Journal of Organometallic Chemistry, 403 (1991) 229–241
Elsevier Sequoia S.A., Lausanne
JOM 21326

Rhodium(I) and iridium(I) complexes of $Ph_2P(S)CH_2P(S)Ph_2$, bis(diphenylphosphino)methane disulfide

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(Received July 27th, 1990)

Abstract

Rhodium(I) and iridium(I) complexes of the ligand bis(diphenylphosphino)methane disulphide (dppmS_2) have been prepared and characterised. The structures of [Rh(dppmS_2)(cod)][ClO_4] and [Rh(dppmS_2)$(CO)_2$][ClO_4] were established in diffraction studies, the latter complex adopting an interesting pseudo-dimeric structure in the solid state.

Introduction

The use of biphosphines, $Ph_2P(CH_2)_nPPh_2$, as chelating or bridging ligands is well known. The chemistry of complexes of dppm, $Ph_2PCH_2PPh_2$, was reviewed by Puddephatt [1], and more recently by Poilblanc [2]. Work on the related diphosphine disulphide ligands has been much less extensive, but *P,S*-coordination has been reported for $Ph_2PCH_2P(S)Ph_2$ [3,4], and *S*- or *S,S*-coordination for $Ph_2P(S)CH_2P(S)Ph_2$ [5–8]. Double metallation of $Ph_2P(S)CH_2P(S)Ph_2$ to give a novel binuclear platinum complex containing a disubstituted methylene bridge with *C,S*-coordination at both platinum centres, has also been reported [8]. Metal complexes of phoshine and arsine sulphides and selenides have been reviewed [9].

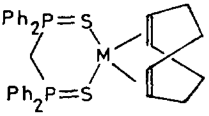
We have previously reported the preparation of rhodium and iridium complexes containing the diphosphine disulfide ligands, $R_2P(S)P(S)R_2$ [10], and the structure of [Rh(cod){$Et_2P(S)P(S)Et_2$}][ClO_4] (cod = 1,5-cyclooctadiene) [11]. We now describe the preparation and characterisation of rhodium and iridium diene and carbonyl complexes containing the ligand $Ph_2P(S)CH_2P(S)Ph_2$ (dppmS_2). The structures of [Rh(cod)(dppmS_2)][ClO_4] and [Rh$(CO)_2$(dppmS_2)][ClO_4] were established in X-ray diffraction studies.

0022-328X/91/$03.50

Results and discussion

Diene and carbonyl complexes

Addition of a stoicheiometric amount of dppmS_2 to a dichloromethane solution of $[M(cod)_2][ClO_4]$ (M = Rh or Ir) led to the formation of $[M(cod)(dppmS_2)][ClO_4]$, **1**. IR spectroscopy showed a decrease in the frequency of ν(P=S) relative to the free ligand, indicating *S*-coordination ($\nu(P{=}S)_{complex} = 580$ cm^{-1}, $\nu(P{=}S)_{uncoordinated} =$ 596–628 cm^{-1}) [6]. Bands due to coordinated alkenes, and uncoordinated perchlorate ions (1100(s) and 620(m) cm^{-1}) were also noted [12]. It is of some note that for the iridium complex, the ^{1}H NMR spectrum obtained differs from that previously reported [6]. In the earlier report, it was stated that two signals at δ 3.38 and 4.13 could be assigned to the alkene protons of the cyclooctadiene ligand, due to a lack of symmetry in the complex. The observation of a single signal in the spectrum of the rhodium complex was attributed to an exchange process. Running the NMR spectrum at a higher field than that at which the spectrum was previously recorded, we noted no splitting of the signal for the alkene protons of the iridium complex (δ 3.95), and there seems to be no reason to suppose that the protons are not in fact equivalent.



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FAB mass spectrometry on the rhodium complex gave a molecular ion for the cation, at *m/z* 659, and a peak at 551 corresponding to the loss of the cyclooctadiene ligand, indicating the mononuclear nature of the complex. The FAB mass spectrum of the iridium complex showed a peak at *m/z* = 748, $[M-1]^+$, and strong peaks at *m/z* 716 and 640 corresponding to loss of sulphur, and the cod ligand respectively.

Table 1

Microanalytical data and IR spectroscopic data for the complexes

Complex	Analysis [a] (%)		IR spectra
	C	H	ν(CO) [b] (cm^{-1})
$[Rh(cod)(dppmS_2)][ClO_4]$	52.4	4.8	
	(52.3)	(4.5)	
$[Ir(cod)(dppmS_2)][ClO_4]$	46.3	4.3	
	(46.6)	(4.0)	
$[Rh(CO)_2(dppmS_2)][ClO_4]$	46.7	4.0	2085
	(46.0)	(4.0)	2020
$[Ir(CO)_2(dppmS_2)][ClO_4]$	39.0	3.0	2070
	(40.1)	(2.8)	2000
$[IrI_2(cod)(dppmS_2)][ClO_4]$	36.4	3.5	
	(36.0)	(3.1)	
$[Rh(CO)(PPh_3)(dppmS_2)][ClO_4]$	56.0	4.2	2002
	(56.2)	(4.0)	

[a] Values in parentheses are those calculated. [b] Recorded in $CHCl_3$ solution, all strong.

Table 2

^{31}P NMR spectroscopic data

Compound	δ
dppmS_2	35.4
$[Rh(cod)(dppmS_2)][ClO_4]$	35.3
$[Ir(cod)(dppmS_2)][ClO_4]$	32.7
$[Rh(CO)_2(dppmS_2)][ClO_4]$	37.2
$[Ir(CO)_2(dppmS_2)][ClO_4]$	36.5

Microanalytical and IR spectroscopic data are given in Table 1 and ^{31}P NMR spectroscopic data in Table 2.

The preparations of $[M(cod)(dppmS_2)][ClO_4]$ ($M = Rh$ or Ir) have previously been reported by another route [6,8]. We intended to investigate the reactivity of the complexes towards carbon monoxide, and to establish the structures of the species unequivocally.

^{31}P NMR spectra of $CDCl_3$ solutions of $[M(cod)(dppmS_2)][ClO_4]$ show resonances at $\delta = 35.4$ for the rhodium complex and $\delta = 32.7$ for the iridium species, only slightly shifted from the resonance for the free ligand ($\delta = 35.3$). This is in sharp contrast to the data for the previously reported complexes $[M(cod)\{R_2P(S)P(S)R_2\}][ClO_4]$ ($R = Me$, Et or Ph). In each of these cases, the ^{31}P shift for the complex is about 30 ppm downfield from that of the free ligand [11]. Coupling between phosphorus and rhodium (^2J(PRh)) was not observed for the complexes, and the small shift suggested that the ligand might not be coordinated in solution. However, our ^{31}P NMR spectroscopic data are in reasonable agreement with those recently reported for $[M(cod)(dppmS_2)][BF_4]$ ($M = Rh$, $\delta = 36.8$, $^2J(RhP) = 4.9$ Hz; $M = Ir$, $\delta = 32.6$).

When carbon monoxide was bubbled through dichloromethane solutions of $[M(cod)(dppmS_2)][ClO_4]$ at room temperature, carbonylated complexes were obtained by displacement of the cyclooctadiene; yellow or red solids were isolated by addition of diethylether, and were relatively stable to air.

The IR spectra of $CHCl_3$ solutions of both complexes showed two carbonyl stretching bands in the 2100–2000 cm^{-1} region of their IR spectra, characteristic of mononuclear *cis*-dicarbonyl complexes [13]. The two bands could also be assigned to a binuclear species $[\{M(CO)_2(dppmS_2)\}_2][ClO_4]_2$, similar to the reported binuclear complexes of dppm [14] or $Et_2SCH_2SEt_2$ [15]. In a KBr disc, the spectrum of the rhodium complex is similar, but the iridium complex shows four carbonyl stretches, possibly due to the existence of different conformations, or metal–metal interactions in the solid state, or to reaction with bromide ion in the matrix. Thus, the nuclearity of the species produced cannot be established unequivocally by consideration of the carbonyl region of the IR spectra.

The ^{31}P NMR spectrum of a $CDCl_3$ solution of the rhodium complex showed a signal at $\delta = 36.9$, and the spectrum was temperature invariant from −60 °C to 25 °C. For the iridium complex the phosphorus chemical shift was δ 36.5, and this spectrum too was temperature independent. The ^{1}H NMR spectrum of $[Ir(dppmS_2)(CO)_2]^+$ showed a phosphorus coupled triplet δ 4.8 ($^2J(PH) = 11$ Hz), similar to that in the established rhodium mononuclear complexes (vide infra). This spectrum, and that of the precursor cod derivative, were temperature independent, effectively ruling out the possibility of a monomer/dimer equilibrium.

The FAB mass spectrum of the rhodium complex showed a molecular ion ($m/z = 607$) for $[Rh(CO)_2(dppmS_2)]^+$, with a strong peak at m/z 551, corresponding to the loss of the two carbon monoxide ligands. No dimers were seen under these conditions (vide infra). The iridium complex gave rise to a molecular ions at

Table 3

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	*y*	*z*
Rh	1212.6(10)	2550.7(13)	653.3(5)
Cl	−4378(4)	4936(5)	1596(2)
S(1)	501(4)	4036(4)	1162(2)
S(2)	443(4)	947(4)	1069(2)
P(1)	323(4)	3364(4)	1894(2)
P(2)	−1114(4)	1515(4)	1156(2)
O(1)	−3965(12)	5876(12)	1990(6)
O(2)	−3669(13)	4020(14)	1762(6)
O(3)	−4261(16)	5225(18)	1053(6)
O(4)	−5541(12)	4740(16)	1599(8)
C(1)	1479(19)	3866(16)	89(7)
C(2)	2527(16)	3718(16)	499(8)
C(3)	3640(19)	2932(19)	485(13)
C(4)	3478(17)	1908(22)	296(8)
C(5)	2327(14)	1388(14)	354(7)
C(6)	1289(15)	1548(14)	−59(6)
C(7)	1101(18)	2200(21)	−585(7)
C(8)	1230(35)	3405(18)	−521(10)
C(9)	−945(11)	2413(14)	1778(6)
C(10)	54(13)	4418(15)	2360(6)
C(11)	−1000(15)	5088(13)	2202(7)
C(12)	−1192(15)	5911(14)	2575(9)
C(13)	−337(17)	6204(24)	3046(8)
C(14)	659(19)	5656(20)	3183(8)
C(15)	873(18)	4716(17)	2854(7)
C(16)	1617(12)	2674(12)	2291(6)
C(17)	2691(14)	3125(14)	2241(7)
C(18)	3688(15)	2776(16)	2629(9)
C(19)	3652(17)	1941(21)	3029(8)
C(20)	2575(17)	1453(18)	3056(8)
C(21)	1565(15)	1865(12)	2695(7)
C(22)	−1890(13)	2236(12)	551(6)
C(23)	−1827(16)	1821(18)	12(7)
C(24)	−2492(19)	2260(24)	−488(7)
C(25)	−3262(17)	3178(16)	−437(8)
C(26)	−3361(17)	3561(20)	73(8)
C(27)	−2694(16)	3068(16)	562(7)
C(28)	−2033(14)	363(17)	1283(7)
C(29)	−3125(16)	128(18)	931(8)
C(30)	−3804(18)	−787(17)	1041(8)
C(31)	−3384(17)	−1392(17)	1496(8)
C(32)	−2319(18)	−1204(16)	1846(8)
C(33)	−1613(17)	−352(15)	1747(8)

$m/z = 697$ for $[Ir(dppmS_2)(CO)_2]^+$, while peaks corresponding to the loss of the carbon monoxide ligands and of sulphur. A detailed analysis of the mass spectra of these species will be reported elsewhere. In order to obtain more information about the structure of the complexes, the structures of the two rhodium complexes were established in X-ray diffraction studies. Attempts to obtain crystals of the iridium complexes suitable for X-ray studies have so far been unsuccessful.

Structures of $[Rh(cod)(dppmS_2)][ClO_4]$ and $[Rh(CO)_2(dppmS_2)][ClO_4]$

There have been rather few structural studies on metal complexes of phosphine sulphide ligands. Two derivatives of the monodentate ligand Me_3PS have been described [6,16], and the structure of $[Rh(cod)\{Et_2P(S)P(S)Et_2\}][ClO_4]$ has recently been reported [11]. The structural data indicate that phosphine sulphides are moderate σ-donors, with minimal π-acceptor properties.

The structure of $[Rh(cod)(dppmS_2)][ClO_4]$ consists of monomeric cationic rhodium(I) species with perchlorate counterions. There are no short anion cation contacts. Atomic coordinates are given in Table 3, and selected bond distances and angles in Table 4. A view of the structure of the cation with the atomic numbering scheme is shown in Fig. 1.

The rhodium atom is in a slightly distorted square-planar environment, coordinated to the carbon–carbon double bonds of the cyclooctadiene, and by the two sulphur atoms of $dppmS_2$, forming a six-membered chelate ring. The rhodium sulphur bonds in **1** (average 2.410(5) Å), although slightly longer, are comparable to those in $[Rh(cod)\{Et_2P(S)P(S)Et_2\}][ClO_4]$ (2.375(3) Å), and the related binuclear species $[Rh_2(\mu\text{-}SPPh_2)_2(cod)_2]$ (average 2.361(3) Å) [17] or $[Rh_2(\mu\text{-}SPPh_2)(\mu\text{-}Cl)(cod)_2]$ (average 2.370(2) Å) [18], in which the anionic group $[SPPh_2]^-$ acts as a bridging ligand, and is bonded through both sulphur and phosphorus centres. The bond lengths fall in the upper part of the range of values corresponding to rhodium(I) thiolate or thioether complexes [19]. The long rhodium–sulphur distances in this complex indicate that, in agreement with the previously reported data, there is no multiple bond component in the rhodium–sulphur bond as a result of back bonding [9].

The average value of the Rh–S–P angle, close to tetrahedral (average value 104.5(2)°) indicates formal sp^3-hybridisation as noted for the related

Table 4

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses [a]

(a) *Bonds*			
Rh–M1	2.03	Rh–M2	2.01
Rh–S(1)	2.403(5)	Rh–S(2)	2.417(5)
Rh–C(1)	2.14(2)	Rh–C(2)	2.16(2)
Rh–C(5)	2.13(2)	Rh–C(6)	2.12(2)
S(1)–P(1)	2.001(6)	S(2)–P(2)	1.994(6)
(b) *Angles*			
M1–Rh–M2	86.7	M1–Rh–S(1)	86.4
M1–Rh–S(2)	173.9	M2–Rh–S(1)	172.3
M2–Rh–S(2)	88.3	S(1)–Rh–S(2)	98.8(2)
Rh–S(1)–P(1)	106.6(2)	Rh–S(2)–P(2)	102.4(2)

[a] M1 and M2 are the mid-points of the C(1)–C(2) and C(5)–C(6) bonds.

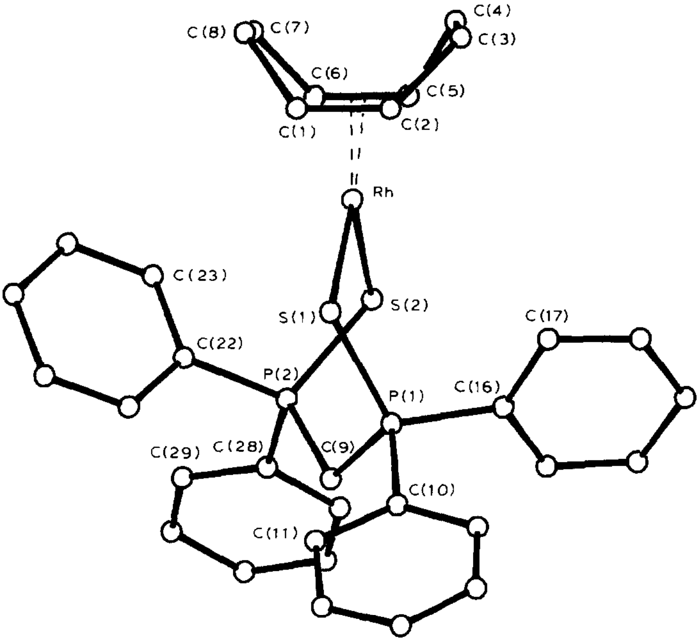

Fig. 1. Structure of the cation of [Rh(dppmS$_2$)(cod)][ClO$_4$].

[Rh(cod){Et$_2$P(S)P(S)Et$_2$}][ClO$_4$] (average 106.8(2)°). The P–S distances are intermediate between those associated with a formal single P–S bond (2.10–2.12 Å) [20] and the range found for uncoordinated phosphorus–sulphur double bonds (1.926–1.966(2) Å) [21].

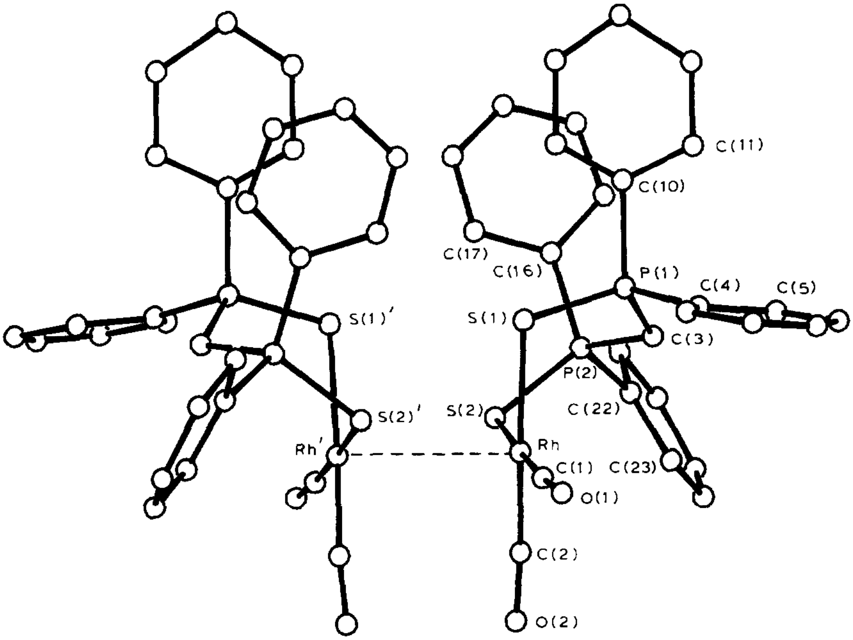

Fig. 2. Structure of the pseudo-dimeric unit of cations of [Rh(dppmS$_2$)(CO)$_2$][ClO$_4$]·0.5Et$_2$O.

Table 5

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
Rh	640.6(2)	2249.5(4)	2682.2(3)
Cl	−7050.4(6)	4405.5(14)	−3102.5(9)
S(1)	682.5(6)	4011.1(13)	3043.9(9)
S(2)	454.5(7)	2711.0(15)	1451.4(9)
P(1)	1389.9(6)	4416.8(12)	2903.4(8)
P(2)	1054.2(6)	3618.2(13)	1355.3(8)
O(1)	932(2)	1720(5)	4216(3)
O(2)	581(2)	39(4)	2239(4)
O(3)	−6833(2)	4492(6)	−2365(3)
O(4)	−7203(3)	3398(5)	−3279(4)
O(5)	−7489(2)	5067(5)	−3285(3)
O(6)	−6670(2)	4706(5)	−3478(3)
C(1)	817(3)	1895(6)	3637(4)
C(2)	612(3)	879(6)	2407(4)
C(3)	1561(2)	3745(5)	2172(3)
C(4)	1930(2)	4143(4)	3638(3)
C(5)	2443(2)	4043(5)	3553(3)
C(6)	2856(3)	3888(6)	4138(4)
C(7)	2765(3)	3833(6)	4795(4)
C(8)	2257(3)	3915(7)	4895(4)
C(9)	1845(3)	4068(6)	4313(3)
C(10)	1386(2)	5781(5)	2765(3)
C(11)	1858(3)	6309(5)	2819(4)
C(12)	1849(3)	7369(6)	2720(4)
C(13)	1390(4)	7898(6)	2571(5)
C(14)	923(3)	7387(6)	2522(5)
C(15)	920(3)	6330(5)	2614(4)
C(16)	844(2)	4889(5)	1052(3)
C(17)	317(3)	5163(6)	932(4)
C(18)	179(3)	6177(7)	700(5)
C(19)	543(4)	6866(7)	589(5)
C(20)	1062(3)	6577(6)	713(5)
C(21)	1224(3)	5597(5)	959(4)
C(22)	1390(2)	3042(5)	736(3)
C(23)	1661(3)	2128(6)	925(4)
C(24)	1899(3)	1634(6)	444(4)
C(25)	1847(3)	2050(7)	−214(4)
C(26)	1588(4)	2950(7)	−411(4)
C(27)	1357(3)	3449(6)	75(4)
C(28)	5021(8)	5218(15)	5300(8)
C(29)	4517(6)	5827(11)	5528(13)

The rhodium–carbon bond distances (2.12–2.16 Å) are very similar to those in other rhodium(I) complexes containing 1,5-cyclooctadiene *trans* to sulphur atoms [10,17]. Both coordinated double bonds (C^1–C^2, C^5–C^6) have lengths (1.40(2) Å) greater than those in free cyclooctadiene [22], as expected.

The diffraction study on $[Rh(CO)_2(dppmS_2)][ClO_4]$ showed two symmetry related mononuclear cations with a rhodium–rhodium distance of 3.245 Å (Fig. 2). Atomic coordinates are given in Table 5 and selected bond distances and angles in Table 6. The rhodium–rhodium distance is substantially longer than rhodium–

Table 6

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses [a]

(a) *Bonds*			
Rh–S(1)	2.383(2)	Rh–S(2)	2.397(2)
Rh–C(1)	1.857(7)	Rh–C(2)	1.851(7)
S(1)–P(1)	1.996(2)	S(2)–P(2)	1.999(2)
P(1)–C(3)	1.808(6)	P(1)–C(4)	1.786(5)
P(1)–C(10)	1.788(6)	P(2)–C(3)	1.815(5)
P(2)–C(16)	1.790(7)	P(2)–C(22)	1.805(7)
C(1)–O(1)	1.117(9)	C(2)–O(2)	1.134(9)
Rh ··· Rh′	3.245(1)		
(b) *Angles*			
S(1)–Rh–S(2)	92.23(7)	S(1)–Rh–C(1)	87.7(2)
S(1)–Rh–C(2)	179.6(2)	S(2)–Rh–C(1)	177.4(2)
S(2)–Rh–C(2)	88.1(2)	C(1)–Rh–C(2)	92.0(3)
Rh–S(1)–P(1)	101.06(9)	Rh–S(2)–P(2)	105.10(8)
S(1)–P(1)–C(3)	112.8(2)	S(1)–P(1)–C(4)	114.7(2)
S(1)–P(1)–C(10)	108.0(2)	C(3)–P(1)–C(4)	103.7(3)
C(3)–P(1)–C(10)	110.6(3)	C(4)–P(1)–C(10)	107.0(3)
S(2)–P(2)–C(3)	113.3(2)	S(2)–P(2)–C(16)	112.7(2)
S(2)–P(2)–C(22)	109.3(2)	C(3)–P(2)–C(16)	107.8(3)
C(3)–P(2)–C(22)	104.5(3)	C(16)–P(2)–C(22)	108.7(3)
Rh–C(1)–O(1)	177.3(7)	Rh–C(2)–O(2)	178.1(6)

[a] Symmetry element ′ is $-x$, y, $0.5-z$.

distances in metal–metal bonds, which lie in the range 2.617(3)–2.796(8) Å [23]. In the case of bis(thioether) bridged dimeric rhodium complexes [15], rhodium–rhodium separations of 3.067 Å have been reported to be consistent with a weak metal–metal interaction. In other complexes of the type $[Rh_2(CO)_2L_2(\mu\text{-}X)_2]$, rhodium–rhodium distances have been in the range 3.06–3.71 Å [24,25]. In one-dimensional stacked complexes, the range of intermolecular rhodium–rhodium distances are greater than that established here, including 3.26 Å for $[Rh(CO)_2(acac)]$ [26], 3.31 Å for $[\{Rh(CO)_2Cl\}_2]$ [27], 3.34 Å for $[Rh(CO)_2(hfacac)]$ [26], 3.393(1) Å for $[Rh_3(\mu_3\text{-}tz)(\mu_2\text{-}Cl)(\eta^3\text{-}C_3H_5)_2(CO)_4]$ [25], 3.425(4) Å for $[Rh_3(\mu_3\text{-}tz)(\mu_2\text{-}Cl)Cl(\eta^4\text{-}tfb)(CO)_4]$ [25] and 3.4522(4) Å for $[Rh(CO)_2Cl(pzH)]$ [28]. There is, however, no evidence for stacking or long range order in our complex (Fig. 3). The only complex which to our knowledge has been shown to have a similar unsupported dimeric structure in the solid state (and in this case also in solution) is $[\{Rh(CNR)_4\}_2][BPh_4]_2$, which has a face-to-face dimeric structure and a rhodium–rhodium separation of 3.193 Å [29]. It is not yet clear if the pseudo-dimeric structure is maintained in solution but this is under investigation. The solution IR spectrum is consistent with a mononuclear *cis*-dicarbonyl complex, though some solution interactions cannot be completely ruled out.

The coordination geometry about each rhodium atom is a slightly distorted square plane, with the carbonyl ligands mutually *cis*. The six-membered ring formed by the diphosphine disulphide is puckered to reduce ring strain and to minimise the interactions of the phenyl rings. The rhodium–sulphur bonds (average 2.390(2) Å) are very similar to those in the $[Rh(cod)(dppmS_2)]$ cation (Rh–S = 2.410(5) Å). Similar bond lengths were noted in complexes of thioether ligands [16,30]. The

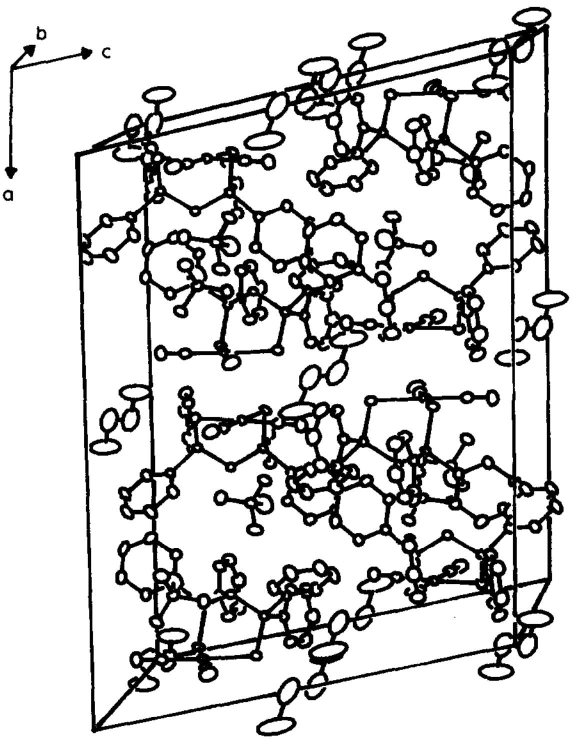

Fig. 3. Packing diagram for $[Rh(dppmS_2)(CO)_2][ClO_4]$.

complex $[Rh(CO)_2(t\text{-}BuSCH{=}CHS\text{-}t\text{-}Bu)][ClO_4]$, which also contains a bidentate S,S-donor ligand, has an Rh–S bond length of 2.364(3) Å [24]. The binuclear rhodium(I) complex $[\{RhCl(CO)(EtSCH_2SEt)\}_2]$, in which the dithioether acts as a bridge between the two rhodium(I) centres, has the two sulphur ligands in a *trans*-arrangement [15]. The Rh–S bond distance (average 2.315(1) Å) is shorter than the bonds in $[Rh(cod)(dppmS_2)][ClO_4]$, $[Rh(cod)\{Et_2P(S)P(S)Et_2\}][ClO_4]$ [11] or $[Rh(CO)_2(t\text{-}BuSCH{=}CHS\text{-}t\text{-}Bu)][ClO_4]$ [24], in which the sulphur ligands are *trans* to cod or CO.

The size of the Rh–S–P angle (average 103.08(9)) indicates formal sp^3-hybridisation for sulphur as expected. The P–S bond lengths are similar to those in the cyclooctadiene complex. The rhodium–carbon bond distances (average 1.854(7) Å) are comparable with the rhodium carbonyl distances in $[Rh(CO)_2(t\text{-}BuSCH{=}CHS\text{-}t\text{-}Bu)][ClO_4]$ (1.96 Å) in which the carbonyl is also *trans* to a sulphur ligand. They are greater than the Rh–C distance in $[\{RhCl(CO)(Et_2SCH_2SEt_2\}_2]$ in which the carbonyl is *trans* to a chloride ligand.

Reactivity of the diene and carbonyl complexes

Like other diphosphine disulfide cationic complexes [11,31], $[Ir(cod)(dppmS_2)][ClO_4]$ undergoes oxidative addition of iodine to give the iridium(III) complex, $[IrI_2(cod)(dppmS_2)][ClO_4]$ which was isolated and characterised (Table 1). No similar reaction was observed with the corresponding rhodium complex. Despite several attempts, under different conditions, no reaction with molecular hydrogen could be achieved for the rhodium complex. Neither complex was active as a catalyst for alkene hydroformylation at 5 bar and 80 °C. The rhodium complexes reacted with neither PhC≡CPh nor HC≡CCOOEt.

Treatment of $[Rh(CO)_2(dppmS_2)][ClO_4]$ with triphenylphosphine resulted in the displacement of a carbonyl ligand, with the formation of the isolable complex $[Rh(CO)(PPh_3)(dppmS_2)][ClO_4]$ (Table 1). The IR spectrum of this complex, both in solution ($CHCl_3$) and in the solid state shows only a single carbonyl stretching band (2002 cm^{-1}, solution, 1995 cm^{-1}, solid state). The ^{31}P NMR spectrum in $CDCl_3$ was somewhat unsatisfactory, showing several signals which could be attributed to redistribution reactions [10].

Experimental

All preparations were carried out under nitrogen by Schlenck techniques. All solvents were distilled and degassed prior to use. Elemental analyses were carried out using a Perkin Elmer 240B microanalyzer. The IR spectra were recorded on a Nicolet 5ZDX-FT spectrometer, in chloroform solution or as KBr discs. ^{1}H and ^{31}P NMR spectra were recorded using a Varian XL200 or Bruker WM360 spectrometers using $CDCl_3$ as solvent, and Me_4Si and 85% H_3PO_4 as references. FAB Mass spectra were recorded using a Kratos MS80RF spectrometer. The starting materials were prepared as previously described [32–35]. $RhCl_3 \cdot H_2O$ was obtained from Johnson Matthey plc, and $Ph_2P(S)CH_2P(S)PPh_2$ was synthesised according the method of Davson and Reger [36].

Preparation of $[M(cod)(dppmS_2)][ClO_4]$

1,2-bis(Diphenylphosphino)methane disulphide (45 mg, 0.1 mmol) was added to a dichloromethane solution of $[Rh(cod)_2][ClO_4]$ (38 mg, 0.09 mmol). The product was immediately precipitated by addition of diethyl ether, collected by filtration, washed with diethyl ether and dried in vacuo to give $[Rh(cod)(dppmS_2)][ClO_4]$ as a yellow powder (55 mg, 80%). The iridium complex was prepared similarly and obtained as a yellow powder in 76% yield.

^{1}H NMR (M=Rh) (CD_2Cl_2) δ 7.5–8.0 (m, 20H, aryl), 4.54 (t, $J(PH) = 12.7$ Hz, 2H, PCH_2P), 4.36 (br, 4H, alkene), 2.33 (m, 8H, CH_2).

(M = Ir) (CD_2Cl_2): δ 7.5–8.0 (m, 20H, aryl), 4.60 (t, $J(PH) = 12.7$ Hz, 2H, PCH_2P), 3.95 (br, 4H, alkene), 2.15 (m, 8H, CH_2).

Preparation of $[M(CO)_2(dppmS_2)][ClO_4]$

Carbon monoxide (1 atm) was bubbled at room temperature through a dichloromethane solution of $[Rh(cod)(dppmS_2)][ClO_4]$ (40 mg in 8 ml, 0.05 mmol) for 10 min. Over this period the colour of the solution darkened. The product was precipitated by addition of diethyl ether, collected by filtration, washed with cold diethyl ether and dried to give $[Rh(CO)_2(dppmS_2)][ClO_4]$ as a red solid (27 mg, 72%). The iridium complex reacted similarly to give $[Ir(CO)_2(dppmS_2)][ClO_4]$ as a deep red solid, in 57% yield.

^{1}H NMR (M = Rh) ($CDCl_3$) δ 7.46–7.88 (m, 20H, aryl), 4.89 (t, $J(PH) = 13$ Hz, 2H, PCH_2P).

(M = Ir) (CD_2Cl_2) δ 7.4–7.7 (m, 20H, aryl), 4.74 (t, $J(PH) = 12.9$ Hz, 2H, PCH_2P).

Preparation of [IrI$_2$(cod)(dppmS$_2$)][ClO$_4$]

Slightly more than the stoicheiometric amount of iodine (26 mg, 0.1 mmol) was added to a solution of [Ir(cod)(dppmS$_2$)][ClO$_4$] (0.08 mmol, prepared in situ) and the mixture stirred for 15 min. The solution became brown, and the product was precipitated by addition of diethyl ether, filtered, washed with diethyl ether, and dried to give [IrI$_2$(cod)(dppmS$_2$)][ClO$_4$] as a brown solid (51 mg, 58%).

Structure of [Rh(CO)$_2$(dppmS$_2$)][ClO$_4$]

A suitable crystal was grown by slow diffusion of ether into a dichloromethane solution of the complex. Data were collected using a crystal fragment ca. 0.2 × 0.2 × 0.1 mm, cut from a large crystal and coated in epoxy glue, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35 \tan \theta)^\circ$, and a maximum scan time of 1 min. A total of 5852 unique reflections were measured for $2 < \theta < 25^\circ$ and $+h + k \pm l$, and 3426 reflections with $|F^2| > 3\sigma(F^2)$ where $\sigma(F^2) = \{\sigma^2(I) + (0.4I)^2\}^{1/2}/\text{Lp}$ were used in the refinement. There was no crystal decay and no absorption correction was applied.

The structure was solved by routine heavy-atom methods and non-hydrogen atoms were refined anisotropically by full-matrix least-squares. A set of four peaks lying across the crystallographic two-fold rotation axis was taken to be part of a molecule of diethyl ether for which the remaining atoms were too disordered to locate. Hydrogen atoms, except for those of the solvent molecule, were included in the refinement, with isotropic temperature factors. The weighting scheme was $\omega = 1/\sigma^2(F)$ and the final residuals were $R = 0.040$, $R' = 0.062$. A final difference map had maximum values of 0.7 e Å^{-3} in the region of the disordered solvent molecule. Programs from the Enraf-Nonius SDP-Plus package were run on a microvax computer.

The crystal was monoclinic, space group $C2/c$, $a = 26.052(8)$, $b = 12.957(4)$, $c = 19.398(5)$ Å, $\beta = 103.62(2)^\circ$, $U = 6363.8$ Å^3, $Z = 8$, $D_{\text{calc}} = 1.55$ g cm^{-3}, $F(000) = 3016$. Monochromated Mo-K$_\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 8.7$ cm^{-1}. A complete table of bond lengths and angles, table of hydrogen atom coordinates and thermal factors, and a list of observed and calculated structure factors are available from P.B.H.

Structure of [Rh(cod)(dppmS$_2$)][ClO$_4$]

Suitable crystals were grown by slow diffusion of ether into a dichloromethane solution of the complex. Data were collected using a crystal ca. 0.3 × 0.25 × 0.05 mm on an Enraf–Nonius CAD-4 diffractometer in the θ–2θ mode with $\Delta\theta = (0.6 + 0.35 \tan \theta)^\circ$ and a maximum scan time of one minute. A total of 5720 unique reflections were measured for $2 < \theta < 25^\circ$ and $+h + k \pm 1$ and 2308 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/\text{Lp}$, were used in the refinement. There was no crystal decay and no correction for absorption was made.

The structure was solved by routine heavy atom methods and refined by full-matrix least-squares with non-hydrogen atoms anisotropic. Hydrogen atoms were held fixed at calculated positions with $U_{\text{iso}} = 1.3U_{\text{eq}}$ for the atom to which they are bonded. The weighting scheme was $w = 1/\sigma^2(F)$, and the final residuals were $R = 0.065$, $R' = 0.101$. A final difference map had a maximum of 1.1 e Å^{-3} near the rhodium atom. Programs from the Enraf–Nonius SDP-Plus package were run on a MicroVAX II computer.

Some of the atoms in the cyclooctadiene have rather high thermal parameters, and that for C(3) is non-positive definite, suggesting that there may be some slight disorder present.

The crystal was monoclinic, space group $P2_1/n$, $a = 11.675(2)$, $b = 11.824(3)$, $c = 24.310(5)$ Å, $\beta = 103.23(2)°$, $U = 3266.9$ Å^3, $Z = 4$, $D_c = 1.54$ g cm^{-3}, $F(000) = 1552$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 8.5$ cm^{-1}. A complete table of bond lengths and angles, tables of thermal parameters and hydrogen atom coordinates, and a list of observed and calculated structure factors are available from P.B.H.

Acknowledgements

This work has been supported by CICYT (project PB85-0008-C02-04), and through the awards of an Acion Integrada from the British Council and the Spanish Ministery of Science, and a CIBA Award for Colloboration in Europe. We thank Mr. A. Greenaway and Mr. A. Aleiwi for the recording of mass spectra, and Drs. A. Avent and G. Muller for the recording of NMR spectra. We thank Dr. K.R. Seddon for useful discussions.

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