Preparation and properties of thiophosphinito-bridged rhodium complexes. Crystal structure of [Rh$_2$(μ-SPPh$_2$)$_2$(COD)$_2$]

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Abstract

Reaction of Ph$_2$P(S)H with [M(acac)(diolefin)] (M = Rh or Ir) yields [M$_2$(SPPh$_2$)$_2$(diolefin)$_2$] complexes. The reactions of [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] with t-butylisocyanide, diphosphine, or carbon monoxide have been studied. Several dirhodium(II) complexes have been prepared by a two centre oxidative-addition reaction, or by exchange reactions of [Rh$_2$(O$_2$CMe)$_4$]. A variety of related complexes is discussed. The crystal structure of [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] has been determined by X-ray diffraction methods. It crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions a 12.152(7), b 16.117(8), c 10.805(7) Å, α 90.42(4), β 112.90(3), γ 109.27(3)°, and $Z = 2$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.0405$ and $R_w = 0.0584$ for 5149 observed reflections. In the dimeric complex two SPPh$_2$-ligands bridge the rhodium atoms through their S and P atoms; the coordination around each metal atom is completed by a COD molecule interacting through the two olefinic bonds. The Rh–Rh distance is of 3.770(1) Å, ruling out the possibility of metal–metal interaction. The two Rh(1)–S(1)–P(2)–Rh(2) and Rh(1)–P(1)–S(2)–Rh(2) units are roughly planar, and the six-atom Rh(1)–S(1)–P(2)–Rh(2)–S(2)–P(1) ring has a boat conformation.

Introduction

During our exploration of the use of difunctional ligands for the construction of bi- and multi-nuclear rhodium complexes, we have studied a variety of binuclear

rhodium complexes [1–5]. In continuation of our interest in this area we have now focused our attention on the $SPPh_2^-$ ligand.

A variety of platinum metal complexes containing the $SPPh_2^-$ or $Ph_2P(S)H$ ligands, either S-bonded [6–8], P-bonded [8–11] or S/P bonded (bridge [12–14] or side-on [15,16]) have been described in recent years. We now describe several binuclear rhodium and iridium complexes, and the crystal structure of $[Rh_2(SPPh_2)_2(COD)_2]$.

Results and discussion

(a) Diolefin complexes

The reactions of complexes of the type [Rh(acac)(diolefin)] (diolefin = 1,5-cyclooctadiene (COD) [17], tetrafluorobenzobarrelene (TFB) [18], norbornadiene (NBD) [17]) and [Ir(acac)(COD)] [19] with a stoichiometric amount of diphenyl-phosphine sulfide ($Ph_2P(S)H$) give complexes of the type $[M_2(SPPh_2)_2(diolefin)_2]$ (I), according to eq. 1.

$$2\left[M(acac)(diolefin)\right] + 2\,Ph_2P(S)H \rightarrow \left[M_2(SPPh_2)_2(diolefin)_2\right] + 2\,Hacac \qquad (1)$$

Molecular weight measurements confirm the dinuclear formulation, although the low stability of the NBD complex prevented determination of its molecular weight by osmometry. The P–S stretching vibrations can be assigned from the IR spectra (Table 1). The lower P–S bond order in the complexes compared with that in the uncoordinated diphenylphosphine sulfide gives rise to a pronounced shift to lower wave numbers (ν(PS) 65–70 cm^{-1}) (see Table 1); this reflects a relatively small influence of the metal atom and the diolefin ligand on the P–S bonding. The proposed binuclear formulation has been confirmed by an X-ray diffraction study in the case of $[Rh_2(SPPh_2)_2(COD)_2]$ (see below). The $[Rh_2(SPPh_2)_2(COD)_2]$ complex reacts readily with different ligands. Thus, addition of t-butyl isocyanide (mole ratio 1/4) in diethyl ether led to displacement of the coordinated diolefin, to give the dinuclear derivative $[Rh_2(SPPh_2)_2(CN-t-Bu)_4]$ (II). When a stoichiometric amount of triphenylphosphine was added to a dichloromethane solution of complex Ia, a compound which analysed for $[Rh(SPPh_2)(PPh_3)_2]$ (III) was formed; this mononuclear complex has been previously prepared by Thewissen [16].

Although the bis(diphenylphosphino)methane (dppm) ligand shows a marked tendency to act as bridge between two metal atoms, forming the $[M_2(dppm)_2]$ unit [20,21], the reaction of $[Rh_2(SPPh_2)_2(COD)_2]$ with dppm yields a yellow-brown complex of formula $[Rh_2(SPPh_2)_2(dppm)_2]$ (IVa), in which the dppm must be acting as chelate. As expected because of the favorable driving force of five-membered chelate ring formation [22], 1,2-bis(diphenylphosphino)ethane (dppe) also reacts with complex Ia (mole ratio 1/2) to give $[Rh_2(SPPh_2)_2(dppe)_2]$ (IVb). On the other hand, addition of bidentate nitrogen donor ligands, such as 1,10-phenanthroline or 2,2′-bipyridine, as well as triphenylphosphine, did not give rise to ligand exchange reactions, and complex Ia was recovered unchanged.

Table 1 lists the analytical data for the isolated complexes.

(b) Carbonyl complexes

The $[Rh_2(SPPh_2)_2(COD)_2]$ complex reacts with carbon monoxide presumably to form the complex $[Rh_2(SPPh_2)_2(CO)_4]$ (V). A better synthetic route involves the

Table 1

Analytical data for the complexes

Complex	Analysis(found(calcd) (%))			Mol.wt. (CHCl$_3$) (found(calcd.))	Yield (%)	ν(PS) (cm^{-1})	ν(CO) (CH$_2$Cl$_2$) (cm^{-1})
	C	H	N				
[Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] (Ia)	56.38 (56.06)	5.43 (5.17)	–	868 (856)	69	565	–
[Rh$_2$(SPPh$_2$)$_2$(TFB)$_2$] (Ib)	52.11 (52.76)	3.05 (2.95)	–	1053 (1092)	60	558	–
[Rh$_2$(SPPh$_2$)$_2$(NBD)$_2$] (Ic)	55.66 (55.85)	4.71 (4.40)	–	–	60	555	–
[Ir$_2$(SPPh$_2$)$_2$(COD)$_2$] (Id)	46.53 (46.40)	3.89 (4.47)	–	1091 (1035)	60	570	–
[Rh$_2$(SPPh$_2$)$_2$(CNt-Bu)$_4$] (II)	54.37 (54.32)	6.22 (5.80)	6.73 (5.76)	997 (973)	88	585	–
[Rh(SPPh$_2$)(PPh$_3$)$_2$] (III)	68.02 (68.17)	4.91 (4.76)	–	777 (845)	63	513	–
[Rh$_2$(SPPh$_2$)$_2$(dppm)$_2$] (IVa)	62.9 (63.0)	4.75 (4.57)	–	1348 (1409)	58	–	–
[Rh$_2$(SPPh$_2$)$_2$(dppe)$_2$] (IVb)	63.74 (63.29)	5.17 (5.09)	–	1449 (1436)	60	–	–
[Rh$_2$(SPPh$_2$)$_2$(CO)$_4$] (V)	44.30 (44.70)	2.95 (2.68)	–	–	82	545	1980
[Rh(SPPh$_2$)(CO)(PPh$_3$)]$_x$ (VI)	60.02 (60.99)	4.24 (4.12)	–	740 (610) ^{a}	79	–	1970
[Rh$_2$(SPPh$_2$)$_2$I$_2$(CO)$_4$] (VII)	33.18 (33.42)	2.37 (2.00)	–	–	61	580	2048
[Rh$_2$(SPPh$_2$)$_2$I$_4$(CO)$_4$] (VIII)	25.47 (26.69)	1.98 (1.60)	–	–	65	540	2085
[Rh$_2$(SPPh$_2$)$_2$I$_2$(CO)$_2$(dppm)] (IX)	45.17 (45.90)	3.59 (3.39)	–	1323 (1334)	61.5	–	2045
[Rh$_2$(SPPh$_2$)$_4$(SPHPh$_2$)$_2$] (X)	56.94 (57.21)	4.32 (4.13)	–	–	70	–	–
[Rh$_2$(SPPh$_2$)$_4$(NCMe)$_2$] (XI)	53.53 (53.8)	3.94 (4.00)	2.38 (2.41)	–	50	–	–
[Rh$_4$(SPPh$_2$)$_6$(COD)$_2$] (XII)	54.37 (54.72)	4.41 (3.47)	–	–	31	–	–
[Rh$_4$(SPPh$_2$)$_6$(TFB)$_2$] (XIII)	53.37 (53.19)	3.54 (3.34)	–	–	30	–	–

^{a} $x = 1$.

reaction of [Rh(acac)(CO)$_2$] [23] with Ph$_2$P(S)H. The IR spectrum of the product shows the presence of only one broad ν(CO) band at 1980 cm^{-1}, which suggests a *trans* disposition of the ligands, as found in [Rh$_2$(dppm)$_2$(NCMe)$_4$][BPh$_4$]$_2$ [24], but a *cis*-disposition of the binucleating ligands is usually observed in complexes of the type [Rh$_2$(μ-L)$_2$(CO)$_4$] [25,26].

The related [Rh(SPPh$_2$)(CO)(PPh$_3$)]$_x$ (VI) complex can likewise be prepared by treating [Rh(acac)(CO)(PPh$_3$)] with Ph$_2$P(S)H or by adding PPh$_3$ to [Rh$_2$(SPPh$_2$)$_2$(CO)$_4$]. Molecular weight measurements do not allow us to distinguish between a mono- and a di-nuclear formulation.

The addition of one equivalent of molecular iodine to an acetone solution of the tetracarbonyl compound V gives a complex of formula [Rh$_2$(SPPh$_2$)$_2$I$_2$(CO)$_4$]

(VII). The observed shift to higher wave numbers of the ν(CO) band of complex VII relative to V suggests that there has been a two center oxidative addition with concurrent metal–metal bond formation, as previously observed for related binuclear complexes containing rhodium atoms in close proximity [21,24]. Complex VII adds a second equivalent of iodine, to give a dirhodium(III) complex of formula $[Rh_2(SPPh_2)_2I_4(CO)_4]$ (VIII). As expected, the ν(CO) stretching vibration is, ca. 100 cm^{-1} higher for the rhodium(III) compound than for the starting rhodium(I) complex V [27]. Finally, the addition of dppm to a solution of $[Rh_2(SPPh_2)_2I_2(CO)_4]$ (mole ratio 1/1) causes displacement of the carbon monoxide and formation of $[Rh_2(SPPh_2)_2I_2(CO)_2(dppm)]$ (IX) (ν(CO): 2045 and 1975 cm^{-1}, Cl_2CH_2). This dirhodium(II) compound is related to the recently reported pyrazolate complex of formula $[Rh_2(Pz)_2I_2(CO)_2(dppm)]$ [27].

(c) Other dirhodium(II) complexes

We have mentioned above that binuclear rhodium(II) complexes containing metal–metal bonds can be prepared by two-center oxidative reactions to rhodium(I) complexes. Another general synthetic route could involve exchange reactions of the well-known $[Rh_2(O_2CMe)_4]$ complex [28] with the diphenylphosphine sulfide ligand. Thus, treatment of $[Rh_2(O_2CMe)_4(MeOH)_2]$ with $Ph_2P(S)H$ (mole ratio 1/6) in methanol leads to replacement of the bridging carboxylate and precipitation of an orange powder that was identified as the complex $[Rh_2(SPPh_2)_4(SPHPh_2)_2]$ (X). The complex probably has four ligands disposed about the dirhodium(II) unit with two S-bonded $Ph_2P(S)H$ molecules occupying the axial sites. The IR spectrum of X shows a band at 2330 cm^{-1} corresponding to the stretching vibration of the P–H bond. The bonds formed by the axial ligands with rhodium in these dimeric complexes are weak compared with the corresponding bonds in mononuclear complexes, and this has been attributed to the *trans*-influence of the covalent Rh–Rh bond [29]. Thus other adducts of rhodium(II) thiophosphinite complexes with neutral ligands could be prepared; when complex X was treated with an excess of acetonitrile the two diphenylphosphine sulfide ligands were replaced by two acetonitrile molecules, to give the yellow adduct $[Rh_2(SPPh_2)_4(NCMe)_2]$ (XI).

The above reactions show the relative flexibility of the thiophosphinito ligand, therefore a wide range of intermetallic separations should be expected for these complexes. The reported reactions are relatively similar to those observed for the analogous binuclear pyrazolate complexes in which intermetallic separations in the range [3.568–2.353 Å) [30–31] have been reported. Both types of ligands have in common the presence of X–Y units (X = P, Y = S or X = Y = N) containing the two donor centers directly bonded.

In view of the well known tendency of the sulfur atoms to bridge two metal centers and of the presence of the potentially bridging group $Ph_2P(S)H$ acting only as monodentate in complex $[Rh_2(SPPh_2)_4(SPHPh_2)_2]$ (X), an attempt was made to construct complexes of higher nuclearity. It was found that addition of [Rh(acac)(diolefin)] compounds (diolefin = 1,5-cyclooctadiene (COD) and tetrafluorobenzobarrelene (TFB)) to acetone suspensions of $[Rh_2(SPPh_2)_4(SPHPh_2)_2]$ gives rise to complexes analysing as $[Rh_4(SPPh_2)_6(diolefin)_2]$ (XII, XIII). A hypothetical structure is shown in Scheme 1, with sulfur atoms bridging two rhodium centres [4]. Unfortunately, the low solubility of the sample prevented molecular weight measurements.

(XII – XIII)

Rh(acac)(diolefin)

(X)

NCMe

(XI)
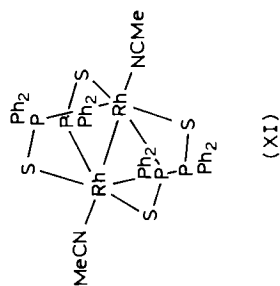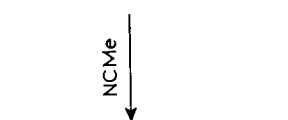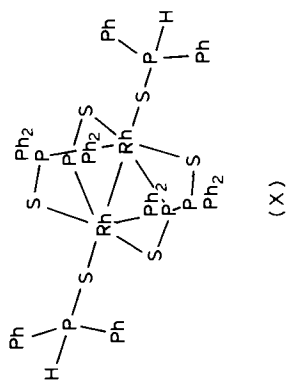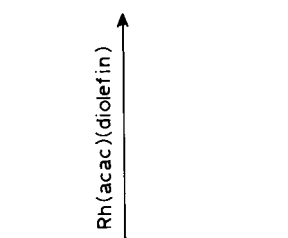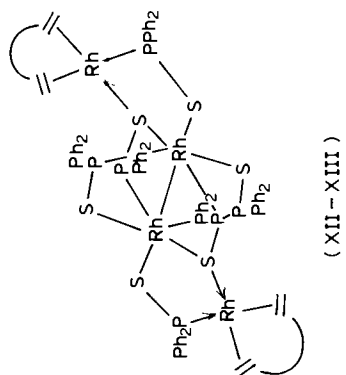
Crystal structure of the complex [Rh$_2$(μ-SPPh$_2$)$_2$(COD)$_2$] (Ia)

The structure of Ia consists of dimeric complexes in which two SPPh$_2$$^-$ ligands bridge the two Rh atoms through their S and P donor atoms. A view of the complex is given in Fig. 1; and selected bond distances and angles are listed in Table 2. The coordination around each Rh atom is completed by a 1,5-cyclooctadiene ligand interacting through the two olefinic bonds. If M(1), M(2), M(3) and M(4) are the mid-points of the C(1)–C(2), C(5)–C(6), C(9)–C(10) and C(13)–C(14) double bonds, the Rh(1)–M(1), Rh(1)–M(2), Rh(2)–M(3) and Rh(2)–M(4) distances are 2.093(10), 2.014(8), 2.087(8) and 2.016(6) Å, respectively. On the basis of these mid-points, the Rh atoms are in slightly distorted square planar environments. The Rh–S bonds, 2.359(2) and 2.363(2) Å, are comparable with those, 2.349(2), 2.339(2) and 2.320(2) Å, found in [Rh$_2$(μ-SC$_5$H$_4$N)$_2$(TFB)$_2$] (TFB = tetrafluorobenzo-barrelene) [4], in which two pyridine-2-thiolato ligands bridge the two Rh atom in two different ways, either through a sulphur atom alone or through a sulphur and a nitrogen atom. The Rh–P bonds, 2.293(2) and 2.282(2) Å are within the normal range observed for similar bonds.

The bridging behaviour of the SPPh$_2$$^-$ ligands in Ia is very similar to that in the complex [Pt$_2$(H)$_2$(P-t-Bu$_3$)$_2$(μ-SPPh$_2$)$_2$] [14]. The S–P bonds are 2.045(2) and 2.045(3) in Ia, 2.040(4) Å in the Pt complex; the distance between the bridged Rh atoms is 3.770(1) in Ia and 3.620(1) Å in the Pt complex, in both cases ruling out the possibility of metal–metal interactions. The two bridges Rh(1)–S(1)–P(2)–Rh(2) and Rh(1)–P(1)–S(2)–Rh(2) are roughly planar, and form a dihedral angle of 99.9(1)°, comparable to that found in the Pt dimer, viz. 97.5°. The six-membered
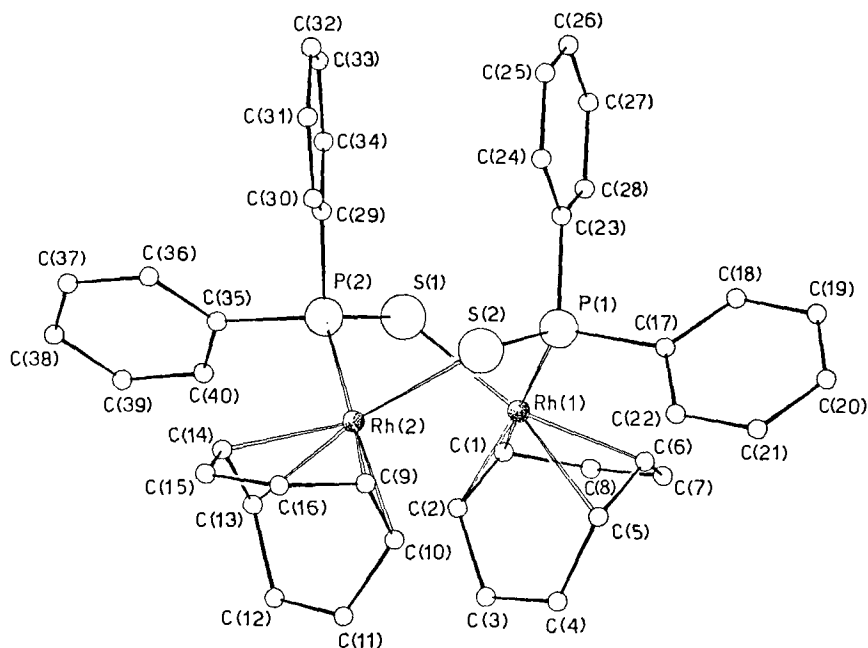

Fig. 1. View of the complex [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] with the atom numbering scheme.

Table 2

Selected bond distances (Å) and angles (°) in the complex Ia [a]

Rh(1)–S(1)	2.359(2)	C(2)–C(3)	1.511(14)
Rh(1)–P(1)	2.293(2)	C(3)–C(4)	1.491(13)
Rh(1)–C(1)	2.206(11)	C(4)–C(5)	1.523(12)
Rh(1)–C(2)	2.201(10)	C(5)–C(6)	1.395(10)
Rh(1)–C(5)	2.119(8)	C(6)–C(7)	1.516(15)
Rh(1)–C(6)	2.145(8)	C(7)–C(8)	1.472(12)
Rh(2)–S(2)	2.363(2)	C(1)–C(8)	1.510(15)
Rh(2)–P(2)	2.282(2)	C(9)–C(10)	1.366(16)
Rh(2)–C(9)	2.194(9)	C(10)–C(11)	1.512(12)
Rh(2)–C(10)	2.198(9)	C(11)–C(12)	1.476(14)
Rh(2)–C(13)	2.130(7)	C(12)–C(13)	1.511(13)
Rh(2)–C(14)	2.130(6)	C(13)–C(14)	1.374(15)
P(1)–S(2)	2.045(2)	C(14)–C(15)	1.514(15)
P(2)–S(1)	2.045(3)	C(15)–C(16)	1.432(13)
C(1)–C(2)	1.380(13)	C(9)–C(16)	1.507(12)
S(1)–Rh(1)–P(1)	89.9(1)	C(2)–C(3)–C(4)	116.1(8)
S(1)–Rh(1)–M(1)	87.8(2)	C(3)–C(4)–C(5)	116.7(8)
M(1)–Rh(1)–M(2)	87.4(3)	C(4)–C(5)–C(6)	125.4(8)
P(1)–Rh(1)–M(2)	94.6(2)	C(5)–C(6)–C(7)	125.3(8)
S(2)–Rh(2)–P(2)	91.5(1)	C(6)–C(7)–C(8)	117.4(9)
S(2)–Rh(2)–M(3)	87.0(2)	C(7)–C(8)–C(1)	116.2(10)
M(3)–Rh(2)–M(4)	86.9(3)	C(10)–C(9)–C(16)	125.8(8)
P(2)–Rh(2)–M(4)	94.0(2)	C(9)–C(10)–C(11)	124.0(10)
Rh(1)–P(1)–S(2)	111.0(1)	C(10)–C(11)–C(12)	116.2(7)
Rh(2)–S(2)–P(1)	111.1(1)	C(11)–C(12)–C(13)	116.2(8)
Rh(2)–P(2)–S(1)	114.1(1)	C(12)–C(13)–C(14)	125.9(8)
Rh(1)–S(1)–P(2)	109.1(1)	C(13)–C(14)–C(15)	125.2(8)
C(2)–C(1)–C(8)	126.6(9)	C(14)–C(15)–C(16)	117.0(9)
C(1)–C(2)–C(3)	124.8(10)	C(15)–C(16)–C(9)	117.7(9)

[a] M(1), M(2), M(3) and M(4) are the midpoints of the C(1)-C(2), C(5)-C(6), C(9)-C(10) and C(13)-C(14) double bonds.

ring Rh(1)–S(1)–P(2)–Rh(2)–S(2)–P(1) has a boat conformation, with the S and P atoms nearly coplanar and the Rh(1) and Rh(2) atoms by 1.463(3) and 1.319(3) Å from the mean plane through the S and P atoms. The same confomation has been observed in the Pt–S–P–Pt′–S–P ring, but in some other complexes containing a $M_2(\mu$-EPR$_2)$ unit (E = O or S) different conformations are adopted [14].

Experimental

General procedures. All rections were carried out anaerobically by conventional Schlenk techniques. Solvents were deoxygenated, and distilled immediately before use. C, H and N analyses were performed with a Perkin–Elmer 240-B micro-analyzer. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer in the range 4000–200 cm^{-1}, with the samples as Nujol mulls or as solutions in matched IR cells, and calibration with polystyrene. Molecular weights were determined with a Knauer vapour pressure osmometer.

Starting materials were prepared by literature procedures as follows: [Rh$_2$Cl$_2$(COD)$_2$] [32], [Rh$_2$Cl$_2$(TFB)$_2$] [18], [Rh$_2$Cl$_2$(NBD)$_2$] [33], [Ir$_2$Cl$_2$(COD)$_2$]

[34], [Rh(acac)(COD)] [17], [Rh(acac)(TFB)] [18], [Rh(acac)(NBD)] [17], [Ir(acac)(COD)] [19], [Rh$_2$(O$_2$CMe)$_4$(MeOH)$_2$] [28] and Ph$_2$P(S)H [35]. Other chemicals were grade reagents, and were used without purification.

Preparation of complexes of the [M$_2$(SPPh$_2$)$_2$(diolefin)$_2$] type (I)

Solid Ph$_2$P(S)H (70.38 mg, 0.32 mmol) was added to a solution of 100 mg (0.32 mmol) of [Rh(acac)(COD)] in 20 ml of methanol. The yellow solution rapidly turned orange, and an orange precipitate of [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] (Ia) was formed inmediately. After 30 min stirring, the volume of the solution was reduced to 5 ml. The orange solid was filtered off, washed with diethyl ether, and dried in vacuo.

Complexes [Rh$_2$(SPPh$_2$)$_2$(TFB)$_2$] (Ib), [Rh$_2$(SPPh$_2$)$_2$(NBD)$_2$] (Ic) and [Ir$_2$(SPPh$_2$)$_2$(COD)$_2$] (Id) were similarly prepared by the route described above, starting from the appropriate amount of [Rh(acac)(TFB)], [Rh(acac)(NBD)] and [Ir(acac)(COD)].

Preparation of [Rh$_2$(SPPh$_2$)$_2$(CNt-Bu)$_4$] (II)

A suspension of [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] (50 mg, 0.058 mmol) in diethyl ether (10 ml) was treated with t-Bu-NC (26 μl; 0.236 mmol). The suspension immediately turned into a red solution, and a yellow solid was then formed. The yellow suspension was stirred for 30 min, then the solvent volume was reduced to 5 ml, and the complex was filtered off, washed with diethyl ether, and vacuum-dried.

Preparation of [Rh(SPPh$_2$)(PPh$_3$)$_2$] (III)

PPh$_3$ (652 mg, 0.236 mmol) was added to a solution of [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] (50 mg, 0.058 mmol) in dichloromethane (10 ml). The orange solution was stirred for 30 min, then the solvent was evaporated off under reduced pressure to ca. 2 ml, and diethyl ether was added, leading to precipitation of a light-orange solid. This was filtered off, washed with diethyl ether, and vacuum-dried.

Preparation of [Rh$_2$(SPPh$_2$)$_2$(dppm)$_2$] (IVa) and [Rh$_2$(SPPh$_2$)$_2$(dppe)$_2$] (IVb)

Addition of dppe (47 mg, 0.118 mmol) to a solution of [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] (50 mg, 0.058 mmol) in dichloromethane (10 ml) caused a colour change from orange to yellow. The solution was stirred for 20 min, than vacuum concentrated, and diethyl ether was added, to give IVb as a yellow powder, which was isolated by vacuum filtration and dried in vacuo.

A similar procedure was used for IVa except that pentane was used instead of diethyl ether; thus compound [Rh$_2$(SPPh$_2$)$_2$(COD)$_2$] (50 mg, 0.058 mmol) and dppm (44.9 mg, 0.116 mmol) gave IVa as a yellow-brown powder.

Preparation of [Rh$_2$(SPPh$_2$)$_2$(CO)$_4$] (V)

Solid Ph$_2$P(S)H (42.2 mg, 0.193 mmol) was added to a solution of [Rh(acac)(CO)$_2$] (50 mg, 0.193 mmol) in 20 ml of acetone; the colour of the solution changed from yellow to red. After 10 min stirring the solvent was evaporated off under reduced pressure to ca. 2 ml and diethyl ether was added, to give a thermally unstable red-brown solid which was filtered off, washed with diethyl ether, and vacuum-dried.

Preparation of [Rh(SPPh$_2$)(CO)(PPh$_3$)]$_x$ (VI)

(a) To a solution of [Rh(acac)(CO)(PPh$_3$)] (50 mg, 0.101 mmol) in acetone (20 ml) was added Ph$_2$P(S)H (22.11 mg, 0.101 mmol). The colour of the solution

changed from yellow to red. After 2 h stirring the solution was concentrated to 2 ml, and hexane was added to give a yellow solid, which was filtered off, washed with diethyl ether, and vacuum-dried.

(b) To a solution of $[Rh_2(SPPh_2)_2(CO)_4]$ (V) (prepared; in situ by treating $[Rh(acac)(CO)_2]$ (50 mg, 0.193 mmol) with $Ph_2P(S)H$ (42.4 mg, 0.193 mmol) in acetone (20 ml)) was added PPh_3 (50.81 mg, 0.193 mmol). The solution was stirred for 30 min then the solvent was evaporated off under reduced pressure, and hexane slowly added to give a yellow-brown solid, which was filtered off, washed with hexane, and air-dried.

Reaction of $[Rh_2(SPPh_2)_2(CO)_4]$ with iodine: $[Rh_2(SPPh_2)_2I_2(CO)_4]$ (VII) and $[Rh_2(SPPh_2)_2I_4(CO)_4]$ (VIII)

To solutions of V (prepared in situ by treating $[Rh(acac)(CO)_2]$ (50 mg, 0.193 mmol) with $Ph_2P(S)H$ (42.3 mg, 0.193 mmol) in acetone (20 ml)) were added the appropriate amounts of iodine (24.58 mg, 0.096 mmol or 49.16 mg, 0.193 mmol) in 5 ml of the same solvent. In each case after 45 min stirring the solution was concentrated under reduced pressure, and pentane was added to give a dark-brown solid, which was filtered off, washed with pentane, and air-dried.

Preparation of $[Rh_2(SPPh_2)_2I_2(CO)_2(dppm)]$ (IX)

Complex VII (60 mg, 0.059 mmol) was suspended in dichloromethane (20 ml), and dppm (22.92 mg, 0.059 mmol) was added. The mixture was stirred for 8 h, during which the dark-brown suspension changed to a red-brown solution. This solution was concentrated under reduced pressure and pentane was slowly added to give a brown solid, which was filtered off, washed with pentane, and air-dried.

Preparation of $[Rh_2(SPPh_2)_4(SPHPh_2)_2]$ (X)

To $[Rh_2(O_2CMe)_4(MeOH)_2]$ (100 mg, 0.197 mmol) suspended in methanol (30 ml) was added $Ph_2P(S)H$ (258.7 mg, 1.182 mmol). After 2 h refluxing the solution became green-orange and an orange precipitate was present. The solid was filtered off, washed with methanol, and vacuum-dried.

Preparation of $[Rh_2(SPPh_2)_4(NCMe)_2]$ (XI)

A suspension of $[Rh_2(SPPh_2)_4(SPHPh_2)_2]$ (50 mg, 0.033 mmol) in acetonitrile (20 ml) was heated at 60°C for 1 h, during which the orange solid gradually turned yellow. The yellow solid was filtered off, washed with acetonitrile, and vacuum-dried.

Preparation of complexes $[Rh_4(SPPh_2)_6(COD)_2]$ (XII) and $[Rh_4(SPPh_2)_6(TFB)_2]$ (XIII)

To a suspension of $[Rh_2(SPPh_2)_4(SPHPh_2)_2]$ (60 mg, 0.039 mmol) in acetone, was added a stoichiometric amount of $[Rh(acac)(COD)]$ (24 mg, 0.078 mmol) $[Rh(acac)(TFB)]$ (33.96 mg, 0.078 mmol). In each case the orange mixture was stirred for 30 min, during which the suspension turned into a dark-red solution and the product separated as a red solid. This was filtered off, washed with acetone, and vacuum-dried.

X-Ray data collection, structure solution and refinement

A prismatic orange crystal of approximate dimensions $0.15 \times 0.27 \times 0.30$ mm was selected and mounted on a Siemens AED single-crystal diffractometer. Unit cell

Table 3

Fractional atomic coordinates ($\times 10^4$) with e.s.d.s. in parentheses for the non hydrogen atoms of Ia

Atom	x	y	z	Atom	x	y	z
Rh(1)	11911(1)	2504(1)	2707(1)	C(18)	13976(6)	4315(4)	6595(7)
Rh(2)	8564(1)	1620(1)	2542(1)	C(19)	14848(7)	4450(5)	7950(8)
S(1)	10493(2)	2976(1)	923(2)	C(20)	14620(7)	3812(5)	8754(8)
S(2)	10012(1)	2756(1)	4412(2)	C(21)	13550(8)	3052(5)	8231(8)
P(1)	11715(1)	3354(1)	4264(1)	C(22)	12664(6)	2910(4)	6877(7)
P(2)	8759(1)	2585(1)	1038(1)	C(23)	11865(5)	4483(4)	3948(6)
C(1)	12572(9)	2168(7)	1204(7)	C(24)	11176(6)	4906(4)	4283(7)
C(2)	11635(9)	1414(6)	1247(6)	C(25)	11326(7)	5770(5)	4033(7)
C(3)	11885(13)	652(6)	1967(9)	C(26)	12139(7)	6189(5)	3448(8)
C(4)	12459(12)	833(5)	3483(10)	C(27)	12823(8)	5767(5)	3098(8)
C(5)	12803(7)	1777(5)	4134(7)	C(28)	12684(7)	4901(5)	3338(7)
C(6)	13760(7)	2531(5)	4087(7)	C(29)	8424(6)	3570(4)	1319(6)
C(7)	14606(8)	2542(8)	3357(9)	C(30)	7755(6)	3584(4)	2112(7)
C(8)	14000(10)	2379(10)	1860(9)	C(31)	7437(7)	4324(5)	2285(7)
C(9)	7942(8)	974(6)	4059(7)	C(32)	7823(8)	5057(5)	1671(8)
C(10)	8726(9)	595(5)	3862(8)	C(33)	8477(8)	5035(5)	869(8)
C(11)	8253(12)	−309(5)	3030(10)	C(34)	8780(6)	4296(4)	686(7)
C(12)	7700(12)	−351(5)	1539(10)	C(35)	7625(6)	2166(4)	−761(6)
C(13)	7465(8)	470(5)	1020(7)	C(36)	6467(6)	2298(4)	−1275(7)
C(14)	6647(7)	824(5)	1210(7)	C(37)	5615(7)	1953(5)	−2631(8)
C(15)	5842(9)	456(7)	1993(10)	C(38)	5887(7)	1470(5)	−3446(7)
C(16)	6499(8)	584(7)	3444(9)	C(39)	7037(8)	1330(5)	−2943(8)
C(17)	12872(6)	3550(4)	6045(6)	C(40)	7904(6)	1679(4)	−1588(7)

parameters were obtained by least-squares refinement of the values of 28 carefully centered reflections. Intensity data were collected at room temperature for θ 3–27° ($\theta/2\theta$ scan) using niobium-filtered Mo-K_α radiation. Of 7278 independent measured reflections, 5149 with $I \geqslant 2\sigma(I)$ were used in the analysis. Corrections were applied for Lorentz polarization, but not for absorption because of the very low absorbance of the sample.

Crystal data. $C_{40}H_{44}P_2Rh_2S_2$, $M = 856.67$, triclinic, a 12.152(7), b 16.117(8), c 10.805(7) Å, α 90.42(4), β 112.90(3), γ 109.27(3)°, V 1818(2) Å^3, $Z = 2$, D_c 1.565 g cm^{-3}, $F(000)$ 872, space group $P\bar{1}$, μ(Mo-K_α) 11.18 cm^{-1}.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using the SHELX system of computer programs [36] with initially isotropic and subsequently anisotropic thermal parameters for all atoms excepting the carbon atoms of the phenyl rings. Half of the hydrogen atoms were clearly located in the final difference Fourier map and the other half were placed at their calculated positions; all were introduced in the final structure factor calculation with isotropic thermal parameters. The atomic scattering factors used, corrected for the anomalous dispersion of the Rh, S and P atoms, were taken from the ref. 37. Unit weights were chosen in the first stages of the refinement, then weights were applied according to $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.688$ and $g = 0.005$. Final R and R_w values were 0.0405 and 0.0584 respectively. Final atomic coordinates for the non-hydrogen atoms are given in Table 3. Coordinates for the hydrogen atoms, thermal parameters, and a list of observed and calculated structure factors are available from the authors.

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