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Synthesis and characterization of rhodium complexes containing atropisomeric sulfur ligands. Structure of $[\{Rh_2(\mu\text{-}L)(CO)_3[P(OC_6H_4Bu^t\text{-}o)_3]\}_2]$ (H_2L = 1,1′-binaphthalene-2,2′-dithiol)

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The addition of the atropisomeric racemic sulfur compound 1,1′-binaphthalene-2,2′-dithiol (H_2L) to a dichloromethane solution of $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$ (cod = cycloocta-1,5-diene) afforded the dithiolate-bridged complexes $[\{Rh_2(\mu\text{-}L)(cod)_2\}_n]$ (n = 2 **1** or 1 **2**). These reacted with carbon monoxide to give the dinuclear tetracarbonyl complex $[Rh_2(\mu\text{-}L)(CO)_4]$ **3**. The reaction of **3** with PR_3 provided the mixed-ligand complexes $[\{Rh_2(\mu\text{-}L)(CO)_2(PR_3)_2\}_2]$ (R = Ph **4** or C_6H_{11} **5**) and $[\{Rh_2(\mu\text{-}L)(CO)_3(PR_3)\}_2]$ **6** [R = $P(OC_6H_4Bu^t\text{-}o)_3$]. The crystal structure of **6** was determined by X-ray diffraction.

Dinuclear thiolate-bridged rhodium complexes are efficient catalysts in the hydroformylation of olefins and other substrates under mild conditions.[1] They are also active hydrogenation catalysts.[2] Their chemistry has been studied in some detail in recent years and several papers dealing with their preparation, structure and reactivity have been published.[3] The catalytic properties of these complexes can be appropriately modulated by changing the nature of the bridging thiolate.[4] Furthermore, if a suitable ligand is chosen, in some cases the costly complex at the end of the hydroformylation reaction can be recovered and reused with no loss of reactivity.[4a]

Despite the high catalytic activity of dinuclear thiolate-bridged complexes in the hydroformylation reaction and the importance of the enantioselective homogeneous catalysis, the use of chiral sulfur derivatives in enantioselective catalysis promoted by transition-metal complexes is a research field which is largely unexplored. The potential of this type of compound has, up to the present, been little discussed.[5] However, some works related to its use in enantioselective catalysis have recently been reported.[6–9]

We were interested in using chiral dithiolate ligands to obtain new dinuclear rhodium complexes which could be catalyst precursors in the hydroformylation reaction. Dinuclear dithiolate-bridged rhodium complexes have hardly been studied at all.[10] We have recently described the synthesis of new complexes $[\{Rh_2[\mu\text{-}S(CH_2)_nS](cod)_2\}_x]$ (n = 2–4, x = 1 or 2; cod = cycloocta-1,5-diene) for which X-ray diffraction studies when n = 2 or 3 showed a bent dinuclear structure.[11] The reactivity of these diolefinic complexes towards carbon monoxide and carbon monoxide–PR_3 was also studied and $[\{Rh_2[\mu\text{-}S(CH_2)_nS](CO)_4\}_x]$ and $[\{Rh_2[\mu\text{-}S(CH_2)_nS](CO)_2(PR_3)_2\}_x]$ (n = 2–4, x = 1 or 2) were obtained by substitution of cod.[12] Likewise we have recently reported the preparation and catalytic activity of dinuclear rhodium complexes with the dithiolate chiral bridge (4*S*,5*S*)-(+)-2,2-dimethyl-1-thia-3-oxolane-4-methanethiol-5-methanol.[8]

As part of our research into rhodium–sulfur complexes and their catalytic chemistry[8,11–13] and in view of the present interest in atropisomeric binaphthyl derivatives,[14] we felt it would be of interest to explore the behaviour of atropisomeric sulfur derivatives. We have recently communicated[6] that dinuclear rhodium complexes with the atropisomeric chiral bridging ligand 1,1′-binaphthalene-2,2′-dithiol (H_2L) are highly active catalysts in the asymmetric hydroformylation of styrene and give a very high yield of the branched aldehyde although the enantiomeric excess is low. When cationic mononuclear rhodium complexes with the corresponding 2,2′-bis(methylsulfanyl) derivative as neutral ligand are used as the catalyst the yields are comparable and enantiomeric excesses slightly higher.

Pursuing our interest in this field we have researched more deeply into some aspects of the co-ordination chemistry of H_2L with rhodium and here we report the synthesis and characterization of some new complexes.

Results and Discussion

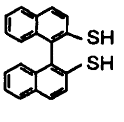
Preparation of the dithiolate complexes

Complexes $[\{Rh_2(\mu\text{-}L)(cod)_2\}_n]$ (n = 2 **1** or 1 **2**) were obtained by adding racemic H_2L to a dichloromethane solution of $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$. Adding methanol caused the precipitation of an orange solid (**1**) the microanalytical data of which match the $[\{Rh_2(\mu\text{-}L)(cod)_2\}_n]$ stoichiometry. Concentration and cooling of the remaining solution yielded a red complex **2** which corresponded to the same stoichiometry. Complexes **1** and **2** are non-electrolytes in acetone (conductivity 4–5 S cm^2 mol^{-1}) and their molecular weights, determined osmometrically in CH_2Cl_2 at 25 °C, indicate that **1** is tetranuclear and **2** is dinuclear. The molecular ion for **2** (m/z = 738) is the heaviest ion in the FAB mass spectra of both **1** and **2**, which suggests that **1** undergoes fragmentation. Attempts to obtain crystals suitable for an X-ray determination were unsuccessful.

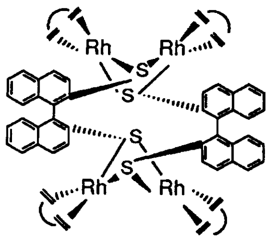
The ^1H NMR spectra of solutions of complexes **1** and **2** show the olefinic proton signals of the co-ordinated cyclooctadiene as two multiplets at δ 4.1 and 4.4. Owing to the bent structure[11] and to the nature of the dithiolate ligand, four non-equivalent sites are expected. However not all non-equivalences were resolved. The *endo*- and *exo*-methylene protons of cod show two multiplet signals at δ 1.7 and 2.2 respectively. The different

Table 1 Atomic coordinates (× 10^4) for complex **6**

Atom	*x*	*y*	*z*
Rh(1)	3671(1)	4751(1)	1741(1)
Rh(2)	4586(1)	6318(1)	1986(1)
P	3217(2)	4681(3)	1124(1)
O(10)	3150(4)	3552(6)	894(3)
C(10)	3243(4)	2524(6)	1050(3)
C(11)	2992(4)	2222(8)	1375(3)
C(12)	3104(4)	1210(9)	1552(3)
C(13)	3466(4)	500(6)	1405(3)
C(14)	3717(4)	802(8)	1080(3)
C(15)	3605(4)	1814(9)	902(3)
C(16)	3875(6)	2106(10)	555(5)
C(17)	4271(6)	3069(11)	613(5)
C(18)	4222(6)	1138(12)	414(4)
C(19)	3439(6)	2351(12)	179(4)
O(20)	3469(4)	5434(6)	812(3)
C(20)	3235(4)	5707(9)	425(2)
C(21)	2758(4)	5209(7)	232(3)
C(22)	2530(4)	5537(8)	−150(3)
C(23)	2779(4)	6362(8)	−340(2)
C(24)	3256(4)	6861(7)	−147(3)
C(25)	3484(4)	6533(8)	236(3)
C(26)	4011(7)	7065(11)	434(5)
C(27)	4493(6)	6267(11)	519(4)
C(28)	3938(7)	7688(11)	810(4)
C(29)	4236(7)	7927(12)	156(5)
O(30)	2592(3)	4961(6)	1079(2)
C(30)	2328(2)	5921(5)	1151(1)
C(31)	2722(2)	6720(4)	1266(1)
C(32)	2560(2)	7732(4)	1391(1)
C(33)	2004(2)	7944(4)	1400(1)
C(34)	1610(2)	7146(5)	1285(1)
C(35)	1771(2)	6134(5)	1160(1)
C(36)	1396(5)	5185(11)	1073(4)
C(37)	1440(6)	4641(11)	663(4)
C(38)	1499(6)	4308(10)	1392(4)
C(39)	778(5)	5521(12)	1034(5)
S(1)	5441(2)	4852(3)	3477(1)
C(40)	4515(1)	3708(3)	3101(1)
C(41)	5079(1)	3703(3)	3243(1)
C(42)	5383(2)	2752(4)	3231(1)
C(43)	5123(2)	1804(4)	3077(1)
C(44)	4558(2)	1809(3)	2935(1)
C(45)	4255(2)	2761(3)	2947(1)
C(46)	3690(2)	2766(2)	2804(1)
C(47)	3430(2)	1819(2)	2651(1)
C(48)	3734(2)	867(2)	2639(1)
C(49)	4298(2)	862(3)	2781(1)
S(2)	4256(2)	4914(3)	2350(1)
C(50)	4199(1)	4761(2)	3149(1)
C(51)	3997(1)	5309(2)	2798(1)
C(52)	3625(2)	6162(2)	2805(1)
C(53)	3455(2)	6467(2)	3162(1)
C(54)	3657(2)	5919(3)	3513(1)
C(55)	4029(2)	5066(3)	3507(1)
C(56)	4231(2)	4518(3)	3858(1)
C(57)	4061(2)	4823(4)	4215(1)
C(58)	3690(2)	5676(4)	4221(1)
C(59)	3488(2)	6224(3)	3871(1)
C(1)	3083(7)	4733(12)	1932(5)
O(1)	2662(5)	4693(10)	2100(4)
C(2)	4941(6)	7210(12)	1689(6)
O(2)	5210(5)	7767(10)	1505(4)
C(3)	4363(7)	7457(14)	2248(6)
O(3)	4228(6)	8236(10)	2402(4)



H_2L



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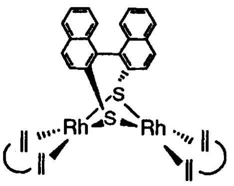

2

signals corresponding to the aromatic protons of the co-ordinated dithiolate can be seen at δ 6.5–7.9. Surprisingly, the ^1H NMR spectra of complexes **1** and **2** do not show differences, as would be expected according to the osmometric measurements.

Bubbling carbon monoxide through dichloromethane solutions of the diene complexes yields carbonyl complexes which are formed by displacing the diene. The elemental analyses match the stoichiometry $[\{Rh_2(\mu\text{-}L)(CO)_4\}_n]$ **3**. The molecular weight (686) was determined osmometrically and suggested that a dinuclear compound had been formed. Furthermore the Fourier-transform IR spectra in solution show three ν(CO) stretching frequencies which are characteristic of dinuclear tetracarbonylrhodium complexes as has been shown previously for this type of complex.[3,4,15]

The dinuclear tetracarbonyl $[Rh_2(\mu\text{-}L)(CO)_4]$ **3** reacts with PR_3 ligands, displacing the CO, giving rise to carbonyl phosphine complexes. In the case of R = Ph or C_6H_{11} the elemental analyses match the stoichiometries $[\{Rh_2(\mu\text{-}L)(CO)_2(PPh_3)_2\cdot 0.5CH_2Cl_2\}_n]$ and $[\{Rh_2(\mu\text{-}L)(CO)_2[P(C_6H_{11})_3]_2\}_n]$. The molecular weights, determined osmometrically in CH_2Cl_2 at 25 °C, show the tetranuclearity of both complexes $[\{Rh_2(\mu\text{-}L)(CO)_2(PPh_3)_2\}_2]\cdot CH_2Cl_2$ **4** (M = 2396) and $[\{Rh_2(\mu\text{-}L)(CO)_2[P(C_6H_{11})_3]_2\}_2]$ **5** (M = 2354).

The Fourier-transform IR spectrum of complex **4** in dichloromethane solution shows three ν(CO) signals at 2059m, 1990(sh) and 1979s cm^{-1}. The $^{31}P\text{-}\{^1H\}$ NMR spectrum in $CDCl_3$ shows a doublet at δ 46.8 [^1J(Rh–P) = 169.3 Hz] which suggests that the phosphorus ligands are in equivalent environments. In the case of **5** the IR spectrum in solution shows four signals, a strong one at 1943 cm^{-1} and three medium ones at 2055, 1991 and 1967 cm^{-1}. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows one doublet at δ 36.9 [^1J(Rh–P) = 117.9 Hz].

Addition of $P(OC_6H_4Bu^t\text{-}o)_3$ to a dichloromethane solution of complex **3** leads to the formation of a brown solid which was recrystallized and characterized as $[\{Rh_2(\mu\text{-}L)(CO)_3[P(OC_6H_4\text{-}Bu^t\text{-}o)_3]\}_2]$ **6**. The structure of this complex was unequivocally established by X-ray crystallography. It is tetranuclear and has C_2 symmetry in the crystal [Fig. 1(*a*)]. Fig. 1(*b*) shows the environments of the four rhodium atoms. Table 1 gives the atom coordinates and Table 2 the most significant intramolecular bond distances and angles. The Rh(1) environment has two sulfur atoms from two different thiolate L ligands (*cis*), S(2) and S(1^I) (I $-x + 1, y, -z + \frac{1}{2}$), one carbonyl group, C(1)–O(1), and the phosphorus atom from the $P(O\text{-}C_6H_4Bu^t\text{-}o)_3$. The co-ordination is approximately square planar [deviations (Å) from the weighted least-squares mean plane defined by the five atoms: Rh(1), −0.008(1); S(2), 0.038(4); S(1^I), −0.003(4); P, 0.042(4); C(1), 0.044(15)]. The main deviations from right angles are observed around the Rh(1)–S(2) bond (Table 2). The Rh(2) environment consists of the same two sulfur atoms bonded to Rh(1), S(2) and S(1^I) (*cis*), and two carbonyl groups,

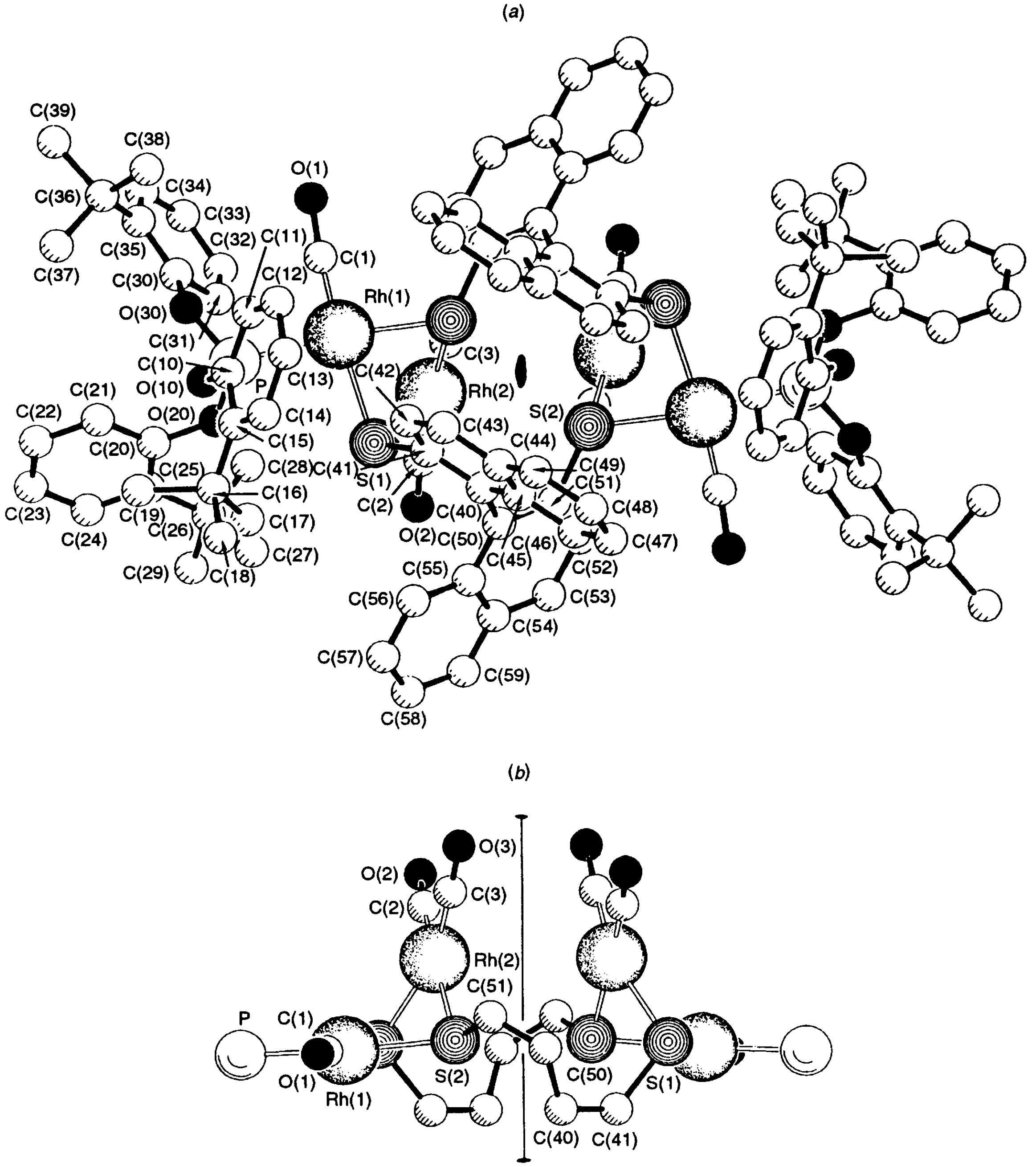

Fig. 1 (*a*) Molecular structure and (*b*) perspective view of $[\{Rh_2(\mu\text{-}L)(CO)_3[P(OC_6H_4Bu^t\text{-}o)_3]\}_2]$ **6** showing the environments of Rh(1) and Rh(2)

Table 2 Selected bond lengths (Å) and angles (°) for complex **6**

Rh(1)–C(1)	1.66(2)	Rh(2)–C(3)	1.79(2)
Rh(1)–P	2.213(4)	Rh(2)–C(2)	1.80(2)
Rh(1)–S(2)	2.333(4)	Rh(2)–S(2)	2.336(4)
Rh(1)–S(1^I)	2.400(4)	Rh(2)–S(1^I)	2.384(4)
Rh(1) ··· Rh(2)	2.973(2)	Rh(2) ··· Rh(2^I)	3.752(2)
C(1)–Rh(1)–P	91.6(5)	C(3)–Rh(2)–C(2)	90.5(8)
C(1)–Rh(1)–S(2)	96.1(5)	C(3)–Rh(2)–S(2)	99.3(6)
P–Rh(1)–S(2)	171.9(2)	C(2)–Rh(2)–S(2)	168.8(5)
C(1)–Rh(1)–S(1^I)	174.7(6)	C(3)–Rh(2)–S(1^I)	160.0(5)
P–Rh(1)–S(1^I)	93.4(2)	C(2)–Rh(2)–S(1^I)	93.5(5)
S(2)–Rh(1)–S(1^I)	78.8(1)	S(2)–Rh(2)–S(1^I)	79.1(1)
C(1)–Rh(1)–Rh(2)	123.9(5)	C(3)–Rh(2)–Rh(1)	111.9(6)
P–Rh(1)–Rh(2)	122.4(1)	C(2)–Rh(2)–Rh(1)	130.2(5)
S(2)–Rh(1)–Rh(2)	50.5(1)	S(2)–Rh(2)–Rh(1)	50.4(1)
S(1^I)–Rh(1)–Rh(2)	51.3(1)	S(1^I)–Rh(2)–Rh(1)	51.8(1)

Symmetry transformation used to generate equivalent atoms: I $-x + 1, y, -z + \frac{1}{2}$.

C(2)–O(2) and C(3)–O(3). The co-ordination is also approximately square planar although more distorted than for Rh(1) [deviations (Å) from the weighted least-squares mean plane defined by the five atoms: Rh(2), 0.003(1); S(2), 0.010(4); S(1^I), −0.018(4); C(2), 0.258(16); C(3), −0.594(18)]. The main deviations from right angles are observed around the Rh(2)–S(2) bond (Table 1). The angle between the Rh(1)–Rh(2) co-ordination planes is 71.8(2)°. In both planes the Rh–S(2) bond distance is shorter than Rh–S(1^I). The Rh(1) and Rh(1^I) co-ordination planes are almost coplanar [dihedral angle 8.7(2)°]. The Rh(2) and Rh(2^I) co-ordination planes are in the same semispace, the dihedral angle being 27.8(2)°. The Rh(1)–Rh(2) distance [2.973(2) Å] is slightly longer than in other dirhodium complexes which have bridging dithiolate ligands, $[Rh_2\{\mu\text{-}(S(CH_2)_2S\}(cod)_2]$ (Rh–Rh 2.876 Å) and $[Rh_2\{\mu\text{-}(S(CH_2)_3S\}(cod)_2]$ (Rh–Rh 2.896 Å).[11] This long distance is indicative of a very weak metal–metal interaction.[16] However, the distance Rh(2) ··· Rh(2^I) [3.752(2) Å] is much longer.

The infrared spectrum of a dichloromethane solution of complex **6** shows three ν(CO) stretching frequencies, 2077m, 2060s and 2007s cm^{-1}. The ^{31}P-{^{1}H} NMR spectrum in C_6D_6 shows one doublet δ 117.4 [^1J(Rh–P) = 272.9 Hz]. It should be pointed out that in this case only two of the CO ligands are substituted by a phosphorus ligand. In the other cases, where phosphines were used (R = Ph or C_6H_{11}), four carbonyl ligands were substituted.

Experimental

All rhodium complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. The complex [{Rh(μ-OMe)(cod)}$_2$] and 1,1′-binaphthalene-2,2′-dithiol were prepared using standard methods.[17,18] Phosphorus reactants were of commercial origin and used without further purification. Tris(*o-tert*-butylphenyl)phosphite was prepared as previously described.[19] All other reagents were commercial samples and were used as purchased. Infrared spectra (KBr pellets or solution) were obtained using a Nicolet 5ZDX spectrophotometer. Elemental analyses were performed on a Carlo Erba microanalyser. Proton and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrophotometer, chemical shifts being quoted in ppm downfield from internal $SiMe_4$, ^{31}P NMR spectra on the same equipment, using external H_3PO_4 as reference.

Preparations

[{Rh$_2$(μ-L)(cod)$_2$}$_n$] ***(n*** **= 2 1 or 1 2).** The compound H_2L (71.82 mg, 0.23 mmol) was added to a solution of [{Rh(μ-OMe)(cod)}$_2$] (100 mg, 0.21 mmol) in dichloromethane. The yellow solution became red. After stirring at room temperature for 10 min, methanol was added to give an orange precipitate of [{Rh$_2$(μ-L)(cod)$_2$}$_2$] **1** which was filtered off and dried *in vacuo* (80.6 mg, 53% yield) (Found: C, 58.3; H, 4.9; S, 8.4. Calc. for $C_{36}H_{36}Rh_2S_2$: C, 58.5; H, 4.9; S, 8.6%). NMR ($CDCl_3$): ^{1}H, δ 7.9 (d, 2 H, *J* = 8.7, aryl H), 7.8 (d, 2 H, *J* = 9, aryl H), 7.7 (d, 2 H, *J* = 9, aryl H), 7.3 (t, 2 H, *J* = 8.6, aryl H), 7.0 (t, 2 H, *J* = 8.7, aryl H), 6.5 (d, 2 H, *J* = 9 Hz, aryl H), 4.4 (br m, 4 H, CH of cod), 4.1 (br m, 4 H, CH of cod), 2.2 (br m, 8 H, CH_2 of cod) and 1.7 (br m, 8 H, CH_2 of cod); ^{13}C-{^{1}H}, δ 132.1, 128.0, 127.9, 126.0, 125.9, 125.8, 124.0 (aryl), 79.1 (CH of cod), 79.0 (CH of cod), 33.3 (CH_2 of cod) and 29.1 (CH_2 of cod). FAB mass spectrum: *m/z* 738, [*M*/2]$^+$; 629.9, [(*M*/2) − cod]$^+$ and 519.8 [(*M*/2) − 2 cod]$^+$. M_r 1476.6 (1610 by osmometry in CH_2Cl_2 at 25 °C).

After separating the orange complex the solvent of the resulting solution was evaporated under reduced pressure to 3 cm^3. After cooling the flask in ice the red product [Rh$_2$(μ-L)(cod)$_2$] **2** was obtained, filtered off, washed with methanol and vacuum dried (63.9 mg, 42% yield). M_r 738.3 (784 by osmometry in CH_2Cl_2 at 25 °C).

[Rh$_2$(μ-L)(CO)$_4$] 3. Carbon monoxide was bubbled through a solution of [{Rh$_2$(μ-L)(cod)$_2$}$_n$] [40 mg, 0.05 mmol (*n* = 1); 0.025 mmol (*n* = 2)] in dichloromethane for 10 min. The initial red solution darkened. Adding methanol gave a dark red precipitate which was filtered off, washed with methanol and dried *in vacuo* (26.8 mg, 78% yield) (Found: C, 45.4; H, 1.9; S, 10.1. Calc. for $C_{24}H_{12}O_4Rh_2S_2$: C, 45.4; H, 1.9; S, 10.1%). IR: (KBr) 2079s, 2059s and 2009s; (CH_2Cl_2) 2076s, 2059s and 2015s cm^{-1}. M_r 634.2 (686 by osmometry in CH_2Cl_2 at 25 °C).

[{Rh$_2$(μ-L)(CO)$_2$(PPh$_3$)$_2$}$_2$]·CH$_2$Cl$_2$ 4. Slightly more (10%) than the stoichiometric amount of triphenylphosphine (27.8 mg, 0.11 mmol) was added to a solution of [Rh$_2$(μ-L)(CO)$_4$] (30 mg, 0.05 mmol) in dichloromethane (5 cm^3). The resulting solution was stirred for 10 min, filtered and the filtrate reduced to 0.5 cm^3 under vacuum. Addition of methanol (5 cm^3) caused the precipitation of a brown solid which was filtered off, washed with cold methanol and dried under vacuum (45.5 mg, 87% yield) (Found: C, 61.6; H, 3.8; S, 5.9. Calc. for $C_{59}H_{44}Cl_2O_2P_2Rh_2S_2$: C, 61.3; H, 3.8; S, 5.6%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 46.8 [d, *J*(P–Rh) = 169.3 Hz]. IR: (KBr) 2057m and 1974s; (CH_2Cl_2) 2059m, 1990sh and 1979s cm^{-1}. M_r 2204.9 (2396 by osmometry in CH_2Cl_2 at 25 °C).

[{Rh$_2$(μ-L)(CO)$_2$[P(C$_6$H$_{11}$)$_3$]$_2$}$_2$] 5. Slightly more (10%) than the stoichiometric amount of tricyclohexylphosphine (29.2 mg, 0.11 mmol) was added to a solution of [Rh$_2$(μ-L)(CO)$_4$] (30 mg, 0.05 mmol) in dichloromethane (5 cm^3). The resulting solution was stirred for 20 min, filtered and the filtrate reduced to 0.5 cm^3 under vacuum. Addition of methanol (5 cm^3) caused the precipitation of a brown solid which was filtered off, washed with cold methanol and dried under vacuum (52.2 mg, 97% yield) (Found: C, 60.9; H, 7.1; S, 5.3. Calc. for $C_{58}H_{78}O_2P_2Rh_2S_2$: C, 61.2; H, 6.9; S, 5.6%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 36.9 [d, *J*(P–Rh) = 117.9 Hz]. IR: (KBr) 2055m, 1992m, 1967m and 1944s; (CH_2Cl_2) 2055m, 1991m, 1967m and 1943s cm^{-1}. M_r 2277.0 (2354 by osmometry in CH_2Cl_2 at 25 °C).

[{Rh$_2$(μ-L)(CO)$_3$[P(OC$_6$H$_4$Bu^t-*o*)$_3$]}$_2$] 6. Tris(*o-tert*-butylphenyl)phosphite (226.2 mg, 0.50 mmol) was added to a solution of [Rh$_2$(μ-L)(CO)$_4$] (30 mg, 0.05 mmol) in dichloromethane (5 cm^3) at a P:Rh ratio = 5:1. The resulting solution was stirred for 30 min, filtered and the filtrate reduced to 0.5 cm^3 under vacuum. Addition of methanol (5 cm^3) caused the precipitation of a brown solid which was filtered off, washed with cold methanol and dried under vacuum (22.7 mg, 44.2% yield). X-Ray-quality crystals were grown by slowly diffusing methanol into a CH_2Cl_2 solution (Found: C, 58.8; H, 4.7; S, 5.9. Calc. for $C_{53}H_{51}O_6PRh_2S_2$: C, 58.7; H, 4.7; S, 5.9%). ^{31}P-{^{1}H} NMR (C_6D_6): δ 117.4 [d, *J*(P–Rh) = 272.9 Hz]. IR (CH_2Cl_2): 2077m, 2060s and 2007s cm^{-1}.

Crystallography

Suitable crystals of complex **6** were grown by slowly diffusing methanol into a methylene chloride solution.

Crystal data. $C_{106}H_{102}O_{12}P_2Rh_4S_4$, *M* = 2169.70, monoclinic, space group *C*2/*c* (no. 15), *a* = 24.45(2), *b* = 12.294(9), *c* = 33.881(7) Å, β = 98.76(4)°, *U* = 10 066(11) Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), *Z* = 4, D_c = 1.432 g cm^{-3}. Brown, air-stable crystals, μ(Mo-Kα) = 8.18 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω–2θ mode with ω scan width = 0.80 + 0.35tan θ, ω-scan speed 1.3–5.5° min^{-1}, graphite-monochromated Mo-Kα radiation. 9590 Reflections measured (1 < θ < 25°, ±*h*, +*k*, +*l*), 8852 unique (Lorentz polarization and empirical absorption correction from ψ scans,[20] minimum, maximum transmission = 0.483, 0.999), 1918 with $I > 2\sigma(I)$.

Structure analysis and refinement. Direct methods (SHELXS 86 program).[21] Full-matrix least-squares refinement on F^2 for all reflections (SHELXL 93 program).[22] Naphthyl and phenyl groups were refined as rigid groups and all the P(OC$_6$H$_4$Bu^t-*o*)$_3$ ligand with restrained geometry. A carbonyl ligand was refined isotropically. The rest of the non-hydrogen atoms were refined anisotropically but similarity restrictions were applied to the phenyl and naphthyl thermal parameters. Hydrogens were placed in calculated positions with isotropic thermal parameters fixed at $1.5U_{eq}$ of the corresponding carbon atoms. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0846P)^2]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Final *R*(*F*) and *wR*(F^2) values were 0.0775 and 0.1663 for reflections with $I > 2\sigma(I)$.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge

Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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