was chromatographed on acidic aluminum oxide. Hexane elution gave a yellow fraction of unchanged starting material and use of a 4:1 hexane–CH_2Cl_2 mixture then gave **4** (15 mg, 6%). Black crystals were obtained from CH_2Cl_2. IR (CH_2Cl_2): 2081w, 2043vs, 2032s, 2022m, 1986w, 1866w cm^{-1}. ^1H-NMR ($CDCl_3$): 2.5 ppm (m), 3.7 ppm (m). Found: C, 23.32; H, 0.84% $Ru_4SC_{17}O_{13}H_8$ calc.: C, 23.84; H, 0.94%.

Table 8
Bond lengths (pm) for $H_2Ru_4(CO)_{12}(SC_4H_8)$ (**3**) and $Ru_4(CO)_{13}(SC_4H_8)$ (**4**)

	3A	3B	4A	4B
Ru(1)–Ru(2)	287.1(1)	284.8(1)	285.2(1)	286.4(1)
Ru(1)–Ru(3)	284.6(1)	283.9(1)	281.2(1)	281.3(1)
Ru(2)–Ru(3)	289.3(1)	292.3(1)	279.5(1)	280.0(1)
Ru(2)–Ru(4)	302.8(1)	302.1(1)	283.9(1)	282.6(1)
Ru(3)–Ru(4)	283.9(1)	285.0(1)	286.4(1)	287.0(1)
Ru(1)–S(1)	238.2(2)	236.8(2)	237.3(1)	238.4(1)
Ru(4)–S(1)	236.9(2)	237.4(2)	238.4(1)	240.0(1)
Ru(1)–C(1)	193.0(6)	192.5(8)	192.2(6)	193.0(6)
Ru(1)–C(2)	187.3(7)	189.1(8)	188.1(6)	188.7(6)
Ru(1)–C(3)	191.3(8)	191.0(7)	191.8(6)	191.2(6)
Ru(2)–C(4)	188.2(5)	190.4(7)	191.5(5)	193.8(6)
Ru(2)–C(5)	189.2(7)	189.4(9)	190.0(6)	191.3(6)
Ru(2)–C(6)	194.9(8)	194.5(6)	193.5(6)	192.3(6)
Ru(3)–C(7)	191.3(6)	190.7(8)	193.9(6)	192.7(6)
Ru(3)–C(8)	191.2(7)	191.3(8)	190.6(7)	191.0(6)
Ru(3)–C(9)	188.5(7)	188.3(8)	188.6(6)	187.3(3)
Ru(4)–C(10)	195.7(6)	193.4(8)	192.1(6)	193.6(6)
Ru(4)–C(11)	190.7(8)	191.2(8)	189.1(6)	190.2(6)
Ru(4)–C(12)	192.0(6)	191.0(11)	189.4(7)	189.4(6)
Ru(2)–C(13)	–	–	203.1(6)	199.9(6)
Ru(3)–C(13)	–	–	203.9(6)	230.2(5)
O(1)–C(1)	112.6(8)	113.9(10)	114.4(7)	114.0(8)
O(2)–C(2)	115.7(9)	114.9(10)	115.2(8)	114.6(7)
O(3)–C(3)	114.2(11)	114.9(8)	112.2(9)	112.0(8)
O(4)–C(4)	114.7(7)	114.0(8)	115.5(6)	115.1(7)
O(5)–C(5)	113.6(9)	114.1(11)	114.1(8)	112.6(7)
O(6)–C(6)	113.5(11)	112.6(8)	112.9(8)	113.5(8)
O(7)–C(7)	114.5(8)	114.4(11)	112.9(8)	113.9(8)
O(8)–C(8)	115.8(9)	114.0(9)	114.2(8)	113.8(7)
O(9)–C(9)	114.9(10)	115.0(10)	114.4(8)	114.8(7)
O(10)–C(10)	112.9(7)	112.7(10)	113.5(8)	112.9(8)
O(11)–C(11)	114.2(10)	114.2(10)	114.0(8)	114.1(8)
O(12)–C(12)	114.5(8)	115 (2)	113.6(9)	114.0(9)
O(13)–C(13)	–	–	115.4(8)	116.4(7)
S(1)–C(41)	185.1(9)	185.0(9)	183.4(5)	183.2(7)
S(1)–C(44)	183.5(6)	183.2(7)	182.6(5)	184.7(6)
C(41)–C(42)	147.5(11)	142.7((14)	150.7(10)	143.0(12)
C(42)–C(43)	144 (2)	139 (2)	150.6(10)	137 (2)
C(43)–C(44)	150.3(12)	149 (2)	150.3(9)	149 (11)

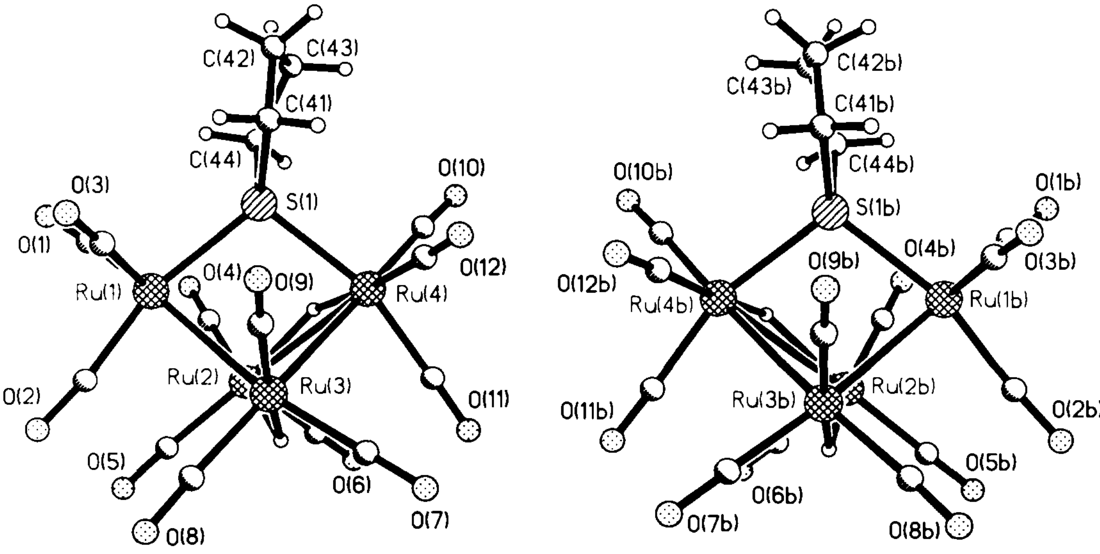

Fig. 3. Structure and numbering scheme of $H_2Ru_4(CO)_{12}(SC_4H_8)$ (3).

Table 9
Selected bond angles (°) for $H_2Ru_4(CO)_{12}(SC_4H_8)$ (3) and $Ru_4(CO)_{13}(SC_4H_8)$ (4)

	3A	3B	4A	4B
Ru(2)-Ru(1)-S(1)	84.0(1)	82.4(1)	84.3(0)	83.2(0)
Ru(3)-Ru(1)-S(1)	82.2(1)	80.7(1)	82.3(0)	83.9(0)
Ru(2)-Ru(1)-C(1)	102.6(3)	106.0(2)	103.6(2)	106.7(2)
Ru(3)-Ru(1)-C(1)	163.3(3)	167.7(2)	162.6(2)	165.7(2)
S(1)-Ru(1)-C(1)	97.9(2)	96.5(2)	95.0(2)	94.2(2)
Ru(2)-Ru(1)-C(2)	84.8(3)	84.8(2)	86.0(2)	85.0(2)
Ru(3)-Ru(1)-C(2)	84.4(2)	86.8(2)	88.0(2)	85.7(2)
S(1)-Ru(1)-C(2)	165.6(3)	165.3(2)	168.9(2)	167.2(2)
Ru(2)-Ru(1)-C(3)	160.2(2)	157.4(2)	158.4(2)	155.3(2)
Ru(3)-Ru(1)-C(3)	99.4(2)	95.7(2)	99.3(2)	96.3(2)
S(1)-Ru(1)-C(3)	94.3(2)	96.6(3)	95.4(2)	97.2(2)
Ru(1)-Ru(2)-C(4)	84.2(3)	81.9(2)	91.0(2)	98.4(2)
Ru(3)-Ru(2)-C(4)	141.1(3)	137.7(2)	123.2(1)	122.7(2)
Ru(4)-Ru(2)-C(4)	105.6(2)	103.2(3)	66.9(2)	63.1(2)
Ru(1)-Ru(2)-C(5)	92.4(3)	93.5(2)	87.3(2)	77.8(2)
Ru(3)-Ru(2)-C(5)	102.8(2)	107.5(2)	130.8(2)	126.6(2)
Ru(4)-Ru(2)-C(5)	160.1(2)	164.7(2)	153.0(2)	143.6(2)
Ru(1)-Ru(2)-C(6)	172.8(2)	174.7(3)	174.3(2)	170.9(2)
Ru(3)-Ru(2)-C(6)	116.2(2)	117.2(2)	115.3(2)	117.9(2)
Ru(4)-Ru(2)-C(6)	95.1(2)	95.5(3)	100.2(2)	106.6(2)
Ru(1)-Ru(3)-C(7)	170.4(2)	172.8(2)	168.8(2)	171.8(2)
Ru(2)-Ru(3)-C(7)	117.6(2)	115.7(2)	108.3(2)	111.7(2)
Ru(4)-Ru(3)-C(7)	89.4(2)	90.8(2)	91.1(2)	92.6(2)
Ru(1)-Ru(3)-C(8)	95.4(2)	91.5(2)	90.2(2)	92.2(2)
Ru(2)-Ru(3)-C(8)	104.5(2)	109.1(3)	117.5(2)	118.4(2)
Ru(4)-Ru(3)-C(8)	168.0(2)	171.9(3)	170.1(2)	172.1(2)
Ru(1)-Ru(3)-C(9)	83.2(2)	87.2(2)	91.0(2)	86.2(2)
Ru(2)-Ru(3)-C(9)	138.2(2)	139.8(2)	138.2(2)	134.8(2)
Ru(4)-Ru(3)-C(9)	93.3(2)	93.2(2)	86.4(2)	85.5(2)
Ru(2)-Ru(4)-S(1)	80.8(1)	78.7(1)	84.4(0)	83.7(0)
Ru(3)-Ru(4)-S(1)	82.6(1)	80.4(1)	81.0(0)	82.4(0)
Ru(2)-Ru(4)-C(10)	114.4(2)	114.5(4)	112.2(2)	117.6(2)
Ru(3)-Ru(4)-C(10)	173.3(2)	173.9(4)	170.8(2)	176.5(2)
S(1)-Ru(4)-C(10)	96.5(2)	96.9(3)	98.1(2)	97.9(2)
Ru(2)-Ru(4)-C(11)	84.7(2)	86.4(3)	81.0(2)	79.6(2)
Ru(3)-Ru(4)-C(11)	83.7(2)	86.0(2)	86.3(2)	83.3(2)
S(1)-Ru(4)-C(11)	163.8(2)	163.5(3)	164.2(2)	162.1(2)
Ru(2)-Ru(4)-C(12)	147.3(2)	147.1(3)	150.4(2)	148.2(2)
Ru(3)-Ru(4)-C(12)	88.4(2)	87.5(3)	91.1(2)	89.8(2)
S(1)-Ru(4)-C(12)	95.4(2)	97.6(2)	95.2(2)	98.2(2)
Ru(1)-Ru(2)-C(13)	–	–	87.6(2)	88.9(2)
Ru(3)-Ru(2)-C(13)	–	–	54.4(2)	54.3(2)
Ru(4)-Ru(2)-C(13)	–	–	110.9(2)	110.1(2)
Ru(1)-Ru(3)-C(13)	–	–	83.5(1)	84.5(1)
Ru(2)-Ru(3)-C(13)	–	–	45.7(1)	44.8(1)
Ru(4)-Ru(3)-C(13)	–	–	102.1(2)	100.2(1)
Ru(1)-S(1)-Ru(4)	102.4(1)	104.4(1)	100.6(0)	99.9(0)
Ru(1)-S(1)-C(41)	118.4(3)	116.5(3)	117.3(2)	116.4(2)
Ru(4)-S(1)-C(41)	115.8(2)	115.6(3)	115.2(2)	113.9(2)
Ru(1)-S(1)-C(44)	116.3(2)	115.2(3)	119.6(2)	117.8(2)
Ru(4)-S(1)-C(44)	111.5(3)	112.8(2)	114.7(2)	117.1(2)
C(41)-S(1)-C(44)	93.1(3)	92.5(3)	90.3(2)	92.8(3)
Ru(1)-C(1)-O(1)	173.2(6)	176.7(6)	177.0(5)	176.1(6)
Ru(1)-C(2)-O(2)	173.9(8)	175.6(6)	177.4(5)	178.4(5)
Ru(1)-C(3)-O(3)	177.8(6)	177.0(8)	177.2(6)	176.5(6)
Ru(2)-C(4)-O(4)	177.0(8)	177.1(5)	164.7(4)	160.1(5)
Ru(2)-C(5)-O(5)	175.8(9)	174.7(5)	172.6(6)	173.5(5)
Ru(2)-C(6)-O(6)	178.2(5)	176.2(7)	172.3(6)	174.2(6)
Ru(3)-C(7)-O(7)	174.9(7)	176.8(6)	175.4(5)	174.2(5)
Ru(3)-C(8)-O(8)	177.4(8)	172.7(8)	178.5(6)	176.2(5)
Ru(3)-C(9)-O(9)	177.6(5)	177.8(7)	175.0(5)	175.7(5)
Ru(4)-C(10)-O(10)	176.7(7)	176.5(8)	176.1(6)	178.1(6)
Ru(4)-C(11)-O(11)	177.2(5)	176.1(6)	175.4(6)	175.9(5)
Ru(4)-C(12)-O(12)	178.0(5)	177.6(7)	177.3(6)	176.8(6)
Ru(2)-C(13)-O(13)	–	–	148.5(5)	148.9(5)
Ru(3)-C(13)-O(13)	–	–	131.6(5)	130.0(4)
S(1)-C(41)-C(42)	106.7(6)	106.2(7)	108.6(4)	106.6(7)
C(41)-C(42)-C(43)	113.9(10)	118.3(11)	111.0(6)	117.6(11)
C(42)-C(43)-C(44)	110.2(7)	111.5(10)	108.2(6)	113.9(7)
S(1)-C(44)-C(43)	105.5(5)	106.6(6)	105.3(4)	106.4(5)

Table 10
Atomic coordinates ($\times 10^4$) for $Ru_4(CO)_{13}(SC_4H_8)$ (4)

Atom	x	y	z
Ru(1)	18(1)	7250(1)	741(1)
Ru(2)	898(1)	7260(1)	128(1)
Ru(3)	322(1)	8570(1)	35(1)
Ru(4)	306(1)	7453(1)	−1054(1)
S(1)	−269(1)	6887(1)	−367(1)
O(1)	−41(2)	5619(3)	1372(3)
O(2)	518(2)	7859(3)	2024(3)
O(3)	−893(2)	7882(4)	1237(3)
O(4)	743(2)	5654(2)	−502(2)
O(5)	1287(2)	6296(3)	1318(3)
O(6)	1866(2)	7437(3)	−430(3)
O(7)	760(2)	9819(3)	−855(3)
O(8)	235(2)	9571(3)	1309(3)
O(9)	−660(2)	9010(3)	−406(3)
O(10)	421(2)	6130(4)	−2076(3)
O(11)	1152(2)	8258(3)	−1588(3)
O(12)	−371(2)	8408(4)	−1930(3)
O(13)	1259(2)	8674(3)	955(3)
C(1)	−21(2)	6219(3)	1119(3)
C(2)	334(2)	7639(3)	1527(3)
C(3)	−562(2)	7641(4)	1040(3)
C(4)	758(2)	6299(3)	−332(3)
C(5)	1130(2)	6693(4)	903(3)
C(6)	1497(2)	7378(3)	−270(3)
C(7)	612(2)	9337(3)	−536(3)
C(8)	267(2)	9187(3)	837(3)
C(9)	−292(2)	8813(3)	−256(3)
C(10)	363(2)	6611(4)	−1691(3)
C(11)	839(2)	7966(4)	−1360(3)
C(12)	−117(2)	8064(4)	−1590(3)
C(13)	1021(2)	8299(3)	600(3)
C(41)	−385(2)	5849(3)	−520(3)
C(42)	−796(3)	5776(4)	−1015(5)
C(43)	−988(2)	6567(4)	−1207(4)
C(44)	−865(2)	7123(3)	−634(3)
Ru(1B)	2474(1)	−175(1)	1046(1)
Ru(2B)	3260(1)	378(1)	1844(1)
Ru(3B)	2754(1)	1393(1)	978(1)
Ru(4B)	2555(1)	1297(1)	2400(1)
S(1B)	2058(1)	257(1)	2002(1)
O(1B)	2359(2)	−1907(3)	1347(3)
O(2B)	3165(2)	−484(3)	−50(2)
O(3B)	1692(2)	−56(4)	−45(3)
O(4B)	3048(2)	−224(3)	3261(2)
O(5B)	3556(2)	−1290(3)	1585(3)
O(6B)	4198(2)	922(4)	2446(3)
O(7B)	3078(2)	3091(3)	1073(3)
O(8B)	2887(2)	1333(3)	−556(2)
O(9B)	1744(2)	1798(3)	714(3)
O(10B)	2398(2)	1153(4)	3934(2)
O(11B)	3358(2)	2436(3)	2580(3)
O(12B)	1882(2)	2648(3)	2240(3)
O(13B)	3798(1)	1006(3)	650(2)

Table 10 (continued)

C(1B)	2407(2)	−1267(3)	1259(3)
C(2B)	2904(2)	−356(3)	362(3)
C(3B)	1974(2)	−96(4)	378(3)
C(4B)	3057(2)	85(3)	2740(3)
C(5B)	3436(2)	−669(3)	1642(3)
C(6B)	3838(2)	744(4)	2247(3)
C(7B)	2973(2)	2450(3)	1066(3)
C(8B)	2837(2)	1328(3)	17(3)
C(9B)	2124(2)	1636(3)	840(3)
C(10B)	2456(2)	1192(4)	3368(3)
C(11B)	3069(2)	1988(3)	2505(3)
C(12B)	2128(2)	2129(4)	2285(3)
C(13B)	3492(2)	886(3)	1005(3)
C(41B)	1944(2)	−475(4)	2655(3)
C(42B)	1472(3)	−375(9)	2832(8)
C(43B)	1185(3)	32(5)	2384(4)
C(44B)	1436(2)	486(4)	1861(3)

3.6. *X-ray crystallography*

Data were collected on a Nicolet R3m diffractometer using Mo-Kα radiation (λ = 71.073 pm). Intensities were corrected for background, polarization and Lorenz factors. An empirical absorption correction was applied, based on ψ-scans. Table 11 presents further crystallographic data. The structures were solved by use of the SHELXTL program. Methylene protons were placed in calculated positions (C–H = 96 pm, U = 800 pm^2).

Table 11
Crystallographic data for $HRuCo_3(CO)_{11}(SC_4H_8)$ (1), $[HRuRh_3(CO)_9]_2[SC_4H_8]_3$ (2), $H_2Ru_4(CO)_{12}(SC_4H_8)$ (3) and $Ru_4(CO)_{13}(SC_4H_8)$ (4)

	1	2	3	4
Formula weight	675.14	1590.29	830.58	856.57
Crystal system	Monocl.	Monocl.	Monocl.	Monocl.
Space group	Pc	$P2/c$	$P2_1/n$	$C2/c$
a (pm)	1132.7(2)	2209.8(9)	1671.5(11)	2886.6(12)
b (pm)	1149.3(2)	1180.1(5)	1924(2)	1715.3(6)
c (pm)	1704.1(3)	3652(2)	1689.1(9)	1958.0(7)
α (°)	90	90	90	90
β (°)	92.88(1)	106.73(3)	116.77(5)	92.33(3)
γ (°)	90	90	90	90
V (pm^3)*10^6	2216(1)	9119(6)	4849(6)	9687(6)
Z	4	8	8	16
No. centering reflections	36	25	27	36
Centering 2θ	17–27	14–23	16–25	29–36
D_{calc} (g cm^{-1})	2.02	2.32	2.28	2.35
Crystal dimensions (mm^3)	0.5*0.5*0.5	0.5*0.5*0.3	0.7*0.3*0.4	0.5*0.5*0.2
2θ-limits	5–55	5–55	5–50	5–55
h, k, l range	15, 15, ±23	27, 15, ±44	20, 23, ±21	38, 23, ±26
No. unique reflections	5349	15889	8524	11194
Observed data $I > 3\sigma(I)$	3572	9110	6183	8284
μ(mm^{-1})	3.00	2.96	2.54	1.30
No. param.	557	523	595	631
R [a]	0.0496	0.0314	0.0268	0.0299
R [b]	0.0468	0.0247	0.0258	0.0318

[a] $R = \Sigma |F_o| - |F_o|/\Sigma |F_o|$. [b] Weight = $1/(\sigma^2(F) + 0.0005*F^2)$.

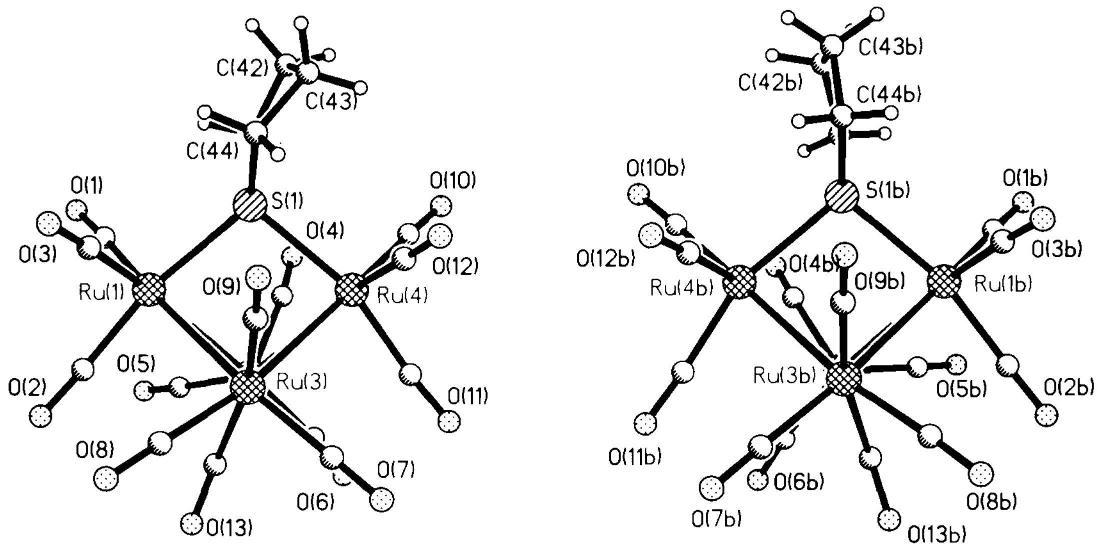

Fig. 4. Structure and numbering scheme of $Ru_4(CO)_{13}(SC_4H_8)$ (**4**).

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