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Diolefin and carbonyl rhodium(I) and iridium(I) complexes with phosphine sulphide ligands. Crystal structure of $[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$

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Abstract

The preparation and properties of new diolefinic or carbonyl cationic rhodium and iridium complexes with phosphine sulphide ligands of the type $[M(COD)L_2]_n^{n+}$ or $[M(CO)_2L_2]_n^{n+}$ ($n = 1$ or 2) (L = Me_3PS, Et_3PS and Ph_3PS, L_2 = $Me_2P(S)(S)PMe_2$, $Et_2P(S)(S)PEt_2$ and $Ph_2P(S)(S)PPh_2$) are described. The complexes have been characterized by elemental analyses, IR spectra, conductance studies and ^{31}P NMR spectroscopy. Oxidative addition of I_2 gives Ir^{III} complexes. Diolefinic complexes with phosphine sulphide are catalyst precursors in the homogeneous hydrogenation of olefins. The crystal structure of $[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$ has been determined by X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/c$, with a 12.754(1), b 13.333(1), c 13.637(1) Å, β 95.30(1)°, $Z = 4$. The cationic complex $[Rh(COD)(Et_2P(S)(S)PEt_2)]^+$ is monomeric, with the Rh atom showing a slightly distorted square-planar environment. The cyclooctadiene ligand is coordinated to the metal through its two olefinic bonds, and a bis(diethylphosphine) disulphide group, bonded through its two S atoms, acts as a bidentate chelating ligand.

Introduction

We recently reported the preparation and properties of cationic rhodium and iridium complexes of types $[M(diolefin)L_2]ClO_4$ and $[M(diolefin)L(PPh_3)]ClO_4$ (M = Rh, diolefin = 1,5-cyclooctadiene (COD) or 2,5-norbornadiene (NBD); M = Ir, diolefin = COD, L = phosphine sulphide ligand) and the use of some of them as catalyst precursors in homogeneous hydrogenation of olefins [1]. We describe here

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the preparation and characterization of new cationic diolefinic complexes with bidentate sulphur ligands $R_2P(S)(S)PR_2$ (R = Et, Ph). Reactions of these diolefinic complexes and of others previously reported [1] with carbon monoxide give the corresponding carbonyl compounds.

Although some related neutral and cationic diolefinic rhodium and iridium complexes containing phosphine sulphides as ligands have been previously reported [2] only two crystal X-ray studies on complexes with this type of ligands have been published, both containing Me_3PS, $[Cr(CO)_5(Me_3PS)]$ and $[Cu(Me_3PS)_3]^+$ [2,3] indicating that this tertiary phosphine sulphide ligand is an σ-donor with minimal π-acceptor properties. No one structures of rhodium complexes with phosphine sulphide ligands have been reported.

Some crystal X-ray studies of related rhodium(I) complexes containing the diphenylthiophosphinite $(SPPh_2^-)$ ligand have been reported recently [4–6], but a different mode of coordination, through both P and S atoms, is observed for this anionic ligand.

We report here the crystal structure of $[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$, in which the bidentate tetraethyl diphosphine disulphide group acts as a chelating ligand.

It is well known that Rh^I and Ir^I cationic complexes $[M(COD)L_2]^+$, L = PR_3, are active catalyst precursors in homogeneous hydrogenation of olefins [7–10]. In the case of sulphur ligands, the catalytic activity observed in the hydrogenation and hydroformylation reactions when dinuclear rhodium(I) complexes with thiolate ligands were used, is noteworthy [11,12]. We have now examined the catalytic activity of some complexes containing phosphine sulphide ligands, and found that the complexes act as precursors in hydrogenation but show no activity in hydroformylation.

Oxidative additions to iridium(I) complexes have been carried out, but only diiodoiridium(III) complexes have been isolated.

Results and discussion

Rh^I and Ir^I diolefin complexes with bidentate disulphide ligands

Addition of phosphine disulphide ligands $R_2P(S)(S)PR_2$ (R = Et, Ph) to dichloromethane solutions of $[M(COD)_2]ClO_4$ (COD = 1,5-cyclooctadiene, M = Rh, Ir) causes rapid displacement of one of the diolefin groups and formation of complexes of general formula $[M(COD)(L-L)]_n(ClO_4)_n$ (**1–4**). These compounds are yellow and moderately air-stable solids. In the IR spectra (Table 1) the P=S stretching frequencies can be seen to have fallen in the usual manner on coordination [2]. In the case of the $[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$ an X-ray diffraction study has established its monomeric nature. The analytical results, conductivity values and IR data for the complexes are listed in Table 1.

Measurements of the equivalent conductivities of acetone or nitromethane solutions at various concentrations of the rhodium complexes with $Et_2P(S)(S)PEt_2$ (**1**) and $Ph_2P(S)(S)PPh_2$ (**2**) gave plots in terms of the Onsager's equation, $\Lambda_e = \Lambda_0 - A\sqrt{c_e}$, with A values characteristic [13,14] of 1 : 1 electrolytes for **1** and 2 : 1 for compound **2**.

However, analogous conductivity measurements carried out on the Ir complexes **3** and **4** gave typical values for 2 : 1 electrolytes [13,14], in accordance with the formation of dinuclear complexes $[(COD)Ir\{\mu\text{-}(L-L)\}_2Ir(COD)](ClO_4)_2$, in which

Table 1

Analytical results, conductivity data and IR data for complexes $[Rh(COD)(L-L)]ClO_4$ and $[(COD)M\{\mu\text{-}(L-L)\}_2M(COD)](ClO_4)_2$ (M = Rh, Ir)

Complex	Elemental analysis (found (calc) (%))			Conductivity data		IR data $\nu(S=P)$ (cm^{-1})
	C	H	S	Λ_M [a]	A [b]	
$[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$ (**1**)	34.9	5.9	11.1	140	550 [a]	545m
	(34.8)	(5.8)	(11.5)			
$[Rh(COD)(Ph_2P(S)(S)PPh_2)]_2(ClO_4)_2$ (**2**)	50.0	4.5	–	126	1530 [c]	553m
	(51.6)	(4.3)				
$[Ir(COD)(Et_2P(S)(S)PEt_2)]_2(ClO_4)_2$ (**3**)	29.2	5.2	–	288	900 [a]	540m
	(29.9)	(5.0)				
$[Ir(COD)(Ph_2P(S)(S)PPh_2)]_2(ClO_4)_2$ (**4**)	46.0	4.4	–	242	979 [a]	520m
	(46.0)	(3.8)				

[a] Measured in acetone solution (Ω^{-1} cm^2 mol^{-1}). [b] Slope found for Onsager's equation $\Lambda_e = \Lambda_0 - A\sqrt{c_e}$. [c] Measured in nitromethane solution.

the bidentate S-donor ligands are assumed to act as bridging ligands between the metal atoms.

The ^{31}P NMR spectra of $CDCl_3$ solutions of the complexes show signals corresponding to the coordinated ligands, which appear downfield compared to those from the free ligand (Table 2). In general, only one signal is observed in accord with the symmetry of the complexes.

In the case of complex $[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$ (**1**), two signals of different intensity are observed (64.9, 79.6 ppm) even over a range of temperatures (308–223 K), suggesting the presence of mono and dinuclear species in solution, arising to the tendency of the bidentate disulphides to act as bridging ligands. Surprisingly, no signal from the free ligand was observed.

In order to obtain further information about the nature of this complex, the crystal structure was determined. It consists of mononuclear cationic rhodium(I) complexes with ClO_4^- counterions packed interacting by ionic and van der Waals forces. Figure 1 shows a molecular representation of the cationic complex and Table 3 lists selected bond distances and angles for this species. In **1** the metal atom is

Table 2

^{31}P NMR data for cyclooctadiene and carbonyl complexes

Compound	δ(P–Rh) (ppm)	$\Delta\delta$(complex – ligand)
$Me_2P(S)(S)PMe_2$	35.25m	–
$Et_2P(S)(S)PEt_2$	34.80m	–
$Ph_2P(S)(S)PPh_2$	38.79m	–
$[Rh(COD)(Me_2P(S)(S)PMe_2)]ClO_4$ [a]	62.67m	27.42
$[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$ (**1**)	64.9m, 79,6m	30.1, 44.8
$[Rh(COD)(Ph_2P(S)(S)PPh_2)]_2(ClO_4)_2$ (**2**)	68.87m	30.08
$[Rh(CO)_2(Et_2P(S)(S)PEt_2)]ClO_4$ (**10**)	79.5m	44.7

[a] Reported in ref. 1.

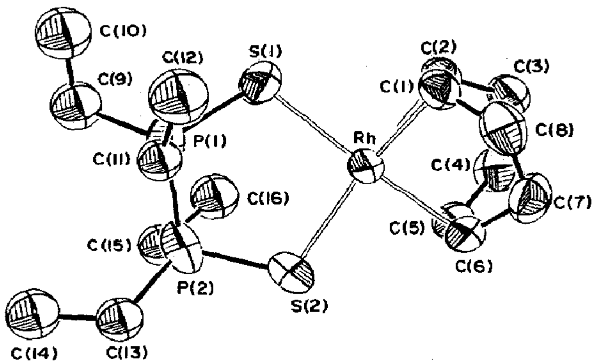

Fig. 1. The cation of $[Rh(COD)(Et_2P(S)(S)PEt_2)]^+$ (from the crystal structure of its perchlorate salt).

bonded to a cyclooctadiene molecule coordinated through both olefinic double bonds, and to a $Et_2P(S)(S)PEt_2$ group, coordinated via both sulphur atoms.

The rhodium atom has a slightly distorted square-planar environment, the deviations of M(1), M(2), S(1) and S(2) (M(1) and M(2) represent the midpoints of the olefinic C(1)–C(2) and C(5)–C(6) bonds) from the mean plane passing through them being −0.308, 0.318, −0.045 and 0.030 Å. The cationic complex has no

Table 3

Selected bond distances (Å) and angles (°) for $[Rh(COD)(Et_2P(S)(S)PEt_2)](ClO_4)$ (1) with e.s.d.'s in parentheses

Rh–S(1)	2.378(3)	Rh–C(5)	2.122(10)
Rh–S(2)	2.373(3)	Rh–C(6)	2.153(11)
Rh–C(1)	2.120(11)	Rh–M(1) [a]	2.019(7)
Rh–C(2)	2.152(9)	Rh–M(2) [a]	2.021(8)
S(1)–P(1)	2.001(4)	P(1)–C(11)	1.779(13)
S(2)–P(2)	1.972(4)	P(2)–C(13)	1.861(13)
P(1)–P(2)	2.215(6)	P(2)–C(15)	1.793(13)
P(1)–C(9)	1.779(17)		
C(1)–C(2)	1.396(15)	C(4)–C(5)	1.522(15)
C(1)–C(8)	1.527(17)	C(5)–C(6)	1.387(15)
C(2)–C(3)	1.499(14)	C(6)–C(7)	1.526(16)
C(3)–C(4)	1.544(15)	C(7)–C(8)	1.505(15)
S(1)–Rh–S(2)	97.5(1)	S(2)–Rh–M(1) [a]	169.0(3)
S(1)–Rh–M(1) [a]	89.4(2)	S(2)–Rh–M(2) [a]	87.4(2)
S(1)–Rh–M(2) [a]	168.1(2)	M(1)–Rh–M(2) [a]	87.5(3)
Rh–S(1)–P(1)	105.1(2)	Rh–S(2)–P(2)	108.7(2)
S(1)–P(1)–P(2)	106.4(2)	S(2)–P(2)–P(1)	103.4(2)
S(1)–P(1)–C(9)	113.8(6)	S(2)–P(2)–C(13)	107.2(5)
S(1)–P(1)–C(11)	113.8(4)	S(2)–P(2)–C(15)	115.3(4)
P(2)–P(1)–C(9)	106.9(6)	P(1)–P(2)–C(13)	113.8(5)
P(2)–P(1)–C(11)	104.0(4)	P(1)–P(2)–C(15)	109.9(4)
C(9)–P(1)–C(11)	111.0(7)	C(13)–P(2)–C(15)	107.5(6)
C(2)–C(1)–C(8)	125.0(9)	C(4)–C(5)–C(6)	126.7(10)
C(1)–C(2)–C(3)	123.7(10)	C(5)–C(6)–C(7)	123.7(10)
C(2)–C(3)–C(4)	112.2(8)	C(6)–C(7)–C(8)	112.9(10)
C(3)–C(4)–C(5)	112.3(9)	C(1)–C(8)–C(7)	113.6(10)

[a] M(1) and M(2) represent the midpoints of the C(1)–C(2) and C(5)–C(6) olefin double bonds.

crystallographic imposed symmetry, but shows a pseudo-C_2 symmetry with the two-fold axis passing through the Rh atom and the midpoint of the P(1) and P(2) bond.

The Rh–S bond lengths in **1** (av. 2.375[4] Å) are very similar to those in the closely related binuclear complexes $[Rh_2(\mu\text{-}SPPh_2)_2(COD)_2]$ (av. 2.361(3) Å) [4], or $[Rh_2(\mu\text{-}SPPh_2)(\mu\text{-}Cl)(COD)_2]$ (av. 2.370(2) Å) [6], in which the anionic group $SPPh_2^-$ is bonded as a bridging ligand through S and P atoms. Another comparable Rh–S bond distance, 2.364(3) Å, was observed for the dicarbonylated complex $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4$, which also contains a bidentate S–S donor ligand [15]. These values are in the long side of the range of bond lengths usually associated with square-planar rhodium(I)-thiolate or -thioether complexes [16].

The possible presence of a partial multiple bond component in the Rh–S bond by back-bonding from the appropriate d_π orbital of the Rh^I centre to an empty sulphur *d* orbital must be ruled out in **1** in the light of the long Rh–S distances observed. In addition, the average value for the Rh–S–P angle, close to tetrahedral (av. 106.8(2)°), indicates formal sp^3 hybridization for sulphur, as reported for the related copper compound $[Cu(SPMe_3)_3]$ [3]. These facts support the suggestion that the phosphine sulphides can be regarded as moderate σ-donor ligands with minimal π-acceptor properties [2].

The P–S bond distances observed (av. 1987(3) Å) are intermediate between those associated with a formal single P–S bond (2.122(1) Å) [17] and the range found for double P=S bonds (1.926–1.966(2) Å) [18], and agree well with the value reported for $[Cu(SPMe_3)_3]$, (av. 1.994(17) Å) [3]. The lengthening of the P–S bond upon coordination from the value observed in the free ligand (av. 1.94(1) Å) [19] is probably due to the lower electronic density available at the sulphur atom after its coordination to the metal centre, and is reflected in the decrease in the (P–S) IR band found in the region 550–520 cm^{-1} (see Table 1).

On the other hand, no significant change is observed for the P–P bond separation (2.215(6) Å) when compared with the value reported for the free tetraethylphosphine disulphide, $Et_2P(S)(S)PEt_2$, 2.22(1) Å [19]. Probably this bond is too far away from the metal to suffer any appreciable modification upon coordination.

The Rh–C bond distances (2.12–2.15 Å) are quite normal when compared with those for other rhodium(I) complexes containing the COD ligand *trans* to S atoms, as in $[Rh_2(\mu\text{-}SPPh_2)_2(COD)_2]$ (av. 2.131(4) Å) [4]. Both coordinated double bonds, C(1)–C(2) and C(5)–C(6), have lengths, 1.396(15) and 1.387(15) Å, greater than those in the free COD molecule (1.34 Å) [20], as expected.

Rhodium(I) carbonyl complexes

Bubbling of carbon monoxide at room temperature through dichloromethane solutions of $[M(COD)L_2]ClO_4$ complexes (M = Rh, Ir; L = $SPMe_3$, $SPPh_3$ (**5–8**); M = Rh, L_2 = $R_2P(S)(S)PR_2$ where R = Me, Et (**9**, **10**) complexes gave the corresponding carbonylated species. Yellow solids were isolated by adding diethyl ether. The solid state and solution IR spectra, show two ν(CO) bands in the 2100–2000 cm^{-1} region, characteristic of *cis*-dicarbonylrhodium(I) complexes [21]. However, for M = Rh, L_2 = $Ph_2P(S)(S)PPh_2$; M = Ir, L_2 = $R_2P(S)(S)PR_2$ where R = Et, Ph, the IR spectra of chloroform solutions of the complexes show three or four (CO) bands in the 2150–1950 cm^{-1} region. Several previously reported tetracarbonylated dinuclear Rh^I and Ir^I compounds exhibit similar CO stretching frequencies in

Table 4

Analytical results, conductivity data and IR data for carbonyl complexes

Complex	Elemental analysis (found (calc) (%))		Conductivity data		IR data [c] ν(CO) (cm^{-1})
	C	H	Λ_M [a]	A [b]	
$[Rh(CO)_2(SPPh_3)_2]ClO_4$ (**5**)	53.4 (53.8)	4.0 (3.6)	148	–	2075s, 2018s
$[Rh(CO)_2(SPMe_3)_2]ClO_4$ (**6**)	20.4 (20.3)	3.7 (3.7)	140	–	2080s, 2010s
$[Ir(CO)_2(SPPh_3)_2]ClO_4$ (**7**)	47.8 (48.8)	3.5 (3.2)	150	–	2070s, 2010s
$[Ir(CO)_2(SPMe_3)_2]ClO_4$ (**8**)	17.0 (17.1)	3.7 (3.2)	143	–	2055s, 2000s
$[Rh(CO)_2(Me_2P(S)(S)PMe_2)]ClO_4$ (**9**)	16.2 (16.2)	3.4 (3.7)	–	–	2080s, 2020s
$[Rh(CO)_2(Et_2P(S)(S)PEt_2)]ClO_4$ (**10**)	24.4 (24.0)	4.5 (4.0)	131	546	2090s, 2030s
$[Ir(CO)_2(Et_2P(S)(S)PEt_2)]_2(ClO_4)_2$ (**11**)	21.6 (22.4)	4.0 (3.8)	248	1100	2074s, 2061s, 2009s, 1994sh
$[Ir(CO)_2(Ph_2P(S)(S)PPh_2)]_2(ClO_4)_2$ (**12**)	39.4 (39.9)	3.6 (2.6)	173	1287	2156s, 2125s, 2090sh, 2055s

[a] Measured in acetone solution (Ω^{-1} cm^2 mol^{-1}). [b] Slope found for Onsager's equation $\Lambda_e = \Lambda_0 - A\sqrt{c_e}$. [c] Measured in chloroform solution.

solution [22,23]. The carbonyl complexes with $SPEt_3$ when M = Rh, Ir, with $Ph_2P(S)(S)PPh_2$ when M = Rh and with $Me_2P(S)(S)Me_2$ when M = Ir, can be detected by IR spectroscopy in solution, but they are not stable enough to be isolated and characterized as pure solids.

Measurements of the equivalent conductivities of the tetracarbonylated complexes in acetone solution at various concentrations gave slopes for the Onsager's equation characteristic of 2 : 1 electrolytes (Table 4). The complexes can be formulated as $[(CO)_2Ir\{\mu\text{-}(L\text{–}L)\}_2Ir(CO)_2](ClO_4)_2$, in accord with the dinuclearity proposed for the corresponding diolefinic compounds.

The ^{31}P NMR spectrum of $[Rh(CO)_2(Et_2P(S)(S)PEt_2)]ClO_4$ in $CDCl_3$ solutions shows a single resonance, $\delta = 79.5$ ppm, indicating equivalence of the two phosphorus atoms in the coordinated bidentate ligand (Table 2).

Oxidative additions to iridium complexes

Several attempts were made to bring about oxidative addition of ICH_3, HCHO, and I_2 to the iridium complexes, but only the oxidative addition of I_2 to the previously reported iridium complex $[Ir(COD)(SPMe_3)_2]ClO_4$ [1] and $[(COD)Ir\{\mu\text{-}(L\text{–}L)\}_2Ir(COD)](ClO_4)_2$ (L–L = $Et_2P(S)(S)PEt_2$) gave the corresponding Ir^{III} mono- and di-nuclear compounds. These complexes show a band due to (Ir–I) in the region 280–350 cm^{-1}, as usually observed when two I atoms are mutually *trans* [24].

Catalytic activity

We have previously described [1] that ethanol solutions of $[Rh(diolefin)(Ph_3PS)_2]ClO_4$ (diolefin = COD, NBD) and dichloromethane solutions of $[Ir(COD)(Ph_3\text{-}$

$PS)_2]ClO_4$ behave as catalyst precursors in the hydrogenation of 1-heptene and shown that the Ir^1 complexes have higher activities than the corresponding Rh^I complexes.

In the present study we examined the use of $[Ir(COD)(Me_3PS)_2]ClO_4$ [1] as a catalyst precursor in hydrogenation of 1-heptene. Dichloromethane solutions of this complex at 25 °C under 1 atm. of hydrogen, with catalyst/1-heptene molar ratio of 1/100, were not catalytically active for the hydrogenation of 1-heptene, but in the presence of an excess of the Me_3PS (Ligand/Rh = 5/1) the solutions became active; 64% of 1-heptene was converted and 51% of heptene was obtained in 12 h. The complexes containing phosphine disulphide ligands $R_2P(S)(S)PR_2$ showed no catalytic activity in hydrogenation of 1-heptene under these conditions.

It seemed of interest to look for catalytic activity of the complexes in hydroformylation of olefins at low pressure and low temperature (5 atm., 80 °C). Dichloroethane solutions of the complexes $[Rh(COD)L_2]ClO_4$ (L = Me_3PS, Ph_3PS, Et_3PS) and $[Rh(COD)LL']ClO_4$ (L' = PPh_3) (prepared as in reference [1]) were used under these mild conditions, with a catalyst/1-heptene molar ratio of 1/400. No hydroformylation was observed, but the hydrogenation product, heptane, was found at the end of the reaction in the case of $[Rh(COD)L_2]ClO_4$ (L = Ph_3PS and Me_3PS) and hydrogenation was complete (5 h) when $[Rh(COD)LL']ClO_4$, (L = Ph_3PS, Me_3PS and L' = PPh_3) was used. No decomposition to rhodium metal was observed.

Experimental

All preparations were carried out under nitrogen by Schlenk techniques. All the solvents were distilled and deoxygenated before use. The elemental analyses were carried out with a Perkin–Elmer 240 B microanalyzer. The IR spectra were recorded on a Nicolet 5ZDX-FT instrument using KBr pellets or dichloromethane solutions. Conductivities were measured in acetone or nitromethane solutions in the range ca. $1 \cdot 10^{-4}$–$5 \cdot 10^{-4}$ M, with a Philips PW9509 conductimeter. Values of A were determined from Onsager's equation $\Lambda_e = \Lambda_0 - A\sqrt{c_e}$, from measurements at several concentrations on acetone or nitromethane solutions in the 10^{-3}–10^{-5} M range. The ^{31}P spectra were recorded on an Bruker WP80 SY spectrometer with $CDCl_3$ as solvent and H_3PO_4 as internal reference. The starting materials were prepared as previously described [25–30]. $RhCl_3 \cdot xH_2O$ was obtained from Johnson Matthey and the phosphine sulphide ligands were purchased from Aldrich and Strem.

Catalytic activity experiments were performed in a conventional hydrogenation apparatus. The order of introduction of reactants into the hydrogenation flask was: 0.03 mmol of the catalyst precursor, 3 mmol of the substrate in 15 cm^3 of ethanol or dichloromethane, (freshly distilled and dried), and finally hydrogen. The mixture was stirred in a thermostat bath at 25 ° C. The hydrogenation rates were determined by analyzing the products with a Hewlett–Packard 5840A chromatograph. The peak areas were obtained with a Hewlett-Packard 5840A computing integrator.

Hydroformylation experiments were carried out in a 150 ml stainless steel magnetically stirred autoclave equipped with a glass inlet. The temperature was kept constant at 80 °C by circulating water through a double jacket. The mixture of Syngas (H_2/CO = 1) was introduced at a constant pressure of 5 bar from a gas reservoir. The fall of pressure in the reservoir was followed with a pressure transducer connected to electronic measuring and printing device. The dichloroethane solution of the catalyst precursors and the 1-hexene were introduced into the evacuated autoclave heated with stirring. When the system had reached thermal equilibrium the Syngas was introduced at 5 bar. After each run the solution was transferred from the autoclave and analyzed by IR spectroscopy and by GLC on a Hewlett-Packard 5840A chromatograph equipped with an OV-17 on Chromosorb W.H.P. 6 m × 1/8″ column.

Preparation of $[M(COD)(L-L)_n(ClO_4)_n$ complexes (1–4)

These compounds were prepared by adding an slight excess of ligand (0.085 mmol) to a dichloromethane solution of $[Rh(COD)_2]ClO_4$ (0.07 mmol). The yellow products which were formed immediately, were precipitated by addition of diethyl ether, filtered off, washed with diethyl ether, and vacuum dried.

Preparation of $[M(CO)_2(SPR_3)_2]ClO_4$ (5–8)

Carbon monoxide (1 atm) was bubbled at room temperature through a dichloromethane solution of $[M(COD)(SPR_3)_2]ClO_4$ (0.1 mmol) for 10 min, during which the colour of the solutions changed. Addition of diethyl ether precipitated the complexes, which were filtered off, washed with cold diethyl ether, and vacuum dried.

Preparation of $[Rh(CO)_2(R_2P(S)(S)PR_2)]ClO_4$ ($R = Me$, Et) and $[Ir(CO)_2(R_2P(S)(S)PR_2)]_2(ClO_4)_2$ ($R = Et$, Ph)

By bubbling of carbon monoxide (1 atm) at room temperature through a dichloromethane solution of $[Rh(COD)_2(R_2P(S)(S)PR_2)]ClO_4$ or $[Ir(COD)_2(R_2P(S)(S)PR_2)]_2(ClO_4)_2$ (0.1 mmol) for 15 min, and subsequent addition of diethyl ether gave the corresponding carbonyl complexes. The solids were filtered off, washed with ether, and vacuum dried.

Preparation of $[Ir(COD)(SPMe_3)(I)_2]ClO_4$ and $[Ir(COD)(Et_2P(S)(S)PEt_2)(I)_2]_2(ClO_4)_2$

$[Ir(COD)(SPMe_3)(I)_2]ClO_4$ (**13**) and $[Ir(COD)(Et_2P(S)(S)PEt_2)(I)_2]_2(ClO_4)_2$ (**14**) were prepared by adding slightly more than the stoichiometric amount (0.1 mmol) of iodine to a dichloromethane solution of $[Ir(COD)(SPMe_3)_2]ClO_4$ or $[Ir(COD)(Et_2P(S)(S)PEt_2)]_2(ClO_4)_2$ (0.08 mmol) prepared "in situ". The yellow solutions became brown after 15 min stirring. Addition of diethyl ether gave the corresponding diiodoiridium(III) complexes. The brown solids were filtered off, washed with diethyl ether, and vacuum dried. **13**: Elemental analysis, found (calc (%)) C, 19.0 (19.3); H, 3.0 (2.8); (Ir–I) 350 cm^{-1}. **14**: C, 20.0 (21.40); H, 3.5 (3.5); (Ir–I) 390 cm^{-1}.

X-Ray structure determination of $[Rh(COD)(Et_2P(S)(S)PEt_2)]ClO_4$

An irregular yellow block of dimensions ca. 0.27 × 0.33 × 0.34 mm was used for the data collection. Unit cell parameters were obtained by least-squares refinement of the values of 53 carefully centered reflections ($20 \leq 2\theta \leq 33°$). Two sets of intensity data were collected on a Stoe-Siemens AED-2 four circles diffractometer within the angular range $3 \leq 2\theta \leq 45°$ ($\omega/2\theta$ scan) using monochromated Mo-K_α radiation. From a total of 6767 measured reflections, averaging of equivalent reflection left 2972 unique reflections (R_{int} 0.025) of which 2539 with $F \geqslant 6\sigma(F)$ were used for the calculations. Two standard reflections were measured every 1 h and showed a slow but progressive loss of intensity ($\leqslant 9\%$); and the correction of this decay was based on this reflection. The structure amplitudes were obtained after the usual Lorentz and polarization corrections. An empirical absorption correction was applied [25]; minimum and maximum absorption corrections were 0.70 and 1.20.

Crystal data. $C_{16}H_{32}ClO_4P_2RhS_2$, M 552.85, monoclinic, space group $P2_1/c$, a 12.754(1), b 13.333(1), c 13.637(1) Å, β 95.30(1)°, U 2309 Å^3, $Z = 4$, D_x 1.59 g cm^{-3}, λ(Mo-K_α) 0.71069 Å, μ 11.73 cm^{-1}, $F(000)$ 1136.

The structure was solved by Patterson and Fourier methods. Refinement was carried out by full-matrix least squares using the SHELX system [32] with initially isotropic and subsequently anisotropic thermal parameters for all atoms except for the carbon atoms of the ethyl groups and the oxygen atoms of the perchlorate anion. Most of the hydrogens were located from a difference Fourier map and the rest were placed at their calculated positions; all were introduced in the final refinement using a riding model and a common isotropic thermal parameter. The function minimized in the least-squares calculations was $\Sigma\omega|\Delta F|^2$; the final

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for the non-hydrogen atoms of the complex [Rh(COD)(Et$_2$P(S)(S)PEt$_2$)](ClO$_4$) (1)

Atom	x	y	z	U_{eq} [a]
Rh	312(1)	2253(1)	1394(1)	481(3)
Cl	−4237(2)	3372(3)	−1578(2)	86(1)
S(1)	1141(2)	1244(2)	253(2)	73(1)
S(2)	1764(2)	3318(3)	1859(2)	79(1)
P(1)	2683(2)	1506(3)	544(2)	69(1)
P(2)	2842(2)	3116(3)	930(2)	73(1)
C(1)	−708(8)	1060(8)	1698(8)	60(4)
C(2)	−1152(7)	1556(7)	859(8)	57(4)
C(3)	−2080(8)	2246(7)	855(9)	67(5)
C(4)	−1745(8)	3351(9)	1018(10)	76(5)
C(5)	−716(8)	3451(7)	1671(8)	60(4)
C(6)	−449(8)	2962(8)	2557(8)	61(4)
C(7)	−1187(10)	2251(8)	3038(9)	79(5)
C(8)	−1069(10)	1176(8)	2729(9)	79(5)
O(1)	−4065(8)	3550(8)	−2570(9)	127(4) *
O(2)	−3495(9)	3835(9)	−922(9)	137(4) *
O(3)	−5266(10)	3501(11)	−1444(9)	150(5) *
O(4)	−4109(13)	2329(12)	−1408(13)	184(6) *
C(9)	3427(13)	1301(12)	−479(12)	108(5) *
C(10)	3349(14)	314(13)	−820(14)	133(6) *
C(11)	3260(10)	875(10)	1610(9)	90(4) *
C(12)	2871(14)	−150(14)	1756(14)	141(7) *
C(13)	4136(10)	3448(11)	1593(10)	95(4) *
C(14)	5043(13)	3408(13)	1037(13)	123(5) *
C(15)	2682(9)	3865(10)	−166(9)	92(4) *
C(16)	1613(11)	3834(12)	−721(11)	107(4) *

[a] Equivalent isotropic U_{eq} defined as one third of the orthogonalized U_{ij} tensor. For Rh atom is expressed in Å$^2 \times 10^4$. * For these atoms U_{iso} is given.

weighting scheme used was $\omega = K/[\sigma^2(F_0) + gF_0^2]$ with $K = 14.396$ and $g = 0.00011$. Final R and R_w values were 0.063 and 0.070. Maximal residual electron density 1.32 e/Å^3, close to P(2). Scattering factors, corrected for the anomalous dispersion of Rh, S, P and Cl atoms, were taken from ref. 33. Final atom coordinates for the non-hydrogen atoms are given in Table 5.

A complete list of bond lengths and angles, structure factors, and a table of H atom coordinates are available from the authors.

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