Journal of Organometallic Chemistry, 441 (1992) 323–331
Elsevier Sequoia S.A., Lausanne
JOM 22989

Synthesis and reactivity of dithiodiphenylphosphinato-derivatives of rhodium. Crystal structure of the square-pyramidal rhodium(III) complex $[RhI(\eta^2\text{-}S_2PPh_2)(COMe)(PPh_3)]$

Javier A. Cabeza, Víctor Riera, María A. Villa-García
Departamento de Química Organometálica, Universidad de Oviedo, 33071 Oviedo (Spain)

Lahcène Ouahab and Smaïl Triki
Laboratoire de Cristallochimie, Université de Rennes I, URA-CNRS 254, Avenue du Général Leclerc, 35042 Rennes Cédex (France)

(Received March 4, 1992)

Abstract

The complexes $[Rh_2(\mu\text{-}Cl)_2L_4]$ (L_2 = 1,5-cyclooctadiene (COD); L = CO) react with $Na[S_2PPh_2]$ to give the mononuclear derivatives $[Rh(S_2PPh_2)L_2]$ (L_2 = COD, **1**; L = CO, **2**). Treatment of complex **2** with PPh_3 affords $[Rh(S_2PPh_2)(CO)(PPh_3)]$ (**3**). Complex **3** reacts with iodine to give a mixture of two isomers of $[RhI_2(S_2PPh_2)(CO)(PPh_3)]$ (**4**). A similar reaction of **3** with methyl iodide gives the pentacoordinate rhodium(III) acyl derivative $[RhI(S_2PPh_2)(COMe)(PPh_3)]$ (**5**), which has a square-pyramidal geometry with the acyl group in the apical position, as determined by X-ray diffraction. The cationic nitrosyl derivative $[Rh(S_2PPh_2)(NO)(PPh_3)]BF_4$ (**6**) has been prepared by reaction of complex **3** with $NOBF_4$. Neither complex **1** nor complex **3** is a catalyst precursor for the homogeneous hydrogenation of alkenes and alkynes.

Introduction

Although the chemistry of square-planar rhodium(I) compounds has been widely studied [1], very few dithiophosphinatorhodium(I) derivatives have so far been reported and their chemistry has been little explored [2,3]. With most platinum-group metals, the dithiophosphinato-ligands act as chelates [4], but some binuclear compounds, such as $[Ru_2(\mu\text{-}S_2PPh_2)_2(CO)_4L_2]$ [5], are also known.

We now describe the synthesis and reactivity of some dithiodiphenylphosphinato-derivatives of rhodium(I). We also report that these complexes are not catalyst precursors for the hydrogenation of alkenes and alkynes under homoge-

---

Correspondence to: Dr. J.A. Cabeza.

neous conditions, although many rhodium(I) complexes are known to have a rich catalytic activity [6,7], even when they contain *S*-donors [7].

Results and discussion

The complex $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (COD = 1,5-cyclooctadiene) reacted with two equivalents of $Na[S_2PPh_2]$ in dichloromethane to give $[Rh(S_2PPh_2)(COD)]$ (**1**) in quantitative yield (Scheme 1). Similarly, the reaction of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with two equivalents of $Na[S_2PPh_2]$ afforded $[Rh(S_2PPh_2)(CO)_2]$ (**2**). Complex **2** exhibits two strong ν(CO) absorptions in its IR spectrum, as expected for a *cis*-dicarbonyl arrangement. Both compounds show characteristic doublet resonances in their $^{31}P\{^1H\}$ NMR spectra (see Experimental) due to coupling of the phosphorus atoms to ^{103}Rh ($I = 1/2$), indicating that they are mononuclear in solution, like the analogous dithiocarbamate derivatives [8,9] (triplet resonances would be expected for binuclear complexes containing $\mu\text{-}S_2PPh_2$ ligands). The dithiophosphate derivative $[Rh\{S_2P(OPh)_2\}(CO)_2]$ is also mononuclear [2]; however, the complex $[Rh_2(\mu\text{-}S_2PF_2)_2(CO)_4]$ has been reported to be a dimer containing $\mu\text{-}S_2PF_2$ ligands [3]. The ruthenium(I) compounds $[Ru_2(\mu\text{-}S_2PPh_2)_2(CO)_4L_2]$ are also binuclear [5].

Carbon monoxide reacted with complex **1**, displacing the COD giving **2** (Scheme 1); however, the reaction was reversed when the CO atmosphere was removed, regenerating complex **1**.

The monocarbonyl derivative $[Rh(S_2PPh_2)(CO)(PPh_3)]$ (**3**) was prepared in high yield by reaction of complex **1** with triphenylphosphine in dichloromethane under carbon monoxide. The reaction could be conveniently monitored by IR spectroscopy, being complete within 1.5 h at room temperature. Complex **3** is the result of the reaction of **2** with triphenylphosphine, since complex **1** does not react with this ligand in absence of carbon monoxide. The $^{31}P\{^1H\}$ NMR spectrum of **3** confirmed that this complex is mononuclear in solution. It shows two doublets, as expected for two phosphorus atoms which do not couple to each other but which couple to one ^{103}Rh nucleus; however, a binuclear structure cannot be excluded since second order AA′XX′ spin systems in dimers may give rise to virtual doublets.

The compounds **1** and **3** did not catalyse the hydrogenation of 1-hexene, 1,5-cyclooctadiene or phenylacetylene at room temperature, under 1 atm of H_2 in tetrahydrofuran (THF) solution (gas chromatography analysis). Although some hydrogenation was observed under more severe conditions (120°C, 20 atm of H_2, 2 h), some decomposition of the complexes to metallic rhodium occurred, though unreacted **1** or **3** was recovered after each run. This contrasts with the high catalytic activity reported for other rhodium(I) complexes containing *S*-donors [7].

Iodine reacted with complex **1** to give an intractable mixture of products. However, a similar reaction with complex **3** gave a 2:1 mixture (by $^{31}P\{^1H\}$ NMR integration) of two isomers of $[RhI_2(S_2PPh_2)(CO)(PPh_3)]$ (**4**). It has been reported that the oxidative addition of iodine to $[Rh(S_2CNMe_2)(RCN)_2]$ gives the *trans*-diiodo-derivative and that the *cis*-adduct is thought to be an intermediate in the reaction [10]. Bearing this in mind and remembering that only one *trans*-diiodo-derivative is possible, we propose that the two isomers of complex **4** are the *cis*-diiodo-derivatives depicted in Scheme 2, because their ratio remained unchanged after heating a THF solution of the mixture under reflux for 2 h. Further, the $^{31}P\{^1H\}$ NMR spectrum of the mixture (see Experimental) consists of two doublets of doublets for each isomer, with very similar J(P–P) and J(P–Rh) coupling constants; since no J(P–P) coupling was observed in compound **3**, which is square-planar, we assume that the PPh_3 ligands in both isomers of complex **4** are *cis* to the sulphur atoms of the S_2PPh_2 ligands, confirming the proposed structures (Scheme 2) for these isomers. In contrast to these observations, the reaction of halogens (I_2, Br_2) with $[Rh\{S_2P(OPh)_2\}(CO)_2]$ gives the binuclear complexes $[Rh_2X_2(\mu\text{-}X)_2\{S_2P(OPh)_2\}_2(CO)_2]$ [2].

Complex **1** remained unchanged after being heated under reflux in methyl iodide for 2 h. However, complex **3** underwent an oxidative addition with methyl iodide, followed by an insertion reaction, to give $[RhI(S_2PPh_2)(COMe)(PPh_3)]$ (**5**) as the final product. The presence of the coordinated acyl group was confirmed by IR and NMR (^1H, $^{13}C\{^1H\}$) spectroscopies (see Experimental), but it was impossible to assign the stereochemistry of this pentacoordinated complex using spectroscopic data alone (several isomers for both trigonal bipyramidal and square pyramidal geometries are possible). An X-ray structure determination (see below) was therefore carried out. No reaction was observed when complex **3** was treated with diiodomethane or allyl bromide.

The molecular structure of complex **5** is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The complex is mononuclear and is square pyramidal, with the base of the iodine, the phosphorus atom of the PPh_3 and both sulphur atoms of the S_2PPh_2 (deviations of these atoms from the best least-squares plane * are −0.028(1), 0.030(2), 0.032(2) and −0.033(2) Å, respectively) and with the acetyl group in the apical position. The rhodium and the carbonyl carbon atoms lie 0.298(1) and 2.247(9) Å, respectively, above the basal plane.

The oxidative addition of alkyl iodides to the anionic complex $[Rh\{S_2C_2(CN)_2\}(CO)(PPh_3)]^-$ has been reported to give pentacoordinate anionic acyl derivatives [11]; the X-ray structure of one, $[RhI\{S_2C_2(CN)_2\}(CO^nPr)(PPh_3)]^-$, is analogous to that of compound **5**.

Complex **3** also reacted with $NOBF_4$ to give a mixture of products from which the solvate $[Rh(S_2PPh_2)(NO)(PPh_3)]BF_4 \cdot 2THF$ (**6**) precipitated when a 2:1 mixture of diethyl ether and THF was used as solvent. The solution contained carbonyl derivatives. The IR spectrum of **6** showed the presence of tetrafluoroborate (ν(BF) = 1080 cm^{-1}) and coordinated NO (1683 cm^{-1}) and the absence of carbonyl ligands; the NMR and microanalytical data also confirm the formulation proposed for this complex, which results from the replacement of a carbonyl by the isoelectronic NO^+. The observation of carbonyl absorptions in the solution of the reaction mixture by IR spectroscopy (2069, 2003 cm^{-1}) at higher wavenumbers than that of complex **3**, suggests that the Lewis acid NO^+ attacks the basic rhodium atom to give an adduct which subsequently decomposes to give **6** and mixed carbonyl-nitrosyl species. As far as we are aware, the substitution of CO by NO^+ in rhodium(I) compounds does not seem to have been reported.

---

* The equation of this plane is $0.8647x - 0.2093y - 0.4565z - 4.5677 = 0$; x, y and z being the orthogonalized coordinates.

Experimental

Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques. The compounds $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ [12] and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ [13] were prepared as described previously; $Na[S_2PPh_2]$ was made by reaction of dithiodiphenylphosphinic acid with sodium carbonate [14]. All other reagents (analytical grade) were purchased (Aldrich) and used as received. The catalytic experiments were performed in a Berghof autoclave and the reactions were monitored with a Perkin Elmer 8600 gas chromatograph. IR spectra were recorded on a Perkin Elmer FT 1720-X spectrophotometer. NMR spectra were run in $CDCl_3$ solutions on a Bruker AC-300 instrument, at 300 MHz (^1H), 121.7 MHz (^{31}P) or 75.5 MHz (^{13}C), using $SiMe_4$ (internal, ^1H and ^{13}C) or 85% H_3PO_4 (external, ^{31}P) as standards ($\delta = 0$ ppm). Microanalyses were obtained with a Perkin Elmer 2400 microanalyzer.

Preparation of $[Rh(S_2PPh_2)(COD)]$ *(1)*

A solution of $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (250 mg, 0.507 mmol) in dichloromethane (10 ml) was treated with $Na[S_2PPh_2]$ (316 mg, 1.160 mmol). After being stirred for 1.5 h, the mixture was evaporated to dryness. The residue was extracted with diethyl ether (3 × 5 ml) to remove the insoluble NaCl and the excess of $Na[S_2PPh_2]$. The combined extracts were evaporated to dryness and the residue washed with hexane to give complex **1** as a yellow solid (394 mg, 84%). Found: C, 53.0; H, 4.8. $C_{20}H_{22}PRhS_2$ calc.: C, 52.2; H, 4.8%. ^1H NMR: 7.8–7.4 (m, 10H, Ph), 4.34 (s, 4H, COD vinyl protons), 2.42 (s, br, 4H, COD allyl protons), 1.79 (m, 4H, COD allyl protons) ppm. $^{31}P\{^1H\}$ NMR: 85.9 (d, $J = 11.0$ Hz) ppm.

Preparation of $[Rh(S_2PPh_2)(CO)_2]$ *(2)*

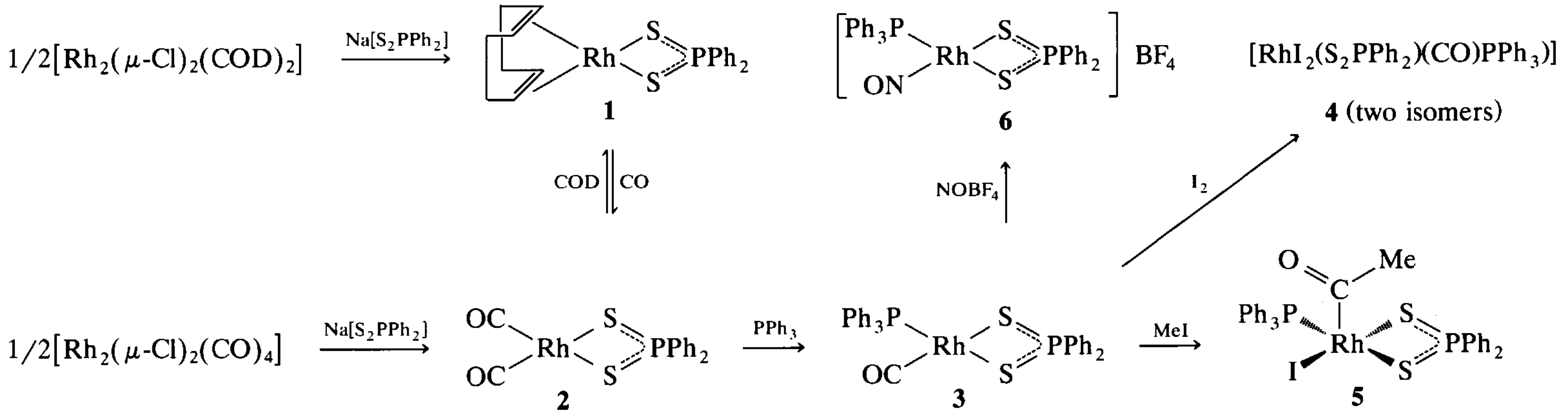
$Na[S_2PPh_2]$ (147 mg, 0.54 mmol) was added to a solution of $[Rh_2(\mu\text{-}Cl_2)(CO)_4]$ (100 mg, 0.257 mmol) in dichloromethane (5 ml). The mixture was stirred for 1 h, filtered, and the resulting solution evaporated to dryness. The residue was washed with hexane to give complex **2** as a pale brown solid (174 mg, 83%). Found: C, 41.3; H, 2.6. $C_{14}H_{10}O_2PRhS_2$ calc.: C, 41.2; H, 2.6%. IR (CH_2Cl_2): $\nu(CO)$ at 2073(s), 2008(s) cm^{-1}. $^{31}P\{^1H\}$ NMR: 102.7 (d, $J = 8.2$ Hz) ppm.

Reaction of complex 1 with carbon monoxide

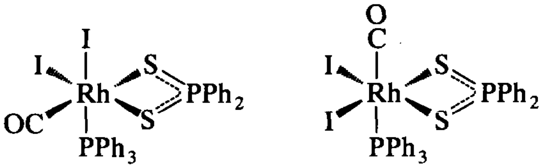
Carbon monoxide was bubbled through a solution of complex **1** (40 mg, 0.087 mmol) in dichloromethane (5 ml) for 30 min. The IR spectrum of this solution showed the presence of complex **2**. The solvent was removed under reduced pressure to give a yellow solid which was washed with hexane. The $^{31}P\{^1H\}$ NMR spectrum of this material indicated that it was a mixture of complexes **1** and **2**, the latter being the minor component. Complex **2** could be prepared pure by bubbling carbon monoxide through a solution of complex **1** in dichloromethane until all the solvent was evaporated and by washing the residue with hexane (to remove COD) under carbon monoxide.

Preparation of $[Rh(S_2PPh_2)(CO)(PPh_3)]$ *(3)*

Carbon monoxide was bubbled for 1.5 h through a solution of complex **1** (380 mg, 0.825 mmol) and triphenylphosphine (220 mg, 0.084 mmol) in dichloromethane


1/2[Rh2(μ-Cl)2(COD)2]
Na[S2PPh2]
1
COD
CO
[Ph3P Rh S PPh2 ON] BF4
6
NOBF4
[RhI2(S2PPh2)(CO)PPh3)]
4 (two isomers)
I2
1/2[Rh2(μ-Cl)2(CO)4]
Na[S2PPh2]
2
PPh3
3
MeI
5

Scheme 1.



Scheme 2. Proposed structures for the two isomers of complex 4

(10 ml). The solvent was removed under reduced pressure and the residue washed with hexane to give complex 3 as a pale yellow solid (450 mg, 85%). Found: C, 57.6; H, 4.0%. $C_{31}H_{25}OP_2RhS_2$ requires: C, 58.0; H, 3.9%. IR (CH_2Cl_2): ν(CO) at 1978(s) cm^{-1}. $^{31}P\{^1H\}$ NMR: 90.4 (d, $J = 7.3$ Hz), 44.3 (d, $J = 163.8$ Hz) ppm.

Reaction of complex 3 with iodine

Iodine (16 mg, 0.063 mmol) was added to a solution of complex 3 (40 mg, 0.062 mmol) in dichloromethane (5 ml). The solution was stirred for 30 min, the solvent was removed under reduced pressure and the residue washed with diethyl ether–hexane (1 : 1) to give complex 4 (two isomers) as a brown solid (50 mg, 89%). Found: C, 41.2; H, 3.0. $C_{31}H_{25}I_2OP_2RhS_2$ calc.: C, 41.5; H, 2.8%. IR (CH_2Cl_2): ν(CO) at 2084(s) cm^{-1}. $^{31}P\{^1H\}$ NMR: minor isomer (*ca.* 33%): 98.1 (dd, $J = 11.4$, 8.0 Hz), 20.4 (dd, $J = 101.8$, 11.4 Hz) ppm; major isomer (*ca.* 66%): 85.0 (dd, $J = 11.8$, 8.8 Hz), 28.2 (dd, $J = 106.8$, 11.8 Hz) ppm.

Preparation of [RhI(S_2PPh_2)(COMe)(PPh_3)] (5)

Complex 3 (60 mg, 0.093 mmol) was stirred in methyl iodide (2 ml) for 1 h. The resulting solution was evaporated to dryness and the oily residue washed with hexane to give complex 5 as a yellow solid (63 mg, 86%). Found: C, 49.4; H, 3.8. $C_{32}H_{28}IOP_2RhS_2$ calc.: C, 49.0; H, 3.6%. IR (CH_2Cl_2): ν(CO) at 1713(s) cm^{-1}. ^1H NMR: 7.9–7.3 (m, 25H, Ph), 3.17 (s, 3H, Me) ppm. $^{31}P\{^1H\}$ NMR: 87.4 (d, $J = 8.2$ Hz), 39.3 (d, $J = 146.0$ Hz) ppm. $^{13}C\{^1H\}$ NMR: 210.6 (dd, $J = 25.7$, 5.0 Hz, CO), 140–127 (m, Ph), 46.4 (s, Me) ppm.

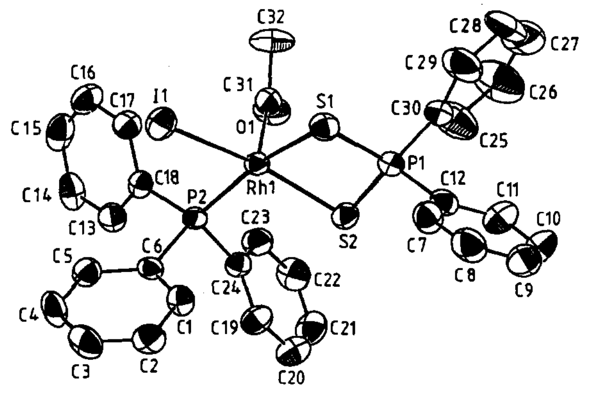


Fig. 1. ORTEP view of the molecule [RhI(S_2PPh_2)(COMe)(PPh_3)] (5) with the atoms shown as 50% vibration ellipsoids.

Table 1

Selected bond distances (Å) and angles (°) in [RhI(S_2PPh_2)(COMe)(PPh_3)] (**5**)

Bond distances					
I(1)–Rh(1)	2.6534(9)	Rh(1)–S(1)	2.441(2)	Rh(1)–S(2)	2.366(2)
Rh(1)–P(2)	2.290(2)	Rh(1)–C(31)	1.96(1)	S(1)–P(1)	2.010(3)
S(2)–P(1)	2.030(3)	P(1)–C(12)	1.801(9)	P(1)–C(30)	1.80(1)
P(2)–C(6)	1.815(9)	P(2)–C(18)	1.826(8)	P(2)–C(24)	1.829(7)
C(31)–O(1)	1.21(1)	C(31)–C(32)	1.58(4)		
Bond angles					
I(1)–Rh(1)–S(1)	89.88(6)	I(1)–Rh(1)–S(2)	163.71(7)	I(1)–Rh(1)–P(2)	91.43(6)
I(1)–Rh(1)–C(31)	100.4(2)	S(1)–Rh(1)–S(2)	82.53(7)	S(1)–Rh(1)–P(2)	166.67(9)
S(1)–Rh(1)–C(31)	99.3(2)	S(2)–Rh(1)–P(2)	92.74(7)	S(2)–Rh(1)–C(31)	95.1(3)
P(2)–Rh(1)–C(31)	93.5(2)	Rh(1)–S(1)–P(1)	84.87(9)	Rh(1)–S(2)–P(1)	86.45(9)
S(1)–P(1)–S(2)	103.4(1)	S(1)–P(1)–C(12)	111.5(3)	S(1)–P(1)–C(30)	114.3(3)
S(2)–P(1)–C(12)	114.2(3)	S(2)–P(1)–C(30)	110.5(3)	C(12)–P(1)–C(30)	103.3(4)
Rh(1)–C(31)–C(32)	114.9(7)	Rh(1)–C(31)–O(1)	123.8(6)	C(32)–C(31)–O(1)	121.3(9)

Preparation of [Rh(S_2PPh_2)(NO)(PPh_3)]BF_4 · 2THF (6)

Complex **3** (80 mg, 0.124 mmol) and $NOBF_4$ (29 mg, 0.248 mmol) were stirred in a mixture of THF and diethyl ether (1 : 2) for 1 h to give a brown-yellow solid. The liquid was decanted and the solid washed with diethyl ether to give complex **6** (40 mg, 37%). Found: C, 52.0; H, 4.7; N, 1.4. $C_{30}H_{25}BF_4NOP_2RhS_2 \cdot 2THF$ calc.: C, 52.1; H, 4.5; N, 1.6%. IR (CH_2Cl_2): ν(NO) at 1683(s) cm^{-1}. ^1H NMR: 7.8–7.0 (m, 25H, Ph), 3.77 (m, 8H, THF), 1.85 (m, 8H, THF) ppm. $^{31}P\{^1H\}$ NMR: 86.2 (d, $J = 12.6$ Hz), 33.5 (d, $J = 148.5$ Hz) ppm.

X-Ray crystal structure of complex 5 · 0.5CH_2Cl_2

Suitable crystals for X-ray diffraction of **5** · $0.5CH_2Cl_2$ were obtained by slow diffusion of hexane layered on a solution of complex **5** in dichloromethane at

Table 2

Crystallographic and refinement data for [RhI(S_2PPh_2)(COMe)(PPh_3)]·$0.5CH_2Cl_2$

Formula	$C_{32}H_{28}IOP_2RhS_2 \cdot 0.5CH_2Cl_2$	F.W.	826.96
Crystal system	monoclinic	Space group	$P2_1/c$
a, Å	13.776(4)	b, Å	15.474(6)
c, Å	17.508(7)	β, deg.	111.60(1)
V, Å^3	3470(2)	Z	4
D_{calcd}, g/cm^3	1.583	crystal size, mm	0.35×0.20×0.18
Radiation (λ, Å)	Mo-K_α (0.71073)	Monochromator	graphite
Temp., K	293	μ(Mo-K_α), cm^{-1}	16.723
F(000)	1640	Scan method	θ–2θ
h, k, l range	0-16, 0-18, ±20	2θ limits, deg	2–50
Measured reflections	6611	Unique reflections	6069
Reflections with $I \geq 3\sigma(I)$	3554	R_{int}	0.029
No. variables	380	R(F) [a]	0.044
$R_w(F)$ [b]	0.062	GOF [c]	1.413
Δ/σ	0.68	$\Delta\rho$, max, min, e/Å^3	1.352, −0.781

[a] $R = \Sigma[\| F_o| - |F_c\|]/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 4F_o^2/[\sigma^2(I) + (0.07|F_o|^2)^2]$. [c] Goodness Of Fit (GOF) = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2}$.

Table 3

Fractional atomic coordinates and equivalent isotropic thermal parameters for $[RhI(S_2PPh_2)(COMe)(PPh_3)]\cdot 0.5CH_2Cl_2$ (estimated standard deviations in parentheses)

Atom	x	y	z	B_{eq} (Å^2)
I(1)	0.23061(5)	0.10881(4)	0.53318(4)	4.30(1)
Rh(1)	0.27044(4)	−0.02964(4)	0.62925(4)	2.39(1)
S(1)	0.1475(2)	−0.1134(2)	0.5170(1)	3.40(5)
S(2)	0.3226(2)	−0.1685(1)	0.6861(1)	3.22(5)
P(1)	0.1926(2)	−0.2134(1)	0.5954(1)	2.89(5)
P(2)	0.4138(2)	0.0354(1)	0.7237(1)	2.37(4)
C(1)	0.5281(6)	0.0011(6)	0.6256(5)	3.3(2)
C(2)	0.5959(7)	0.0187(6)	0.5860(5)	3.9(2)
C(3)	0.6346(7)	0.1022(7)	0.5889(6)	4.7(2)
C(4)	0.6093(7)	0.1672(6)	0.6342(6)	4.7(2)
C(5)	0.5445(7)	0.1467(6)	0.6769(5)	3.6(2)
C(6)	0.5034(6)	0.0638(5)	0.6733(4)	2.6(2)
C(7)	0.2269(7)	−0.3041(6)	0.4713(6)	4.2(2)
C(8)	0.2405(8)	−0.3784(7)	0.4311(7)	5.2(3)
C(9)	0.2442(8)	−0.4566(7)	0.4661(6)	5.4(3)
C(10)	0.2351(9)	−0.4631(7)	0.5417(7)	5.6(3)
C(11)	0.2187(8)	−0.3902(6)	0.5817(6)	4.7(2)
C(12)	0.2136(6)	−0.3093(6)	0.5452(5)	3.3(2)
C(13)	0.4871(6)	0.1601(5)	0.8463(5)	3.4(2)
C(14)	0.4779(7)	0.2325(6)	0.8902(5)	4.0(2)
C(15)	0.3837(8)	0.2763(6)	0.8678(6)	5.1(2)
C(16)	0.3001(7)	0.2500(6)	0.8015(6)	4.6(2)
C(17)	0.3079(7)	0.1780(6)	0.7560(5)	3.7(2)
C(18)	0.4021(6)	0.1325(5)	0.7790(4)	2.6(2)
C(19)	0.5673(7)	−0.0906(6)	0.8040(5)	3.6(2)
C(20)	0.6140(7)	−0.1498(6)	0.8655(6)	4.3(2)
C(21)	0.5856(8)	−0.1549(6)	0.9337(5)	4.2(2)
C(22)	0.5087(7)	−0.1024(6)	0.9377(5)	4.2(2)
C(23)	0.4590(6)	−0.0440(6)	0.8753(5)	3.5(2)
C(24)	0.4875(6)	−0.0369(5)	0.8076(4)	2.6(2)
C(25)	0.1223(8)	−0.2642(9)	0.7178(6)	6.4(3)
C(26)	0.0459(9)	−0.300(1)	0.7461(7)	8.3(4)
C(27)	−0.0506(9)	−0.3172(9)	0.6963(7)	7.5(3)
C(28)	−0.0806(8)	−0.296(1)	0.6111(9)	8.7(4)
C(29)	−0.0051(8)	−0.2612(8)	0.5812(7)	6.7(3)
C(30)	0.0971(6)	−0.2472(6)	0.6368(5)	3.5(2)
C(31)	0.1819(6)	−0.0061(5)	0.6922(5)	3.3(2)
C(32)	0.0705(7)	0.0140(8)	0.6415(6)	5.3(3)
O(1)	0.2129(4)	−0.0070(5)	0.7661(3)	4.3(1)
Cl(1)	0.1522(5)	0.4723(4)	0.7559(4)	6.5(2)
Cl(2)	0.0651(6)	0.3638(6)	0.6173(4)	10.3(2)
C(33)	0.046(2)	0.438(2)	0.672(2)	11(1)

−20°C. Intensity data were collected on an Enraf Nonius CAD4 diffractometer with graphite-crystal monochromatized Mo-K_α radiation. The cell dimensions were determined and refined by least-squares methods from the setting angles of 25 centred reflections in the range $16 < 2\theta < 22°$. Intensities were collected using the θ–2θ scan mode. Three standard reflections measured every hour revealed no fluctuations in intensities. One set of reflections was collected up to $2\theta = 50°$.

Lorentz and polarization corrections were applied. Absorption corrections were performed using the DIFABS procedure [15]. The structure was solved by direct methods [16] and successive Fourier difference syntheses and was refined by weighted anisotropic full-matrix least-squares methods. After refinement of positional and anisotropic (β_{ij}) thermal parameters for all non-hydrogen atoms, the positions of the H atoms were calculated [d(C–H) = 1 Å, B_{eq} = 5 Å^2] and included as a fixed contribution to F_c. Scattering factors and corrections for anomalous dispersion were from ref. 17. Structure illustrations were drawn with ORTEP [18]. All calculations were performed on a MicroVax 3100 computer using the SDP package [19]. Selected bond lengths and angles are given in Table 1. Crystal data are summarized in Table 2. Atomic coordinates are given in Table 3.

The following material will be deposited with the Cambridge Crystallographic Data Centre: atomic coordinates, complete tables of bond lengths and angles and H-atom coordinates. Tables of thermal parameters, least-squares planes and structure factors are available from the authors.

Acknowledgments

We thank the DGICYT (Spain) and the CNRS (France) for financial support and the Departamento de Química Inorgánica of the University of Zaragoza (Spain) for C, H, N microanalyses.

References

1 See, for example, R.P. Hughes, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 5, Pergamon Press, Oxford, 1982, p. 277.
2 F. Faraone, J. Chem. Soc., Dalton Trans., (1975) 541.
3 F.A. Hartman and M. Lustig, Inorg. Chem., 7 (1968) 2669.
4 See, for example, D.J. Cole-Hamilton and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1974) 739 and refs. therein.
5 R.H. Hilts and M. Cowie, Inorg. Chem, 29 (1990) 3349.
6 C. Masters, Homogeneous Transition-Metal Catalysis, Chapman and Hall, London, 1981.
7 C. Claver, Ph. Kalck, M. Ridmy, A. Thorez, L.A. Oro, M.T. Pinillos, M.C. Apreda, F.H. Cano and C. Foces-Foces, J. Chem. Soc., Dalton Trans., (1988) 1523, and refs. therein.
8 F.A. Cotton and J.A. McCleverty, Inorg. Chem., 3 (1964) 1398.
9 C. O'Connor, J.D. Gilbert and G. Wilkinson, J. Chem. Soc. A, (1969) 84.
10 R. Kuwae, T. Tanaka and K. Kawakami, Bull. Chem. Soc. Jpn., 52 (1979) 437.
11 C.H. Cheng, B.D. Spivack and R. Eisenberg, J. Am. Chem. Soc., 99 (1977) 3003.
12 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 3178.
13 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.
14 W.A. Higgins, P.W. Vogel and W.G. Craig, J. Am. Chem. Soc., 77 (1955) 1864; R.G. Cavell, W. Byers and E.D. Day, Inorg. Chem., 10 (1971) 2710.
15 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 39 (1983) 158.
16 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Deleclercq and M.M. Woolfson, MULTAN84, a System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Universities of York (England) and Louvain (Belgium), 1984.
17 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, England, 1974. Present distributor D. Reidel, Dordrecht, (The Netherlands).
18 C.K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
19 B.A. Frenz & Associates, SDP Structure Determination Package, College Station, Texas (USA) and Enraf Nonius, Delft (The Netherlands), 1985.