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Dithiolate complexes of ruthenium and osmium: X-ray structures of $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ and $[\{(\mu\text{-}H)M_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ ($M=Ru$, Os)

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Abstract

A comparison between the reactivity of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ with 1,2-ethanedithiol ($HSCH_2CH_2SH$) and 1,3-propanedithiol ($HSCH_2CH_2CH_2SH$) is reported. The reaction of $[Ru_3(CO)_{12}]$ with 1,2-ethanedithiol at 68°C afforded $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (**1**) in 40% yield, whereas the reaction with 1,3-propanedithiol yielded $[\{(\mu\text{-}H)Ru_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**2**) and $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$ (**3**) in 30 and 19% yields respectively. Treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with 1,2-ethanedithiol gave $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2SH)]$ (**4**) in 60% yield and with 1,3-propanedithiol it afforded $[\{(\mu\text{-}H)Os_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**5**) in 30% yield. Compounds **1** and **3** both react with equimolar amounts of PPh_3 at room temperature to give the monosubstituted products $[Ru_2(CO)_5(\mu\text{-}SCH_2CH_2S)(PPh_3)]$ (**6**) and $[Ru_2(CO)_5(\mu\text{-}SCH_2CH_2S)(PPh_3)]$ (**7**) respectively. When heated to 68°C, compound **2** transformed into **3**. The compounds have been characterized by spectroscopic studies, and in the case of **1**, **2** and **5** by X-ray crystallography.

Keywords: Dithiolate complexes; Ruthenium; Osmium; X-ray structures

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1. Introduction

The use of alkanedithiolates to stabilize transition metal cluster compounds by serving as chelating or bridging ligands and preventing cluster fragmentation during the course of catalytic reactions has received considerable attention [1–21]. The reactivity of polythiocycloalkanes towards metal carbonyl clusters is also of interest. It has been shown that some reactions proceed with retention of the cluster structure, while in other cases fragmentation into a dinuclear species as well as ring opening of the ligand takes place. For example, the reaction of $[Ru_3(CO)_{12}]$ with 1,2,5,6-tetrathiacyclooctane at 40°C gave a mixture of products from which the dinuclear and trinuclear complexes $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$, *anti*-$[Ru_3(CO)_7(\mu\text{-}SCH_2CH_2S)_2]$ and *syn*-$[Ru_3(CO)_7(\mu\text{-}SCH_2CH_2S)_2]$ containing the 1,2-ethanedithiolate ligand were isolated [22]. On the other hand, reactions of $[Ru_3(CO)_{12}]$ with 1,3-dithiacyclohexane, 1,3,5-trithiacyclohexane and 1,4,7-trithiacyclononane, yielded the respective complexes $[(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}1,3\text{-dithiacyclohexane})]$, $[Ru_3(CO)_9(\mu\text{-}\eta^3\text{-}1,3,5\text{-trithiacyclohexane})]$ and $[Ru_3(CO)_9(\mu\text{-}\eta^3\text{-}1,4,7\text{-trithiaheptane})]$ involving entirely different coordination modes of the ligands [23]. Recently, we have investigated the reactions of various dithiols with unsaturated triosmium clusters $[(\mu\text{-}H)Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ and $[(\mu\text{-}H)Os_3(CO)_9\{C_9H_5(R)N\}]$ ($R=H$ or Me) [24,25] and saturated triruthenium clusters $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ and $[Ru_3(CO)_{10}(\mu\text{-dppe})]$ [26], and observed several bonding modes of the dithiolate ligand depending on the cluster and the dithiol used. In the present work we report on the reactions of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ with 1,2-ethanedithiol and 1,3-propanedithiol and also the substitution reactions of the resulting diruthenium complexes with triphenylphosphine.

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2. Results and discussion

Treatment of $[Ru_3(CO)_{12}]$ with 2 equiv. of 1,2-ethanedithiol afforded $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (**1**) (Scheme 1) in 40% yield. This compound was previously reported from the thermal degradation of $[Ru_3(CO)_7(\mu\text{-}CO)_2(1,1,1\text{-}\eta^3\text{-}9S3)]$ (9S3 = 1,4,7-trithiacyclononane) at 68°C in 16% yield [27] as well as from the reaction of $[Ru_3(CO)_{12}]$ with 1,2,5,6-tetrathiacyclooctane at 40°C in 26% yield [22], and characterized on the basis of spectroscopic data only. We undertook an X-ray structure determination of **1** to confirm the coordination mode of the ethanedithiolate ligand.

The X-ray structure of **1** is shown in Fig. 1, and selected bond distances and angles are presented in Table 1. The molecule is based on two ruthenium atoms, each containing three linear terminal carbonyl groups and mutually bridged by both the sulfur atoms of the ethanedithiolate ligand. The molecule possesses a non-crystallographic *mm* symmetry with the $[Ru_2(CO)_6]$ unit adopting the classic 'sawhorse' arrangement. The Ru–Ru bond at 2.6790(8) Å is significantly shorter than that (2.854 Å) in the parent compound $[Ru_3(CO)_{12}]$ [28], but close to the metal–metal distance (2.710(1) Å) in the osmium analog $[Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ which has been reported from the pyrolysis of $[Os_3(CO)_{11}(SCH_2CH_2SCH_2CH_2)]$ as well as from the direct reaction of $[Os_3(CO)_{12}]$ with 1,4-dithiacyclohexane [29]. The ethanedithiolate ligand serves as a bidentate bridging ligand across the metal–metal bond and donates six electrons to make **1** a 34-electron valence saturated bimetallic compound, with each metal atom achieving the expected 18-electron configuration. The Ru–S–Ru bridges are symmetrical with distances Ru(1)/Ru(2)–S(1) = 2.375(2)/2.374(2) and Ru(1)/Ru(2)–S(2) = 2.370(2)/2.370(2) Å. These values are comparable to those found in *syn*-$[Ru_3(CO)_7(\mu\text{-}SCH_2CH_2S)_2]$ (2.365 Å, average) [22] and $[Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (2.392 Å, average) [29]. The Ru–S–Ru angles are highly acute with the values 68.69(5) and 68.84(4)° at S(1) and S(2) respectively.

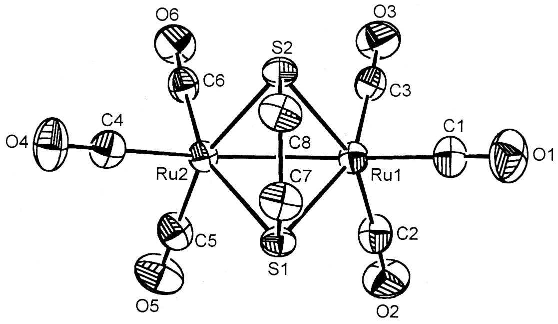
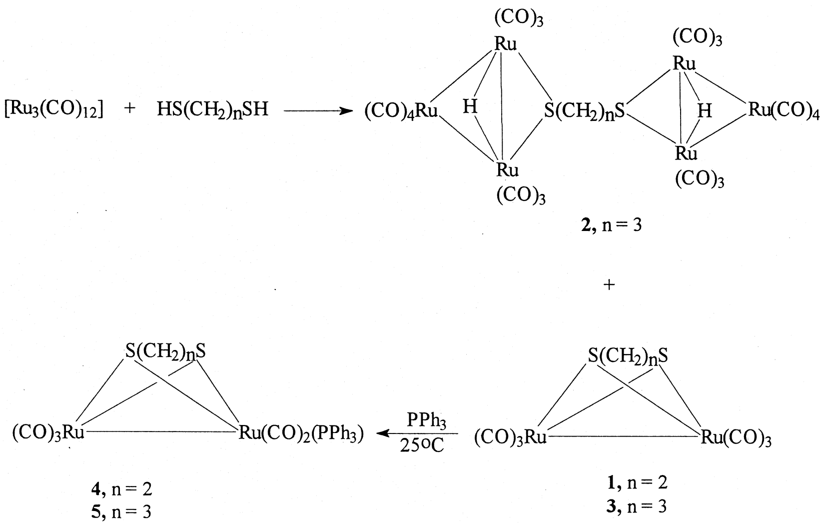


Fig. 1. Solid state structure of $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (**1**) showing the atom labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for **1**

Ru(1)–Ru(2)	2.6790(8)	Ru(1)–S(1)	2.375(2)
Ru(1)–S(2)	2.370(2)	Ru(2)–S(1)	2.374(2)
Ru(2)–S(2)	2.370(2)	S(1)–C(7)	1.818(6)
S(2)–C(8)	1.825(6)		
C(3)–Ru(1)–C(2)	92.9(3)	C(3)–Ru(1)–C(1)	99.7(3)
C(2)–Ru(1)–C(1)	97.3(3)	C(3)–Ru(1)–S(2)	90.3(2)
C(2)–Ru(1)–S(2)	159.3(2)	C(1)–Ru(1)–S(2)	102.3(2)
C(3)–Ru(1)–S(1)	155.9(2)	C(2)–Ru(1)–S(1)	91.4(2)
C(1)–Ru(1)–S(1)	103.3(2)	S(2)–Ru(1)–S(1)	77.81(6)
C(6)–Ru(2)–C(5)	90.2(3)	C(6)–Ru(2)–C(4)	98.7(3)
C(5)–Ru(2)–C(4)	98.5(3)	C(6)–Ru(2)–S(2)	92.6(2)
C(5)–Ru(2)–S(2)	160.9(2)	C(4)–Ru(2)–S(2)	99.7(2)
C(6)–Ru(2)–S(1)	157.0(2)	C(5)–Ru(2)–S(1)	92.4(2)
C(4)–Ru(2)–S(1)	103.5(2)	S(2)–Ru(2)–S(1)	77.84(5)
Ru(2)–S(1)–Ru(1)	68.69(5)	Ru(2)–S(2)–Ru(1)	68.84(4)

The reaction of $[Ru_3(CO)_{12}]$ with 1,3-propanedithiol yielded the trimetallic and dimetallic compounds $[\{(\mu\text{-}H)(Ru_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**2**) and $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$ (**3**) (Scheme 1) in 30 and 19% yields respectively. Compound **2** has been characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopic data and by an X-ray study.



Scheme 1.

The structure of **2** is shown in Fig. 2, and selected bond distances and angles are presented in Table 2. An interesting feature of **2** is the presence of two $\{(\mu\text{-H})Ru_3(CO)_{10}\}$ moieties linked by a propanedithiolate ligand. The overall structure of **2** is very similar to that of the methanedithiolate osmium analog $[\{(\mu\text{-H})Os_3(CO)_{10}\}_2(\mu\text{-}\eta^2\text{-SCH}_2S)]$ obtained from the reaction of $[(\mu\text{-H})_2Os_3(CO)_{10}]$ with CS_2 [30,31]. Each $\{(\mu\text{-H})Ru_3(CO)_{10}\}$ unit in **2** consists of an approximately equilateral traingle of three ruthenium atoms with Ru–Ru distances lying in a narrow range 2.8212(8)–2.8429(9) Å. These values are very similar to the Ru–Ru distances found in $[(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-SCH}_2COOH)]$ (2.827(5)–2.839(4) Å) [32]. The positions of the hydride ligands were obtained from difference maps and they are found to bridge the same edge of each triangle as the sulfur atom. Large angles for the *cis* carbonyl groups (e.g. Ru(3)–Ru(1)–C(2)/C(3) = 111.1(2)/115.4(2), Ru(1)–Ru(3)–C(8)/C(9) = 113.1(2)/116.6(2), Ru(6)–Ru(4)–C(11)/C(13) = 113.9(2)/114.0(2), Ru(4)–Ru(6)–C(18)/C(19) = 113.5(2)/116.1(2)°) are consistent with the location of the bridging hydrides along the Ru(1)–(Ru(3) and Ru(4)–Ru(6) edges in the two Ru_3 triangles. The sulfur bridges are symmetrical with distances Ru(1)/Ru(3)–S(1) = 2.386(2)/2.391(2) and Ru(4)/Ru(6)–S(2) = 2.388(2)/2.379(2) Å. These values are comparable with the Ru–S distances found in **1** and also in *anti*-$[(\mu\text{-H})Ru_3(CO)_7(\mu\text{-}\eta^2\text{-SCH}_2CH_2S)_2]$ (2.376(2)–2.384(2) Å) [22]. The $Ru_2S(1)$ and $Ru_2S(2)$ planes are inclined from the corresponding Ru_3 planes by 77.93(4) and 76.25(4)° respectively. The C–S bond distances of S(1)–C(21) = 1.839(6) and S(2)–C(23) = 1.824(6) Å are very similar to the C–S single bond distances 1.80–1.82 Å observed in several thioalkanes [33–36].

The IR, ^{1}H and ^{13}C NMR spectra of **2** are consistent with the proposed formulation and X-ray structure. The ^{1}H NMR spectrum of **2** contains a triplet at δ 2.25, a quartet at δ 2.05 and a singlet at δ −15.41 with relative intensities 2:1:1. The triplet and quartet are due to the six methylene protons in a slightly different environment, whilst the singlet is attributed to the two bridging hydrides in identical stereochemical environment. The ^{13}C NMR spectrum exhibits two resonances at δ 52.5 and 35.7 due to the carbon atoms of the dithiolate ligand as well as signals at δ 204.1, 202.6, 198.1, 192.8, 191.5 and 185.5 due to the carbonyl carbons. The ν(CO) stretching frequencies are similar to those of $[\{\mu\text{-H})(Os_3(CO)_{10}\}_2(\mu\text{-SCH}_2S)]$ [30,31].

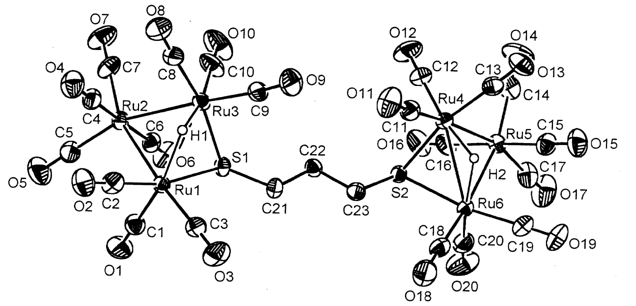


Fig. 2. Solid state structure of $[\{(\mu\text{-H})Ru_3(CO)_{10}\}_2(\mu\text{-SCH}_2CH_2CH_2S)]$ (**2**) showing the atom labeling scheme. Hydrogen atoms other than the bridging hydrides are omitted for clarity. Thermal ellipsoids are drawn at 40% probability level.

Table 2
Bond lengths (Å) and angles (°) for **2**

Ru(1)–Ru(3)	2.8212(8)	Ru(1)–Ru(2)	2.8338(7)
Ru(2)–Ru(3)	2.8429(9)	Ru(1)–S(1)	2.386(2)
Ru(3)–S(1)	2.391(2)	Ru(4)–S(2)	2.388(2)
Ru(4)–Ru(5)	2.8162(8)	Ru(4)–Ru(6)	2.8344(9)
Ru(5)–Ru(6)	2.8414(8)	Ru(6)–S(2)	2.379(2)
S(1)–C(21)	1.839(6)	S(2)–C(23)	1.824(6)
C(2)–Ru(1)–C(1)	95.5(3)	C(2)–Ru(1)–C(3)	94.4(3)
C(1)–Ru(1)–C(3)	96.3(3)	C(2)–Ru(1)–S(1)	165.0(2)
C(1)–Ru(1)–S(1)	96.5(2)	C(3)–Ru(1)–S(1)	93.2(2)
C(2)–Ru(1)–Ru(3)	111.1(2)	C(1)–Ru(1)–Ru(3)	135.6(2)
C(3)–Ru(1)–Ru(3)	115.4(2)	S(1)–Ru(1)–Ru(3)	53.88(4)
C(2)–Ru(1)–Ru(2)	90.3(2)	C(1)–Ru(1)–Ru(2)	85.7(2)
C(3)–Ru(1)–Ru(2)	174.7(2)	S(1)–Ru(1)–Ru(2)	81.68(4)
Ru(3)–Ru(1)–Ru(2)	60.36(2)	C(5)–Ru(2)–C(4)	92.2(3)
C(5)–Ru(2)–C(7)	100.0(3)	C(4)–Ru(2)–C(7)	92.4(3)
C(5)–Ru(2)–C(6)	90.5(3)	C(4)–Ru(2)–C(6)	175.7(3)
C(7)–Ru(2)–C(6)	90.4(3)	C(5)–Ru(2)–Ru(1)	98.4(2)
C(4)–Ru(2)–Ru(1)	86.8(2)	C(7)–Ru(2)–Ru(1)	161.6(2)
C(6)–Ru(2)–Ru(1)	89.5(2)	C(5)–Ru(2)–Ru(3)	157.9(2)
C(4)–Ru(2)–Ru(3)	85.3(2)	C(7)–Ru(2)–Ru(3)	102.0(2)
C(6)–Ru(2)–Ru(3)	91.0(2)	Ru(1)–Ru(2)–Ru(3)	59.60(2)
C(10)–Ru(3)–C(8)	94.3(4)	C(10)–Ru(3)–C(9)	97.3(3)
C(8)–Ru(3)–C(9)	90.0(3)	C(10)–Ru(3)–S(1)	95.9(3)
C(8)–Ru(3)–S(1)	166.8(2)	C(9)–Ru(3)–S(1)	97.0(2)
C(10)–Ru(3)–Ru(1)	135.0(3)	C(8)–Ru(3)–Ru(1)	113.1(2)
C(9)–Ru(3)–Ru(1)	116.6(2)	S(1)–Ru(3)–Ru(1)	53.72(4)
C(10)–Ru(3)–Ru(2)	85.8(2)	C(8)–Ru(3)–Ru(2)	91.0(2)
C(9)–Ru(3)–Ru(2)	176.6(2)	S(1)–Ru(3)–Ru(2)	81.41(4)
Ru(1)–Ru(3)–Ru(2)	60.04(2)	C(12)–Ru(4)–C(13)	92.9(3)
C(12)–Ru(4)–C(11)	97.4(3)	C(13)–Ru(4)–C(11)	94.9(3)
C(12)–Ru(4)–S(2)	93.5(2)	C(13)–Ru(4)–S(2)	165.7(2)
C(11)–Ru(4)–S(2)	97.0(2)	C(12)–Ru(4)–Ru(5)	89.5(2)
C(13)–Ru(4)–Ru(5)	84.7(2)	C(11)–Ru(4)–Ru(5)	173.1(2)
S(2)–Ru(4)–Ru(5)	82.59(4)	C(12)–Ru(4)–Ru(6)	135.4(2)
C(13)–Ru(4)–Ru(6)	114.0(2)	C(11)–Ru(4)–Ru(6)	113.9(2)
S(2)–Ru(4)–Ru(6)	53.38(4)	Ru(5)–Ru(4)–Ru(6)	60.38(2)
C(14)–Ru(5)–C(15)	91.1(3)	C(14)–Ru(5)–C(17)	101.6(3)
C(15)–Ru(5)–C(17)	91.7(3)	C(14)–Ru(5)–C(16)	92.2(3)
C(15)–Ru(5)–C(16)	174.5(3)	C(17)–Ru(5)–C(16)	91.9(3)
C(14)–Ru(5)–Ru(4)	95.5(2)	C(15)–Ru(5)–Ru(4)	88.4(2)
C(17)–Ru(5)–Ru(4)	162.9(3)	C(16)–Ru(5)–Ru(4)	87.0(2)
C(14)–Ru(5)–Ru(6)	155.1(2)	C(15)–Ru(5)–Ru(6)	83.5(2)
C(17)–Ru(5)–Ru(6)	102.9(3)	C(16)–Ru(5)–Ru(6)	91.7(2)
Ru(4)–Ru(5)–Ru(6)	60.13(2)	C(20)–Ru(6)–C(19)	93.5(3)
C(20)–Ru(6)–C(18)	98.6(4)	C(19)–Ru(6)–C(18)	91.8(3)
C(20)–Ru(6)–S(2)	94.3(2)	C(19)–Ru(6)–S(2)	169.7(2)
C(18)–Ru(6)–S(2)	93.7(2)	C(20)–Ru(6)–Ru(4)	134.2(2)
C(19)–Ru(6)–Ru(4)	116.1(2)	C(18)–Ru(6)–Ru(4)	113.5(2)
S(2)–Ru(6)–Ru(4)	53.67(4)	C(20)–Ru(6)–Ru(5)	87.3(3)
C(19)–Ru(6)–Ru(5)	91.5(2)	C(18)–Ru(6)–Ru(5)	173.0(2)
S(2)–Ru(6)–Ru(5)	82.19(4)	Ru(4)–Ru(6)–Ru(5)	59.50(2)
C(21)–S(1)–Ru(1)	109.4(2)	C(21)–S(1)–Ru(3)	110.0(2)
Ru(1)–S(1)–Ru(3)	72.40(5)	C(23)–S(2)–Ru(6)	109.7(2)
C(23)–S(2)–Ru(4)	111.1(2)	Ru(6)–S(2)–Ru(4)	72.95(5)
C(22)–C(21)–S(1)	110.3(4)	C(21)–C(22)–C(23)	110.4(5)
C(22)–C(23)–S(2)	110.2(4)		

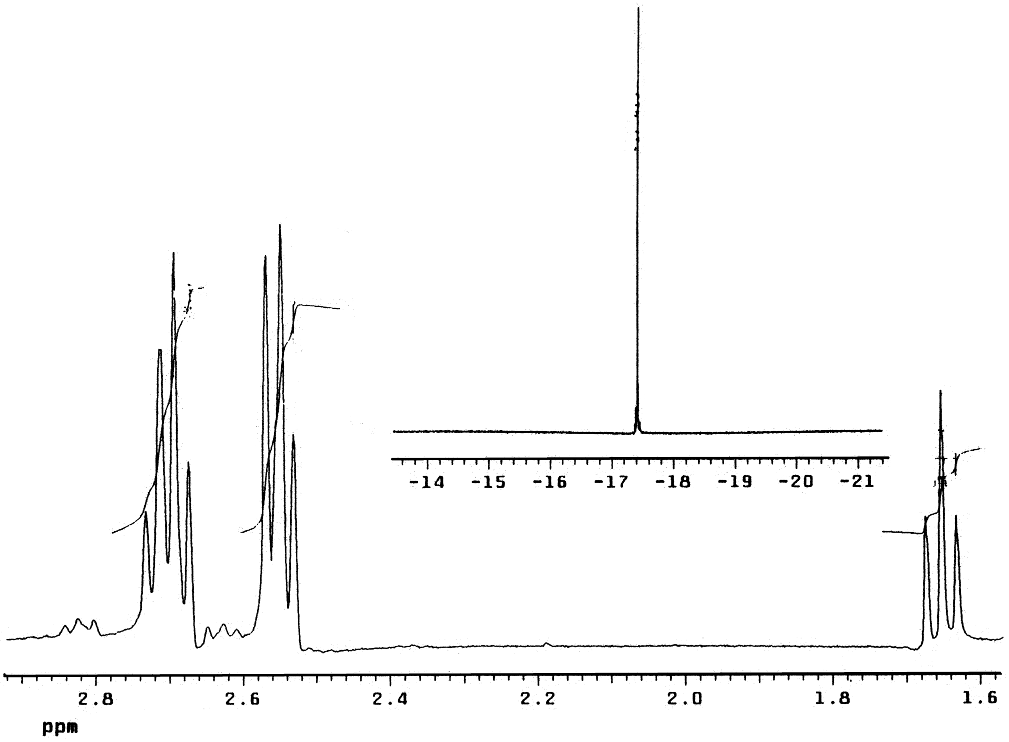
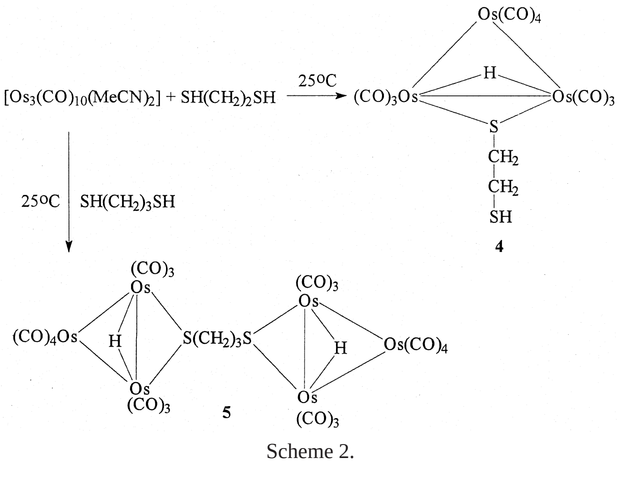


Fig. 3. ^{1}H NMR spectrum of [(μ-H)$Os_3(CO)_{10}$(μ-SCH_2CH_2SH)] (**4**) in $CDCl_3$.

The complex **3** has been characterized by elemental analysis, IR, ^{1}H NMR and mass spectroscopic data. The IR spectrum of **3** is very similar to that of **1** indicating that they are structurally similar. The ^{1}H NMR spectrum shows multiplets at δ 2.19 and 1.89 in a relative intensity of 2:1. The mass spectrum shows the molecular ion peak at *m/z* 478 as expected and the stepwise loss of six carbonyl groups is also observed. The structure of this complex is thus proposed as in Scheme 1.

The reaction of 1,2-ethanedithiol with [$Os_3(CO)_{10}$-$(MeCN)_2$] afforded [(μ-H)$Os_3(CO)_{10}$(μ-SCH_2CH_2SH)] (**4**) in 60% yield. The compound has been characterized by elemental analysis, IR, ^{1}H NMR and mass spectroscopic data. The IR spectrum of **4** in the carbonyl stretching region is very similar to that of [(μ-H)$Os_3(CO)_{10}$(μ-SR)] [37,38], suggesting that they have very similar structures. The ^{1}H NMR and mass spectra indicated the formation of a decacarbonyl compound by oxidative addition of one S–H bond while the other S–H bond remains free. The mass spectrum shows the molecular ion peak at *m/z* 950 with sequential loss of ten carbonyl ligands. The ^{1}H NMR spectrum (Fig. 3) contains four signals at δ 2.70 (dt, 2H, $J = 8.0$ Hz), 2.55 (t, 2H, $J = 8.0$ Hz), 1.65 (t, 1H, $J = 8.0$ Hz) and -17.42 (s, 1H). The S–H proton is observed at δ 1.65 as a triplet with $J = 8.0$ Hz presumably due to coupling with the adjacent methylene protons. The triplet at δ 2.55 is due to the methylene protons attached to the coordinated sulfur atom while the doublet of a triplet (deceptively appearing as a quartet) at δ 2.70 is assigned to the methylene protons adjacent to the sulfur atom of the free S–H group. The other possible structure with activation of both the S–H bonds can easily be ruled out, because such activation would result in a singlet resonance for methylene protons of the dithiolate ligand. Thus the spectroscopic data are consistent with the proposed structure for **4** (Scheme 2).

In contrast, 1,3-propanedithiol reacts with [$Os_3(CO)_{10}$-$(MeCN)_2$] at room temperature to give [{(μ-H)-$Os_3(CO)_{10}$}$_2$(μ-$SCH_2CH_2CH_2S$)] (**5**). This compound was previously structurally characterized by Lewis and co-workers [39], but no spectroscopic data were reported. We have now characterized it by both spectroscopic data and X-ray crystallography. The IR spectrum of **5** is different from that of the methanedithiolate dicluster [{(μ-H)$Os_3(CO)_{10}$}$_2$(μ-SCH_2S)] but is very similar to that of the propanedithiolate ruthenium analog **2** and the monocluster **4**. The ^{1}H NMR spectrum of **5** shows a pattern similar to



Scheme 2.

2 and contains a triplet at δ 2.44 for four equivalent methylene protons of the 1,3-propanedithiolate ligand, a quintet at δ 1.99 for the other two methylene protons and a high field singlet at δ -17.42 for the two equivalent bridging hydride ligands (one from each cluster). Compound **5** is found to be isostructural with **2**, in which two $\{(\mu\text{-H})Os_3(CO)_{10}\}$ groupings are bridged by the $SCH_2CH_2CH_2S$ ligand and each sulfur bridges two osmium atoms in separate Os_3 cluster units (Fig. 4). The molecular geometry parameters in **5** (Table 3) are comparable with the corresponding values in **2** and also with those obtained from the earlier study [39]. The Os–Os, Os–S and S–C distances (2.8441(10)–2.8652(10), 2.401(4)–2.414(4), 1.82(2)–1.83(2) Å) in **5** are virtually identical with the respective reported values (2.840(3)–2.860(3), 2.397(5)–2.424(5), 1.83(3)–1.85(4) Å) [39].

We have recently [26] found that substitution reaction of the iron-dithiolate compound $[Fe_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S]$ with tertiary phosphines gives $[Fe_2(CO)_5(\mu\text{-}SCH_2CH_2CH_2S)(PR_3)]$. Keeping this in mind we investigated the CO substitution reaction of **1** and **3** with PPh_3 and observed that an easy reaction occurs yielding the mono-substituted compounds $[Ru_2(CO)_5(\mu\text{-}SCH_2CH_2S)(PPh_3)]$ (**6**) and $[Ru_2(CO)_5(\mu\text{-}SCH_2CH_2CH_2S)(PPh_3)]$ (**7**). Suitable single crystals could not be grown for **6** and **7** for X-ray analysis; however, they are proposed to be structurally similar to $[Fe_2(CO)_5(\mu\text{-}SCH_2CH_2CH_2S)(PR_3)]$ on the basis of elemental analysis, IR, ^1H and $^{31}P\{^1H\}$ NMR and mass spectroscopic data. The mass spectra of **6** and **7** contain the molecular ion peaks at *m/z* 698 and 712 respectively with successive loss of five CO groups. The ^{31}P NMR spectra of **6** and **7** consist of a single resonance and do not show any significant change on varying the recording temperature. This suggests that **6** and **7** exist as single isomers. As expected, in addition to the signals for the phenyl protons of triphenylphosphine, the ^1H NMR spectra contain resonances due to dithiolate ligands. The IR spectra of **6** and **7** are very similar to that reported for $[Fe_2(CO)_5(\mu\text{-}SCH_2CH_2CH_2S)(PR_3)]$ in which the triphenylphosphine is coordinated at an axial site of one of the metal atoms [26]. When heated to reflux in hexane compound **2** was transformed into **3** by cluster degradation.

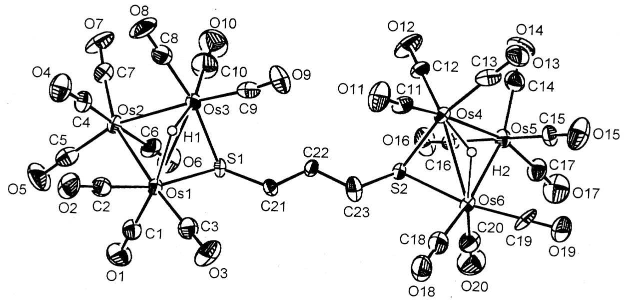


Fig. 4. Solid state structure of $[\{(\mu\text{-H})Os_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**5**) showing the atom labeling scheme. Hydrogen atoms other than the bridging hydrides are omitted for clarity. Thermal ellipsoids are drawn at 40% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Os(1)–Os(3)	2.8445(10)	Os(1)–Os(2)	2.8577(10)
Os(2)–Os(3)	2.8652(10)	Os(1)–S(1)	2.405(4)
Os(3)–S(1)	2.412(5)	Os(4)–Os(5)	2.8441(10)
Os(4)–Os(6)	2.8594(10)	Os(5)–Os(6)	2.8643(11)
Os(4)–S(2)	2.414(4)	Os(6)–S(2)	2.401(4)
S(1)–C(21)	1.82(2)	S(2)–C(23)	1.83(2)
C(1)–Os(1)–C(2)	93.4(8)	C(1)–Os(1)–C(3)	94.7(8)
C(2)–Os(1)–C(3)	94.5(7)	C(1)–Os(1)–S(1)	97.9(6)
C(2)–Os(1)–S(1)	165.9(6)	C(3)–Os(1)–S(1)	93.0(5)
C(1)–Os(1)–Os(3)	137.4(6)	C(2)–Os(1)–Os(3)	112.0(6)
C(3)–Os(1)–Os(3)	115.6(6)	S(1)–Os(1)–Os(3)	53.93(11)
C(1)–Os(1)–Os(2)	87.1(6)	C(2)–Os(1)–Os(2)	90.4(5)
C(3)–Os(1)–Os(2)	174.6(5)	S(1)–Os(1)–Os(2)	81.73(10)
Os(3)–Os(1)–Os(2)	60.33(2)	C(5)–Os(2)–C(4)	93.4(8)
C(5)–Os(2)–C(7)	99.2(8)	C(4)–Os(2)–C(7)	91.6(8)
C(5)–Os(2)–C(6)	90.1(8)	C(4)–Os(2)–C(6)	174.8(7)
C(7)–Os(2)–C(6)	91.6(7)	C(5)–Os(2)–Os(1)	98.7(6)
C(4)–Os(2)–Os(1)	87.0(5)	C(7)–Os(2)–Os(1)	162.1(6)
C(6)–Os(2)–Os(1)	88.7(5)	C(5)–Os(2)–Os(3)	158.2(6)
C(4)–Os(2)–Os(3)	83.8(5)	C(7)–Os(2)–Os(3)	102.5(6)
C(6)–Os(2)–Os(3)	91.5(6)	Os(1)–Os(2)–Os(3)	59.61(2)
C(10)–Os(3)–C(8)	92.3(9)	C(10)–Os(3)–C(9)	98.9(9)
C(8)–Os(3)–C(9)	90.3(7)	C(10)–Os(3)–S(1)	96.8(8)
C(8)–Os(3)–S(1)	168.1(6)	C(9)–Os(3)–S(1)	95.9(5)
C(10)–Os(3)–Os(1)	134.6(8)	C(8)–Os(3)–Os(1)	114.5(5)
C(9)–Os(3)–Os(1)	116.0(5)	S(1)–Os(3)–Os(1)	53.70(10)
C(10)–Os(3)–Os(2)	84.3(8)	C(8)–Os(3)–Os(2)	91.8(5)
C(9)–Os(3)–Os(2)	176.1(5)	S(1)–Os(3)–Os(2)	81.45(10)
Os(1)–Os(3)–Os(2)	60.07(2)	C(13)–Os(4)–C(12)	90.3(8)
C(13)–Os(4)–C(11)	96.1(8)	C(12)–Os(4)–C(11)	95.9(8)
C(13)–Os(4)–S(2)	166.4(6)	C(12)–Os(4)–S(2)	95.5(6)
C(11)–Os(4)–S(2)	95.6(6)	C(13)–Os(4)–Os(5)	85.3(6)
C(12)–Os(4)–Os(5)	90.7(6)	C(11)–Os(4)–Os(5)	173.2(5)
S(2)–Os(4)–Os(5)	82.33(10)	C(13)–Os(4)–Os(6)	115.1(6)
C(12)–Os(4)–Os(6)	137.5(6)	C(11)–Os(4)–Os(6)	113.3(5)
S(2)–Os(4)–Os(6)	53.35(10)	Os(5)–Os(4)–Os(6)	60.29(3)
C(17)–Os(5)–C(15)	92.3(8)	C(17)–Os(5)–C(14)	102.6(9)
C(15)–Os(5)–C(14)	89.6(8)	C(17)–Os(5)–C(16)	92.8(8)
C(15)–Os(5)–C(16)	173.9(8)	C(14)–Os(5)–C(16)	92.6(8)
C(17)–Os(5)–Os(4)	162.9(6)	C(15)–Os(5)–Os(4)	88.2(5)
C(14)–Os(5)–Os(4)	94.5(6)	C(16)–Os(5)–Os(4)	85.9(5)
C(17)–Os(5)–Os(6)	102.9(6)	C(15)–Os(5)–Os(6)	84.5(5)
C(14)–Os(5)–Os(6)	154.1(6)	C(16)–Os(5)–Os(6)	91.1(5)
Os(4)–Os(5)–Os(6)	60.12(3)	C(20)–Os(6)–C(19)	93.4(8)
C(20)–Os(6)–C(18)	97.5(9)	C(19)–Os(6)–C(18)	92.6(8)
C(20)–Os(6)–S(2)	95.3(6)	C(19)–Os(6)–S(2)	169.0(6)
C(18)–Os(6)–S(2)	92.9(6)	C(20)–Os(6)–Os(4)	136.7(6)
C(19)–Os(6)–Os(4)	115.3(6)	C(18)–Os(6)–Os(4)	111.9(6)
S(2)–Os(6)–Os(4)	53.78(11)	C(20)–Os(6)–Os(5)	89.8(6)
C(19)–Os(6)–Os(5)	91.3(6)	C(18)–Os(6)–Os(5)	171.5(6)
S(2)–Os(6)–Os(5)	82.13(10)	Os(4)–Os(6)–Os(5)	59.59(2)
C(21)–S(1)–Os(1)	109.6(5)	C(21)–S(1)–Os(3)	110.2(6)
Os(1)–S(1)–Os(3)	72.37(12)	C(23)–S(2)–Os(6)	109.0(6)
C(23)–S(2)–Os(4)	109.9(6)	Os(6)–S(2)–Os(4)	72.87(12)
C(22)–C(21)–S(1)	112.5(11)	C(21)–C(22)–C(23)	112.9(13)
C(22)–C(23)–S(2)	109.2(11)		

This work shows that the methylene chain length of the ditholate ligands as well as the metal atoms of the clusters have an important effect on product formation when reacted with trimetallic compounds. Longer methylene chain lengths favor dimer formation whilst a short chain length results in the formation of bidentate chelate as well as monodentate thiolate bridge.

3. Experimental

All the reactions were routinely carried out under a prepurified nitrogen atmosphere. Reagent grade solvents were freshly distilled from appropriate drying agents. Infrared spectra were recorded on a Schimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Varian Unity Plus 400 spectrometer. $[Ru_3(CO)_{12}]$ was purchased from Strem Chemicals Inc. and used without further purification. $[Os_3(CO)_{10}(MeCN)_2]$ was prepared according to the known procedure [40].

3.1. Reaction of $[Ru_3(CO)_{12}]$ with 1,2-ethanedithiol

A THF solution (80 ml) of $[Ru_2(CO)_{12}]$ (0.200g, 0.312 mmol) and 1,2-ethanedithiol (0.059 g, 0.626 mmol) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (9:1, v/v) gave two bands. The major band afforded the known compound $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (0.050 g, 40%) as pale yellow crystals after recrystallization from hexane/CH_2Cl_2 at -20°C. IR (ν(CO), hexane): 2085m, 2056vs, 2018vs, 2004s, 1995m, 1968w cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.37 (s). ^{13}C {^1H} NMR ($CDCl_3$): carbonyl region, 196.2 (4C), 188.6 (2C), hydrocarbon region, 36.1 (2C). MS (*m/z*): 464, M^+, 436 $[M-CO]^+$, 408 $[M-2CO]^+$, 380 $[M-3CO]^+$, 352 $[M-4CO]^+$, 324 $[M-5CO]^+$, 296 $[M-6CO]^+$. *Anal*. Calc. for $C_8H_4O_6Ru_2S_2$: C, 20.78; H, 0.87. Found: C, 20.95; H, 0.95%.

3.2. Reaction of $[Ru_3(CO)_{12}]$ with 1,3-propanedithiol

To a THF solution (100 ml) of $[Ru_3(CO)_{12}]$ (0.400 g, 0.625 mmol) was added 1,3-propanedithiol (0.135 g, 1.25 mmol) and the reaction mixture was refluxed for 1 h. The solvent and excess thiol were removed in vacuo and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (9:1, v/v) developed two bands. The faster moving band afforded $[\{(\mu\text{-}H)Ru_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**2**) (0.120 g, 30%) as orange crystals after recrystallization from hexane/CH_2Cl_2 at -20°C. Analytical and spectral data for **2**: (IR ν(CO), hexane): 2105m, 2067vs, 2057s, 2027vs, 2010w, 1998w cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.25 (t, 4H, $J=7.6$ Hz), 2.05 (q, 2H, $J=7.6$ Hz), -15.41 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): carbonyl region, δ 204.1 (2C), 202.6 (2C), 198.1 (4C), 192.8 (4C), 191.5 (4C), 184.5 (4C), hydrocarbon region, δ 55.1 (2C), 35.7 (1C). *Anal*. Calc. for $C_{23}H_8O_{20}Ru_6S_2$: C, 21.67; H, 0.63. Found: C, 21.82; H, 0.75%. The second band gave $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$ (**3**) (0.056 g, 19%) as pale yellow crystals after recrystallization from hexane/CH_2Cl_2 at -20°C. Analytical and spectral data for **3**: IR (ν(CO), hexane): 2086s, 2055vs, 2018vs, 2004s, 1994s, 1966w cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.19 (s, 4H), 1.89 (s, 2H). MS (*m/z*): 478, M^+, 450 $[M-CO]^+$, 422 $[M-2CO]^+$, 394 $[M-3CO]^+$, 366 $[M-4CO]^+$, 338 $[M-5CO]^+$, 310 $[M-6CO]^+$. *Anal*. Calc. for $C_9H_6O_6Ru_2S_2$: C, 22.69; H,1.27. Found: C, 22.78; H, 1.43%.

*3.3. Thermolysis of **2***

A THF solution (30 ml) of **2** (0.120 g, 0.094 mmol) was refluxed for 1.5 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (9:1, v/v) afforded **3** (0.012 g, 34%) as pale yellow crystals.

3.4. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 1,2-ethanedithiol

To a dichloromethane solution (15 ml) of $[Os_3(CO)_{10}(MeCN)_2]$ (0.194 g, 0.208 mmol) was added 1,2-ethanedithiol (0.039 g, 0.414 mmol) and the reaction mixture was stirred at room temperature for 5 h. The solvent was removed by rotary evaporation and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (4:1, v/v) gave two bands. The faster moving major band gave $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2SH)]$ (**4**) as yellow crystals (0.117 g, 60%) from hexane/CH_2Cl_2 at 20°C and the second band gave too small an amount of a compound for complete characterization. Spectral and analytical data for **4**: IR (ν(CO) hexane): 2110m, 2069vs, 2060s, 2026vs, 2021m, 2001s, 1992m, 1986w cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.70 (q, 2H, $J=8.4$ Hz), 2.55 (t, 2H, $J=8.4$ Hz), 1.65 (t, 1H, $J=8.4$ Hz), -17.41 (s, 1H). *Anal*. Calc. for $C_{12}H_6O_{10}Os_3S_2$: C, 15.25; H, 0.64. Found: C, 15.42; H, 0.78%. MS (*m/z*): 950 (M^+), 922 $[M-CO]^+$, 894 $[M-2CO]^+$, 866 $[M-3CO]^+$, 838 $[M-4CO]^+$, 810 $[M-5CO]^+$, 782 $[M-6CO]^+$, 754 $[M-7CO]^+$, 726 $[M-8CO]^+$, 698 $[M-9CO]^+$, 670 $[M-10CO]^+$.

3.5. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 1,3-propanedithiol

1,3-Propanedithiol (0.046 g, 0.428 mmol) was added to a dichloromethane solution (15 ml) of $[Os_3(CO)_{10}(MeCN)_2]$ (0.200 g, 0.214 mmol) in CH_2Cl_2 (15 ml) and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed by TCL on silica gel. Elution with hexane/CH_2Cl_2 (4:1, v/v) gave one major band which afforded $[\{\mu\text{-}H)Os_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ (**5**) (0.056 g, 30%) as yellow crystals from hexane/CH_2Cl_2 at -20°C. Analytical and spectral data for **5**: IR (ν(CO), hexane): 2110w, 2070s, 2060m, 2027s, 2022m, 2000m, 1991m cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.44 (t, 4H, $J=7.4$ Hz), 1.91 (q, 2H, $J=7.4$ Hz), -17.42 (s, 2H). *Anal*. Calc. for

$C_{23}H_8O_{20}Os_6S_2$: C, 15.26; H, 0.44. Found: C, 15.49; H, 0.58%.

3.6. Reaction of **1** with PPh_3

A mixture of **1** (0.050 g, 0.108 mmol) and triphenylphosphine (0.028 g, 0.107 mmol) in hexane (35 ml) was stirred at room temperature for 1 h. The color of the solution changed from yellow to orange. The solvent was rotary evaporated and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 gave a single band which afforded $[Ru_2(CO)_5(\mu\text{-}SCH_2CH_2S)(PPh_3)]$ (**6**) (0.041 g, 55%) as orange crystals after recrystallization from hexane/CH_2Cl_2 at −20°C. Analytical and spectral data for **6**: IR (ν(CO), CH_2Cl_2): 2060vs, 2004vs, 2024vw 1985w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.53–7.38 (m, 15H), 1.83 (m, 2H), 1.14 (m, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.6 (s). MS (*m/z*): 698, M^+, 670 $[M-CO]^+$, 642 $[M-2CO)]^+$, 614 $[M-3CO]^+$, 586 $[M-4CO]^+$, 558 $[M-5CO]^+$. *Anal.* Calc. for $C_{25}H_{19}O_5PRu_2S_2$: C, 43.10; H, 2.75. Found: C, 43.32; H, 2.92%.

3.7. Reaction of **3** with PPh_3

A similar reaction to that above of **3** (0.030 g, 0.063 mmol) and PPh_3 (0.017 g, 0.065 mmol) in hexane (30 ml) followed by similar workup and chromatographic separation yielded $[Ru_2(CO)_5(\mu\text{-}SCH_2CH_2CH_2S)(PPh_3)]$ (**7**) (0.020 g, 44%) as orange crystals from hexane/CH_2Cl_2 at −20°C. Analytical and spectral data for **7**: IR (ν(CO), CH_2Cl_2): 2060vs, 2004vs, 1985m, 1946m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.67–7.42 (m, 15H), 1.81 (m, 2H), 1.37 (m, 2H), 0.98 (m, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 42.1 (s). MS (*m/z*): 712, M^+, 684 $[M-CO]^+$, 656 $[M-2CO]^+$, 628 $[M-3CO]^+$, 600 $[M-4CO]^+$, 572 $[M-5CO]^+$. *Anal.* Calc. for $C_{26}H_{21}O_5PRu_2S_2$: C, 43.94; H, 2.98. Found: C, 44.18; H, 3.15%.

3.8. X-ray crystallography

Crystallographic data for **1** and **5** were recorded on a Delft Instruments FAST TV area detector and those for **2** were measured on a Turbo CAD4 diffractometer using monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) [41]. All data sets were corrected for absorption using DIFABS [42]. The structures were solved by direct methods (SHELXS-86) [43], developed via difference syntheses, and refined on F^2 by full-matrix least-squares (SHELXL-96) [44] using all unique data with intensities greater than zero. In all cases the non-hydrogen atoms were anisotropic. The bridging hydrides (H(1) and H(2)) in **2** were located from difference maps but not refined; all other hydrogen atoms were included in calculated positions (riding model). Compound **5** is isostructural with **2**, and so the refinement was carried out starting from the atomic coordinates for **2**. The crystallographic data are summarized in Table 4.

Table 4
Crystal data and details of data collection and structure refinement for **1**, **2** and **5** [a]

	Compound **1**	Compound **2**	Compound **5**
Chemical formula	$C_8H_4O_6Ru_2S_2$	$C_{23}H_8O_{20}Ru_6S_2$	$C_{23}H_8O_{20}Os_6S_2$
Formula weight	362.31	1274.83	1809.61
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	8.695(2)	14.748(3)	14.7855(11)
b (Å)	16.128(3)	14.088(2)	14.072(3)
c (Å)	9.957(2)	17.893(4)	17.867(2)
β (°)	98.22(2)	91.94(2)	91.981(12)
V ($Å^{-3}$)	1381.9(5)	3715.5(12)	3715.4(9)
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Z	4	4	4
Crystal size (mm)	0.12×0.10×0.08	0.45×0.20×0.06	0.20×0.16×0.12
Shape	prism	plate	prism
Colour	yellow	yellow	yellow
θ Range for data collection (°)	2.42–24.95	1.38–25.26	1.84–25.07
Reflections collected	5386	7246	14862
Unique reflections	2039	6704	5550
R_{int}	0.0491	0.0082	0.0549
Data/parameters in the refinement	2039/163	6704/460	5550/461
Goodness-of-fit on F^2	0.904	1.065	0.923
Final R [b] indices	$R_1 = 0.0726$ (0.0324) [c]	$R_1 = 0.0536$ (0.0393) [c]	$R_1 = 0.0702$ (0.0417) [c]
	$wR_2 = 0.0744$ (0.0726) [c]	$wR_2 = 0.1342$ (0.1188) [c]	$wR_2 = 0.0939$ (0.0884) [c]

[a] All measurements were done at 293(2) K.

[b] $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)\}^2]^{1/2}$.

[c] R_1 and wR_2 values for all unique data; those calculated for data with $I > 2\sigma(I)$ are given in parentheses.

Supplementary data

Full details of data collection and structure refinements are deposited with the Cambridge Crystallographic Data Centre, 2 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), CCDC reference numbers 139585 (**1**), 139586 (**2**) 139587 (**5**).

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