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Binuclear ruthenium complexes containing bridging dithiolate and dppm ligands: X-ray structures of $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2CH_2S)(\mu\text{-}dppm)]$ and $[Ru_2(CO)_4\{(\mu\text{-}SC_6H_3(CH_3)S\}(\mu\text{-}dppm)]$

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Abstract

The reactions of $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ (**4**) with 1,2-ethanedithiol, 1,3-propanedithiol and 3,4-toluenedithiol in refluxing THF afforded the dinuclear dithiolato complexes $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2S)(\mu\text{-}dppm)]$ (**5**), $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2CH_2S)(\mu\text{-}dppm)]$ (**6**) and $[Ru_2(CO)_4\{\mu\text{-}SC_6H_3(CH_3)S\}(\mu\text{-}dppm)]$ (**7**), respectively. Protonation of complexes **5** and **6** by tetrafluoroboric acid in CD_2Cl_2 resulted in the formation of cationic hydrido complexes $[(\mu\text{-}H)Ru_2(CO)_4(\mu\text{-}SCH_2CH_2S)(\mu\text{-}dppm)]^+$ (**8**) and $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2CH_2S)(\mu\text{-}dppm)]^+$ (**9**) isolated as their PF_6^- salts. Compounds **5** and **6** are also obtained from the reactions of dppm with $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (**10**) and $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$ (**11**), respectively. Protonation of **10** and **11** with tetrafluroboric acid gives the mono-protronated species $[(\mu\text{-}H)Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]^+$ (**12**) and $[(\mu\text{-}H)Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]^+$ (**13**), respectively. All the compounds have been characterised by IR, ^1H NMR, $^{31}P\{^1H\}$ and mass spectroscopic data, together with single crystal X-ray diffraction studies for **6** and **7**.

Keywords: Dithiolate complexes; Ruthenium clusters; Protonation; X-ray structures

1. Introduction

Diphosphines are versatile ligands in coordination and organometallic chemistry, owing to their ability to stabilise a great variety of metal complexes in a number of oxidation states [1–3] as well as to their application in homogeneous catalysts [4]. The chemistry of the diphosphine substituted complex $[Ru_3(CO)_{10}((\mu\text{-}dppm)]$ (**4**) (dppm = $Ph_2PCH_2PPh_2$) is characterised by its enhanced reactivity over that of the unsubstituted carbonyl $[Ru_3(CO)_{12}]$. The reactivities of **4** are of special interest because of the rigid geometry of the dppm ligand in maintaining the metal framework intact during chemical reactions [5–14]. Like diphosphines, alkane/arene-dithiolates also behave similarly in cluster chemistry [15]. There are plenty of examples, where the dithiols react with trimetallic clusters either by retaining the cluster structure intact or by breaking-down it into a dinuclear species as well as the ring opening of the ligand. For example, the dithiolato bridged dinuclear complexes $[Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$, $[Fe_2(CO)_6\{\mu\text{-}SC_6H_3(CH_3)S\}]$ and $[Fe_2(CO)_6(\mu\text{-}SCCHCHCHCHCS)]$ have been reported by several groups from the reactions of $[Fe_3(CO)_{12}]$ with respective dithiols [16–19]. In a previous report [20] we have shown that di- and trinuclear ruthenium complexes $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$, $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$, and $[\{(\mu\text{-}H)Ru_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$ are formed by the reaction of $[Ru_3(CO)_{12}]$ with 1,2-ethanedithiol and 1,3-propanedithiol, respectively, but the labile cluster $[Os_3(CO)_{10}(MeCN)_2]$ leads to the oxidative addition product $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2SH)]$ and $[\{(\mu\text{-}H)Os_3(CO)_{10}\}_2(\mu\text{-}SCH_2CH_2CH_2S)]$, respectively, when it reacts with the same ligands at room temperature. The

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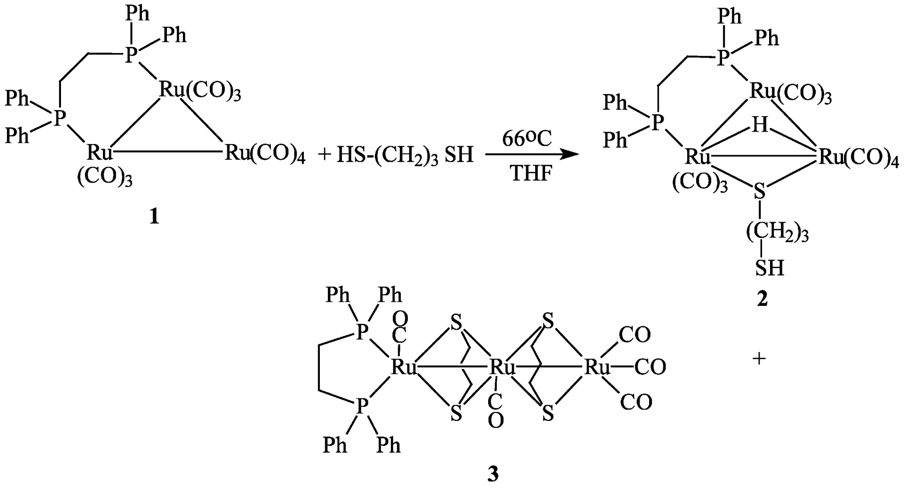
dinuclear compound [$Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)$] was first reported by Adams et al. [21] from the thermal degradation of [$Ru_3(CO)_7(\mu\text{-}CO)_2(\eta^3$-1,4,7-trithiacyclononane)] at 68 °C as well as from the reaction of [$Ru_3(CO)_{12}$] with 1,2,5,6-tetrathiacyclooctane at 40 °C by a ring opening cleavage reaction of the ligand [22]. The osmium analog [$Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)$] was reported [23] from the direct reaction of [$Os_3(CO)_{12}$] with 1,4-dithiacyclohexane as well as from the pyrolysis of [$Os_3(CO)_{11}(SCH_2CH_2SCH_2CH_2)$] at 128 °C. Arenethiolato-bridged dinuclear complexes [$M_2(CO)_6((\mu$-bdt)] (M = Fe, Ru, Os] (bdt = benzene-1,2-dithiolate) can easily be prepared from the reaction of corresponding trinuclear metal carbonyl with an excess of bdt ligand [24]. We have an intense interest in complexes bearing both the diphosphine and dithiolato ligands owing to their various coordination modes with metal centre. It is noteworthy that in such case, the binding of the ligands to the metal site are accomplished either by activation of S–H/S–S/P–C and C–H bonds of the ligands or by simple coordination through the donor atoms depending on the ligand geometry as well as the reaction condition. Recently, we have shown [25] that the reaction of the dppe complex [$Ru_3(CO)_{10}((\mu$-dppe)] (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$) with 1,3-propanedithiol leads to the formation of [$(\mu\text{-}H)Ru_3(CO)_8\{\mu\text{-}S(CH_2)_3\text{-}SH\}(\mu$-dppe)] (**2**) and [$Ru_3(CO)_5\{\mu_2\text{-}S(CH_2)_3S\}_2(\eta^2$-dppe)] (**3**), respectively (Scheme 1).

This observation prompted us to investigate the reaction of the corresponding dppm analog **4** with various dithiols such as, 1,2-ethanedithiol, 1,3-propanedithiol and 3,4-toluenedithiol and the results are described in the present paper. The protonation reactions of **10**, **11** and their dppm substituted analogs **5** and **6** with tetrafluoroboric acid are also reported.

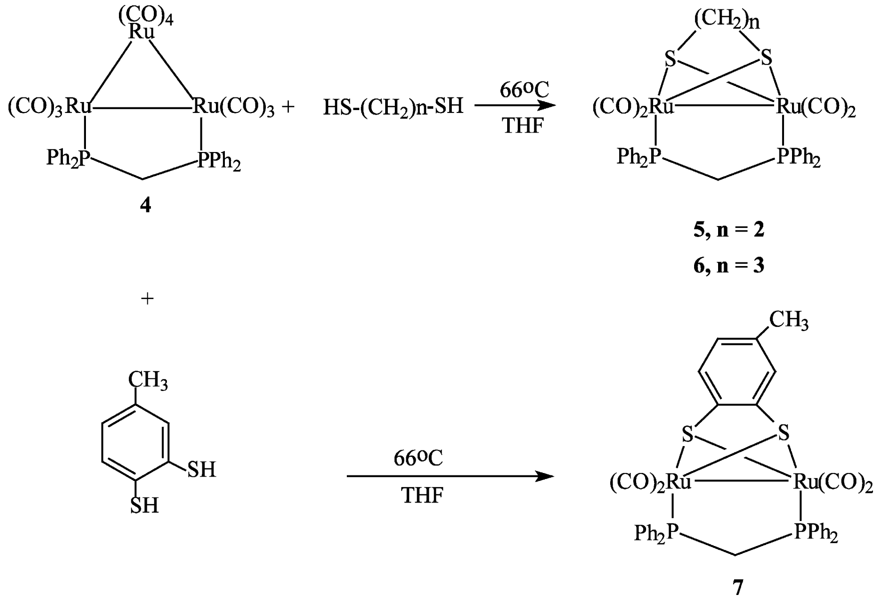
2. Results and discussion

In contrast to the reaction of **1** with 1,3-propanedithiol which afforded the trinuclear compounds **2** and **3** [25], the reactions of **4** with 1,2-ethanedithiol, 1,3-propanedithiol and 3,4-toluenedithiol in THF at reflux temperature followed by chromatographic separation resulted in the isolation of the dinuclear compounds, [$Ru_2(CO)_4(\mu\text{-}SCH_2CH_2S)(\mu$-dppm)] (**5**), [$Ru_2(CO)_4(\mu\text{-}SCH_2CH_2CH_2S)(\mu$-dppm)] (**6**) and [$Ru_2(CO)_4\{(\mu\text{-}SC_6H_3(CH_3)S)\}(\mu$-dppm)] (**7**), respectively, in 28, 30 and 45% yields, respectively (Scheme 2).

The compounds have been characterised on the basis of elemental analysis, infrared, ^{1}H NMR and mass spectroscopic data together with single crystal X-ray diffraction studies on **6** and **7**. The binuclear formulations of **5**–**7** were indicated by their microanalysis and mass spectra which showed the molecular ions (m/z 790 for **5**; 804 for **6** and 851 for **7**) and successive loss of four CO ligands. The similarity of their IR spectra in the carbonyl region suggested a similar arrangement of the carbonyl ligands while the presence of bridging dppm ligands has been confirmed by the $^{31}P\{^1H\}$ NMR spectra {δ 28.6 (s) for **5**, 25.8 (s) for **6**}. In addition to the methylene and phenyl resonances of the dppm ligand, the ^{1}H NMR spectra display well-separated signals for the dithiolato ligands. The ^{1}H NMR spectrum of **5**, in the aliphatic region, contains three multiplets at δ 3.35, 2.37 and 2.21 each integrating for two hydrogens. The multiplets at δ 2.37 and 2.21 have been assigned to the methylene protons of 1,2-ethanedithiolate ligand while the other at δ 3.35 is due to the methylene protons of the dppm ligand. The multiplet centred at δ 7.33 is due to the aromatic protons of the dppm ligand. The $^{13}C\{^1H\}$ NMR spectrum of **5** in the carbonyl region indicates the presense of four terminal



Scheme 1.



Scheme 2.

carbonyl ligands as 2 non-equiv. pairs giving siganls at δ 208.2 (t, 2C, $J = 5.3$ Hz) and 195.3 (t, 2C; $J = 3.0$ Hz). The aliphatic region of the ^{1}H NMR spectrum of **6** contains five multiplets of 1:1:2:2:2 relative intensity at δ 3.35, 3.32, 2.05 2.25 and 2.40, respectively. The multiplets centred at δ 3.35 and 3.32 are due to the methylene protons of the dppm ligand, and those at δ 2.05, 2.25 and 2.40 are assigned to the methylene protons of the 1,3-propanedithiolate ligand. The ^{1}H NMR spectrum of **7** contains a singlet at δ 2.09 due to the methyl protons of the dithiolate ligand and a multiplet at δ 3.56 assigned to the methylene protons of the dppm ligand. The ring proton resonances of the toluenedithiolate ligand are overlapped with the phenyl resonances of the dppm ligand.

The structures of **6** (Fig. 1) and **7** (Fig. 2) were determined unambiguously by X-ray crystallography. Selected bond distances and angles for the two compounds are given in Tables 1 and 2, respectively. The compounds are very similar regarding the attachment of the carbonyl, dithiolate and dppm ligands to the metal sites. Both structures consist of a ruthenium–ruthenium back-bone, ligated terminally by four carbonyl ligands adopting the $Ru_2(CO)_4$ classical 'sawhorse' arrangement, and bridged by a dithiolate as well as a dppm ligand. The S(2) atom in both structures lies on the opposite side of the Ru_2P_2 plane while S(1) is nearly perpendicular to it. The Ru–S distances lie in the narrow ranges 2.3890(12)–2.4103(12) Å (**6**) and 2.413(2)–2.439(2) Å (**7**) and this indicates that the dithiolato bridges are quite symmetrical in both compounds. The Ru–S–Ru angles are highly acute with the values at S(1) and S(2) of 67.37(3)° and 67.96(3)°, respectively, for **6**, and 65.98(5)° and 66.52(5)°, respectively, for **7**. The Ru–P distances are also nearly equal as shown by the values 2.3237(12) and 2.3433(12) Å for **6** and 2.305(2) and 2.325(2) Å for **7**. The P–C–P angles of the short-bite dppm ligand in **6** and **7** {P(1)–C(8)–P(2) = 114.4(2)° for **6** and P(1)–C(12)–P(2) = 113.0(3)° for **7**} are comparable with the corresponding values in $[Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_5(\mu\text{-}\eta^2\text{-dppm})_2]$ {112.0(6)° and 114.4(7)°} [26] and $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8(\mu\text{-dppm})]$ {115.2(2)°} [27]. The interesting features of the molecular structures of **6** and **7** are their very short Ru–Ru distances. The Ru–Ru distances of 2.6720(7) Å in **6** and

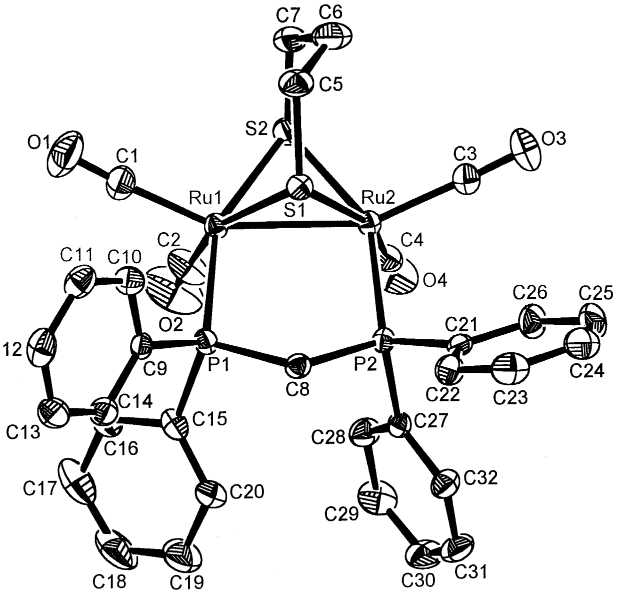


Fig. 1. X-ray structure of $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2CH_2S)(\mu\text{-dppm})]$ (**6**) showing the atom labelling scheme. Thermal ellipsoids are drawn at 35% probability level. The hydrogen atoms are omitted for clarity.

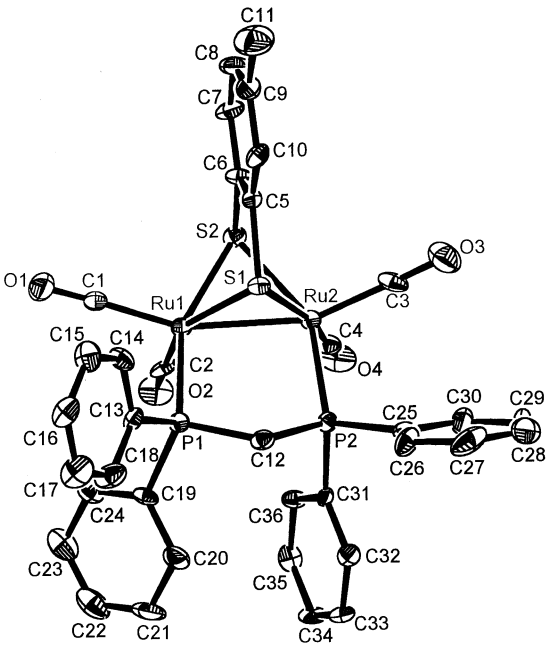


Fig. 2. X-ray structure of [Ru$_2$(CO)$_4${(μ-SC$_6$H$_3$(CH$_3$)S)}(μ-dppm)] (**7**) showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level. The hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for [Ru$_2$(CO)$_4$(μ-SCH$_2$CH$_2$CH$_2$S)(μ-dppm)] (**6**)

Bond distances			
Ru(1)–Ru(2)	2.6720(7)	Ru(1)–P(1)	2.3237(12)
Ru(1)–S(1)	2.4071(12)	Ru(2)–P(2)	2.3433(12)
Ru(1)–S(2)	2.3916(12)	S(1)–C(5)	1.837(5)
Ru(2)–S(1)	2.4103(12)	S(2)–C(7)	1.820(5)
Ru(2)–C(4)	1.870(5)	Ru(2)–C(3)	1.889(5)
Ru(1)–C(1)	1.904(5)	Ru(1)–C(2)	1.842(6)
Ru(2)–S(2)	2.3890(12)		
Bond angles			
Ru(1)–S(1)–Ru(2)	67.37(3)	P(1)–C(5)–P(2)	114.(2)
S(2)–Ru(2)–Ru(1)	56.07(3)	P(1)–Ru(1)–S(2)	152.45(4)
S(2)–Ru(2)–S(1)	82.51(4)	S(2)–Ru(1)–S(1)	82.53(4)
P(2)–Ru(2)–S(2)	149.12(4)	S(2)–Ru(1)–Ru(2)	55.97(3)
S(1)–Ru(1)–Ru(2)	56.37(3)	P(2)–Ru(2)–S(1)	84.62(4)
P(1)–Ru(1)–Ru(2)	97.00(3)	P(2)–Ru(2)–Ru(1)	93.60(3)
P(1)–Ru(1)–S(1)	86.18(4)	S(1)–Ru(2)–Ru(1)	56.25(3)
		Ru(2)–S(2)–Ru(1)	67.96(3)

Table 2
Selected bond distances (Å) and angles (°) for [Ru$_2$(CO)$_4${(μ-SC$_6$H$_3$(CH$_3$)S)}(μ-dppm)] (**7**)

Bond distances			
Ru(1)–Ru(2)	2.6481(9)	Ru(1)–P(1)	2.305(2)
Ru(1)–S(1)	2.439(2)	Ru(2)–P(2)	2.325(2)
Ru(1)–S(2)	2.413(2)	S(1)–C(5)	1.787(6)
Ru(1)–C(1)	1.889(8)	Ru(2)–C(3)	1.863(8)
Ru(1)–C(2)	1.861(7)	Ru(2)–C(4)	1.872(6)
Ru(2)–S(1)	2.424(2)	S(2)–C(6)	1.777(6)
Ru(2)–S(2)	2.416(2)		
Bond angles			
Ru(1)–S(1)–Ru(2)	65.98(5)	P(1)–C(12)–P(2)	113.0(3)
S(2)–Ru(2)–Ru(1)	56.68(4)	P(1)–Ru(1)–S(2)	154.77(6)
S(2)–Ru(2)–S(1)	77.80(6)	S(2)–Ru(1)–S(1)	77.57(6)
P(2)–Ru(2)–Ru(1)	92.13(5)	S(2)–Ru(1)–Ru(2)	56.79(4)
S(1)–Ru(2)–Ru(1)	57.29(4)	P(2)–Ru(2)–S(1)	88.08(6)
P(1)–Ru(1)–Ru(2)	98.15(5)	P(2)–Ru(2)–S(2)	148.66(7)
P(1)–Ru(1)–S(1)	86.03(6)	S(1)–Ru(1)–Ru(2)	56.74(4)
		Ru(2)–S(2)–Ru(1)	66.52(5)

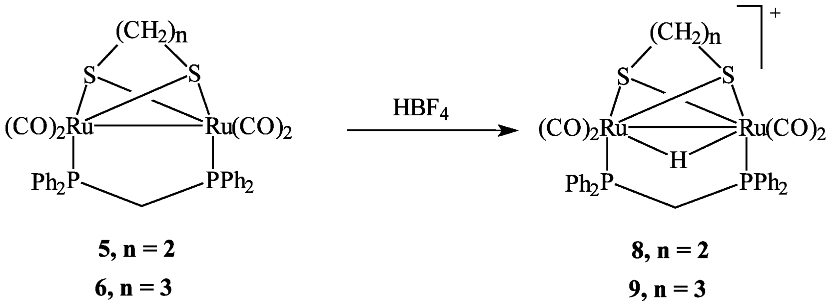
2.6481(9) Å in **7** are significantly shorter than the corresponding Ru–Ru distances {2.8564(10) Å} in the parent compound **4** [28], but are comparable with the corresponding values found in the dinuclear ruthenium complexes such as, [Ru$_2$(CO)$_6$(μ-SCH$_2$CH$_2$S] {2.679(8) Å} [20], [Ru$_2$(CO)$_4$(μ-SC$_6$H$_4$S)(PPh$_3$)$_2$] {2.677(5) Å} [29], and [Ru$_2$(CO)$_6$(μ-SC$_6$H$_4$S)] {2.650(2) Å} [24]. This relative shortening of the Ru–Ru bond in both **6** and **7** compared with the parent compound **4** is presumably due to the 'pincer' effect exerted by the bridging dithiolate ligand [24]. The dithiolate ligands serve as bidentate bridging ligand across the metal–metal bond and donate six electrons to make **6** and **7** electron precise with 36 valence electrons, each metal atom achieving the expected 18-electron configuration.

2.1. *Protonation reactions of **5** and **6***

Cabeza et al. demonstrated that binuclear ruthenium complexes [Ru$_2$(CO)$_6$(μ-SCCHCHCHCHCS)] and [Ru$_2$(μ-dan)(CO)$_4$(L)$_2$] (H$_2$dan = 1,8-diamminonapthalene; L = CO, PR$_3$) [30,31] undergo protonation to give cationic hydrido derivatives but these reactions cannot be generalised. For example, [Ru$_2$(CO)$_6$(μ-dmpz)$_2$] (Hdmpz = 3,5-dimethylpyrazole) does not undergo protonation even in concentrated sulfuric acid [32]. We have studied protonation of **5** and **6** to see whether protonation of the more electron rich dppm substituted compound occurs more smoothly with acids.

Treatment of **5** and **6** with an excess of tetrafluoroboric acid afforded cationic hydrido derivatives which were isolated as their PF$_6^-$ salts [(μ-H)Ru$_2$(CO)$_4$(μ-SCH$_2$CH$_2$S)(μ-dppm)][PF$_6$] (**8**) and [(μ-H)Ru$_2$(CO)$_4$(μ-SCH$_2$CH$_2$CH$_2$S)][PF$_6$] (**9**), respectively, as pale yellow solids (Scheme 3) by treatment with NH$_4$PF$_6$. Suitable single crystals could not be grown for either of the complexes for X-ray analysis. So, the structures of **8** and **9** are proposed on the basis of their analytical and spectroscopic data.

The ν(CO) stretching frequencies of both **8** and **9** are shifted to higher wave numbers than those of their parent compounds. This increase in the wave numbers for the protonated species with respect to **5** and **6** is due to the reduction of electron density of the metals causing the C–O bond order to be enhanced, which in turn, decrease the electron donation by the metal to π*CO orbitals. In addition to the expected resonances for phenyl and methylene protons of the dppm and



Scheme 3.

dithiolato ligands, the ^1H NMR spectrum of **8** in the hydride region shows a triplet of doublets at δ −13.16 ($J_{P-H} = 16.0$ Hz, $J_{H-H} = 2.8$ Hz) in agreement with the assumption that the hydride is bridging the two ruthenium atoms which are also bridged by the dppm and dithiolate ligands. The proton decoupling experiment reveals that the hydride is coupled equally to the 2 equiv. ^{31}P nuclei ($J_{P-H} = 16.0$ Hz) and to one of the methylene protons of dppm ligand ($J_{H-H} = 2.8$ Hz). Thus when the CH_2 resonance at δ 4.72 is decoupled, the hydride resonance becomes a triplet. This four-bond coupling ($J_{H-H} = 2.8$ Hz) must arise from the *trans* arrangement of the bridging hydride with one of the CH_2 protons. Similar coupling of one of the methylene protons of dppm ligand with the cluster bound hydride ligand has been observed by Smith et al. [33] in the protronated species $[(\mu\text{-H})Os_3Au(CO)_8\{Ph_2CH_2P(Ph)C_6H_4\}]^+$ and $[(\mu\text{-H})_2Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]^+$. The $^{31}P\{^1H\}$ NMR spectrum of **8** in CD_2Cl_2 exhibits a singlet at δ 32.2 for the 2 equiv. ^{31}P nuclei of dppm ligand. The ^1H NMR spectrum of **9** in the hydride region contains a doublet of triplets at δ −11.92 ($J_{P-H} = 16.0$ Hz, $J_{H-H} = 2.4$ Hz). The multiplicity of the hydride resonances and the size of the coupling constants are very similar to those of **8**, indicating that they have similar structures. In agreement with this, the $^{31}P\{^1H\}$ NMR spectrum of **9** exhibits a sharp singlet at δ 31.9 for the 2 equiv. ^{31}P nuclei of dppm ligand.

2.2. *Protonation reactions of* ***10*** *and* ***11***

In order to compare the protonation reactions of the unsubstituted dithiolato compounds $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]$ (**10**) and $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]$ (**11**) with those of the dppm substituted analogs **5** and **6**, we have investigated the reaction of **10** and **11** with tetrafluoroboric acid (Scheme 4).

As expected, both the compounds **10** and **11** underwent protonation to give the cationic hydrido derivatives $[(\mu\text{-H})Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)]^+$ (**12**) and $[(\mu\text{-H})Ru_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2S)]^+$ (**13**). These compounds were precipitated as yellow solids from the acidic solutions but undergo spontaneous deprotonation when treated with aqueous NH_4PF_6. The structures proposed for the **12** and **13** are based on their spectroscopic data. In addition to the usual resonances for the methylene protons, the hydride region of the ^1H NMR spectra contain characteristic hydride resonances (δ −12.98 for **12**, and −13.92 for **13**). As expected, the ν(CO) stretching frequencies of **12** and **13** in presence of excess acid shifted to higher wave numbers compared with **10** and **11**.

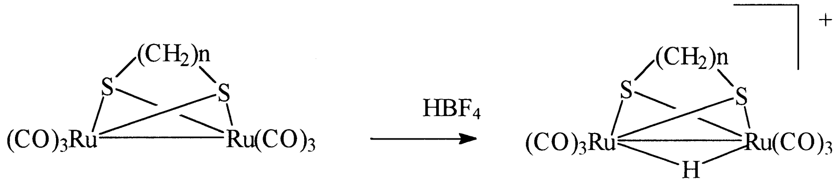
An interesting finding of the investigation is that S–H activation of the dithiolate ligand is accompanied by the degradation of the parent complex **4** leading to a dinuclear species. The short-bite dppm behaves as a ‘spectator’ ligand. At least one feature is worth noting that the basic geometry of the parent cluster **4** is not preserved in either **6** or **7**.

3. Experimental

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All glassware was either flame dried under vacuum or dried in an oven prior to use. Tetrahydrofuran was freshly distilled under a nitrogen atmosphere from sodium benzophenone ketyl. Dichloromethane was distilled under nitrogen from phosphorus pentoxide. Infrared spectra were recorded on a Shimadzu FT IR 8101 spectrophotometer. ^1H NMR spectra were recorded on a Bruker DPX 400 spectrometer. 1,2-Ethanedithiol, 1,3-propanethdiol and 3,4-toluenedithiol were purchased from Merck and used as received. Mass spectra were recorded on a Varian Mat 312 mass spectrometer. The compound $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ (**4**), **10** and **11** were prepared according to the published procedure [34].

3.1. *Reaction of* ***4*** *with 1,2-ethanedithiol*

1,2-Ethanedithiol (0.041 g, 0.435 mmol) was added to a THF (40 cm^3) solution of **4** (0.210 g, 0.217 mmol) and the reaction mixture was heated to reflux for 30 min. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (4:1, v/v) gave one major and two minor bands. The major band afforded



10, n = 2
11, n = 3

12, n = 2
13, n = 3

Scheme 4.

$[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2S)(\mu\text{-dppm})]$ (**5**) (0.048 g, 28%) as yellow crystals after recrystallisation from hexane–CH_2Cl_2 at −15 °C. *Anal.* Calc. for $C_{31}H_{26}O_4P_2Ru_2S_2$: C, 47.08; H, 3.32. Found: C, 47.25; H, 3.40%. IR ν(CO, CH_2Cl_2): 2004s, 1981vs and 1938s cm^{-1}; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 204.24 (t, 2C, $J = 5.3$ Hz), 195.30 (t, 2C, $J = 3.0$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.6 (s); ^1H NMR ($CDCl_3$): δ 2.21(m, 4H), 2.37 (m, 2H), 3.35 (m, 2H), 7.33 (m. 20H); mass spectrum: *m/z* 790 (M^+), 762 ($M^+ -$CO), 734 ($M^+ -$2CO), 706 ($M^+ -$3CO), 678 ($M^+ -$4CO).

3.2. Reaction of 4 with 1,3-propanedithiol

A similar reaction to that of above of **4** (0.210 g, 0.217 mmol) with 1,3-propanedithiol (0.044 g, 0.407 mmol) followed by similar chromatographic work-up gave two bands. The first band was too small for complete characterisation. The second band gave $[Ru_2(CO)_4\{\mu\text{-}S(CH_2)_3S\}(\mu\text{-dppm})]$ (**6**) (0.065 g, 37%) as yellow crystals from hexane–CH_2Cl_2 at −15 °C. *Anal.* Calc. for $C_{32}H_{28}O_4P_2Ru_2S_2$: C, 47.75; H, 3.51. Found: C, 48.03; H, 3.65%. IR ν(CO, CH_2Cl_2): 2004s, 1981vs, 1938s cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.9 (s); ^1H NMR ($CDCl_3$): δ 2.05 (m, 2H), 2.25 (m, 2H), 2.40 (m, 2H), 3.32 (m, 1H), 3.35 (m, 1H), 7.33 (m, 20H); mass spectrum: *m/z* 804 (M^+), 776 ($M^+ -$CO), 748 ($M^+ -$2CO), 720 ($M^+ -$3CO), 692 ($M^+ -$4CO).

3.3. Reaction of 4 with 3,4-toluenedithiol

A similar treatment of **4** (0.210 g, 0.217 mmol) with 3,4-toluenedithiol (0.064 g, 0.410 mmol) followed by similar chromatographic work-up afforded $[Ru_2(CO)_4\{\mu\text{-}S(C_6H_3)(CH_3)S\}(\mu\text{-dppm})]$ (**7**) $(CH_3)_2CO$ (0.107 g, 54%) as yellow crystals after recrystallisation from acetone–ethanol at room temperature (r.t.). *Anal.* Calc. for $C_{39}H_{33}O_5P_2Ru_2S_2$: C, 51.47; H, 3.66. Found: C, 51.71; H, 3.57%. IR ν(CO, CH_2Cl_2): 2008s, 1986vs, 1945s cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.09 (m, 3H), 3.56 (m, 2H), 7.27 (m, 23H); mass spectrum: *m/z* 851 [M^+], 823 [$M^+ -$CO], 795 [$M^+ -$2CO], 767 [$M^+ -$3CO], 739 [$M^+ -$4CO].

3.4. Protonation of 5

An excess of $HBF_4 \cdot OEt_2$ (one drop from a pasteur pipette) was added to a solution of **5** (0.016 g, 0.020 mmol) in CD_2Cl_2 (0.5 cm^3) in an NMR tube. After recording ^1H and $^{31}P\{^1H\}$ NMR spectra, the volatiles were removed under vacuum, and the residue was dissolved in methanol (5 cm^3). Addition of a methanolic solution of ammonium hexafluorophosphate (0.022 g) followed by a few drops of water gave a yellow precipitate which was recrystallised from CH_2Cl_2–Et_2O to give $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2S)(\mu\text{-dppm})][PF_6]$ (**8**) as yellow crystals (0.010 g, 63%). *Anal.* Calc. for $C_{31}H_{26}O_4P_3Ru_2S_2F_6$: C, 39.74; H, 2.80. Found: C, 39.92; H, 2.99%. IR ν(CO, CH_2Cl_2): 2060vs, 2020vs, 1981w, 1943w cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.01 (m, 2H), 3.11 (m, 2H) 4.72 (m, 2H), 7.39 (m, 20H), −13.16 (dt, 1H, $J_{P–H} = 16.0$ Hz, $J_{H–H} = 2.8$ Hz) $^{31}P\{^1H\}$ NMR (CD_2Cl_2}: δ 32.2 (s).

3.5. Protonation of 6

A similar protonation of **6** (0.018 g, 0.022 mmol) as employed for **5** with excess $HBF_4 \cdot OEt_2$, followed by usual work-up as mentioned above, afforded $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2CH_2S)(\mu\text{-dppm})][PF_6]$ (**9**) as yellow crystals (0.012g, 62%). *Anal.* Calc. for $C_{32}H_{28}O_4P_3Ru_2S_2F_6$: C, 40.42; H, 2.97. Found: C, 40.43; H, 2.94%. IR ν(CO, CH_2Cl_2): 2058vs, 2018vs, 1981w, 1943w cm^{-1}; ^1H NMR (CD_2Cl_2): δ 2.30 (m, 4H), 2.07 (m, 2H), 3.34–3.70 (m, 2H), 7.45 (m, 20H), −11.92 (dt, 1H, $J_{P–H} = 16.0$ Hz, $J_{H–H} = 2.4$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.9 (s).

3.6. Reaction of $[Ru_2(CO)_6(\mu\text{-}SCH_2CH_2S)$ (10) with dppm

Dppm (0.075 g, 0.195 mmol) was added to a THF (20 cm^3) solution of **10** (0.045 g, 0.097 mmol) and the resulting mixture was heated to reflux for 2 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane–CH_2Cl_2 (4:1, v/v) gave one major and several minor bands. The major band gave $[Ru_2(CO)_4(\mu\text{-}SCH_2CH_2S)(\mu\text{-dppm})]$ (**5**) (0.019 g, 25%) as yellow crystals after recrystallisation from hexane–CH_2Cl_2 at −15 °C.

3.7. *Reaction of [$Ru_2(CO)_6(\mu$-$SCH_2CH_2CH_2S$) (**11**) with dppm*

A similar reaction of dppm (0.073 g, 0.190 mmol) with **11** (0.045 g, 0.094 mmol) followed by similar chromatographic work-up gave two bands. The first band was too small for complete characterisation. The second band gave [$Ru_2(CO)_4\{\mu$-$S(CH_2)_3$–$S\}(\mu$-dppm)] (**6**) (0.023 g, 30%) as yellow crystals after recrystallisation from hexane–CH_2Cl_2 at −15 °C.

3.8. *Protonation of **10***

Tetrafluoroboric acid (one drop from a Pasteur pipette) was added to a CD_2Cl_2 solution of **10** (0.025 g, 0.011 mmol) in an NMR tube. After recording the ^1H NMR the volatiles were removed under reduced pressure. Treatment of the residue with aqueous solution of $[NH_4][PF_6]$ afforded the starting material **10**. ^1H NMR indicated complete protonation to give $[(\mu$-$H)Ru_2(CO)_6(\mu$-$SCH_2CH_2S)]^+$ (**12**). IR ν(CO, CH_2Cl_2): 2145w, 2129s, 2085vs, 2054vs, 2008vs, 1967w, 1942w, 1923w cm^{-1}; ^1H NMR (CD_2Cl_2): δ 1.97 (m, 2H), 2.45 (m, 2H), −12.98 (s, 1H).

3.9. *Protonation of **11***

A similar protonation of **11** (0.018 g, 0.022 mmol), as employed for **10**, with tetrafluoroboric acid followed by usual work-up as mentioned above, afforded $[(\mu$-$H)Ru_2(CO)_6(\mu$-$SCH_2CH_2CH_2S)]^+$ (**13**) as yellow solid (0.012 g, 62%). IR ν(CO, CH_2Cl_2): 2143w, 2127s, 2085vs, 2054vs, 2008vs, 1967w, 1942w, 1923w, 1909vw cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.05 (m, 2H), 2.42 (m, 4H), −13.92 (s, 1H).

3.10. *X-ray crystallography*

Crystals of **6** and **7** suitable for X-ray diffraction were grown from a hexane–CH_2Cl_2 solution of **6** or by layering an acetone solution with ethanol at −4 °C for **7**. Crystallographic data were collected using a FAST area detector diffractometer and Mo Kα radiation (λ = 0.71069 Å) by following previously described procedure [35]. The unit cell parameters were determined by the least-square refinement of the diffractometer angles for 250 reflections and the data were corrected for absorption using DIFABS [36]. The structures were solved by direct methods (SHELXS-96) [37] and refined on F^2 by full-matrix least-squares (SHELXL-97) [38] using all unique data. All non-hydrogen atoms were anisotropic. The hydrogen atoms were included in calculated position (riding model). The crystal data and refinement details are summarised in Table 3.

Table 3
Crystal data and details of data collection and structure refinement[a] for **6** and **7**·$(CH_3)_2CO$

	6	**7**
Empirical formula	$C_{32}H_{28}O_4P_2Ru_2S_2$	$C_{37}H_{28}O_4P_2Ru_2S_2$, C_2H_6O
Formula weight	804.74	910.86
Temperature (K)	293(2)	150(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	10.433(2)	8.885(2)
b (Å)	17.103(2)	23.834(5)
c (Å)	18.693(2)	17.775(4)
β (°)	104.698(12)	90.56(3)
V (Å^3)	3226.3(6)	3763.9(14)
Z	4	4
D_{calc} (g cm^{-3})	1.657	1.607
Absorption coefficient (cm^{-1})	12.00	10.41
F(000)	1608	1832
Crystal size (mm)	0.40 × 0.35 × 0.30	0.32 × 0.28 × 0.20
θ Range for data collection (°)	2.02–25.06	2.06–25.12
Index ranges	$-9 \le h \le 11$, $-18 \le k \le 18$, $-22 \le l \le 21$	$-9 \le h \le 8$, $-27 \le k \le 22$, $-17 \le l \le 20$
Reflections collected	13 263	14 802
Independent reflections	4844	5880
R_{int}	0.0400	0.0992
Data/parameters	4844/379	5880/454
Goodness-of-fit on F^2	0.964	0.989
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0313$, $wR_2 = 0.0693$	$R_1 = 0.0476$, $wR_2 = 0.0797$
R indices (all data)	$R_1 = 0.0443$, $wR_2 = 0.0714$	$R_1 = 0.0927$, $wR_2 = 0.0876$
Largest difference peak and hole (e Å^{-3})	0.888 and −0.360	0.919 and −0.569

[a] Details in common: X-radiation, Mo Kα, λ = 0.71069 Å; refinement method: full-matrix least-squares on F^2 using all unique data.

4. Supplementary material

Atomic coordinates and full tables of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, CCDC reference numbers 196703 (**6**) and 196704 (**7**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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