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Reactions of a diruthenium complex with sulfur, selenium and sulfur dioxide

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Reaction of the complex [$Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2$] **1** (dppm = $Ph_2PCH_2PPh_2$) with sulfur or selenium gave the corresponding [$Ru_2(CO)_4(\mu\text{-}E)(\mu\text{-}dppm)_2$] (E = **2** or **3**) in high yield. Both **2** and **3** reacted with an excess of sulfur to give the disulfido, μ-sulfido complex [$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(S_2)(\mu\text{-}dppm)_2$] **4**. Complex **1** reacted readily with SO_2 to give [$Ru_2(CO)_4(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$] **5**, containing a bridging S-bonded SO_2 ligand. The complexes **1**, **4** and **5** have been characterized by crystal structure determinations and are shown to contain Ru–Ru single bonds.

The complex [$Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2$] **1** (dppm = $Ph_2PCH_2PPh_2$),[1–3] like related diphosphine derivatives of the unstable [$Ru_2(CO)_9$],[4] displays high reactivity towards both electrophilic and nucleophilic reagents and so is an interesting reagent for study of co-ordination chemistry at a diruthenium centre.[1–4] Although this topic is of current interest and though there are many examples of ruthenium complexes with bridging sulfur- or selenium-donor ligands,[5–10] there appear to be no reports on complexes derived from **1** with sulfur or selenium reagents.[4] Since it seemed probable that interesting chemistry relevant to the role of RuS_2 in catalytic hydrodesulfurization[5] would result, such a study was initiated and this article reports the reactions of **1** with the reagents sulfur (and some other potential sulfur atom donors), selenium, and sulfur dioxide.

Results and Discussion

The chemistry below leads to a series of complexes [$Ru_2(CO)_4(\mu\text{-}E)(\mu\text{-}dppm)_2$] (E = S, Se or SO_2) by displacement in complex **1** with E = CO. It was of interest to compare the properties of these complexes. The structure of **1** as a solvate with 1,2-$C_2H_4Cl_2$ has been determined but the data were of poor quality,[2] so we have therefore redetermined it, this time as the acetone solvate. Whilst this work was in progress the structure of **1** as the acetonitrile solvate was reported.[1] The new structure is shown in Fig. 1 and selected distances and angles are given in Table 1.

The structure contains a *trans,trans*-$Ru_2(\mu\text{-}dppm)_2$ unit in the extended boat conformation with the methylene flaps directed away from the bridging carbonyl ligand. Hence, the axial phenyl groups are all directed towards the bridging carbonyl, which is small enough to fit between them (Fig. 1). The bond distances and angles are similar to those found in the other solvates.[1,2] Thus, the Ru–Ru distance is 2.903(2), 2.903(2) and 2.907(9) Å in the acetone, 1,2-dichloroethane[2] and acetonitrile[1] solvates respectively.

Reactions with sulfur and selenium

When [$Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2$] **1** was treated with elemental sulfur in a ratio $Ru_2:S = 1:1$ the bridging sulfido complex [$Ru_2(CO)_4(\mu\text{-}S)(\mu\text{-}dppm)_2$] **2** was obtained by displacement of the bridging carbonyl by the sulfide ligand. The reaction was complete in 10 min at room temperature and the product was obtained as an air-stable, orange-brown solid in high yield. The same product **2** was obtained by reaction of **1** with either of the sulfur atom donors H_2S or propylene sulfide, with evolution of hydrogen or propene respectively as well as CO (Scheme 1). No intermediates were observed when the reactions were monitored by ^1H and ^{31}P NMR spectroscopy, though, at least with H_2S as reagent, they must be formed transiently. Complex **2** did not react further with either H_2S or with propylene sulfide, but did react with an excess of sulfur as described later.

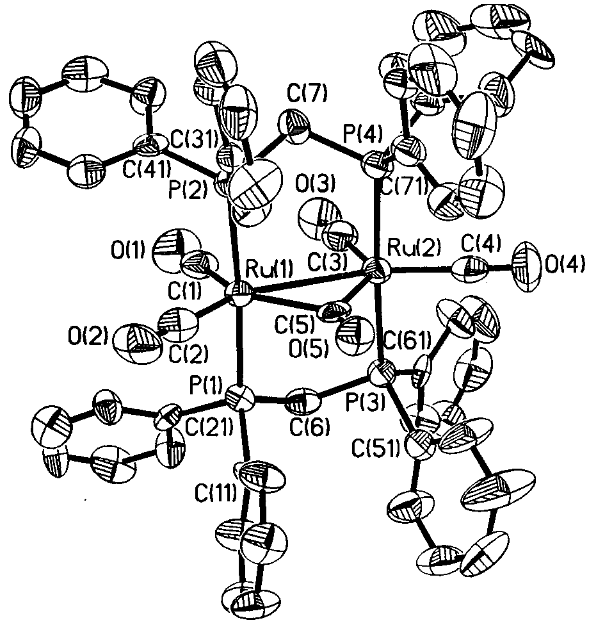


Fig. 1 View of the structure of [$Ru_2(CO)_4(\mu\text{-}CO)(\mu\text{-}dppm)_2$] **1**

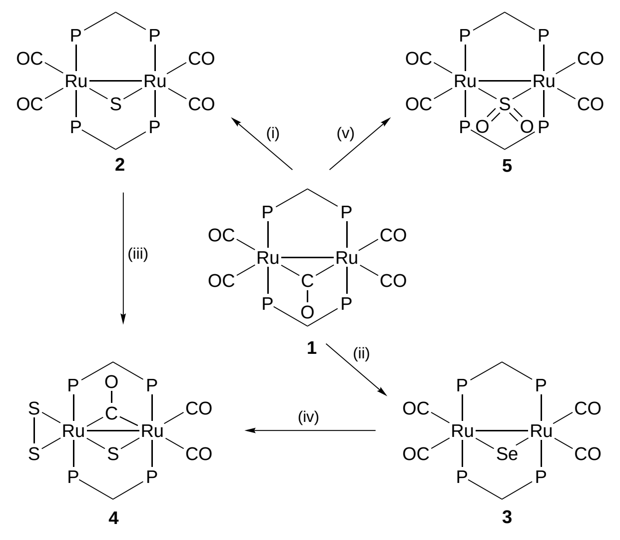
Complex **2** was readily characterized by analytical and spectroscopic methods. The significant feature which differentiated the IR spectrum from that of its precursor was the four terminal carbonyl stretching bands but no bridging carbonyl band (observed at 1701 cm^{-1} for **1**).[2] The ^1H NMR spectrum was typical of an 'A-frame' complex, containing two multiplets due to the CH^aH^b protons of the dppm ligands at δ 5.1 and 3.1. The ^{31}P NMR spectrum showed a singlet at δ 27.5 as expected for a symmetrical compound.

The reaction of complex **1** with grey selenium proceeded in an analogous way to give the bridging selenido complex **3** (Scheme 1), which was isolated as a stable, dark brown solid. Its spectroscopic properties were very similar to those of **2**. In addition, it gave a parent ion in the FAB mass spectrum, as well as peaks due to fragments from sequential loss of the four carbonyl ligands.

The reaction of complex **1** or **2** with an excess of sulfur gave a new complex characterized as [$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(S_2)(\mu\text{-}dppm)_2$] **4** (Scheme 1), and this could be isolated as air-stable red crystals. The reaction with **1** proceeded sequentially to give **2** and then **4**, as monitored by ^1H and ^{31}P NMR spectroscopy.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**·0.5Me_2CO

Ru(1)–C(1)	1.98(2)	Ru(1)–C(2)	1.90(2)
Ru(1)–C(5)	2.13(2)	Ru(1)–P(1)	2.346(4)
Ru(1)–P(2)	2.352(4)	Ru(1)–Ru(2)	2.903(2)
Ru(2)–C(3)	1.96(2)	Ru(2)–C(4)	1.87(2)
Ru(2)–C(5)	2.13(2)	Ru(2)–P(3)	2.347(4)
Ru(2)–P(4)	2.327(4)	O(1)–C(1)	1.11(2)
O(2)–C(2)	1.13(2)	O(3)–C(3)	1.14(2)
O(4)–C(4)	1.13(2)	O(5)–C(5)	1.18(2)
C(2)–Ru(1)–C(1)	115.8(7)	C(2)–Ru(1)–C(5)	98.9(6)
C(1)–Ru(1)–C(5)	145.3(7)	C(2)–Ru(1)–P(1)	91.3(5)
C(1)–Ru(1)–P(1)	85.1(5)	C(5)–Ru(1)–P(1)	92.8(4)
C(2)–Ru(1)–P(2)	89.5(5)	C(1)–Ru(1)–P(2)	88.4(5)
C(5)–Ru(1)–P(2)	93.8(4)	P(1)–Ru(1)–P(2)	173.1(2)
C(2)–Ru(1)–Ru(2)	145.8(5)	C(1)–Ru(1)–Ru(2)	98.4(5)
C(5)–Ru(1)–Ru(2)	47.0(4)	P(1)–Ru(1)–Ru(2)	91.9(1)
P(2)–Ru(1)–Ru(2)	91.2(1)	C(4)–Ru(2)–C(3)	118.1(7)
C(4)–Ru(2)–C(5)	107.9(7)	C(3)–Ru(2)–C(5)	133.9(7)
C(4)–Ru(2)–P(4)	87.1(5)	C(3)–Ru(2)–P(4)	90.3(5)
C(5)–Ru(2)–P(4)	89.7(4)	C(4)–Ru(2)–P(3)	90.2(5)
C(3)–Ru(2)–P(3)	90.3(5)	C(5)–Ru(2)–P(3)	91.8(4)
P(4)–Ru(2)–P(3)	117.2(2)	C(4)–Ru(2)–Ru(1)	154.9(6)
C(3)–Ru(2)–Ru(1)	86.9(5)	C(5)–Ru(2)–Ru(1)	47.0(4)
P(4)–Ru(2)–Ru(1)	91.1(1)	P(3)–Ru(2)–Ru(1)	91.7(1)
O(1)–C(1)–Ru(1)	178(2)	O(2)–C(2)–Ru(1)	177(2)
O(3)–C(3)–Ru(2)	178(2)	O(4)–C(4)–Ru(2)	177(2)
O(5)–C(5)–Ru(1)	138(1)	O(5)–C(5)–Ru(2)	136(1)
Ru(1)–C(5)–Ru(2)	86.0(6)		



Scheme 1 Reagents: (i) S_8, −CO; (ii) Se, −CO; (iii) S_8, −CO; (iv) S_8, −CO, −Se; (v) SO_2, −CO

The IR spectrum of **4** contained three carbonyl bands at 2020, 1960, and 1836 cm^{-1}, consistent with the presence of two terminal carbonyls and one bridging carbonyl group. The ^1H NMR spectrum contained two broad multiplets at δ 2.8 and 4.5 due to the CH^aH^b protons of the dppm ligands, while the ^{31}P NMR spectrum contained two multiplets of equal intensity at δ 10.5 and 18.0, indicating the inequivalence of the two ruthenium centres. The FAB mass spectrum showed the parent peak for $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(S_2)(\mu\text{-}dppm)_2]^+$ at $m/z = 1151$ and fragmentation peaks at $m/z = 1087$, 1059, 1031 and 1003, attributed to ions formed by sequential loss of S_2, followed by one, two, and three CO groups respectively.

The spectroscopic data did not define the nature of the sulfur-donor ligands in complex **4** so it was also characterized by a crystal structure determination. A view of the structure is given in Fig. 2 and selected bond distances and angles are in Table 2. There was disorder between the μ-S and μ-CO ligands of **4**, but this was successfully resolved; Fig. 2 shows only one of the two arrangements.

Table 2 Selected bond distances (Å) and bond angles (°) in $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(S_2)(\mu\text{-}dppm)_2]\cdot Me_2CO$

Ru(1)–C(1)	2.18(3)	Ru(1)–P(1)	2.395(6)
Ru(1)–P(2)	2.403(6)	Ru(1)–S(1)	2.404(9)
Ru(1)–S(2)	2.430(7)	Ru(1)–S(3)	2.434(7)
Ru(1)–Ru(2)	2.935(3)	Ru(2)–C(3)	1.80(2)
Ru(2)–C(2)	1.86(3)	Ru(2)–C(1)	2.25(3)
Ru(2)–P(3)	2.415(6)	Ru(2)–P(4)	2.415(6)
Ru(2)–S(1)	2.535(9)	S(2)–S(3)	2.13(1)
C(2)–O(2)	1.15(3)	C(3)–O(3)	1.22(2)
C(1)–Ru(1)–P(1)	95(2)	C(1)–Ru(1)–P(2)	90(2)
P(1)–Ru(1)–P(2)	174.0(2)	C(1)–Ru(1)–S(1)	105.1(7)
P(1)–Ru(1)–S(1)	90.9(3)	P(2)–Ru(1)–S(1)	91.5(3)
C(1)–Ru(1)–S(2)	107.1(7)	P(1)–Ru(1)–S(2)	82.3(2)
P(2)–Ru(1)–S(2)	92.8(2)	S(1)–Ru(1)–S(2)	147.5(3)
C(1)–Ru(1)–S(3)	156.6(8)	P(1)–Ru(1)–S(3)	92.1(2)
P(2)–Ru(1)–S(3)	82.1(2)	S(1)–Ru(1)–S(3)	97.1(3)
S(2)–Ru(1)–S(3)	51.8(3)	C(1)–Ru(1)–Ru(2)	49.5(7)
P(1)–Ru(1)–Ru(2)	93.3(1)	P(2)–Ru(1)–Ru(2)	92.6(2)
S(2)–Ru(1)–Ru(2)	156.0(2)	S(3)–Ru(1)–Ru(2)	152.2(2)
C(3)–Ru(2)–C(2)	92(1)	C(3)–Ru(2)–C(1)	83(1)
C(2)–Ru(2)–C(1)	171(2)	C(3)–Ru(2)–P(3)	91.3(8)
C(2)–Ru(2)–P(3)	87.4(8)	C(1)–Ru(2)–P(3)	85(2)
C(3)–Ru(2)–P(4)	89.3(8)	C(2)–Ru(2)–P(4)	91.8(8)
C(1)–Ru(2)–P(4)	96(2)	P(3)–Ru(2)–P(4)	179.0(2)
C(3)–Ru(2)–S(1)	174.6(8)	C(2)–Ru(2)–S(1)	86.7(9)
C(1)–Ru(2)–S(1)	98.8(7)	P(3)–Ru(2)–S(1)	93.8(3)
P(4)–Ru(2)–S(1)	85.5(3)	C(3)–Ru(2)–Ru(1)	130.1(9)
C(2)–Ru(2)–Ru(1)	137.9(9)	Ru(1)–S(1)–Ru(2)	72.9(2)
O(1)–C(1)–Ru(1)	134(2)	O(1)–C(1)–Ru(2)	143(2)
Ru(1)–C(1)–Ru(2)	83(1)	S(3)–S(2)–Ru(1)	64.2(3)
S(2)–S(3)–Ru(1)	64.0(3)	O(2)–C(2)–Ru(2)	177(3)
O(3)–C(3)–Ru(2)	177(2)		

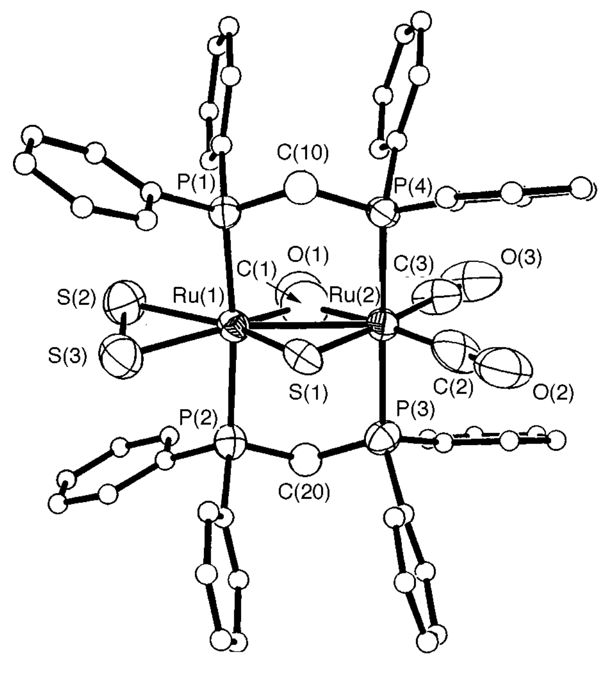


Fig. 2 View of the structure of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(S_2)(\mu\text{-}dppm)_2]$ **4**. Only one of the arrangements of the disordered μ-S and μ-CO groups is shown

The structure contains the expected *trans,trans*-$Ru_2(\mu\text{-}dppm)_2$ unit in an extended chair conformation. This conformation results in the presence of two axial phenyl groups on each side of the molecule, and so to two similarly sized cavities for the μ-S and μ-CO ligands to fit into. Atom Ru(1) is bonded to a terminal η^2-disulfide ligand while Ru(2) is bonded to two terminal carbonyls. There is a bridging sulfide ligand and a bridging carbonyl. The Ru–Ru distance of 2.935(3) Å indicates the presence of a metal–metal bond; although the distance is at the long end of the Ru–Ru single bond range [2.707(6)–3.02(1)],[1–4] there are precedents for the elongation of metal–metal bonds when they are bridged by sulfur.[11] Hence each ruthenium atom can be considered to be seven-co-ordinate with highly distorted pentagonal bipyramidal stereochemistry. Since Ru(1) is bound to three sulfur atoms and Ru(2) is bound to only one, the simplest way of dealing with the electron configuration is to consider that Ru(1) and Ru(2) carry a negative and a positive charge respectively; each ruthenium is then co-ordinatively saturated and has a formal oxidation state of ii. If the ruthenium atoms are initially considered to be neutral, the formal oxidation states are $\mathrm{Ru^{III}}(1)$ and $\mathrm{Ru^{I}}(2)$ and then a donor–acceptor bond(2)→Ru(1) must be invoked in order for each ruthenium to attain the 18-electron configuration, leading to effectively the same electron configuration as in the situation above.

The bridging sulfide ligand is bound asymmetrically, as indicated by the distances Ru(1)–S(1) and Ru(2)–S(1) of 2.404(9) and 2.535(9) Å respectively. The disulfide ligand is bound in a symmetrical η^2-chelate mode with Ru(1)–S(2) and Ru(1)–S(3) distances of 2.430(7) and 2.434(7) Å respectively. The S–S distance S(2)–S(3) 2.13(1) Å is at the long end of the range found in other disulfido complexes for which the S–S distances range between the S=S double bond (1.88 Å) and S–S single bond (2.09 Å) distances.[5–7,12] Although η^2 chelation by disulfide ligands is common for many transition metals,[5] complex **4** appears to be the first example for a diruthenium complex.[4–7] In the known disulfido complexes of ruthenium, the disulfido group bridges in the bridging η^2-|| bonding mode and there is evidence for partial SS and RuS double bonding. For example, the complex $[\mathrm{Ru_2(\mu\text{-}S_2)(\mu\text{-}SPr^i)_2(\eta\text{-}C_5Me_5)_2}]$ has Ru–S 2.215(4) and 2.209(5) and S–S 2.008(6) Å, all significantly shorter than the corresponding distances in **4**.[6]

Attempts were made to prepare mixed chalcogenide complexes but without success. Thus complex **2** failed to react with an excess of selenium. Complex **3** did react with an excess of sulfur but the only product formed in detectable quantity was **4**; hence this reaction leads to displacement of the bridging selenide ligand in **3** by sulfide.

Reaction of complex 1 with sulfur dioxide

Complex **1** reacts readily with sulfur dioxide to give $[\mathrm{Ru_2(CO)_4(\mu\text{-}SO_2)(\mu\text{-}dppm)_2}]$ **5**, which was isolated as air-stable yellow crystals (Scheme 1). The reaction involves the displacement of the bridging carbonyl of **1** by a bridging S-bonded $\mathrm{SO_2}$ ligand. Complexes **5** and **2** are closely related, but efforts to prepare **5** by oxidation of the sulfide ligand in **2** using hydrogen peroxide or trimethylamine N-oxide were unsuccessful. The symmetrical nature of complex **5** is shown by the ^{31}P NMR spectrum, which contains a sharp singlet at δ 34.7 due to the equivalent phosphorus atoms of the dppm ligands. The ^{1}H NMR spectrum exhibited two resonances at δ 2.7 and 4.6 due to the $\mathrm{CH^aH^b}$ protons of the dppm ligands, as expected for an A-frame structure. The IR spectrum contained only terminal carbonyl stretching bands at 2070, 2007, 1972 and 1943 $\mathrm{cm^{-1}}$. The ν(SO) bands were observed at 1210 (sym. stretch) and 1050 $\mathrm{cm^{-1}}$ (asym. stretch), and their separation of 160 $\mathrm{cm^{-1}}$ indicates a symmetrical S-bonded co-ordination of the $\mathrm{SO_2}$ ligand.[13]

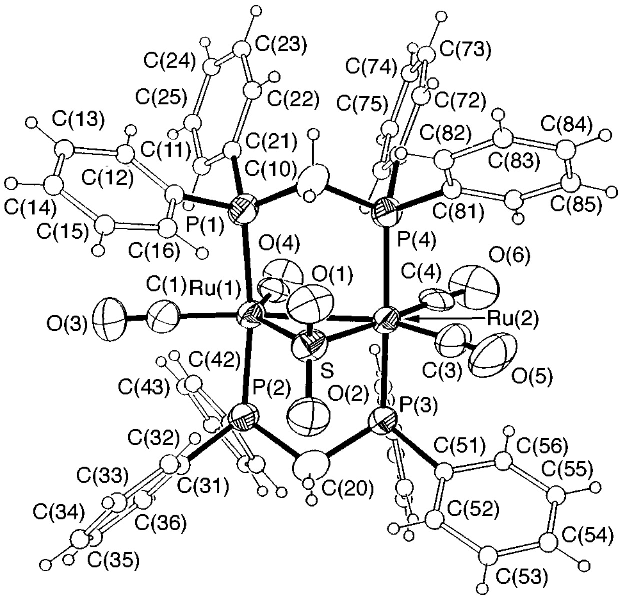


Fig. 3 View of the structure of $[\mathrm{Ru_2(CO)_4(\mu\text{-}SO_2)(\mu\text{-}dppm)_2}]$ **5**

Table 3 Selected bond distances (Å) and angles (°) in $[\mathrm{Ru_2(CO)_4(\mu\text{-}SO_2)(\mu\text{-}dppm)_2}]\cdot\mathrm{EtOH}\cdot\mathrm{H_2O}$

Ru(1)–C(1)	1.90(2)	Ru(1)–C(2)	1.90(2)
Ru(1)–S	2.386(4)	Ru(1)–P(2)	2.391(4)
Ru(1)–P(1)	2.393(4)	Ru(1)–Ru(2)	2.925(2)
Ru(2)–C(3)	1.91(2)	Ru(2)–C(4)	1.95(2)
Ru(2)–S	2.354(4)	Ru(2)–P(3)	2.386(4)
Ru(2)–P(4)	2.402(4)	S–O(1)	1.48(1)
S–O(2)	1.53(1)	C(1)–O(3)	1.16(2)
C(2)–O(4)	1.16(2)	C(3)–O(5)	1.13(2)
C(4)–O(6)	1.21(2)		
C(1)–Ru(1)–C(2)	110.6(7)	C(1)–Ru(1)–S	115.2(6)
C(2)–Ru(1)–S	134.2(5)	C(1)–Ru(1)–P(2)	86.4(5)
C(2)–Ru(1)–P(2)	91.3(4)	S–Ru(1)–P(2)	91.1(1)
C(1)–Ru(1)–P(1)	85.8(5)	C(2)–Ru(1)–P(1)	92.7(4)
S–Ru(1)–P(1)	91.0(1)	P(2)–Ru(1)–P(1)	172.1(2)
C(1)–Ru(1)–Ru(2)	166.6(6)	C(2)–Ru(1)–Ru(2)	82.8(5)
S–Ru(1)–Ru(2)	51.4(1)	P(2)–Ru(1)–Ru(2)	93.8(1)
P(1)–Ru(1)–Ru(2)	93.5(1)	C(3)–Ru(2)–C(4)	96.9(8)
C(3)–Ru(2)–S	90.0(6)	C(4)–Ru(2)–S	173.0(5)
C(3)–Ru(2)–P(3)	92.4(5)	C(4)–Ru(2)–P(3)	87.1(4)
S–Ru(2)–P(3)	91.6(2)	C(3)–Ru(2)–P(4)	91.8(5)
C(4)–Ru(2)–P(4)	89.8(4)	S–Ru(2)–P(4)	91.0(1)
P(3)–Ru(2)–P(4)	175.1(1)	C(3)–Ru(2)–Ru(1)	142.4(6)
C(4)–Ru(2)–Ru(1)	120.7(5)	P(3)–Ru(2)–Ru(1)	89.2(1)
P(4)–Ru(2)–Ru(1)	89.1(1)	O(1)–S–O(2)	108.5(7)
O(1)–S–Ru(2)	114.7(6)	O(2)–S–Ru(2)	114.8(5)
O(1)–S–Ru(1)	120.3(5)	O(2)–S–Ru(1)	119.2(5)
Ru(2)–S–Ru(1)	76.2(1)	O(3)–C(1)–Ru(1)	174(2)
O(4)–C(2)–Ru(1)	176(1)	O(5)–C(3)–Ru(2)	176(2)
O(6)–C(4)–Ru(2)	169(2)		

Complex **5** was further characterized by a crystal structure determination of a solvate **5**·EtOH·$\mathrm{H_2O}$. A view of the structure is given in Fig. 3 and selected bond distances and angles are in Table 3. The structure contains the *trans,trans*-$\mathrm{Ru_2(\mu\text{-}dppm)_2}$ unit in the extended boat conformation. This conformation with the methylene flaps towards the μ-$\mathrm{SO_2}$ ligand creates a larger cavity on this side of the molecule, since the phenyl substituents are all equatorial, as needed to accommodate the $\mathrm{SO_2}$ ligand. Note that in **1**, with the smaller μ-CO ligand, the extended boat conformation is also observed but with the methylene flaps away from the bridging ligand (Fig. 1). In **5** each ruthenium has two terminal carbonyl ligands and the $\mathrm{SO_2}$ ligand adopts the symmetrical bridging mode, as predicted from the spectroscopic data. Nevertheless the arrangement of the carbonyl ligands is much less symmetrical and this appears to be due to steric effects with the axial phenyl substituents of the dppm ligands. Note for example the large differences in bond angles C(2)–Ru(1)–Ru(2) 82.8(5) and C(4)–Ru(2)–Ru(1) 120.7(5), and C(1)–Ru(1)–Ru(2) 166.6(6) and C(3)–Ru(2)–Ru(1) 142.4(6)°. In order to avoid the axial phenyl groups C(2)O(4) moves from its natural position towards Ru(2) while C(4)O(6) moves away from Ru(1). The Ru–Ru separation of 2.925(2) Å indicates the presence of a metal–metal single bond.[1–4] The acute Ru–S–Ru angle of 76.2(1)° also indicates compression along the Ru–Ru axis and is comparable to other such values where $\mathrm{SO_2}$ bridges a metal–metal bond [69.6(1)–79.8(1)°];[14] the M–S–M angle is significantly larger [91.2(1)–

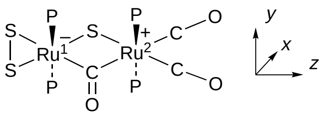
118.0(2)°] when SO_2 bridges two non-bonded metal atoms.[13,14] Thus, each ruthenium atom is considered to have distorted octahedral stereochemistry. The symmetrical bridging of the SO_2 is illustrated by the similarity of the Ru–S distances Ru(1)–S and Ru(2)–S of 2.386(4) and 2.354(4) Å respectively, while the S=O distances S–O(1) 1.48(1) and S–O(2) 1.53(1) Å are significantly different although within the range for other μ-SO_2 complexes.[13,14] The elongation of the S=O bonds compared to those in free SO_2 [1.432(3) Å] is expected since the orbital used for M–SO_2 back bonding is S–O antibonding in nature.[7,13–15]

These are few other binuclear SO_2 complexes of ruthenium.[7,10,13–15] The complex $[Ru_2(\mu\text{-}SO_4)_2(SO_2)_2(PPh_3)_4]$ contains a sulfur dioxide molecule co-ordinated to each ruthenium as a terminal S-bonded ligand.[10] The closest analogy to **5** appears to be $[Ru_2(CO)_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}SO_2)]$, which is characterized as having a bridging SO_2 group from its spectroscopic properties.[10] Complex **5** is thus the first $Ru_2(\mu\text{-}SO_2)$ complex to be characterized crystallographically.

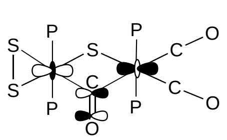
Conclusion

The reactions described between complex **1** and sulfur or selenium lead to formal oxidation of the complexes from the initial Ru^0Ru^0 state. Thus, **2** and **3** are considered as Ru^IRu^I complexes, while **4** can be considered either as $Ru^{II}Ru^{II}$ or Ru^IRu^{III}. The SO_2 complex **5** would normally be considered as Ru^0Ru^0, with its formation involving a simple ligand displacement. However, all the complexes contain a metal–metal single bond whose distance appears to depend primarily on the nature of the bridging group(s). Thus, **1**, which has a bridging carbonyl only, has the shortest Ru–Ru distance of 2.903(2) Å, while **4** and **5**, which each have a sulfur donor bridge, have approximately equal but longer Ru–Ru distances of 2.935(3) and 2.925(2) Å respectively.

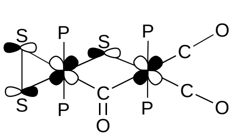
The bonding in complex **4** is of interest since the metal atoms have high co-ordination numbers for a $M_2(dppm)_2$ complex. If the axes are defined as in **4A**, the ruthenium atoms use the orbitals $4d_{yz}$, $4d_{x^2-y^2}$, $4d_{z^2}$, 5s, $5p_x$, $5p_y$, $5p_z$ primarily for σ bonding, while $4d_{xy}$ and $4d_{yz}$ are used in π bonding. Strong interactions are expected between the π orbitals of the sulfide ligand and the filled π* orbitals of the disulfide ligand with the metal orbitals of π symmetry.[5–7] Extended Hückel molecular orbital calculations indicate that the HOMO (highest occupied molecular orbital) is an antibonding combination of such filled orbitals as shown in **4B**, while the LUMO (lowest unoccupied molecular orbital) is a combination of the metal–metal σ* orbital (mostly d_{z^2}–d_{z^2}) and π* orbitals of the carbonyl ligands shown as **4C**.



4A



4B



4C

Another interesting feature of the structures is that the dppm ligands adopt different conformations in the complexes **1**, **4** and **5**. Complexes with the *trans,trans*-$M_2(\mu\text{-dppm})_2$ group usually adopt an envelope conformation of each $M_2(\mu\text{-dppm})$ group with the CH_2 flap directed towards the side of the molecule where the bulkier ligands are located. This naturally leads to the phenyl groups on this side of the molecule being equatorial and there is a larger natural cavity in which the other ligands must fit. In complex **4** the μ-S and μ-CO groups have about equal size (thus allowing them to be disordered on either side) and there is also one S and one CO on either side. Hence, the elongated chair conformation is adopted, leading to equal sized cavities on each side of the $Ru_2(\mu\text{-dppm})_2$ plane. In complexes **1** and **5** there is a μ-CO and μ-SO_2 group respectively on one side of the molecule and two terminal axial carbonyls on the other. Both adopt the extended boat conformation, but in **1** the methylene flaps are away from the μ-CO ligand whereas in **5** they are towards the μ-SO_2 ligand. We suggest that this occurs because the steric effects follow the series μ-SO_2 > 2 × terminal CO > μ-CO. In **5** it seems that steric effects with the axial phenyl groups cause a major distortion of the angles involving the terminal carbonyl ligands.

In terms of reactivity complex **1** is electron-rich and is air-sensitive. All the complexes **2**–**5** are air-stable and presumably all have lower electron density at ruthenium. This can be attributed to formal oxidation in the case of **2**, **3** and, especially, **4**, but to the better electron-withdrawing ability of μ-SO_2 compared to μ-CO in **5**.

Experimental

Complex **1** was synthesized as reported elsewhere,[2] and all experiments were carried out using Schlenk techniques with an atmosphere of nitrogen. The NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer and chemical shifts are given with respect to $SiMe_4$ (^1H) or phosphoric acid (^{31}P).

Preparations

$[Ru_2(CO)_4(\mu\text{-S})(\mu\text{-dppm})_2]$ 2. The complex $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (0.11 g) was mixed with elemental sulfur (0.0032 g) and CH_2Cl_2 (15 cm^3) added. The reaction mixture was stirred under nitrogen for 0.5 h. Solvent was then removed under reduced pressure. The orange-brown compound thus obtained was washed with pentane (5 cm^3) and dried under vacuum. Yield = 96%. It was recrystallized from CH_2Cl_2–pentane (Found: C, 57.5; H, 4.0. Calc. for $C_{54}H_{44}O_4P_4Ru_2S$: C, 58.2; H, 3.9%). IR (Nujol): $\tilde{\nu}$(CO) 2035, 1980, 1943 and 1916 cm^{-1}. NMR (acetone): δ(^1H) 3.1 (m, 2 H, $^2J_{HH} = 13$, $J_{PH} = 4$, CH^aH^b), 5.1 (m, 2 H, $^2J_{HH} = 13$, $J_{PH} = 5$ Hz, CH^aH^b) and 7.0–8.0 (m, 40 H, C_6H_5); δ(^{31}P) 27.3 (s, dppm).

To a stirring solution of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (0.15 g) in tetrahydrofuran (thf) (20 cm^3) was injected H_2S (10 cm^3). The reaction mixture was then stirred for 3 h after which the solvent was removed under vacuum. The brown solid thus obtained was characterized as $[Ru_2(CO)_4(\mu\text{-S})(\mu\text{-dppm})_2]$ by IR, ^1H and ^{31}P NMR spectroscopy. Yield = 94%.

Propylene sulfide (10 μl) was added to a solution of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ in thf (20 cm^3) After stirring the reaction mixture for 3 h it was evaporated to dryness. The resulting orange-brown solid was then washed with hexane (10 cm^3) and dried *in vacuo*. The product was identified as $[Ru_2(CO)_4(\mu\text{-S})(\mu\text{-dppm})_2]$ by its IR, ^1H and ^{31}P NMR spectra. Yield = 96%.

$[Ru_2(CO)_4(\mu\text{-Se})(\mu\text{-dppm})_2]$ 3. To a mixture of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (0.15 g) and elemental grey selenium (0.035 g) was added thf (25 cm^3). The reaction mixture was then stirred for 5 h. The unchanged selenium (excess) was filtered off. Removal of solvent yielded the product as a dark brown solid. Yield = 97%. It was recrystallized from CH_2Cl_2–pentane (Found: C, 56.2; H, 3.9. Calc. for $C_{54}H_{44}O_4P_4Ru_2Se$: C, 55.8; H, 3.8%). IR (Nujol): $\tilde{\nu}$(CO) 2036, 1981, 1944 and 1921 cm^{-1}. NMR (acetone): δ(^1H) 3.5 (m, 2 H, $^2J_{HH} = 13$, $J_{PH} = 4$, CH^aH^b), 5.5 (m, 2 H, $^2J_{HH} = 13$, $J_{PH} = 6$ Hz, CH^aH^b) and 7.0–7.8 (m, 40 H, C_6H_5); δ(^{31}P) 27.8 (s, dppm). FAB mass spectrum: $m/z = 1161$ (M^+), 1133, 1105 and 1049.

$[Ru_2(CO)_2(\mu\text{-CO})(\mu\text{-S})(S_2)(\mu\text{-dppm})_2]$ 4. The complex $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (0.11 g) was mixed with an excess

Table 4 Crystal data and structure refinements* for complexes **1**, **4** and **5**

	1$\cdot 0.5(CH_3)_2CO$	**4**$\cdot (CH_3)_2CO$	**5**$\cdot C_2H_5OH\cdot H_2O$
Formula	$C_{56.5}H_{47}O_{5.5}P_4Ru_2$	$C_{56}H_{50}O_4P_4Ru_2S_3$	$C_{56}H_{52}O_8P_4Ru_2$
M	1139.96	1209.16	1211.06
T/K	295	298	298
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	11.989(2)	12.877(5)	20.700(3)
b/Å	22.496(3)	37.69(1)	12.944(2)
c/Å	22.188(5)	13.303(5)	22.913(4)
β/°	104.94(3)	117.46(1)	91.08(1)
U/Å^3	5782(2)	5729(4)	6138(2)
D_c/Mg m^{-3}	1.310	1.402	1.284
μ/mm^{-1}	0.676	0.790	0.695
T_{min}, T_{max}	0.312, 0.339	0.844, 0.896	0.723, 0.827
F(000)	2312	2456	2416
No. observations [$I > 2\sigma(I)$]	6620	3515	4864
No parameters	632	348	402
$R1$, $wR2$	0.0834, 0.1931	0.1146, 0.2334	0.0963, 0.2715

* In each case the wavelength of X-rays was 0.710 73 Å, monoclinic, $Z = 4$.

of elemental sulfur (0.026 g) and thf (20 cm^3) added. The reaction mixture was stirred overnight upon which a yellow-brown precipitate was formed. This was filtered off, washed with pentane (2 × 5 cm^3) and dried under vacuum. Recrystallization from CH_2Cl_2 gave red crystals. Yield = 55% (Found: C, 55.0; H, 4.0. Calc. for $C_{53}H_{44}O_3P_4Ru_2S_3$: C, 55.2; H, 3.8%). IR (Nujol): $\tilde{\nu}$(CO) 2020, 1960 and 1836 cm^{-1}. NMR (CD_2Cl_2): $\delta(^1H)$ 2.82 (m, 2 H, CH^aH^b), 4.5 (m, 2 H, CH^aH^b) and 6.9–8.0 (m, 40 H, C_6H_5); $\delta(^{31}P)$ 10.5 and 18.0 (m, dppm). FAB mass spectrum: m/z = 1151, 1087, 1059, 1031 and 1003.

Alternatively, $[Ru_2(CO)_4(\mu\text{-Se})(\mu\text{-dppm})_2]$ (0.10 g) was mixed with elemental sulfur (0.025 g) to which thf (15 cm^3) was added. The reaction mixture was stirred under nitrogen overnight. Solvent was than removed under reduced pressure. The brown solid product thus obtained was crystallized from CH_2Cl_2, and identified by its IR and ^1H and ^{31}P NMR spectra. Yield = 32%.

$[Ru_2(CO)_4(\mu\text{-}SO_2)(\mu\text{-dppm})_2]$ 5. Sulfur dioxide was bubbled into a greenish yellow solution of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (0.15 g) in CH_2Cl_2 (15 cm^3) for 5 min. Ethanol (40 cm^3) was added to the resulting wine-red solution and the mixture was set aside. The product, which slowly deposited as yellow needles, was filtered off, washed with ethanol and vacuum dried. Yield = 61% (Found: C, 55.2; H, 4.4. Calc. for $C_{54}H_{44}O_6P_4SRu_2\cdot C_2H_5OH\cdot H_2O$: C, 55.5; H, 4.3%). IR (Nujol): $\tilde{\nu}$(CO) 2070, 2007, 1972 and 1943 cm^{-1}. NMR ($CDCl_3$): $\delta(^1H)$ 2.68 (m, 2 H, $^2J_{HH} = 12$, $J_{PH} = 4$, CH^aH^b), 4.6 (m, 2 H, $^2J_{HH} = 12$, $J_{PH} = 6$ Hz, CH^aH^b) and 6.6–7.6 (m, 40 H, C_6H_5); $\delta(^{31}P)$ 34.7 (s, dppm).

X-Ray crystallography

The structure determinations were carried out using a Siemens P4 diffractometer, with XSCANS software and the crystals were sealed in glass capillary tubes. The data processing, solution by direct methods and refinements were carried out using SHELXTL programs.[16] For complexes **1** and **5** an empirical absorption correction was made using ψ scans, while for **4** a Gaussian absorption correction was applied to the data. Full details are given in Table 4.

In refinement of the structure of complex **1** an acetone molecule with occupancy of 0.5 was located and refined, but a second area of residual electron density (1.44 e Å^{-3}) could not be modelled; it may due to partial occupation by a disordered water molecule.

During the least-squares cycles refinement for complex **4** the positions of the bridging groups S(1) and C(1)–O(1) were found to be disordered. This disorder was successfully resolved by refining site occupancy factors to each bridging unit 0.6:0.4. The sulfur atom S(1) having occupancy of 0.6 was refined anisotropically whereas only isotropic refinement was possible for S(1a), C(1), O(1), C(1a) and O(1a). The C–O distances C(1)–O(1) and C(1a)–O(1a) were fixed at 1.20 Å. Isotropic thermal parameters were refined for all the phenyl carbon atoms and a C_2 symmetry restraint was imposed on all the phenyl rings. All hydrogen atoms were placed in the calculated positions for the purpose of structure-factor calculations only. The Fourier-difference map revealed two regions of disordered acetone. In one region the disordered methyl carbons were related by rotation along the C=C bond and in the other region the carbonyl carbon atom was found at the origin (crystallographic disorder). The site occupancies of these disorder models are arbitrary and were not refined in the least-squares cycles. Ideal constraints were imposed on the geometry (C–C 1.54 and C=O 1.20 Å). Common isotropic thermal parameters were refined for each set of disordered solvent molecules and no hydrogen atoms were included for the solvent molecules.

The crystals of complex **5** diffracted weakly. In the neutral molecule all the non-hydrogen atoms except the phenyl carbons were assigned anisotropic thermal parameters and refined. Isotropic thermal parameters were refined for all the phenyl carbon atoms. A C_2 symmetry restraint was imposed on all these phenyl rings. All hydrogen atoms were placed in the calculated positions for the purpose of structure-factor calculations only. The Fourier-difference map revealed the regions of highly disordered solvent molecule and they were assigned to be one ethanol (in three regions with occupancies of 0.5, 0.25 and 0.25) and one water molecule (in four positions in the crystal lattice with occupancy of 0.25 each). Ideal constraints were imposed on the geometry of ethanol molecules (C–C 1.54, C–O 1.40 Å). Common isotropic thermal parameters were refined for each set of disordered solvent molecules and no hydrogen atoms were included for them.

CCDC reference number 186/783.

See http://www.rsc.org/suppdata/dt/1998/285/ for crystallographic files in .cif format.

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