

Oxidative-addition reactions on planar chloranilate rhodium systems.

Crystal structure of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{Me}_2\text{I}_2(\text{CO})_2(\text{PPh}_3)_2]$

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The binuclear chloranilate complexes $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{L}_4]$ $\{\text{L} = \text{CO}$ **1** or CNR (R = toluene-*p*-sulfonylmethyl) **2**, $\text{L}_4 = (\text{CO})_2(\text{CNR})_2$ **3**, $(\text{CO})_2(\text{PPh}_3)_2$ **4** or $(\text{CO})_2[\text{P}(\text{OMe})_3]_2$ **5** $\}$ have been prepared and oxidative addition of the electrophiles MeI and I_2 investigated. Addition of XI (X = Me or I) to compounds **4** and **5**, in a Rh:XI = 1:1 molar ratio, led to the symmetrical complexes $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{X}_2\text{I}_2(\text{CO})_2(\text{PR}_3)_2]$ (X = Me, R = Ph **6**; X = I, R = Ph **7**; X = I, R = OMe **8**). Interaction of **4** and **5** with 1 mol of XI (X = Me or I) gave equimolecular mixtures of Rh^{I}_2 and Rh^{III}_2 systems. The crystal structure of **6** has been determined by X-ray diffraction methods.

The synthesis of transition-metal complexes containing *o*- or *p*-quinones and their substituted derivatives has been of interest in recent years. The quinones can co-ordinate to a metal centre in three different oxidation states: catecholate,¹⁻³ semiquinonate⁴⁻⁶ and quinone.^{7,8} In this area we recently reported the synthesis and characterization of the binuclear rhodium(I) compound $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ (cod = cycloocta-1,5-diene).⁹ In this compound the chloranilate dianion $\text{C}_6\text{Cl}_2\text{O}_4^{2-}$ is planar with the delocalization confined to upper and lower regions of the ligand ring.

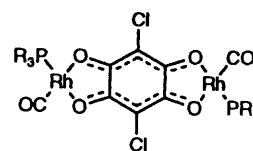
Transition-metal complexes of quinone ligands have been attracting increasing attention due to their structural and electrochemical properties. In addition to metal-localized redox processes,^{10,11} these complexes usually show rich electrochemistry with ligand-localized redox processes corresponding to the reduction of the quinone ligand to a semiquinone and then to a catecholate. In this context the binuclear compound $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ undergoes two sequential reversible one-electron reductions, which can reasonably be attributed to the quinone-semiquinonate and to the semiquinonate-catecholate couples in agreement with a ligand-centred transfer process.⁹

The present investigation was undertaken in order to explore the reactivity of the binuclear rhodium complexes $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{L}_2]$ $[\text{L}_2 = (\text{CO})_2$ or $(\text{CO})(\text{PR}_3)$; R = Ph or OMe] towards oxidative-addition reactions of MeI and I_2 . The molecular structure of the rhodium(III) compound $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{Me}_2\text{I}_2(\text{CO})_2(\text{PPh}_3)_2]$ is also reported.

Results and Discussion

The complex $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ has been prepared by the reaction of $[\text{Rh}_2(\mu\text{-OMe})_2(\text{cod})_2]$ with $\text{C}_6\text{Cl}_2\text{O}_2(\text{OH})_2$ (chloranilic acid) in a 1:1 molar ratio. The chloranilate dianion $\text{C}_6\text{Cl}_2\text{O}_4^{2-}$, in the *p*-quinone form, chelates to each rhodium(I) through two oxygen atoms, thus acting as a tetradentate ligand, bridging the bimetallic complex.⁹

Bubbling carbon monoxide through a diethyl ether suspension of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ leads to displacement of the cycloocta-1,5-diene ligands and to formation of the



1 R = Ph **4** or OMe **5**

carbonyl derivative $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_4]$ **1** [$\nu(\text{CO})$ (CH_2Cl_2): 2090 and 2024 cm^{-1}]. Interestingly, a more complicated IR spectrum in the $\nu(\text{C}\equiv\text{O})$ region is observed in the solid state. Considering the dark blue colour of the complex, these data point to the possible presence of intermolecular rhodium interactions.^{12,13}

Reaction of isocyanide ligands with $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ or $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_4]$, in a molar ratio toluene-*p*-sulfonylmethyl isocyanide: Rh = 2:1 or 1:1, respectively, gives the compounds $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CNR})_4]$ **2** or $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{CNR})_2]$ **3** (R = toluene-*p*-sulfonylmethyl), both brown. The analytical data confirm the displacement of both cyclooctadiene ligands or two carbon monoxide ligands, respectively.

The addition of triphenylphosphine or trimethyl phosphite to dichloromethane suspensions of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_4]$ also displaces two carbonyl ligands and affords $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PR}_3)_2]$ (R = Ph **4** or OMe **5**). The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of these compounds show the presence of one doublet corresponding to two equivalent phosphorus atoms coupled to the nearest rhodium centre (δ 29.4, J_{RhP} 127 **4**; 132.4, 262 Hz **5**). The presence of only one signal at 1975 **4** or 2000 cm^{-1} **5** in the IR spectra confirms the symmetrical disposition of the terminal ligands.^{14,15} We suggest that a *trans* configuration is, thus, present in complexes **4** and **5** (see **I**).

We have studied some oxidative-addition reactions of halogens and alkyl halides to the binuclear complexes $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PR}_3)_2]$ (R = Ph **4** or OMe **5**). All these reactions involve oxidation at both rhodium centres leading to dirhodium(III) bimetallic systems. In contrast, Bosnich

and co-workers¹⁶ reported binuclear rhodium(III)-rhodium(I) complexes bridged by a tetradentate ligand.

Reaction of methyl iodide with $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PPh}_3)_2]$

The addition of methyl iodide to a dichloromethane solution of compound **4** in a 2:1 molar ratio leads to a change from brown to orange. After stirring for 16 h the infrared spectrum shows only one band at 2062 cm^{-1} from the terminal carbonyl ligands, while the band at 1975 cm^{-1} corresponding to the starting material **4** has completely disappeared. This shift to higher wavenumber suggests reduced back donation, possible due to an increase in metal oxidation state.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum shows the presence of two doublets of different intensities (δ 35.1, J_{RhP} 110, a; 34.7, 111 Hz, b). This indicates the formation of two symmetrical isomers, the rhodium centres of which are equivalent, with rhodium coupling constants consistent with those of other rhodium(III) complexes.^{17,18} Removal of the solvent and addition of hexane gives an orange solid.

On the basis of the above data and the microanalysis, the complex was characterized as $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{Me}_2\text{I}_2(\text{CO})_2(\text{PPh}_3)_2]$ **6**, in which each rhodium centre carries one iodide and one methyl group. Compound **6** was correctly described as a (Me)IRh^{III}...Rh^{III}I(Me) system. In contrast with the behaviour reported for other bi- or poly-nuclear rhodium systems no acetyl compound has been detected.^{19,20}

Crystals suitable for X-ray diffraction studies were obtained from CH_2Cl_2 -hexane solutions of compound **6**. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum in CDCl_3 solution of this crystallized material shows the presence of only one isomer (δ 35.1, J_{RhP} 110 Hz).

Crystal structure of complex **6**

The structure of the binuclear complex **6**, having a crystallographically imposed C_i symmetry, is shown in Fig. 1, together with the atomic numbering scheme; selected bond distances and angles are given in Table 1. The chloranilate $\text{C}_6\text{Cl}_2\text{O}_4^{2-}$ ligand, lying across the inversion centre, displays the more common *p*-quinone form and bridges the two Rh atoms acting as a tetradentate, bis-chelating ligand, through the four oxygen atoms. Each Rh completes an octahedral co-ordination from a terminal carbonyl group [Rh-C(1) 1.810(10) Å], a methyl ligand [Rh-C(2) 2.083(9) Å], an I atom [Rh-I 2.699(2) Å] and a P atom [Rh-P 2.336(2) Å], where the PPh_3 and I ligands are *trans* disposed. The lengths of the two Rh-O bonds [Rh-O(2) 2.190(4) and Rh-O(3) 2.090(5) Å] are very different reflecting the *trans* effect of the methyl group, whereas those for the two C-O bonds, of the *p*-quinone [C(3)-O(2) 1.266(9) and C(4)-O(3) 1.269(7) Å], are practically equal. The five-membered chelate rings are essentially planar, with the Rh atom only 0.093(1) Å out of plane.

The chloranilate $\text{C}_6\text{Cl}_2\text{O}_4^{2-}$ ligand is planar with π -electron delocalization confined to upper and lower regions of the ligand, thus the C(3)-C(4) bond length of 1.522(9) Å is indicative of negligible conjugation between the halves of the ligand; for comparison the values of the other C(4)-C(5) and C(3)-C(5') bonds are 1.387(9) and 1.389(9) Å. The bonding of the $\text{C}_6\text{Cl}_2\text{O}_4^{2-}$ in **6** is very similar to that in the binuclear complex $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$,⁹ in which the Rh atoms are in a tetrahedral environment and the Rh-O bonds are essentially equivalent [2.089(8) and 2.100(9) Å].

Taking into account the molecular structure described above, the reaction involving $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PPh}_3)_2]$ and methyl iodide can be interpreted as a *cis*-oxidative addition of a molecule of MeI to each rhodium centre leading to the rhodium(III) derivative **6**.

The nature of the co-ordination of the chloranilate dianion in these binuclear systems maintains a large metallic separation; thus, each metal centre might behave relatively independently

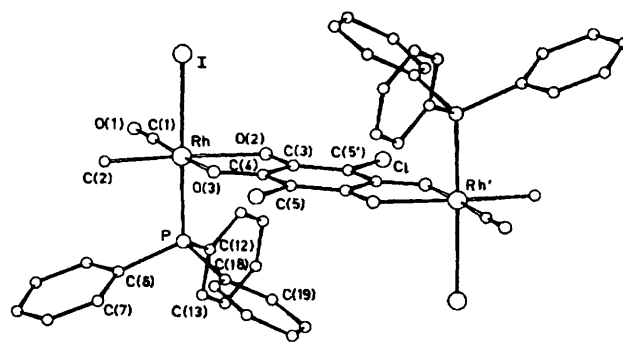


Fig. 1 View of the structure of the binuclear complex $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{Me}_2\text{I}_2(\text{CO})_2(\text{PPh}_3)_2]$ **6** with the atomic numbering scheme

Table 1 Selected bond distances (Å) and angles ($^\circ$) with estimated standard deviations in parentheses for complex **6**

Rh-I	2.699(2)	Rh-P	2.336(2)
Rh-O(2)	2.190(4)	Rh-O(3)	2.090(5)
Rh-C(1)	1.810(10)	Rh-C(2)	2.083(9)
Cl-C(5)	1.727(7)	P-C(6)	1.833(7)
P-C(12)	1.818(8)	P-C(18)	1.800(8)
O(1)-C(1)	1.124(13)	O(2)-C(3)	1.266(9)
O(3)-C(4)	1.269(7)	C(3)-C(4)	1.522(9)
C(3)-C(5')	1.389(9)	C(4)-C(5)	1.387(9)
C(1)-Rh-C(2)	86.5(4)	O(3)-Rh-C(2)	92.9(3)
O(2)-Rh-C(1)	104.6(3)	O(2)-Rh-O(3)	75.9(2)
P-Rh-C(2)	93.1(3)	P-Rh-C(1)	90.3(3)
P-Rh-O(3)	93.4(1)	P-Rh-O(2)	87.6(1)
I-Rh-C(2)	89.6(3)	I-Rh-C(1)	86.7(3)
I-Rh-O(3)	89.6(1)	I-Rh-O(2)	90.4(1)
Rh-O(2)-C(3)	114.1(4)	Rh-O(3)-C(4)	117.7(4)
O(2)-C(3)-C(4)	116.2(6)	O(2)-C(3)-C(5')	123.6(7)
C(4)-C(3)-C(5')	120.2(6)	C(3)-C(4)-C(5)	119.2(6)
O(3)-C(4)-C(3)	115.8(5)	O(3)-C(4)-C(5)	125.0(6)
C(3')-C(5)-C(4)	120.6(6)	Cl-C(5)-C(4)	119.2(5)
Cl-C(5)-C(3')	120.2(5)		

Primed atoms are related to the unprimed ones by the symmetry operation $1 - x, -y, 1 - z$

with regard to reactions which take place at the neighbouring metal site. Therefore we thought to prepare a mixed-valent compound by addition of only one molecule of methyl iodide to one rhodium centre. However, the reaction of methyl iodide with $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PPh}_3)_2]$ in a molar ratio of 1:1 gave only an equimolar mixture of compounds **4** and **6**.

Reaction of molecular iodine with $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PR}_3)_2]$ (R = Ph or OMe)

Similar oxidative addition takes place on reaction with molecular iodine and dichloromethane solutions of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PPh}_3)_2]$ **4** or $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ **5**. The addition of 2 mol of molecular iodine gave compounds $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{I}_4(\text{CO})_2(\text{PR}_3)_2]$ (R = Ph **7** or OMe **8**). The increase of the formal oxidation number from I to III parallels the increase in the carbonyl stretching wavenumbers from 1975 to 2081 cm^{-1} when R = Ph, and from 2000 to 2100 cm^{-1} for R = OMe. Despite the large number of potential isomers possible for **7** and **8**, the NMR spectra indicate that only one of them is produced in this reaction. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra show a doublet at δ -2.2 (J_{RhP} 78) **7** or 95.9 (153 Hz) **8** arising from a symmetrical compound. Thus the reaction implies the co-ordination of two iodide groups to each rhodium metal centre suggesting a structure comparable to that of **6**.

Again the addition of only 1 mol of iodine to dichloromethane solutions of compounds **4** and **5** failed to yield a mixed-oxidation-state compound, only mixtures of the

starting materials **4** or **5** and the respective dirhodium(III) products **7** or **8** were obtained.

In conclusion, a study of the addition of methyl iodide and halogens to binuclear dirhodium(I) complexes containing the planar chloranilate dianion as bridging ligand has been undertaken leading to the synthesis of dirhodium(III) complexes. All attempts to prepare rhodium(I)–rhodium(III) compounds have so far proved unsuccessful.

Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). The compounds $[\text{Rh}(\text{acac})(\text{cod})]$ (acac = acetylacetonate)²¹ and $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ ⁹ were prepared according to literature methods. Solvents were purified by standard procedures and distilled under nitrogen prior to use. All other reagents were obtained from Aldrich and used as received. Solution infrared spectra were recorded on a Nicolet Magna 550 spectrometer, ¹H and ³¹P-¹H NMR spectra in CDCl₃ solutions at room temperature on a Varian XL 300 spectrometer; ³¹P chemical shifts are positive downfield from external 85% H₃PO₄ in D₂O. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser.

Preparations

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_4]$ 1. Carbon monoxide was bubbled through a solution of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ (300 mg, 0.47 mmol) in dichloromethane (15 cm³), during 20 min, to give a dark blue suspension. Evaporation of the solvent to dryness and addition of diethyl ether (15 cm³) gave a dark blue solid which was filtered off, washed with diethyl ether and vacuum dried (yield 88%) (Found: C, 23.1; H, 0.0. Calc. for C₂₂H₂₄Cl₂O₄Rh₂: C, 22.8; H, 0.0%). IR (CH₂Cl₂): 2090 and 2024 cm⁻¹ [ν(CO)].

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CNR})_4]$ 2 (R = toluene-*p*-sulfonylmethyl). Solid CNR (248 mg, 1.27 mmol) was added to a solution of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{cod})_2]$ (200 mg, 0.31 mmol) in dichloromethane (15 cm³). The starting red solution immediately became dark green. After stirring for 30 min the solvent was evaporated to dryness. Addition of diethyl ether (8 cm³) gave a brown solid which was filtered off, washed with hexane and vacuum dried (yield 97%) (Found: C, 42.9; H, 3.6; N, 4.5. Calc. for C₄₂H₃₆Cl₂N₄O₁₂Rh₂S₄: C, 42.2; H, 3.6; N, 4.6%). IR (CH₂Cl₂): 2180 cm⁻¹ [ν(CN)]. ¹H NMR (CDCl₃): δ 7.65 (m, Ph), 5.43 (br, CH₂) and 2.42 (s, CH₃).

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{CNR})_2]$ 3 (R = CH₂O₂SC₆H₄Me-*p*). To a suspension of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_4]$ (200 mg, 0.38 mmol), in dichloromethane (15 cm³), was added a stoichiometric amount of solid CNR (148 mg, 0.76 mmol). The starting blue suspension became a dark brown solution, with the evolution of carbon monoxide. The solution was stirred for 40 min and the solvent evaporated to dryness. Addition of diethyl ether (1 cm³) and hexane (6 cm³) gave a dark brown solid which was filtered off, washed with hexane and dried under vacuum (yield 85%) (Found: C, 35.9; H, 2.1; N, 3.4. Calc. for C₂₆H₁₈Cl₂N₂O₁₀Rh₂S₂: C, 36.3; H, 2.5; N, 3.4%). IR (CH₂Cl₂): 2168 cm⁻¹ [ν(CN)] and 2082, 2020 cm⁻¹ [ν(CO)]. ¹H NMR (CDCl₃): δ 7.61 (m, Ph), 4.65 (br, CH₂) and 2.30 (s, CH₃).

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PPh}_3)_2]$ 4. A stoichiometric amount of solid triphenylphosphine (499 mg, 1.90 mmol) was added to a suspension of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_4]$ **1** (500 mg, 0.95 mmol) in dichloromethane (15 cm³) and the resulting dark brown solution stirred for 4 h. Concentration of the solvent to 2 cm³ and addition of diethyl ether (2 cm³) followed by hexane (10

cm³) gave a brown solid which was filtered off, washed with hexane and dried under vacuum (yield 96%) (Found: C, 53.8; H, 3.5. Calc. for C₄₄H₃₀Cl₂O₆P₂Rh₂: C, 53.2; H, 3.0%). IR (CH₂Cl₂): 1975 (br) cm⁻¹ [ν(CO)]. ³¹P-¹H NMR (CDCl₃): δ 29.4 (d, *J*_{RhP} 127 Hz).

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ 5. Addition of trimethyl phosphite (135 μl, 1.14 mmol) to a suspension of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_4]$ **1** (300 mg, 0.57 mmol) in dichloromethane (15 cm³) led to evolution of carbon monoxide. The resulting dark green solution was evaporated to ca. 1 cm³ and diethyl ether (1 cm³) followed by hexane (10 cm³) added after 15 min of stirring. The dark brown solid obtained was filtered off, washed with hexane and vacuum dried (yield 66%) (Found: C, 23.7; H, 2.6. Calc. for C₁₄H₁₈Cl₂O₂P₂Rh₂: C, 23.4; H, 2.6%). IR (CH₂Cl₂): 2000 cm⁻¹ [ν(CO)]. ³¹P-¹H NMR (CDCl₃): δ 132.4 (d, *J*_{RhP} 262 Hz).

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{Me}_2\text{I}_2(\text{CO})_2(\text{PPh}_3)_2]$ 6. Methyl iodide (37.76 μl, 0.60 mmol) was added to a solution of the complex $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PPh}_3)_2]$ **4** (300 mg, 0.30 mmol) in dichloromethane (15 cm³). The mixture was stirred at room temperature for 16 h changing from brown to orange. The solvent was removed under reduced pressure to 1 cm³, and the addition of diethyl ether (3 cm³) and hexane (5 cm³) afforded an orange solid which was filtered off and recrystallized from dichloromethane–hexane (yield 79%) (Found: C, 43.5; H, 2.7. Calc. for C₄₆H₃₆Cl₂I₂O₆P₂Rh₂: C, 43.2; H, 2.8%). IR (CH₂Cl₂): 2062 cm⁻¹ [ν(CO)]. ³¹P-¹H NMR (CDCl₃): δ 35.1 (d, *J*_{RhP} 110, a) and 34.7 (d, *J*_{RhP} 111 Hz, b).

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{I}_4(\text{CO})_2(\text{PPh}_3)_2]$ 7. Iodine (51 mg, 0.20 mmol) was added to a solution of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2(\text{PPh}_3)_2]$ **4** (100 mg, 0.10 mmol) in dichloromethane (15 cm³). The resulting dark brown solution was stirred at room temperature. After 60 min the IR spectrum revealed the absence of starting material. Concentration of the solvent (1 cm³) and addition of diethyl ether (3 cm³) followed by hexane (5 cm³) gave a brown solid which was filtered off and washed with hexane (yield 64%) (Found: C, 35.4; H, 2.1. Calc. for C₄₄H₃₀Cl₂I₄O₆P₂Rh₂: C, 35.2; H, 1.9%). IR (CH₂Cl₂): 2081 cm⁻¹ [ν(CO)]. ³¹P-¹H NMR (CDCl₃): δ -2.2 (d, *J*_{RhP} 78 Hz).

$[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)\text{I}_4(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ 8. The stoichiometric amount of molecular iodine (66 mg, 0.26 mmol) was added to a solution of $[\text{Rh}_2(\mu\text{-C}_6\text{Cl}_2\text{O}_4)(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ **5** (100 mg, 0.13 mmol) in dichloromethane (15 cm³). After stirring for 20 min, at room temperature, the solution changed from brown to red. The solvent was evaporated to 2 cm³ and diethyl ether (10 cm³) was added to give a brown solid, which was filtered off, washed with diethyl ether and dried under vacuum (yield 75%) (Found: C, 13.8; H, 1.2. Calc. for C₁₄H₁₈Cl₂I₄O₁₂P₂Rh₂: C, 13.7; H, 1.4%). IR (CH₂Cl₂): 2100 cm⁻¹ [ν(CO)]. ³¹P-¹H NMR (CDCl₃): δ 95.9 (d, *J*_{RhP} 153 Hz).

Crystallography

A crystal of complex **6** approximate dimensions 0.18 × 0.22 × 0.25 mm was used for the X-ray analysis.

Crystal data. C₄₆H₃₆Cl₂I₂O₆P₂Rh₂, *M* = 1277.26, monoclinic, space group *P*2₁/*n*, *a* = 12.340(2), *b* = 12.763(2), *c* = 15.354(3) Å, β = 96.11(2)°, *U* = 2404.4(7) Å³, λ = 0.710 73 Å, *Z* = 2, *D*_c = 1.764 g cm⁻³, *F*(000) = 1240, μ(Mo-Kα) = 21.93 cm⁻¹.

Data were collected at room temperature on a Siemens AED single-crystal diffractometer using niobium-filtered Mo-Kα radiation and the θ–2θ scan mode. The intensity of one standard reflection was measured after every 100 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 necessary. The individual profiles have been analysed according to Lehmann and Larsen.²² All reflections with θ in the range 3–30° were measured; of 7007 independent reflections, 2757, having $I > 2\sigma(I)$, were considered observed and used in the analysis.

The structure was solved by Patterson and Fourier methods, and refined (on F) 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 the g value was 0.0012.

Final R and R' values were 0.0409 and 0.0414. The SHELX 76 and SHELXS 86 systems of computer programs were used.²³ Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 24. All calculations were carried out on the GOULD POWERNODE 6040 computer of the Centro di Studio per la Strutturistica Diffattometrica del C. N. R., Parma.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/24.

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References

- 1 D. Sanna and K. N. Raymond, *Inorg. Chem.*, 1990, **29**, 1586.
- 2 F. Harlt, A. Vlcek, jun., L. A. deLearie and C. G. Pierpont, *Inorg. Chem.*, 1990, **29**, 1073.
- 3 H. Kang, S. Liu, S. N. Shaikh, T. Nicholson and J. Zubieta, *Inorg. Chem.*, 1989, **28**, 920.
- 4 W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187.
- 5 C. Benelli, A. Dei, D. Gatteschi and L. Pardi, *Inorg. Chem.*, 1990, **29**, 3409.
- 6 A. Dei, D. Gatteschi, L. Pardi and L. Russo, *Inorg. Chem.*, 1991, **30**, 2589.
- 7 C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
- 8 W. K. Seok and T. J. Meyer, *J. Am. Chem. Soc.*, 1988, **110**, 7358.
- 9 M. A. Calvo, A. M. Manotti Lanfredi, L. A. Oro, M. T. Pinillos, C. Tejel, A. Tiripicchio and F. Uguzzoli, *Inorg. Chem.*, 1993, **32**, 1147.
- 10 F. Harlt and A. Vlcek, jun., *Inorg. Chem.*, 1992, **31**, 2869.
- 11 K. Lu and J. E. Earley, *Inorg. Chem.*, 1993, **32**, 189.
- 12 F. Bonati, L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreda, C. Foces-Foces and F. H. Cano, *J. Organomet. Chem.*, 1989, **369**, 253.
- 13 L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreda, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1988, 1927.
- 14 F. A. Cotton, *Chemical Applications of Group Theory*, Wiley, New York, 1990.
- 15 D. Mountanzon, Ph. Kalck and R. Poilblanc, *J. Organomet. Chem.*, 1980, **186**, 121.
- 16 T. G. Schenck, C. R. C. M. Hilne, J. F. Sawyer and B. Bosnich, *Inorg. Chem.*, 1985, **24**, 2338.
- 17 M. T. Pinillos, A. Elduque, L. A. Oro, F. J. Lahoz, F. Bonati, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1990, 989.
- 18 A. Elduque, L. A. Oro, M. T. Pinillos, A. Tiripicchio and F. Uguzzoli, *J. Chem. Soc., Dalton Trans.*, 1994, 385.
- 19 A. Mayanza, J. J. Bonnet, J. Galy, Ph. Kalck and R. Poilblanc, *J. Chem. Res.*, 1980, (S) 146; (M) 2101.
- 20 M. T. Pinillos, A. Elduque, E. Martín, N. Navarro, L. A. Oro, A. Tiripicchio and F. Uguzzoli, *Inorg. Chem.*, 1995, **34**, 3105.
- 21 F. Bonati and C. G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.
- 22 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
- 23 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976; SHELXS 86, Program for the solution of crystal structures, University of Göttingen, 1986.
- 24 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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