

## $\eta^5$ -Cyclopentadienylrhodium(I) Complexes containing Diphosphines and their Reactions with the Electrophiles $H^+$ and $Me^+$ . Crystal and Molecular Structure of $[Rh(\eta-C_5H_5)(CO)(Ph_2PCH_2PPh_2)]$ ,† a Complex with a Unidentate Bis(diphenylphosphino)methane Ligand

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The compounds  $[Rh(\eta-C_5H_5)(dppm)(CO)]$  (2),  $[Rh(\eta-C_5H_5)(dppe)]$  (3), and  $[Rh(\eta-C_5H_5)(dppp)]$  (4) were obtained from the reactions of  $[Rh(\eta-C_5H_5)(CO)_2]$  (1) with bis(diphenylphosphino)-methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,3-bis(diphenylphosphino)propane (dppp) respectively. The X-ray structure determination of (2) shows it to crystallize in the space group  $P2_1/n$  with unit-cell dimensions  $a = 13.734(4)$ ,  $b = 9.771(3)$ ,  $c = 20.440(8)$  Å,  $\beta = 103.9(1)^\circ$ , and  $Z = 4$ .  $R' = 0.05$  for 2 864 observed reflections. Some relevant bond distances are Rh-(centroid of  $C_5H_5$  ring) = 1.932, Rh-P = 2.238(2), and Rh-C(carbonyl) = 1.806(8) Å. The bonding of the dppm ligand is, unusually, unidentate to the metal. The reactions of (2), (3), (4), and of the previously reported complex  $[{Rh(\eta-C_5H_5)(CO)}_2(\mu-dppb)]$  (6) [dppb = 1,4-bis(diphenylphosphino)butane], with the electrophilic agents  $H^+$  and  $Me^+$  have been studied. Complex (3) reacts with  $HBF_4$  to give the cationic hydride  $[Rh(\eta-C_5H_5)H(dppe)]BF_4$  (5); in the same reaction (4) and (6) gave unstable products. The protonic attack of HCl on (3), (4), and (6) results in the formation of compounds devoid of co-ordinated cyclopentadienyl ion. The binuclear complex  $[{Rh(CO)}_2(\mu-Cl)}_2(\mu-dppb)]$  (7) was the product of the reaction of (6) with HCl; for this reaction a possible mechanism is proposed. The reactions of HCl with (3) and (4) are more complex and mixtures containing  $[{Rh(P-P)Cl}_n]$  and the rhodium(III) hydride  $[{RhH(P-P)Cl}_2]_n$  ( $n = 1$  or  $2$ , P-P = dppe or dppp) were isolated. The compound  $[{Rh(dppe)Cl}_2]$  was formed by the reaction of (5) with  $[AsPh_4]Cl$ . The electrophilic attack of MeI on (2) takes place either at the metal or at the unco-ordinated phosphorus atom of dppm and the reaction product is  $[Rh(\eta-C_5H_5)(COMe)I(Ph_2PCH_2PMePh_2)]I$ . MeI reacts with (3) and (4) to give  $[Rh(\eta-C_5H_5)Me(dppe)]I$  and  $[Rh(\eta-C_5H_5)Me(dppp)]I$ , which are very unstable in solution.

The synthesis of the cyclopentadienylrhodium(I) complexes containing phosphines and their reactions with electrophile reagents have been widely studied.<sup>1</sup> As a part of our studies in this area we recently started to investigate the reaction of  $[Rh(\eta-C_5H_5)(CO)_2]$  with chelating diphosphines of the type  $Ph_2P(CH_2)_nPPh_2$  ( $n = 1-4$ ); for  $n = 4$  we have already synthesized the binuclear complex  $[\mu-1,4\text{-bis(diphenylphosphino)butane}]_2\text{-dicarbonylbis}(\eta\text{-cyclopentadienyl})\text{dirhodium(I)}$ , whose reactions and crystal and molecular structure have been recently published.<sup>2</sup> Here we report the synthesis of mononuclear cyclopentadienylrhodium(I) complexes containing the diphosphines dppm, dppe, and dppp [dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane] and the X-ray structure determination of the complex  $[Rh(\eta-C_5H_5)(dppm)(CO)]$ . As far as we are aware, the solid-state structure reported here is the second<sup>3</sup> crystallographic example of a unidentate dppm ligand.

We also report on the electrophilic attack of  $H^+$  and  $Me^+$  on the new compounds and on the binuclear complex  $[{Rh(\eta-C_5H_5)(CO)}_2(\mu-dppb)]$  [dppb = 1,4-bis(diphenylphosphino)butane]. Here the protonic attacks were carried out for the sake of ascertaining the influence of the anionic counterpart of the electrophilic agent on the course of reaction.<sup>4</sup> We have already reported<sup>5,6</sup> that when the electrophilic agents are hydrohalogenic acids, the reactions with  $\eta$ -cyclopentadienyl-

rhodium(I) complexes can cause elimination of cyclopentadiene and the formation of dimeric rhodium(I) complexes.

### Results and Discussion

**Cyclopentadienylrhodium(I) Complexes with Diphosphines.**—The course of the reactions of  $[Rh(\eta-C_5H_5)(CO)_2]$  (1) with  $Ph_2P(CH_2)_nPPh_2$  ( $n = 1-4$ ) and the nature of the products obtained depends on the chelate diphosphine chain length. We have already reported<sup>2</sup> that the binuclear complex  $[{Rh(\eta-C_5H_5)(CO)}_2(\mu-dppb)]$  (6) is the product of the reaction of (1) with dppb. By refluxing a heptane solution of (1) with dppm, the initial yellow colour slowly changes to orange and the i.r. spectra show the disappearance of the  $\nu(CO)$  bands of the starting material and the contemporary appearance of a new  $\nu(CO)$  band. At the end of the reaction the complex  $[Rh(\eta-C_5H_5)(dppm)(CO)]$  (2) was isolated from the mixture as a yellow-orange solid.

Complex (2) is soluble in the most common solvents including saturated hydrocarbons; in the solid state it is stable for a long time whereas its stability is limited in chlorinated solvents. Molecular weight measurements, analytical, and i.r. and  $^1H$  n.m.r. spectral data indicate that the complex is mononuclear with the dppm bonded in the unidentate fashion. The existence in the i.r. spectrum of a single  $\nu(CO)$  band at  $1940\text{ cm}^{-1}$  rules out bridge-bonded carbonyl groups; in the  $^1H$  n.m.r. spectrum the resonance of the cyclopentadienyl proton was observed as a triplet at  $\tau$  4.87 ( $C_6D_6$ ),  $J(H-P)$  and  $J(H-Rh)$  being of the same order (0.6 Hz). The expected small value of the coupling constant of the unco-ordinated phosphorus atom of the dppm ligand could not be detected because it was beyond the capability of the  $^1H$  n.m.r. machine used. The molecular structure and atomic numbering of (2) are illustrated in Figure 1. Bond lengths and bond angles are listed in Table 1.

†  $[Bis(diphenylphosphino)methane-P]carbonyl(\eta\text{-cyclopentadienyl})\text{-rhodium(I)}$ .

Supplementary data available (No. SUP 23456, 26 pp.): observed and calculated structure factors, thermal parameters, hydrogen atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

**Table 1.** Some relevant interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Distances			
Rh—C(1)	2.256(7)	P(1)—C(7)	1.839(6)
Rh—C(2)	2.284(7)	P(1)—C(11)	1.822(5)
Rh—C(3)	2.273(8)	P(1)—C(17)	1.844(5)
Rh—C(4)	2.240(8)	P(2)—C(7)	1.852(7)
Rh—C(5)	2.298(8)	P(2)—C(21)	1.856(5)
Rh—C(6)	1.806(8)	P(2)—C(27)	1.843(5)
Rh—P(1)	2.238(2)	C(6)—O	1.159(8)
Rh—(C <sub>5</sub> H <sub>5</sub> )*	1.932		
(b) Angles			
C(6)—Rh—P(1)	93.7(3)	P(1)—C(7)—P(2)	114.4(4)
(C <sub>5</sub> H <sub>5</sub> )*—Rh—C(6)	135.1(3)	C(7)—P(2)—C(23)	98.3(3)
(C <sub>5</sub> H <sub>5</sub> )*—Rh—P(1)	131.1(5)	C(7)—P(2)—C(29)	103.2(3)
Rh—P(1)—C(7)	119.4(2)	C(23)—P(2)—C(29)	102.1(2)
Rh—P(1)—C(11)	115.5(2)	C(1)—C(2)—C(3)	107.9(8)
Rh—P(1)—C(17)	112.4(2)	C(2)—C(3)—C(4)	108.1(7)
C(7)—P(1)—C(11)	101.1(3)	C(3)—C(4)—C(5)	108.0(8)
C(7)—P(1)—C(17)	101.8(3)	C(4)—C(5)—C(1)	106.2(8)
Rh—C(6)—O(1)	178.4(8)		

(C<sub>5</sub>H<sub>5</sub>)\* represents centroid of cyclopentadienyl ring.

The crystal structure, as shown in Figure 1, is built up of discrete mononuclear molecules. The dppm ligand is unidentate to the rhodium atom through the phosphorus; the co-ordination sphere is completed by the η<sup>5</sup>-bonded cyclopentadienyl ligand and the carbon atom of the carbonyl group. The co-ordination about each rhodium atom is trigonal if the centre of the cyclopentadienyl ring is considered as one co-ordination position, or pentagonal with the η-C<sub>5</sub>H<sub>5</sub> ring occupying three co-ordination sites. The bond distances in the inner co-ordination sphere of this complex are quite similar to those reported for the dimeric complex (6); Rh—C(cyclopentadienyl) bond distances are in the range 2.240(8)—2.298(8) Å in the present determination and 2.24(1)—2.30(1) Å in the dimeric derivative. The Rh—P(1) bond distance is 2.238(2) Å, comparable with the corresponding value of 2.246(2) Å in the dimer, as is the Rh—CO distance [1.806(8) *cf.* 1.80(1) Å]. The rhodium atom lies 1.932 Å from the centroid of the C<sub>5</sub>H<sub>5</sub> ring, which is perpendicular to the trigonal plane (see Table 2).

In most of the reported complexes the dppm ligand bridges two rhodium atoms; <sup>7-11</sup> only in a few cases has it been found <sup>12,13</sup> that dppm acts, in rhodium(I) complexes, as a chelating ligand with the formation of a four-membered ring. Compounds in which the dppm behaves as a unidentate two-electron donor ligand <sup>3,14-18</sup> are less common; no cobalt, rhodium, or iridium compounds of this type have been reported so far.

The three co-ordination modes of dppm in rhodium complexes is further evidence for its ability to adopt different conformations due to the flexibility of the P—C—P angle and to rotation around the P—C (methylene) bond. The P—C—P angle is 95.4° (averaged value <sup>12,13</sup>) in the rhodium chelate, about 109° in bimetallic rhodium complexes with dppm as a bridging group, <sup>7-11</sup> and 114.4(4)° in the rhodium complex with unidentate dppm (this work).

Within the Rh(dppm) framework we found that the Rh—P distance [2.238(2) Å] is, as expected, shorter than values for the Rh—P distances reported in rhodium complexes with dppm as a bridging [2.309(2)—2.346(2) Å] or chelating ligand (average 2.343(2) Å for [Rh(dppm)<sub>2</sub>(CO)]<sup>+</sup> (ref. 13)). The conformation of the ligand is characterized by the torsion angle P(2)—C(7)—P(1)—Rh of 72.6° and by two almost parallel Ph rings (see Table 2).

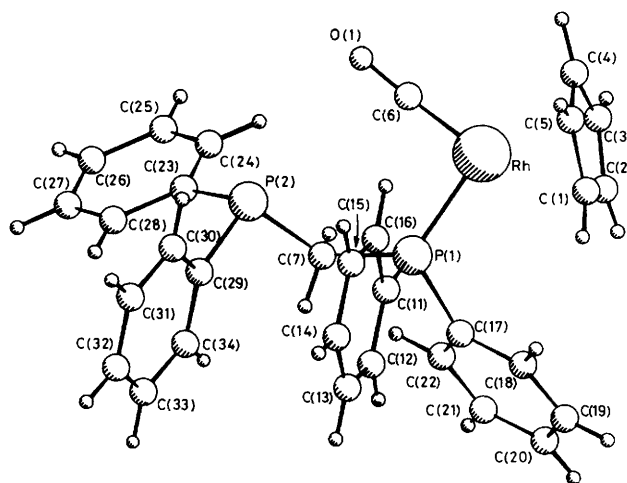
**Table 2.** Least-squares planes [deviations of relevant atoms from the planes (Å) are given in square brackets]

Plane 1: C(1)—C(5), (C <sub>5</sub> H <sub>5</sub> )*	13.2081X + 0.2400Y - 10.1385Z = -11.7454
[C(1) 0.018, C(2) -0.006, C(3) -0.009, C(4) 0.020, C(5) -0.023]	
Plane 2: (C <sub>5</sub> H <sub>5</sub> )*, C(6), P	2.4543X - 7.2542Y + 11.932Z = 9.5225
[Rh -0.048, C(7) 0.380]	
Plane 3: C(11)—C(16) (phenyl)	13.4112X + 2.0735Y - 5.5415Z = -4.5864
Plane 4: C(17)—C(22) (phenyl)	-4.9772X + 1.9890Y + 19.8257Z = 16.1576
Plane 5: C(23)—C(28) (phenyl)	1.6147X + 9.7024Y + 0.3251Z = 1.9046
Plane 6: C(29)—C(34) (phenyl)	12.9879X + 2.3988Y - 0.4146Z = 2.4339
Plane 7: P(2), C(7), P(1)	-0.369X + 3.0156Y + 18.9956Z = 15.7186

Angles (°) between the planes

1—2	88.7	3—4	69.8
2—5	44.9	2—6	82.9
2—3	89.6	5—6	69.0
3—5	71.0	2—7	66.7
2—4	68.2	4—7	20.4
4—5	80.1	5—7	71.6
4—6	84.3	6—7	75.3
3—6	14.6	3—7	89.8

(C<sub>5</sub>H<sub>5</sub>)\* represents centroid of cyclopentadienyl ring.

**Figure 1.** Molecular structure of (2) showing the atom numbering

Use of space-filling molecular models clearly shows that in cyclopentadienylrhodium(I) complexes the co-ordination of the dppm as chelate is sterically unfavourable and that the formation of the binuclear species  $[\{\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})\}_2(\mu\text{-dppm})]$  is again prevented by steric interactions. On refluxing (2) in heptane the complex was recovered unchanged; addition of (1) to the mixture and refluxing produced no change in the complex. Neither  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{dppm})]$  nor  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-dppm})(\text{CO})_2]$  are formed in the reaction of (1) with dppm.

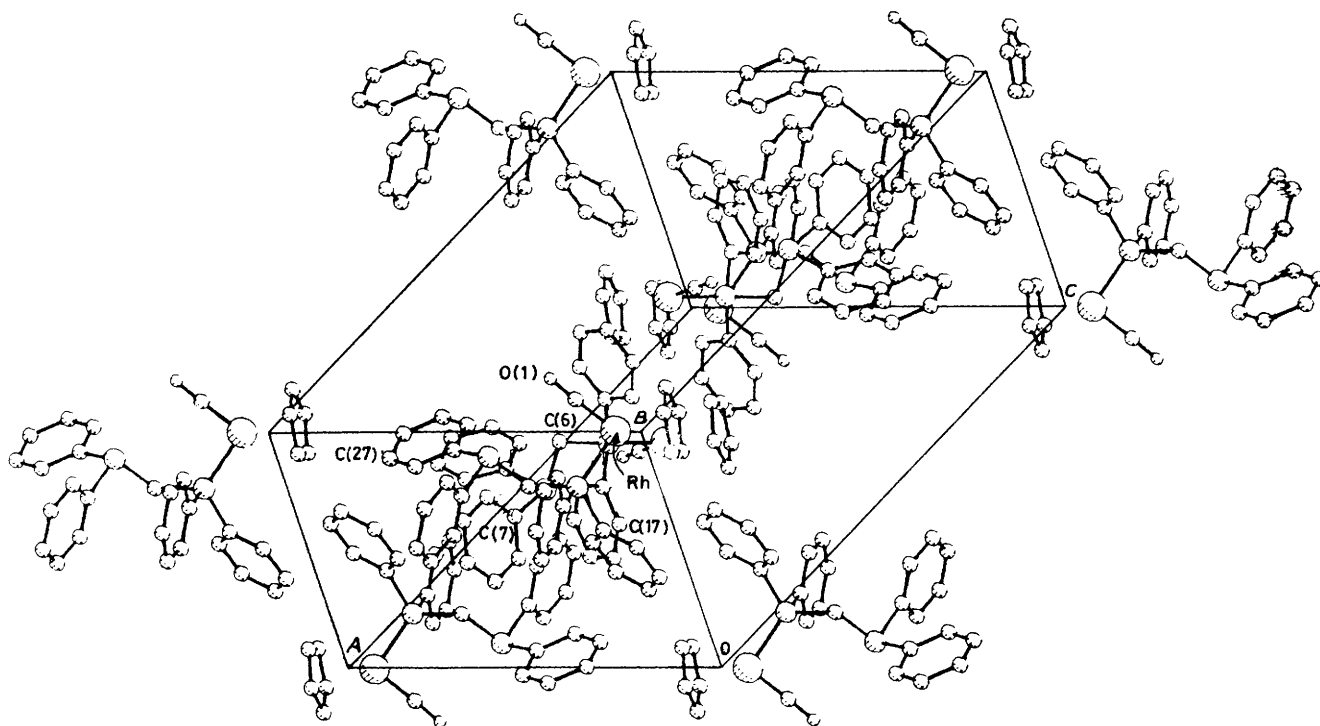


Figure 2. Unit-cell contents for (2)

The course of the reactions of (1) with dppe and dppp is different from the analogous one with dppm; in fact, following the reactions by i.r. spectra we only observed the disappearance of the  $\nu(\text{CO})$  bands of the starting material. We carried out the reaction in refluxing light petroleum (b.p. 80–120 °C) but we verified that a lower temperature neither influences the course of the reactions nor the nature of the products. From the previous reactions we isolated the complexes  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{dppe})]$  (3) and  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{dppp})]$  (4) which are orange solids, soluble in the common organic solvents and unstable in air even as solids. Compound (4) decomposes more rapidly than (3); this is probably due to the greater stability of the five-membered chelate ring of dppe compared to the six-membered ring of dppp. A similar suggestion was proposed to explain the different behaviour of  $[\text{Rh}(\text{dppe})_2]^+$  and  $[\text{Rh}(\text{dppp})_2]^+$  towards carbon monoxide;<sup>19,20</sup> while the former does not interact with CO, the latter readily gives the adduct  $[\text{Rh}(\text{dppp})_2(\text{CO})]^+$ . The  $^1\text{H}$  n.m.r. spectra of the complexes (3) and (4) show the cyclopentadienyl proton resonances at  $\tau$  4.66 and 4.96 respectively. This significant difference presumably results from a complicated variation in effective ligand basicity. The ligands dppe and dppp in the complexes are weakly bonded to the metal; in fact, in dichloromethane solution at room temperature, they are easily displaced by CO to yield (1).

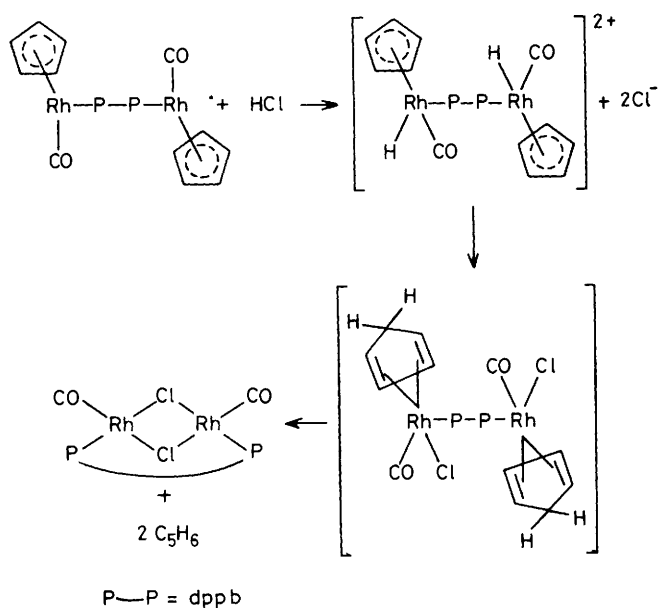
**Reactions with the Electrophiles  $\text{H}^+$  and  $\text{Me}^+$ .**—The site of electrophilic attack on some sandwich or half-sandwich metal complexes has been previously investigated.<sup>1,4,21–27</sup> We can conclude that for cyclopentadienyl-cobalt(II), -rhodium(II), and -iridium(II) metal complexes, the attack by an electrophilic reagent, E, is likely to be always initially directed towards the central metal atom, M.<sup>1,2,5,6,21–25,28–32</sup> In some cases, particularly when the electrophilic reagent is  $\text{H}^+$ ,<sup>5,6,27</sup> in a second stage of the reaction (after the formation of the M–E bond), a reversible or irreversible migration of the electrophile onto the cyclopentadienyl ligand can take place. We studied the reactions of the cyclopentadienylrhodium(II) diphosphine complexes with HCl and  $\text{HBF}_4$  to gain useful information on

the stages subsequent to the protonic attack on the metal centre.

Complex (3) reacts (in dichloromethane) with  $\text{HBF}_4$ , leading to the formation of the cationic hydride  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{H}(\text{dppe})]\text{BF}_4$  (5), which was isolated also as the tetraphenylborate salt. Both the salts are yellow, stable in solution for a few days, while in the solid state they are stable for some weeks. The  $^1\text{H}$  n.m.r. spectrum in  $\text{CDCl}_3$  shows the resonance of the cyclopentadienyl protons at  $\tau$  4.35 [ $J(\text{H-P}) = 1.5$ ,  $J(\text{H-Rh}) = 0.4$  Hz] while the resonance of the hydride proton was not detected owing to the low solubility of the compound; in the i.r. spectrum  $\nu(\text{Rh-H})$  was observed at  $2032\text{ cm}^{-1}$ .

Complexes (4) and (6) appear to react with  $\text{HBF}_4$  in the same way as (3), but the hydrides are too unstable to isolate and fully characterise them. The solid crude product shows in the i.r. spectrum  $\nu(\text{CO})$  at  $2060\text{ cm}^{-1}$  with shoulders at  $2085\text{w}$  and  $2015\text{m cm}^{-1}$ . The crude product partially regenerates the starting compound (6) in dichloromethane.

The course of the reactions of protonic attack of HCl on (3), (4), and (6) is different from that with  $\text{HBF}_4$ , leading only to compounds without the co-ordinated cyclopentadienyl. A yellow compound formulated as  $[\{\text{Rh}(\text{CO})(\mu\text{-Cl})\}_2(\mu\text{-dppb})]$  (7) was the main product of the reaction of (6) with HCl. It is insoluble in saturated hydrocarbons and diethyl ether, but soluble in benzene, chlorinated solvents, and methanol. The i.r. spectrum shows  $\nu(\text{CO})$  at  $1980\text{vs, br cm}^{-1}$  and  $\nu(\text{Rh-Cl})$  at  $280\text{ cm}^{-1}$ ; the  $^1\text{H}$  n.m.r. spectrum, apart from the resonance of the aromatic protons, does not show any evidence of co-ordinated cyclopentadienyl; through analytical and spectroscopic data we could deduce that the compound was binuclear, with the Cl and the dppb ligands bridge-bonded between the two rhodium atoms. According to our suggestion<sup>5,6</sup> on the reactions of the mononuclear cyclopentadienylrhodium(II) complexes  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{L}]$  (L = CO or  $\text{PPh}_3$ ) and  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]$  with HCl, we believe the mechanism shown in the Scheme to operate. This involves the formation of a dicationic di-hydrido-complex which, by nucleophilic attack



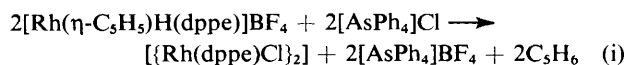
Scheme.

of  $\text{Cl}^-$  on the metal, undergoes hydrogen ion migration on the cyclopentadienyl ring leading to the formation of a very labile diene complex, which on releasing cyclopentadiene gives the chloro-bridged derivative.

The reactions of  $\text{HCl}$  with (3) and (4) proceed in the same way leading to the chloro-bridged complexes  $[\{\text{Rh}(\text{dppe})\text{Cl}\}_2]$  and  $[\{\text{Rh}(\text{dppp})\text{Cl}\}_2]$ .

A complicating factor in these reactions is the equilibrium existing in solution between the dimer and monomer species<sup>33-35</sup>  $[\{\text{Rh}(\text{P}-\text{P})\text{Cl}\}_2] \rightleftharpoons 2[\text{Rh}(\text{P}-\text{P})\text{Cl}]$  ( $\text{P}-\text{P} = \text{dppe}$  or  $\text{dppp}$ ). Further, in equilibrium conditions it is probable that  $\text{HCl}$  adds oxidatively to the species  $[\{\text{Rh}(\text{P}-\text{P})\text{Cl}\}_2]$  and  $[\text{Rh}(\text{P}-\text{P})\text{Cl}]$  with formation of rhodium(III) hydrido-complexes. For this reason we could not obtain satisfactory analyses for the reaction products, which are a mixture of compounds that we were not able to separate. Thus, the crude product obtained from the reaction of (4) shows, in the i.r. spectrum, apart from bands at 320, 290, and  $280\text{ cm}^{-1}$  attributable to  $\nu(\text{Rh}-\text{Cl})_{\text{terminal}}$  and  $\nu(\text{Rh}-\text{Cl})_{\text{bridge}}$ , others at 2060 and  $1988\text{ cm}^{-1}$  which could be assigned to  $\nu(\text{Rh}-\text{H})$  of  $[\{\text{Rh}-\text{H}(\text{dppp})\text{Cl}\}_2]$  and of the five-co-ordinate complex  $[\text{RhH}(\text{dppp})\text{Cl}_2]$  respectively. The former complex could be generated by addition of  $\text{HCl}$  to  $[\{\text{Rh}(\text{dppp})\text{Cl}\}_2]$  and the latter by addition to the monomer species  $[\text{Rh}(\text{dppp})\text{Cl}]$ . Analytical data indicate that the hydride mixture contains also some  $[\{\text{Rh}(\text{dppp})\text{Cl}\}_n]$  ( $n = 1$  or  $2$ ).

The formation of the complex  $[\{\text{Rh}(\text{dppe})\text{Cl}\}_2]$  by the reaction of (5) with  $[\text{AsPh}_4]\text{Cl}$  is remarkable: equation (i). Thus



the migration of the hydrogen ion on the cyclopentadienyl ring and the consequent release of  $\text{C}_5\text{H}_6$  is promoted by the nucleophilic attack of  $\text{Cl}^-$  on the metal.

The reactions of (2) with  $\text{HBF}_4$  and  $\text{HCl}$  produced compounds which we could not characterise; the possible protonic attack on the unco-ordinated phosphorus can add complications to these reactions.

As expected,  $\text{MeI}$  reacts with (3) and (4) to give the rhodium(III) derivatives  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{Me}(\text{dppe})]\text{I}$  (8) and  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{Me}(\text{dppp})]\text{I}$  (9). They are whitish solids which darken if left in air; in solution they are even less stable, releasing

$\text{MeI}$ . We have described the reactions of (6) with  $\text{MeI}$  in a previous paper.<sup>2</sup>

Treatment of (2) with neat  $\text{MeI}$  gives the salt  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{I}(\text{Ph}_2\text{PCH}_2\text{PMePh}_2)]\text{I}$  (10); since the reaction required an excess of  $\text{MeI}$ , it was impossible to detect whether the initial attack of  $\text{MeI}$  occurred at the metal or at the phosphorus atom, so as to compare the Lewis basicity of the two centres. Other authors have recently been able to establish that, in the reaction of  $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{CO})(\text{P}_2\text{Me}_4)]$  with  $\text{MeI}$ , the metal shows a Lewis basicity greater than the unco-ordinated phosphorus atom.<sup>32</sup> According to its formulation, (10) shows in the i.r. spectrum  $\nu(\text{CO})$  at  $1646\text{ cm}^{-1}$ , and in the  $^1\text{H}$  n.m.r. spectrum bands at  $\tau$  4.79 [ $J(\text{H}-\text{P}) = 2\text{ Hz}$ ], 7.03 [ $J(\text{H}-\text{P}) = 0.7\text{ Hz}$ ], and 7.68 [ $J(\text{H}-\text{P}) = 14\text{ Hz}$ ] attributable, respectively, to the resonance of the cyclopentadienyl protons, the methyl of the acetyl group, and methyl bonded to the phosphorus.

### Experimental

The complexes  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  and  $[\{\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})\}_2(\mu\text{-dppb})]$  were prepared by literature methods.<sup>2,36</sup> 1,3-Bis(diphenylphosphino)propane, 1,2-bis(diphenylphosphino)ethane, and bis(diphenylphosphino)methane were Strem products. Other reagents were used as obtained from commercial sources. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using a polystyrene film for calibration. A Perkin-Elmer R 24B spectrometer was used to obtain  $^1\text{H}$  n.m.r. spectra. Molecular weights were determined with a Knauer vapour pressure osmometer. Conductivity measurements were made with a WTW LBR conductivity meter. Elemental analyses were performed by Bernhardt Mikroanalytisches Laboratorium, Elbach, Germany, and by the microanalytical laboratory of the Organic Chemistry Institute of Milan.

All the reactions were carried out under an atmosphere of oxygen-free nitrogen. Analytical and characteristic i.r. and  $^1\text{H}$  n.m.r. data of the compounds are reported in Table 3.

*[Bis(diphenylphosphino)methane]carbonyl(η-cyclopentadienyl)rhodium(I) (2).*—A mixture containing  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  (obtained in heptane from  $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$  (0.150 g) and excess  $\text{Ti}(\text{C}_5\text{H}_5)$ ) and  $\text{dppm}$  (0.296 g) in heptane ( $150\text{ cm}^3$ ) was heated under reflux until the i.r. spectrum showed disappearance of the  $\nu(\text{CO})$  of the starting material (about 9 h). The solution was filtered under  $\text{N}_2$ , concentrated, and transferred to a heptane-containing silica column. Elution with heptane gave a yellow fraction which was concentrated by evaporation at reduced pressure. The product was obtained as yellow-orange crystals by cooling to  $-30^\circ\text{C}$ ; additional product was obtained from mother-liquors, by evaporation (yield, 30%).

*[1,2-Bis(diphenylphosphino)ethane]η-cyclopentadienylrhodium(I) (3).*— $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  [obtained initially in pentane from  $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$  (0.200 g) and excess  $\text{Ti}(\text{C}_5\text{H}_5)$ ] and  $\text{dppe}$  (0.410 g) in light petroleum (b.p.  $80\text{--}120^\circ\text{C}$ ) were heated under reflux. The reaction was monitored by i.r. and stopped when the  $\nu(\text{CO})$  band of the starting material disappeared (about 9 h). During this time the solution turned from yellow to red. The mixture was left to stand overnight and then filtered under  $\text{N}_2$ . The resulting red solution, after concentration, was cooled to  $-30^\circ\text{C}$  giving red crystals; additional product was obtained by evaporation of the solvent (yield, 62%).

*[1,3-Bis(diphenylphosphino)propane]η-cyclopentadienylrhodium(I) (4).*—This compound was prepared in the same manner as (3), starting from  $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$  and  $\text{dppp}$  (yield, 45%).

Table 3. Analytical and characteristic i.r. and <sup>1</sup>H n.m.r. data

Compound	Colour	Analysis (%) <sup>a</sup>			I.r. <sup>b</sup> (v/cm <sup>-1</sup> )	<sup>1</sup> H N.m.r. (τ) <sup>c</sup>	
		C	H	Halogen		C <sub>5</sub> H <sub>5</sub>	CH <sub>3</sub>
(2) [Rh(η-C <sub>5</sub> H <sub>5</sub> )(dppm)(CO)]	Orange	64.0 (64.1)	4.75 (4.7)		1 940vs, ν(CO)	4.87 (t) <sup>d</sup>	
(3) [Rh(η-C <sub>5</sub> H <sub>5</sub> )(dppe)]	Red-orange	65.45 (65.75)	5.2 (5.15)			4.66 (dt) <sup>d</sup>	
(4) [Rh(η-C <sub>5</sub> H <sub>5</sub> )(dppp)]	Brown	66.2 (66.2)	5.25 (5.4)			4.96 (dt) <sup>d</sup>	
(5) [Rh(η-C <sub>5</sub> H <sub>5</sub> )H(dppe)]BF <sub>4</sub>	Pale yellow	57.0 (56.9)	4.4 (4.25)		2 032mw, ν(Rh-H)	4.35 (td) <sup>e</sup>	
(7) [{Rh(CO)(μ-Cl)} <sub>2</sub> (μ-dppb)]	Yellow	47.7 (47.45)	3.9 (3.7)	9.0 (9.35)	1 980vs, ν(CO) 280m, ν(Rh-Cl)		
(8) [Rh(η-C <sub>5</sub> H <sub>5</sub> )Me(dppe)]I	Off-white	54.35 (54.25)	4.6 (4.55)	17.9 (17.9)		<i>f</i>	<i>f</i>
(9) [Rh(η-C <sub>5</sub> H <sub>5</sub> )Me(dppp)]I	Cream	54.7 (54.85)	4.7 (4.75)	17.3 (17.55)		4.69 (m) <sup>e</sup>	9.16 (m) <sup>e</sup>
(10) [Rh(η-C <sub>5</sub> H <sub>5</sub> )(COMe)I(Ph <sub>2</sub> PCH <sub>2</sub> PMePh <sub>2</sub> )]I	Yellow	45.9 (45.85)	3.85 (3.85)	29.3 (29.35)	1 646s, br, ν(COMe)	4.79 (d) <sup>e</sup>	7.03 (s) <sup>e</sup> 7.68 (s)
[{RhH(dppp)Cl <sub>2</sub> }] <sub>n</sub>	Yellow	56.0 (55.2)	5.0 (4.65)	11.55 (12.45)	2 060w, ν(Rh-H) 1 988w, ν(Rh-Cl) <sub>t</sub> 320m, ν(Rh-Cl) <sub>t</sub> 290m, 280m, ν(Rh-Cl) <sub>b</sub>		

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Nujol mulls; t = terminal, b = bridging. <sup>c</sup> Using SiMe<sub>4</sub> as internal standard; *J*[(C<sub>5</sub>H<sub>5</sub>)-P] values are in the range 0.6–0.8 Hz for rhodium(i) and 1.2–1.8 Hz for rhodium(iii) complexes; *J*[(C<sub>5</sub>H<sub>5</sub>)-Rh] values are in the range 0.5–0.7 Hz. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub> solution. <sup>e</sup> In CDCl<sub>3</sub> solution. <sup>f</sup> Unstable in solution (see text).

Table 4. Final fractional atomic co-ordinates (× 10<sup>4</sup>) for non-hydrogen atoms with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Rh	-552(0)	1 551(1)	8 997(0)	C(15)	-1 133(4)	2 746(4)	6 561(3)
P(1)	-4(1)	383(2)	8 214(1)	C(16)	-789(4)	2 283(4)	7 222(3)
P(2)	1 835(1)	1 997(2)	7 993(1)	C(17)	-291(3)	-1 460(4)	8 223(2)
O(1)	1 385(4)	2 967(7)	9 530(3)	C(18)	-1 288(3)	-1 885(4)	8 016(2)
C(1)	-2 209(6)	1 083(9)	8 715(4)	C(19)	-1 537(3)	-3 251(4)	8 090(2)
C(2)	-1 779(6)	264(9)	9 279(4)	C(20)	-789(3)	-4 191(4)	8 372(2)
C(3)	-1 391(7)	1 116(10)	9 808(4)	C(21)	207(3)	-3 766(4)	8 580(2)
C(4)	-1 571(7)	2 497(10)	9 578(5)	C(22)	456(3)	-2 400(4)	8 505(2)
C(5)	-2 124(6)	2 462(10)	8 899(5)	C(23)	3 186(3)	1 714(5)	8 386(2)
C(6)	633(6)	2 408(8)	9 314(4)	C(24)	3 471(3)	1 690(5)	9 089(2)
C(7)	1 344(5)	363(7)	8 243(3)	C(25)	4 478(3)	1 533(5)	9 419(2)
C(11)	-526(4)	912(4)	7 345(3)	C(26)	5 202(3)	1 401(5)	9 046(2)
C(12)	-607(4)	4(4)	6 808(3)	C(27)	4 917(3)	1 424(5)	8 344(2)
C(13)	-952(4)	467(4)	6 148(3)	C(28)	3 909(3)	1 581(5)	8 014(2)
C(14)	-1 215(4)	1 838(4)	6 024(3)				

[1,2-Bis(diphenylphosphino)ethane](η-cyclopentadienyl)-hydridorhodium(iii) Tetrafluoroborate (5).—Aqueous HBF<sub>4</sub> was added dropwise to a stirred dichloromethane solution of (3). The solution changed rapidly from red to pale yellow. By adding diethyl ether a pale yellow solid was obtained. This was collected, washed with diethyl ether, and crystallized from dichloromethane-hexane. The corresponding tetraphenylborate salt was prepared by adding Na[BPh<sub>4</sub>] dissolved in methanol to a methanolic solution of the corresponding BF<sub>4</sub><sup>-</sup> salt.

Reaction of (5) with [AsPh<sub>4</sub>]Cl.—To a dichloromethane solution of (5) was added [AsPh<sub>4</sub>]Cl in the same solvent. The mixture was left, with stirring, for 4 h. The solution was filtered and the solvent evaporated off. A yellow solution was obtained by extraction with benzene; [{Rh(dppe)Cl}]<sub>2</sub> was obtained as yellow-orange solid on addition of heptane.

[μ-1,4-Bis(diphenylphosphino)butane]bis-[carbonyl-μ-chloro-rhodium(i)] (7).—Aqueous HCl was added dropwise to a

stirred diethyl ether solution of [{Rh(η-C<sub>5</sub>H<sub>5</sub>)(CO)}<sub>2</sub>(μ-dppb)]. A yellow-orange precipitate was rapidly formed. This was collected and washed several times with diethyl ether. The crude product was washed (2 or 3 times) with small portions of CH<sub>3</sub>OH (the product is soluble in methanol) until the i.r. spectra did not show the weak band at 2 100 cm<sup>-1</sup>. The yellow solid was washed with pentane and dried.

Preparation of [Rh(η-C<sub>5</sub>H<sub>5</sub>)(COMe)I(Ph<sub>2</sub>PCH<sub>2</sub>MePPh<sub>2</sub>)]I (10).—A mixture of (2) and MeI (3 cm<sup>3</sup>) was stirred at room temperature for about 2 h. Excess MeI was partially removed by evaporation; on adding hexane the product was obtained as a yellow solid. This was collected, washed several times with hexane, and dried.

Preparation of [1,3-Bis(diphenylphosphino)propane]η-cyclopentadienyl(methyl)rhodium(iii) Iodide (9).—An excess of MeI was added dropwise to a stirred solution of (4) in pentane. A cream precipitate was rapidly formed. This was collected, washed several times with pentane, and dried.

The complex [1,3-bis(diphenylphosphino)ethane] $\eta$ -cyclopentadienyl(methyl)rhodium(III) iodide (8) was prepared in the same manner as an off-white solid.

**X-Ray Data Collection.**—A single crystal of (2) of approximate dimensions ca.  $0.1 \times 0.1 \times 0.12$  mm was lodged in a glass capillary. Rotation and Weissenberg photographs indicated a monoclinic lattice. Intensity data were collected using a Siemens-Stoe four-circle diffractometer in the range  $6 \leq 2\theta \leq 50^\circ$  with Mo- $K\alpha$  radiation (graphite monochromator,  $\theta$ — $\omega$  scan mode, scan width  $1.4^\circ$ , scan speed  $0.04^\circ \text{ s}^{-1}$ , and a 15 s background count at each end of the scan range). During the data collection two standard reflections were measured every 120 min to check the stability of the crystal and electronics of the diffractometer. Using the criterion  $I \geq 2.5\sigma(I)$  where  $\sigma(I)$  is the estimated standard deviation derived from counting statistics 2 864 of the 4 300 intensities recorded with  $k, l \geq 0$  were deemed independent and observed and were used in the solution and refinement of the structure. Corrections were made for Lorentz and polarization effects but not for absorption.

**Crystal Data.**— $\text{C}_{31}\text{H}_{27}\text{OP}_2\text{Rh}$ ,  $M = 580.4$ , Monoclinic,  $a = 13.734(4)$ ,  $b = 9.771(3)$ ,  $c = 20.440(8)$  Å,  $\beta = 103.9(1)^\circ$ ,  $U = 2\,662.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.45$  g cm<sup>-3</sup>,  $F(000) = 1\,184$ ,  $\mu(\text{Mo-}K\alpha) = 6.9$  cm<sup>-1</sup>. Space group  $P2_1/n$  from systematic absences ( $h0l$ ,  $h + l \neq 2n$ ;  $0k0$ ,  $k \neq 2n$ ).

**Structure Determination.**—A three-dimensional Patterson map revealed the position of the rhodium atoms. The first difference-Fourier map, calculated by subtracting the contribution of the rhodium atoms, revealed some of the non-hydrogen atoms, including phosphorus. A further difference-Fourier map was sufficient to determine the positions of the missing non-hydrogen atoms. The structure was then refined by a full-matrix least-squares procedure. The function minimized was  $\sum w[|F_o| - |F_c|]^2$  in which  $w = 3.0203/[\sigma^2(F_o) + 0.000\,179 F_o^2]$ .

The scattering factors for the non-hydrogen atoms were taken from ref. 37 and those for the hydrogen atoms from ref. 38. Corrections for the real and imaginary parts of the anomalous dispersion were applied for Rh and P.<sup>39</sup>

The refinement was carried out with the phenyl rings treated as rigid groups and restricted to their normal geometry ( $D_{6h}$  symmetry, C—C = 1.395 Å), using the group refinement procedure. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. Rh, P, O, and C(carbonyl) atoms were allowed to vibrate anisotropically. Hydrogen atom contributions were included as fixed atoms in calculated positions:  $d(\text{C—H}) = 0.95$  Å and  $B_{\text{iso}} = 6$  Å<sup>2</sup>.

The final  $R$  value for the 2 864 reflections with  $I \geq 2.5\sigma(I)$  was 0.052 ( $R' = 0.050$ ). (The total number of measured independent reflections with  $k, l \geq 0$  was 3 113.) The calculations were carried out on the IBM computer of the Centro di Calcolo, University of Messina, with the SHELX-76 system of crystallographic programs.<sup>40</sup>

Fractional atomic co-ordinates for the non-hydrogen atoms are in Table 4.

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