Stereoselective Oxidative-addition Reaction of Molecular Iodine and Mercury(II) Halides to Rhodium Dithiolate Compounds. Crystal Structure of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$†

Anabel Elduque,[a] **Luis A. Oro,***[,a] **M. Teresa Pinillos,**[a] **Antonio Tiripicchio**[b] **and Franco Ugozzoli**[b]

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, E-50009 Zaragoza, Spain*

[b] *Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy*

The binuclear complexes $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(L_2)_2]$ [L_2 = cycloocta-1,5-diene (cod) **1**, $L_2 = (CO)_2$ **2**] and $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PR_3)_2]$ (R = Ph **3** or OPh **4**) have been prepared and oxidative addition of the electrophiles I_2 and HgX_2 (X = Cl or I) investigated. Compounds **3** and **4** undergo stepwise addition of molecular iodine to yield the symmetrical complexes $[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_n(CO)_2(PR_3)_2]$ [*n* = 2, R = Ph **5**, R = OPh **6**; *n* = 4, R = Ph **7**, R = OPh **8**]. However, interaction of **3** with HgX_2 (X = Cl or I) affords the unsymmetrical compounds $[Rh_2\{\mu\text{-}S(CH_2)_2S\}X_2(CO)_2(PPh_3)_2]$ (X = Cl **9** or I **10**). The crystal structure of **9** has been determined by X-ray diffraction methods.

The synthesis, structure and reactivity of binuclear metal complexes have attracted considerable interest in recent years.[1,2] Part of this interest has been stimulated by their potential use as models of co-operative effects between adjacent centres in heterogeneous catalytic reactions.[3,4] Of particular relevance is the reactivity of binuclear complexes in oxidative-addition reactions, systems containing $M_2(\mu\text{-pz})_2$[5-7] (pz = pyrazolate), $M_2(\mu\text{-pz})(\mu\text{-SR})$,[8-10] $M_2(\mu\text{-SR})_2$[11,12] (M = Rh or Ir) and $Ir_2(\mu\text{-}C_5H_4NS)_2$[13] moieties being the subject of detailed investigations.

Many reactions of divalent mercury compounds with mononuclear d^8 transition-metal complexes have been reported. However, related chemistry involving binuclear transition-metal compounds has been scarcely explored.[14,15] In this area we have studied the reaction of mercury(II) chloride with the binuclear dirhodium compound $[Rh_2(\mu\text{-pz})_2(CO)_2(PPh_3)_2]$. The reaction can be interpreted as resulting from the oxidative addition of $HgCl_2$ to one rhodium centre and simultaneous Lewis acid–base bond formation between the mercury and the other rhodium centre.[16] A similar situation has been found for $[Rh_2(\mu\text{-pz})(\mu\text{-SBu}^t)(\mu\text{-HgCl})Cl(CO)_2(PPh_3)_2]$. In this compound the individual rhodium centres are joined by one exobidentate pyrazolate ligand and one SBu^t group.[17]

The present investigation was undertaken in order to explore the use of the dianionic sulfur donor ethane-1,2-dithiolate as a bridging ligand. We have also carried out a study of the oxidative addition of I_2 and HgX_2 (X = Cl or I) to $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$. Two geometrical isomers of the compound $[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_2(CO)_2(PPh_3)_2]$ have been isolated.

Results and Discussion

The reaction of the monomeric rhodium(I) compound [Rh(acac)(cod)] (acac = acetylacetonate, cod = cycloocta-1,5-diene) with 1,2-ethanedithiol, in a 2:1 molar ratio, affords the binuclear rhodium(I) complex $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(cod)_2]$ **1** which has been fully characterised by spectroscopic data (see Experimental section).

Bubbling carbon monoxide through a dichloromethane solution of complex **1** leads to displacement of the cycloocta-1,5-diene ligands and to the formation of the carbonyl derivative $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_4]$ **2** [ν(CO)(CH_2Cl_2): 2070, 2050, 2010 and 1980 cm^{-1}]. Interestingly in the solid state, this exhibits a very complex IR spectrum in the ν(CO) region. These spectra and the dark green colour of the complex could be indicative of the presence of intermolecular rhodium–rhodium interactions.[18]

As expected, addition of triphenylphosphine or triphenyl phosphite to dichloromethane suspensions of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_4]$ caused the evolution of carbon monoxide and formation of derivatives *cis*-$[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PR_3)_2]$ (R = Ph **3** or OPh **4**). The $^{31}P\text{-}\{^1H\}$ NMR spectra of these show the presence of one doublet corresponding to two equivalent phosphorus atoms coupled to the nearest rhodium centre (δ 38.4, J_{RhP} 156 **3**; δ 121.8, J_{RhP} 266 Hz **4**). Also, the presence of only one signal at 1970 (**3**) or 1997 cm^{-1} (**4**) is indicative of a *cis* disposition of the terminal ligands.[19]

Compounds **3** and **4** undergo stepwise addition of molecular iodine, yielding first $[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_2(CO)_2(PR_3)_2]$ (R = Ph **5** or OPh **6**) and, then, $[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_4(CO)_2(PR_3)_2]$ (R = Ph **7** or OPh **8**) all of them stable and brown. The increase of the formal oxidation number from I to II and then to III parallels the increase in the carbonyl stretching wavenumbers, from 1970 to 2025 and 2065 cm^{-1} when R = Ph, and from 1997 to 2050 and 2095 cm^{-1} when R = OPh.

The NMR spectra of complexes **5** and **6** indicate that only one of the possible isomers is produced in this reaction. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **5** shows a doublet at δ 30.1 (J_{RhP} = 117 Hz) arising from a symmetrical compound. Thus the reaction implies a one electron removal to each rhodium centre and on the basis of the above-mentioned data we propose for compound **5** the symmetrical structure shown. The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra of **6** are very similar to those of **5**. These spectroscopic data provide good evidence that complexes **5** and **6** have identical structures. The NMR spectra of compound **7**

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

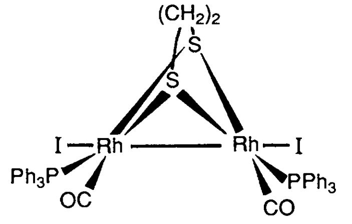

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Table 1 Bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **9**

Rh(1)–Rh(2)	2.648(2)	S(1)–C(3)	1.822(13)
Rh(1)–S(1)	2.317(3)	S(2)–C(4)	1.823(12)
Rh(1)–S(2)	2.296(4)	P(1)–C(5)	1.816(11)
Rh(1)–P(1)	2.345(3)	P(1)–C(11)	1.842(7)
Rh(1)–Cl(1)	2.399(4)	P(1)–C(17)	1.821(11)
Rh(1)–C(1)	1.935(10)	P(2)–C(23)	1.828(12)
Rh(2)–S(1)	2.350(2)	P(2)–C(29)	1.820(9)
Rh(2)–S(2)	2.350(3)	P(2)–C(35)	1.812(10)
Rh(2)–P(2)	2.314(2)	O(1)–C(1)	1.075(12)
Rh(2)–Cl(2)	2.432(4)	O(2)–C(2)	1.155(15)
Rh(2)–C(2)	1.868(11)	C(3)–C(4)	1.489(14)
Cl(1)–Rh(1)–C(1)	92.3(3)	Rh(1)–Rh(2)–S(1)	54.8(1)
P(1)–Rh(1)–C(1)	93.6(3)	Cl(2)–Rh(2)–C(2)	103.9(3)
P(1)–Rh(1)–Cl(1)	93.1(1)	P(2)–Rh(2)–C(2)	90.6(3)
S(2)–Rh(1)–C(1)	90.5(3)	P(2)–Rh(2)–Cl(2)	92.5(1)
S(2)–Rh(1)–Cl(1)	158.2(1)	S(2)–Rh(2)–Cl(2)	97.8(1)
S(2)–Rh(1)–P(1)	108.3(1)	S(2)–Rh(2)–P(2)	97.2(1)
S(1)–Rh(1)–Cl(1)	91.7(1)	S(1)–Rh(2)–C(2)	90.6(3)
S(1)–Rh(1)–P(1)	103.5(1)	S(1)–Rh(2)–Cl(2)	97.6(1)
S(1)–Rh(1)–S(2)	79.6(1)	S(1)–Rh(2)–S(2)	77.8(1)
Rh(2)–Rh(1)–C(1)	106.1(3)	Rh(1)–S(1)–Rh(2)	69.1(1)
Rh(2)–Rh(1)–Cl(1)	102.4(1)	Rh(2)–S(1)–C(3)	100.9(4)
Rh(2)–Rh(1)–S(2)	56.2(1)	Rh(1)–S(1)–C(3)	105.0(4)
Rh(2)–Rh(1)–S(1)	56.0(1)	Rh(1)–S(2)–Rh(2)	69.5(1)
Rh(1)–Rh(2)–C(2)	102.4(3)	Rh(2)–S(2)–C(4)	101.6(4)
Rh(1)–Rh(2)–P(2)	114.5(1)	Rh(1)–S(2)–C(4)	104.3(4)
Rh(1)–Rh(2)–S(2)	54.3(1)		

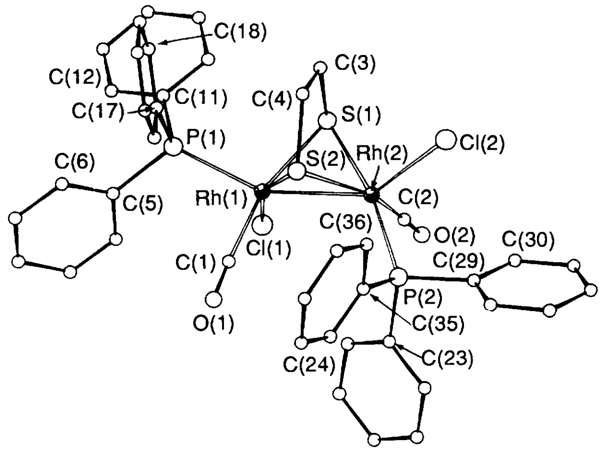

Fig. 1 Perspective view of the molecular structure of the complex $[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$ **9**, showing the atomic numbering scheme

show the presence of a small quantity of an isomer which has escaped isolation upon fractional crystallisation.

Reaction of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ *with Mercury*(II) *Halides.*—Addition of mercury(II) chloride (1 : 1 molar ratio) to a dichloromethane solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$, at room temperature, resulted in a change from yellow to red. Work-up of the resulting solution, as described in the Experimental section, gave the complex $[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$ **9** as a red solid. The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits one pair of doublets of doublets indicating an unsymmetrical structure. The doublet splitting of 120 or 124 Hz is due to rhodium–phosphorus coupling and that of 11 Hz could be assigned to phosphorus–phosphorus coupling. It is of interest that the two $^{103}Rh\text{–}^{31}P$ coupling constants have similar values within the range described for other rhodium(II) complexes.[6,17] The reaction between $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ and $HgCl_2$ indicates that the $HgCl_2$ can act as a two-electron oxidant. Use of 1 equivalent of $HgCl_2$ rapidly produced the dirhodium(II) derivative $[Rh_2\{\mu\text{-}S(CH_2)S\}_2Cl_2(CO)_2(PPh_3)_2]$ and metallic mercury when the reaction was carried out in dichloromethane.

Crystal Structure of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$ **9**.—The structure of complex **9** is shown in Fig. 1 together with the atomic numbering scheme; selected bond distances and angles are given in Table 1. In the unsymmetrical binuclear rhodium(II) complex each of the two sulfur atoms of the ethanedithiolate acts as a symmetrical bridge between the two metals [Rh(1)–S(1) 2.317(3) and Rh(2)–S(1) 2.350(2); Rh(1)–S(2) 2.296(4) and Rh(2)–S(2) 2.350(3) Å], which are at a distance of 2.648(2) Å, consistent with a metal–metal bond. The two Rh_2S bridges form a dihedral angle of 79.2(1)° and the S(1)···S(2) separation is 2.952(3) Å. Each metal is in a distorted-octahedral arrangement, involving the other Rh atom, two S atoms, one terminal Cl atom, one P atom from a PPh_3 ligand and one C atom from a terminal carbonyl group. The Rh(1)–P(1) bond distance [2.345(3) Å], *trans* to the Rh(1)–Rh(2) bond, is longer than Rh(2)–P(2) [2.314(2) Å], *trans* to Rh(2)–S(1), so the Rh(2)–Cl(2) bond distance [2.432(4) Å], *trans* to the Rh(1)–Rh(2) bond, is longer than Rh(1)–Cl(1) [2.399(4) Å], *trans* to Rh(1)–S(2). In the ethanedithiolate ligand the S–C [1.822(13) and 1.823(12) Å] and C–C [1.489(14) Å] bond distances are quite regular.*

Qualitative studies of oxidative-addition reactions of mercury(II) halides to binuclear transition-metal complexes indicated that the reactivity increases in the order $HgCl_2 > HgI_2$.[21] So we turned our attention to the reaction of HgI_2 with $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ in the hope that some intermediate species might be detected in solution. Upon addition of mercury(II) iodide to a solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ at −50 °C, in dichloromethane, reaction occurred immediately, as indicated by a change from yellow to violet. The intermediate compound formed displayed two doublets at δ 34.2 (J_{RhP} = 114) and 19.7 (J_{RhP} = 136 Hz) indicating that it is unsymmetrical having chemically different phosphorus environments. We propose structure **b**, Scheme 1, to rationalise the spectra. This structure corresponds to the oxidative addition of HgI_2 to a single metal centre in the binuclear starting complex. After 45 min of reaction, precipitation of metal mercury was observed. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the resulting compound **10** shows two doublets of doublets at δ 36.3 (J_{RhP} = 123, $^3J_{PP}$ = 11) and at 17.4 (J_{RhP} = 124, $^3J_{PP}$ = 11 Hz). The rhodium coupling constants are in the range corresponding to other rhodium(II) complexes and are similar to that found for the symmetrical isomer **5**. The spectroscopic data indicated that complexes **9** and **10** have identical structures. Furthermore, it is worth noting that there is no evidence for the isomerisation of the binuclear rhodium(II) complexes **5** and **10** in solution. Their spectra are invariant over the range +25 to −50 °C.

The spectroscopic data provide the basis for a consistent interpretation of the reaction involving $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ and mercury(II) halides as shown in Scheme 1. The first step is the formation of a violet rhodium(III)–

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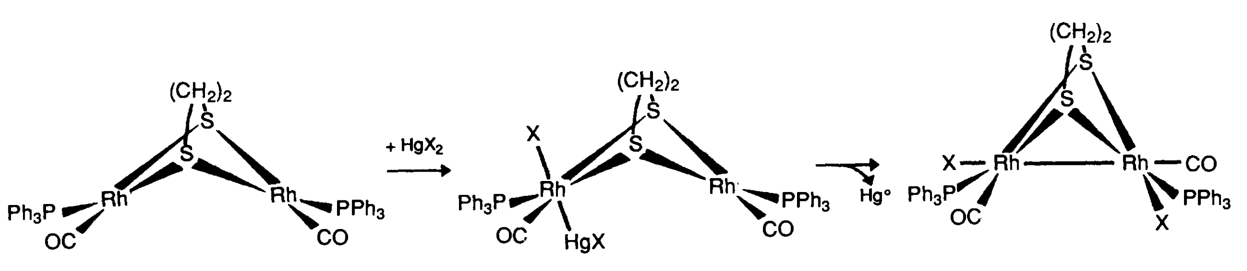
* *Note added at proof.* The preparation and crystal structure of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(cod)_2]$ has been independently reported by Claver and co-workers.[20]



a

b

X = Cl or I

c

	X
9	Cl
10	I

Scheme 1

rhodium(I) mercury-bonded species, resulting from the oxidative addition of the HgI and I fragments to the same rhodium centre of the starting compound $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ **3**. The second step would be the precipitation of metal mercury, migration of one iodide ligand to the rhodium(I) centre and consequent formation of a rhodium(II)–rhodium(II) bond leading to compound **10**. Such HgX transfer yielding metals in the same oxidation state appears to be promoted in related binuclear systems in which the bridging groups favour a compression of the metal–metal interaction.[22]

In conclusion, the addition of iodine to binuclear complexes containing ethane-1,2-dithiolate leads to symmetrical dirhodium(II) and dirhodium(III) compounds. However, the addition of mercury(II) salts gives unsymmetrical halogenated dirhodium(II) derivatives. Formation of a $Rh^{III}\text{–}Hg\cdots Rh^{I}$ intermediate has been proposed in the former reactions.

Experimental

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer, ^1H and ^{31}P NMR in $CDCl_3$ solution at room temperature on a Varian XL 200 spectrometer. The ^1H chemical shifts were reported with respect to $SiMe_4$ and the ^{31}P shifts to external 85% H_3PO_4, without correction for susceptibility. All preparations were carried out under nitrogen on a vacuum line using Schlenk techniques. Solvents were purified by standard methods prior to use. The reactants were of commercial origin and used without further purification. The complex [Rh(acac)(cod)] was prepared according to literature methods.[23]

Preparation of the Complexes.—$[Rh_2\{\mu\text{-}S(CH_2)_2S\}(cod)_2]$ **1**. Ethane-1,2-dithiol (13.52 μl, 0.16 mmol) was added to a solution of [Rh(acac)(cod)] (100 mg, 0.32 mmol) in dichloromethane (20 cm^3). The colour changed from yellow to orange. The reaction was continued for 20 min to afford a red suspension. Then the solvent was evaporated under reduced pressure to 1 cm^3. Addition of hexane (15 cm^3) gave a red solid which was filtered off, washed with hexane and dried under vacuum (yield 82%) (Found: C, 42.1; H, 5.9. Calc. for $C_{18}H_{28}Rh_2S_2$: C, 42.0; H, 5.5%). ^1H NMR($CDCl_3$): δ 2.35 [m, H_2C, cod, $S(CH_2)_2S$], 2.57 [m, H_2C, cod, $S(CH_2)_2S$], 4.29 (s, HC=, cod) and 4.62 (s, HC=, cod).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_4]$ **2**. Carbon monoxide was bubbled through a solution of complex **1** (100 mg, 0.19 mmol) in dichloromethane (15 cm^3), during 15 min, to give a dark red suspension. Evaporation of the solvent to dryness and addition of hexane (12 cm^3) caused the precipitation of a dark green solid which was filtered off, washed with hexane and vacuum dried (yield 75%) (Found: C, 17.5; H, 1.0. Calc. for $C_6H_4O_4Rh_2S_2$: C, 17.5; H, 0.9%). IR(CH_2Cl_2): 2070, 2050, 2010 and 1980 cm^{-1} [ν(CO)]. ^1H NMR($CDCl_3$): δ 2.17 [s, $S(CH_2)_2S$].

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ **3**. A stoichiometric amount of solid triphenylphosphine (101 mg, 0.38 mmol) was added to a suspension of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_4]$ **2** (78 mg, 0.19 mmol) in dichloromethane (15 cm^3) and the resulting yellow solution was stirred for 15 min. Concentration of the solvent to 2 cm^3 and addition of diethyl ether (2 cm^3) and then hexane (10 cm^3) gave an orange solid which was filtered off, washed with hexane and dried under vacuum (yield 70%) (Found: C, 54.5; H, 4.1. Calc. for $C_{40}H_{34}O_2P_2Rh_2S_2$: C, 54.6; H, 3.9%). IR($CH_2Cl_2$): 1970 (br) cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.73 [br, $S(CH_2)_2S$], 7.39 (m, PPh_3) and 7.68 (m, PPh_3); $^{31}P\text{-}\{^1H\}$, δ 38.4 (d, J_{RhP} 156 Hz).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2\{P(OPh)_3\}_2]$ **4**. Addition of triphenylphosphite (191.6 μl, 0.73 mmol) to a suspension of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_4]$ **2** (147 mg, 0.36 mmol) in dichloromethane (15 cm^3) caused evolution of carbon monoxide. The resulting yellow solution was evaporated to *ca.* 1 cm^3 and hexane (10 cm^3) was added to give a yellow solid which was filtered off, washed with hexane and vacuum dried (yield 75%) (Found: C, 41.9; H, 3.7. Calc. for $C_{40}H_{34}O_8P_2Rh_2S_2$: C, 42.2; H, 3.5%). IR($CH_2Cl_2$): 1997 cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.38 [br, $S(CH_2)_2S$] and 7.30 [s, $P(OPh)_3$]; $^{31}P\text{-}\{^1H\}$, δ 121.8 (d, J_{RhP} 266 Hz).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_2(CO)_2(PPh_3)_2]$ **5**. To a solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ **3** (100 mg, 0.11 mmol) in dichloromethane (15 cm^3) was added the stoichiometric amount of molecular iodine (28.8 mg, 0.11 mmol). After stirring for 1 h, at room temperature, the solution changed from yellow to brown. Then the solvent was evaporated to 2 cm^3 and hexane (10 cm^3) was added to give a dark brown solid which was filtered off, washed with hexane and dried under vacuum (yield 80%) (Found: C, 42.1; H, 2.9. Calc. for $C_{40}H_{34}I_2O_2P_2Rh_2S_2$: C, 42.4; H, 3.0%). IR($CH_2Cl_2$): 2025 cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.28 [br, $S(CH_2)_2S$] and 7.56 (m, PPh_3); $^{31}P\text{-}\{^1H\}$, δ 30.1 (d, J_{RhP} 117 Hz).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}_2I_2(CO)_2\{P(OPh)_3\}_2]$ **6**. Iodine (26.1 mg, 0.10 mmol) was added to a solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2\{P(OPh)_3\}_2]$ **4** (100 mg, 0.10 mmol) in dichloromethane (20 cm^3). The resulting brown solution was stirred at room temperature. After 5 h the IR spectra revealed the absence of starting material. Concentration of the solvent (2 cm^3) and addition of hexane (10 cm^3) gave a brown solid which was filtered off, washed with hexane and dried under vacuum (yield 70%) (Found: C, 38.9; H, 2.7. Calc. for $C_{40}H_{34}I_2O_8P_2Rh_2S_2$: C, 39.1; H, 2.8%). IR($CH_2Cl_2$): 2050 cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.34 [br, $S(CH_2)_2S$] and 7.42 [m, $P(OPh)_3$]; $^{31}P\text{-}\{^1H\}$, δ 99.9 (dd, J_{RhP} 174, J_{PP} 8 Hz).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_4(CO)_2(PPh_3)_2]$ **7**. To a solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ **3** (100 mg, 0.11 mmol) in dichloromethane (15 cm^3) was added the stoichiometric amount of molecular iodine (28.8 mg, 0.11 mmol) to give after 1 h of stirring complex **5** and after 3 d the complex **10** (monitored by IR spectroscopy). The resulting brown solution was concentrated (1 cm^3) and addition of diethyl ether (2 cm^3) and

Table 2 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of complex **9**

Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	2037(1)	1200(1)	2362(1)
Rh(2)	2245(1)	−666(1)	3325(1)
S(1)	908(1)	813(2)	4062(2)
S(2)	1937(2)	−57(2)	1094(2)
P(1)	1228(2)	2801(2)	1534(2)
P(2)	3683(1)	−1908(2)	2378(2)
Cl(1)	2365(2)	1955(2)	4208(3)
Cl(2)	1518(2)	−1913(2)	3693(3)
O(1)	3831(5)	921(7)	184(10)
O(2)	2684(7)	−542(7)	6164(9)
C(1)	3188(7)	1071(7)	986(11)
C(2)	2525(7)	−628(7)	5085(10)
C(3)	197(6)	630(8)	3016(12)
C(4)	712(7)	230(7)	1501(11)
C(5)	1924(6)	3522(7)	633(9)
C(6)	1789(7)	4072(7)	−603(10)
C(7)	2274(7)	4663(8)	−1213(12)
C(8)	2882(8)	4775(8)	−560(14)
C(9)	3027(8)	4243(9)	667(15)
C(10)	2564(7)	3625(8)	1254(11)
C(11)	278(6)	3757(6)	2846(9)
C(12)	91(6)	4784(7)	2688(10)
C(13)	−665(7)	5505(7)	3621(11)
C(14)	−1253(7)	5171(8)	4693(12)
C(15)	−1072(7)	4150(8)	4829(12)
C(16)	−304(7)	3431(7)	3928(11)
C(17)	731(6)	2618(6)	135(9)
C(18)	−207(7)	3012(8)	281(12)
C(19)	−534(8)	2799(10)	−792(14)
C(20)	64(10)	2194(10)	−2009(13)
C(21)	991(8)	1800(8)	−2172(10)
C(22)	1320(7)	2006(7)	−1101(10)
C(23)	4631(6)	−1701(7)	2787(9)
C(24)	4545(7)	−718(7)	3056(11)
C(25)	5256(8)	−537(9)	3353(12)
C(26)	6041(7)	−1347(10)	3443(12)
C(27)	6109(8)	−2339(10)	3251(14)
C(28)	5413(7)	−2512(8)	2901(13)
C(29)	3833(6)	−3197(6)	3018(10)
C(30)	3475(8)	−3335(8)	4463(11)
C(31)	3632(10)	−4300(10)	4997(15)
C(32)	4142(10)	−5167(9)	4087(18)
C(33)	4507(9)	−5027(8)	2653(15)
C(34)	4348(7)	−4037(7)	2115(12)
C(35)	3985(6)	−2084(7)	418(10)
C(36)	3388(7)	−2316(7)	−212(11)
C(37)	3578(9)	−2403(8)	−1703(13)
C(38)	4345(10)	−2274(9)	−2609(12)
C(39)	4929(10)	−2074(9)	−2024(12)
C(40)	4745(7)	−1954(0)	−498(10)

hexane (10 cm^3) caused the precipitation of a dark brown solid which was filtered off, washed with hexane and dried under vacuum (yield 68%) (Found: C, 34.5; H, 2.3. Calc. for $C_{40}H_{34}I_4O_2P_2Rh_2S_2$: C, 34.6; H, 2.4%). IR($CH_2Cl_2$): 2065 cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.71 [br, $S(CH_2)_2S$], 7.77 (m, PPh_3) and δ 3.10 [br, $S(CH_2)_2S$], 7.56 (m, PPh_3); $^{31}P-\{^1H\}$, δ 24.1 (d, J_{RhP} 91) and 25.2 (d, J_{RhP} 104 Hz).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_4(CO)_2\{P(OPh)_3\}_2]$ **8**. Molecular iodine (52.1 mg, 0.20 mmol) was added to a solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2\{P(OPh)_3\}_2]$ **4** (100 mg, 0.10 mmol) in dichloromethane (20 cm^3). The resulting brown solution was stirred at room temperature. After 4 d of stirring the IR spectrum revealed the absence of starting material. Concentration of the solvent (2 cm^3) and addition of hexane (10 cm^3) gave a brown solid which was filtered off, washed with hexane and dried under vacuum (yield 65%) (Found: C, 32.3; H, 2.4. Calc. for $C_{40}H_{34}I_4O_8P_2Rh_2S_2$: C, 32.4; H, 2.3%). IR($CH_2Cl_2$): 2095 cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.38 [br, $S(CH_2)_2S$] and 7.35 (m, $P(OPh)_3$]; $^{31}P-\{^1H\}$, δ 82.5 (dd, J_{RhP} 82, J_{PP} 21 Hz).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$ **9**. To a solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ **3** (100 mg, 0.11 mmol) in dichloromethane (15 cm^3) was added solid mercury(II) chloride (30 mg, 0.11 mmol). The solution changed from yellow to dark red and a dark precipitate of metallic mercury was formed. After 30 min of stirring the solution was filtered through Kieselguhr to remove the precipitate. Then the solvent was evaporated to 2 cm^3 and hexane (10 cm^3) was added to give a dark red crystalline solid which was filtered off, washed with hexane and dried under vacuum (yield 65%) (Found: C, 50.3; H, 3.4. Calc. for $C_{40}H_{34}Cl_2O_2P_2Rh_2S_2$: C, 50.6; H, 3.6%). IR($CH_2Cl_2$): 2050 and 2020 cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.37 [br, $S(CH_2)_2S$], 2.65 [br, $S(CH_2)_2S$] and 7.52 (m, PPh_3); $^{31}P-\{^1H\}$, δ 16.1 (dd, J_{RhP} 120, J_{PP} 11) and 37.5 (dd, J_{RhP} 124, J_{PP} 11 Hz).

$[Rh_2\{\mu\text{-}S(CH_2)_2S\}I_2(CO)_2(PPh_3)_2]$ **10**. Solid mercury(II) iodide (20 mg, 0.11 mmol) was added to a solution of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}(CO)_2(PPh_3)_2]$ **3** (100 mg, 0.11 mmol) in dichloromethane (20 cm^3). The solution changed from yellow to violet and, after 30 min of stirring, to dark red with precipitation of metallic mercury. This suspension was filtered off through Kieselguhr to remove the mercury. Then the filtrate was evaporated under vacuum and precipitated from hexane to provide a dark red solid which was filtered off and vacuum dried (yield 75%) (Found: C, 42.1; H, 2.9. Calc. for $C_{40}H_{34}I_2O_2P_2Rh_2S_2$: C, 42.4; H, 3.0%). IR($CH_2Cl_2$): 2030 cm^{-1} [ν(CO)]. NMR($CDCl_3$): ^1H, δ 2.15 [br, $S(CH_2)_2S$], 2.72 [br, $S(CH_2)_2S$] and 7.45 (m, PPh_3); $^{31}P-\{^1H\}$, δ 17.4 (dd, J_{RhP} 124, J_{PP} 11) and 36.3 (dd, J_{RhP} 123, J_{PP} 11 Hz).

Crystal Structure Determination of $[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$ **9**.—A crystal of approximate dimensions 0.20 × 0.25 × 0.35 mm was used for the X-ray analysis.

Crystal data. $C_{40}H_{34}Cl_2O_2P_2Rh_2S_2$, $M = 949.49$, triclinic, space group $P\bar{1}$, $a = 16.384(7)$, $b = 14.091(5)$, $c = 9.553(5)$ Å, $\alpha = 85.85(2)$, $\beta = 74.25(2)$, $\gamma = 67.54(2)°$, $U = 1960(2)$ Å^3, $\lambda = 0.710\,73$ Å, $Z = 2$, $D_c = 1.608$ g cm^{-3}, $F(000) = 952$, μ(Mo-Kα) = 11.82 cm^{-1}.

Data were collected at room temperature on Siemens AED single-crystal diffractometer using niobium-filtered Mo-Kα radiation and the θ–2θ scan mode. All reflections with θ in the range 3–26° were measured; of 7731 independent reflections, 5087, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analysed according to Lehmann and Larsen.[24] The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. No correction for absorption effects was applied.

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. The hydrogen atoms were placed at their calculated positions (C–H 0.96 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence g was 0.0137. Final R and R' values were 0.0692 and 0.0684. The SHELX 76 and SHELXS 86 systems of computer programs were used.[25] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 26. Final atomic coordinates for the non-hydrogen atoms are given in Table 2. All calculations were carried out on the Gould POWERNODE 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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