Synthesis, Reactivity, and Crystal and Molecular Structures of [μ-1,4-Bis(diphenylphosphino)butane]-dicarbonylbis-(ηcyclopentadienyl)-dirhodium(I)

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The title compound (1) was obtained from the reaction of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ with 1,4-bis(diphenylphosphino)-butane (dppb). An *X*-ray structure determination of (1) has shown that it crystallises in space group $P\bar{1}$ with $a = 7.650(2)$, $b = 9.323(3)$, $c = 13.253(3)$ Å, $\alpha = 106.1(1)$, $\beta = 100.1(1)$, $\gamma = 93.4(1)°$. Its structure has been determined from three-dimensional *X*-ray data collected by counter methods. The final *R* factor obtained by full-matrix least-squares refinement of 2 022 reflections was 0.051. The crystal consists of discrete dimeric molecules of $\bar{1}$ symmetry held together by the bridging dppb group. The centrosymmetrically related rhodium atoms occupy the centre of a triangle at the vertices of which are planarly disposed a terminal carbonyl group, the centre of the cyclopentadienyl ring, and the phosphorus of the dppb ligand.

The reactions of the binuclear rhodium(I) complex (1) with small molecules have been studied. The dinitrosyl rhodium complex $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(NO)_2][PF_6]_2$ was obtained by treating (1) with $[NO][PF_6]$. Complex (1) reacts with halogens to give the rhodium(III) dicationic compounds $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2X_2]X_2$ (X = Cl, Br, or I). The diacetyl derivative $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(COMe)_2I_2]$ is the product of the reaction of (1) with MeI; the dicationic rhodium(III) compounds $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2(CH_2CN)_2]^{2+}$ and $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Me_2]^{2+}$ are obtained in the reactions with CH_2ClCN and $[OMe_3][PF_6]$. Mercury(II) chloride forms with (1) the adduct $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2(HgCl_2)_2]$. The i.r. and ^1H n.m.r. spectra of the new compounds are discussed.

WHILE several reports of the reactions of $[M(\eta\text{-}C_5H_5)(CO)_2]$ (M = Rh or Ir) with tertiary phosphines have appeared,[1] studies of the analogous reactions with chelating phosphines have not been reported. We have recently started to investigate the reaction of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ with the chelating phosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$—4).[2] Although this study is still in progress [2] we have established that the course of the reaction is dependent on the chelate chain length.

In this work we report the synthesis, reactivity, and crystal and molecular structures of the title compound, obtained as one of the products of the reaction between $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and 1,4-bis(diphenylphosphino)-butane (dppb). Because of their implications in homogeneous catalysis, the studies of the reactions of the binuclear metal complex with small molecules and on the co-ordination modes of these molecules to the metal are of interest.[3] In connection with our concern for the activation reactions of small molecules by co-ordination to a transition metal in a low valent state we have explored the behaviour of $[(\eta\text{-}C_5H_5)(CO)Rh\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}Rh(CO)(\eta\text{-}C_5H_5)]$, (1), in some reactions of this type. Recent investigations [4-8] on the reactions of the formally five-co-ordinate 18-electron complexes $[M(\eta\text{-}C_5H_5)LL']$ (M = Rh or Ir; L = CO or C_2H_4; L' = tertiary phosphine) with XY addenda have resulted in the isolation of ionic complexes indicating that the metal acts as a nucleophile. In some cases these ionic complexes can then undergo loss of L or migration of X to L, with co-ordination of Y to metal, to yield neutral metal(III) derivatives. It appeared interesting, therefore, to establish whether the same behaviour was displayed by binuclear complexes containing two rhodium(I) atoms formally five-co-ordinated.

RESULTS AND DISCUSSION

Synthesis and Characterisation of $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2]$, (1).—On refluxing a benzene solution of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and dppb the yellow colour changes slowly to red-brown and the i.r. spectra show, together with the disappearance of the ν(CO) bands of the starting material, the appearance of a new ν(CO) band at 1 935 cm^{-1}. Such behaviour has not been observed with the chelating phosphines of smaller chain length, *e.g.* dppe and dppp [dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane]; in these cases the i.r. spectra have shown only the disappearance of the ν(CO) of the starting material. In the reaction of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ with dppb at least two products are formed; these were separated by column chromatography on silica which had been packed in benzene. Elution with benzene removed a yellow fraction which, as reported in the experimental section, gave the product (1). Further elution with methanol gave a yellow uncharacterised product which does not contain a co-ordinated cyclopentadienyl ligand (cp). The full characterisation of the products of the reaction of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ with the other chelating phosphines used will be reported in a further paper.[2] It has been proved that (1) is not a reaction intermediate; in fact no reaction occurs when (1) is refluxed in benzene with an excess of dppb. The complex (1) is a solid, soluble in benzene, methanol (in which it is a non-electrolyte), and chlorinated solvents and moderately soluble in diethyl ether; as a solid it is indefinitely stable and its solutions are stable at room temperature at least for a period of weeks. The molecular weight, analytical data, and spectroscopic properties suggest for (1) a

binuclear structure with the chelating diphosphine dppb symmetrically bridging two metal atoms. The presence in the i.r. spectrum of a single ν(CO) band at 1 930 cm^{-1} is not consistent with the presence of bridging carbonyl groups; in the ^1H n.m.r. the cyclopentadienyl protons resonance was observed as a triplet at τ 4.95, the phosphorus and rhodium couplings to the cyclopentadienyl ring protons being of the same order [J(HP) = J(HRh) = 0.6 Hz]. This agrees with related assignments on mononuclear cyclopentadienylphosphinerhodium(I) complexes even though, in some cases, the magnitude of the coupling constants of the cyclopentadienyl ring protons to phosphorus is slightly different.[1,5,8,9]

TABLE 1

Final atomic fractional parameters for non-hydrogen atoms (×10^4) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Rh	1 378(1)	2 137(1)	2 957(1)
P	1 724(3)	−308(2)	2 686(2)
O(1)	−2 171(11)	1 650(10)	3 497(8)
C(1)	1 607(17)	4 400(11)	2 647(11)
C(2)	2 557(16)	4 589(11)	3 699(10)
C(3)	3 989(15)	3 743(12)	3 625(10)
C(4)	3 867(15)	2 991(12)	2 539(11)
C(5)	2 467(17)	3 451(12)	1 919(9)
C(6)	−766(15)	1 833(11)	3 286(9)
C(19)	3 715(11)	−715(9)	3 529(6)
C(20)	4 118(11)	225(10)	4 687(7)
C(7)	−157(11)	−1 512(9)	2 809(7)
C(8)	−141(13)	−2 019(11)	3 703(8)
C(9)	−1 642(15)	−2 956(13)	3 735(10)
C(10)	−3 005(16)	−3 360(13)	2 916(9)
C(11)	−3 089(15)	−2 867(12)	2 036(9)
C(12)	−1 653(13)	−1 940(11)	1 982(8)
C(13)	2 067(11)	−1 352(9)	1 346(7)
C(14)	2 340(14)	−642(13)	604(9)
C(15)	2 703(16)	−1 451(14)	−374(10)
C(16)	2 691(15)	−2 960(13)	−633(9)
C(17)	2 391(14)	−3 695(12)	81(8)
C(18)	2 063(13)	−2 902(11)	1 069(8)

Although several cases have already been reported,[10-18] the ability of dppb to promote the formation of binuclear complexes by bridging two metal atoms rather than chelating to one is unusual.

Description of the Structure (I).—The crystals of [$Rh_2(\mu$-dppb)(η-C_5H_5)$_2$(CO)$_2$] are formed by the packing of discrete dimeric molecules having $\bar{1}$ symmetry with the centre located at ½, 0, ½, which make only van der Waals contacts with one another. The asymmetric unit is half of the molecule and the co-ordinates of all non-hydrogen atoms in this unit are given in Table 1. The carbon atoms of the phenyl ring were refined isotropically, while all other non-hydrogen atoms were refined anisotropically. The structure of the dimeric molecule is shown in Figure 1 and the atomic numbering scheme is defined.

The co-ordination about each rhodium atom can be considered either as trigonal, the co-ordination positions being occupied by the centre of the cyclopentadienyl ring, the phosphorus, and the carbon atom C(6) of the carbonyl ligand, or pentagonal with the η-C_5H_5 ring occupying three co-ordination sites. The individual Rh–C distances (see Table 2) (from the cyclopentadienyl ring) show significant variations, possibly due to the carbon atoms experiencing different intermolecular repulsions. The C–C distances and C–C–C angles have the expected values. The average Rh–C distance is 2.276 Å and the carbocyclic system is planar within the limits of experimental error. The rhodium atom lies 1.941 Å below the plane of the five-membered ring. The orientation of the cp ring is perpendicular to the trigonal co-ordination plane. In Table 3 are reported the mean planes through

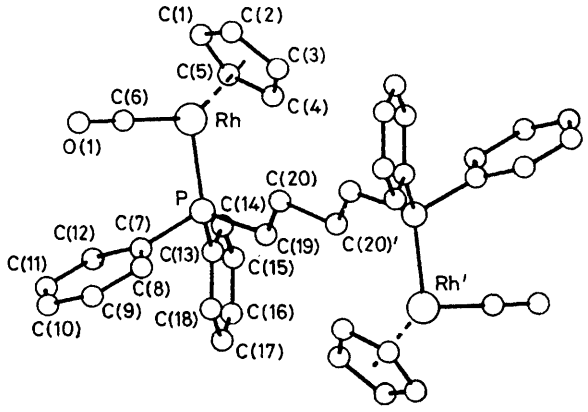


FIGURE 1 A view of the dimeric molecule of (I) down c showing the atom numbering

TABLE 2

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

(*a*) Distances

Rh–C(1)	2.26(1)	P–C(19)	1.849(8)
Rh–C(2)	2.28(1)	C(19)–C(20)	1.51(1)
Rh–C(3)	2.30(1)	C(7)–C(8)	1.39(1)
Rh–C(4)	2.24(1)	C(8)–C(9)	1.42(1)
Rh–C(5)	2.30(1)	C(9)–C(10)	1.32(2)
Rh–C(6)	1.80(1)	C(10)–C(11)	1.36(1)
Rh–P	2.246(2)	C(11)–C(12)	1.38(1)
C(6)–O(1)	1.17(1)	C(7)–C(12)	1.39(1)
C(1)–C(2)	1.41(2)	C(13)–C(14)	1.37(1)
C(2)–C(3)	1.39(2)	C(14)–C(15)	1.39(2)
C(3)–C(4)	1.40(2)	C(15)–C(16)	1.35(2)
C(4)–C(5)	1.40(2)	C(16)–C(17)	1.35(1)
C(1)–C(5)	1.40(2)	C(17)–C(18)	1.39(1)
P–C(7)	1.831(8)	C(18)–C(13)	1.39(1)
P–C(13)	1.844(8)	C(20)–C(20)'	1.60(2)

(*b*) Angles

C(6)–Rh–P	90.5(3)	C(3)–C(4)–C(5)	110(1)
C(19)–P–Rh	115.5(3)	C(4)–C(5)–C(1)	106(1)
C(7)–P–Rh	116.5(3)	C(5)–C(1)–C(2)	109(1)
C(13)–P–Rh	116.6(3)	C(7)–C(8)–C(9)	119(1)
C(13)–P–C(7)	100.3(4)	C(8)–C(9)–C(10)	120(1)
C(7)–P–C(19)	105.6(4)	C(9)–C(10)–C(11)	123(1)
C(13)–P–C(19)	99.9(4)	C(10)–C(11)–C(12)	118(1)
O(1)–C(6)–Rh	179.2(9)	C(12)–C(7)–C(8)	119(1)
C(19)–C(20)–C(20)'	110(1)	C(7)–C(12)–C(11)	121(1)
C(20)–C(19)–P	115.5(6)	C(13)–C(14)–C(15)	120(1)
C(8)–C(7)–P	122.2(7)	C(14)–C(15)–C(16)	121(1)
C(12)–C(7)–P	119.1(7)	C(15)–C(16)–C(17)	120(1)
C(14)–C(13)–P	121.9(7)	C(16)–C(17)–C(18)	120(1)
C(18)–C(13)–P	120.1(7)	C(17)–C(18)–C(13)	121(1)
C(1)–C(2)–C(3)	108(1)	C(18)–C(13)–C(14)	118(1)
C(2)–C(3)–C(4)	107(1)		

Primed atoms are related to the unprimed ones by the centre of symmetry.

the dimer. Since structural details are not available for any other compound containing the μ-dppb group the comparison has been made with $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2(CH_2)]$,[19] $[Rh_2(\eta\text{-}C_5H_5)(CO)_2(\mu\text{-}CO)]$,[20] and $[Rh_2(dppm)_2(CO)_2(\mu\text{-}Cl)][BF_4]$ [21] where different bridging groups are present. Although direct Rh–Rh interactions exist in the quoted compounds their values for the Rh–C(cp), Rh–C(=O), and Rh–C=O are, within the limit of error, comparable with the values of 1.94(1) Å Rh–C(cp), 1.80(1) Å Rh–C(=O), and 179.2(2)° Rh–C=O found in the title compound where no direct Rh–Rh interactions are present. The Rh–P distance [2.246(2) Å] is comparable with the values of 2.271(2) and 2.228(2) Å reported for $[Rh(dppe)(mac)][BF_4]$.[22] [dppm = $Ph_2PCH_2PPh_2$, mac = (*Z*)-methyl-α-acetamidocinnamate.]

TABLE 3

Squares planes through the dimer, (1) (deviations of relevant atoms from the planes (Å) are given in square brackets)

Plane 1: Rh, Rc, *C(6), P
$1.8989X - 1.1038Y + 11.8356Z = 3.5375$
[Rh −0.012, Rc 0.005, C(6) 0.004, P 0.003]

Plane 2: C(1), C(2), C(3), C(4), C(5)
$4.2847X + 7.3846Y - 5.1158Z = 2.5970$
[C(1) −0.013, C(2) −0.005, C(3) 0.022, C(4) −0.030, C(5) 0.027]

Plane 3: C(7), C(8), C(9), C(10), C(11), C(12)
$-4.2822X + 6.8697Y + 4.0434Z = 0.1714$
[C(7) −0.007, C(8) −0.001, C(9) 0.011, C(10) −0.014, C(11) 0.005, C(12) 0.005]

Plane 4: C(13), C(14), C(15), C(16), C(17), C(18)
$7.0558X - 0.3866Y + 2.6237Z = 1.8516$
[C(13) 0.012, C(14) −0.017, C(15) 0.014, C(16) −0.005, C(17) −0.000, C(18) −0.003]

Angles (°) between the planes

1–2	89.9	1–3	78.0	1–4	53.2
2–3	75.7	2–4	59.5	3–4	70.2

* Rc = Ring centre.

The conformation of the aliphatic chain is *trans* as required by symmetry conditions. Figure 2 shows the crystal packing arrangement which is determined by coulombic forces and van der Waals interactions.

Reactions of (1) *with Small Molecules.*—When (1) is treated with $[NO][PF_6]$ in dry benzene-methanol (1 : 1), carbon monoxide is evolved and, from the brown-yellow solution, the dinitrosyl complex $[(\eta\text{-}C_5H_5)(NO)Rh(\mu\text{-dppb})Rh(NO)(\eta\text{-}C_5H_5)][PF_6]_2$, (2), is obtained as a yellow solid. The conductivity in methanol or acetone solution lies in the range expected for 1 : 2 electrolytes. The ν(NO) vibration at 1 820 cm^{-1} observed in the i.r. spectrum suggests [23–25] that NO is co-ordinated as NO^+. Furthermore, complex (2) must be formally considered as a binuclear nitrosyl complex of rhodium(I) and the reaction of (1) with $[NO][PF_6]$ as a substitution reaction of carbon monoxide by the nitrosonium ion. This is also confirmed by the magnitude of the phosphorus coupling of the cp protons which agrees with other literature values for cyclopentadienylphosphinerhodium(I) complexes. In the rhodium(III) complexes the phosphorus coupling to the cyclopentadienyl protons is higher than that found for analogous rhodium(I) derivatives.[5–9] For complex (2), as well as for the other compounds here described, the splitting of the cyclopentadienyl resonance by rhodium atoms seems to be beyond the resolution of the spectrophotometer and not calculable.

In view of the formation of rhodium(III) complexes by oxidative addition reactions of cyclopentadienylcarbonylphosphinerhodium(I) complexes it was expected that the rhodium(I) complex (1) should undergo chemical

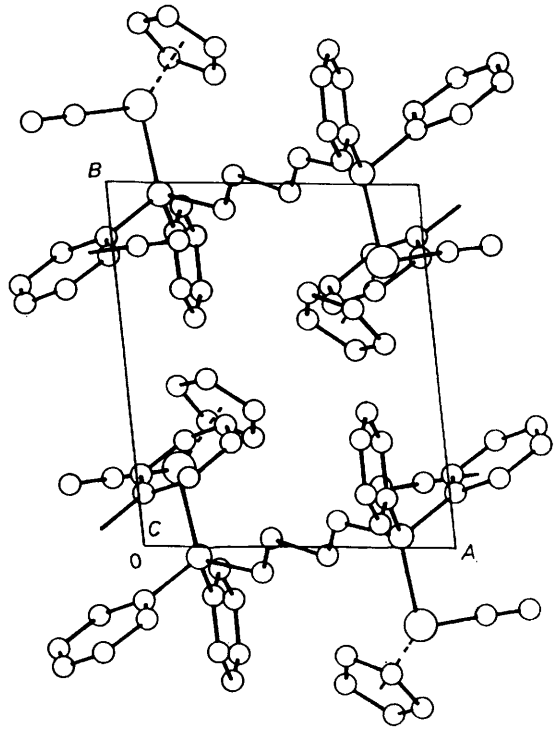


FIGURE 2 Projection down *c* of the unit cell of complex (1)

oxidation to produce rhodium(III) bimetallic compounds. Therefore we have carried out some reactions dealing particularly with the formation of Rh–C σ bonds.

Halogens react with (1), in diethyl ether, at room temperature to give the rhodium(III) dicationic compounds $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2X_2]X_2$ (X = Cl or Br) (3) and $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2I_2][I_3]_2$, (3a), whose stabilities increase from the chloro- to the iodo-derivative. The chloro-derivative decomposes as a solid and in solution, over a period of an hour forming a complex mixture, but the iodo-derivative is stable as a solid and in solution it decomposes more slowly. Oxidative additions on (1) result in an increase in ν(CO), confirming that the process involves both rhodium(I) atoms; the increase in ν(CO) reflects the extent of metal to carbon monoxide ligand back-bonding which decreases as the formal oxidation state of the rhodium atoms increases.

From the reaction of (1) with methyl iodide, the diacetyl derivative $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(COMe)_2I_2]$, (4), is easily obtained. In line with the reaction of [Rh(η-

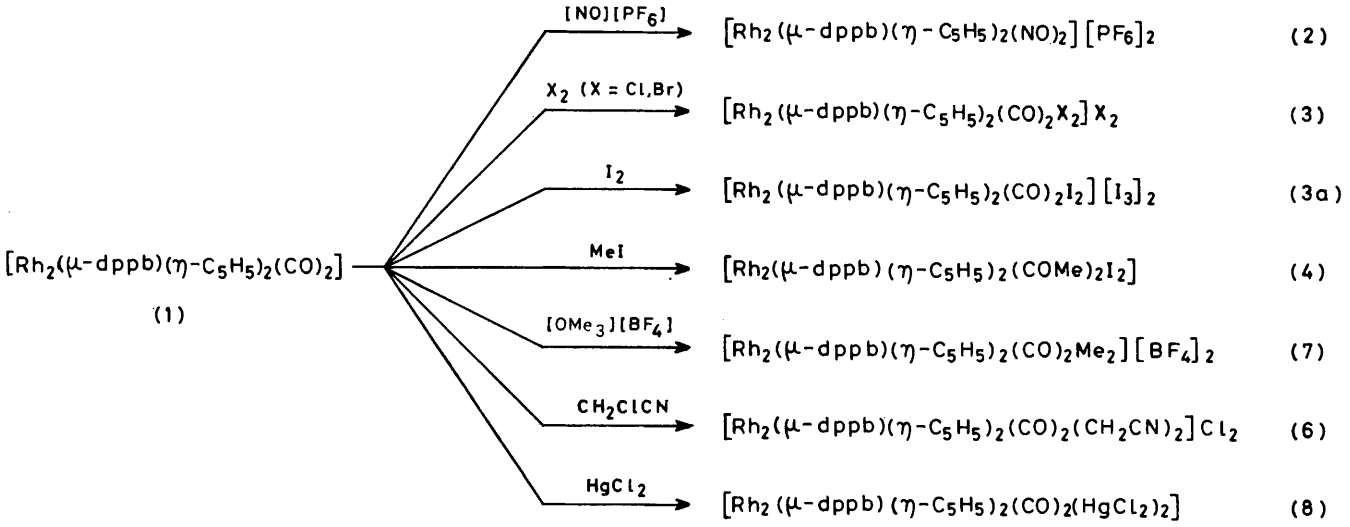
TABLE 4

Analytical and characteristic i.r. and ^{1}H n.m.r. data

Compound [a]	Colour	Analysis (%) [b] C	H	Halogen	ν(CO) [c]/cm^{-1}	^{1}H n.m.r. (τ) [d] C_5H_5	Other
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2]$	Orange	58.6 (58.7)	4.70 (4.70)		1 928vs	4.94t [e]	
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(NO)_2][PF_6]_2$	Yellow	41.1 (41.05)	3.50 (3.45)	2.45 [f] (2.50)	1 820vs [g]	4.16d [h]	
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Cl_2]Cl_2$	Orange	50.1 (50.05)	4.05 (4.00)	14.7 (14.75)	2 105vs	4.84d [e]	
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Br_2]Br_2$	Orange	42.2 (42.2)	3.40 (3.35)	28.15 (28.1)	2 100vs	4.85d [e]	
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2I_2][I_3]_2$	Red-brown	26.3 (26.2)	2.00 (2.10)	55.3 (55.3)	2 090vs	3.63d [h]	
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(COMe)_2I_2]$	Red-brown	45.6 (45.75)	4.10 (4.00)	23.1 (23.0)	1 650vs,br	4.87d [e]	7.14s (CCH_3)
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2(CH_2CN)_2][BPh_4]_2$	Yellow	71.7 (71.4)	5.40 (5.35)	1.80 [f] (1.80)	2 080vs [i]	4.05d [h]	
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Me_2][PF_6]_2$	Yellow	44.4 (44.3)	3.95 (3.90)		2 065vs	4.13d [h]	8.94dd (CH_3) [j]
$[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2(HgCl_2)_2]$	Yellow	35.3 (35.3)	2.85 (2.80)	10.35 (10.4)	2 040s	[k]	

[a] dppb = $Ph_2P(CH_2)_4PPh_2$. [b] Calculated values are given in parentheses. [c] Nujol mulls. [d] Using $SiMe_4$ as internal standard; the J(P-C_5H_5) values are 0.6 Hz for rhodium(I) and in the range 1.2—2.0 Hz for rhodium(III) complexes. [e] In $CDCl_3$. [f] Referring to N. [g] Referring to ν(NO). [h] In [$^2H_6$]acetone. [i] ν(CN) at 2 210m cm^{-1}. [j] J(Me—P) 4.5 Hz and J(Rh—Me) 2.0 Hz. [k] Insoluble.

$C_5H_5)(CO)(PPh_3)]$ with alkyl halides,[6,8] we assume that the reaction occurs first by formation of the dicationic intermediate $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Me_2]I_2$, (5), and subsequently by nucleophilic attack by halide ions on the metal and migration of the alkyl groups to the co-ordinated carbonyls. As reported in Table 4, the i.r. and ^{1}H n.m.r. spectra of (4) show the characteristic absorptions of the various constituents of the compound. shows a band at 2 210 cm^{-1} and a very strong one at 2 080 cm^{-1} which can be assigned to ν(CN) and ν(CO) respectively; in the ^{1}H n.m.r. spectrum ([$^2H_6$]acetone) the only sharp resonances arise from cp and phenyl rings; the resonances of the methylenic groups of the diphosphine ligand and of CH_2CN are very broad and overlap. Also this reaction, as well as that of (1) with CH_3I, initially involves nucleophilic attack on the metal



SCHEME Summary of the transformations carried out on complex (1)

We have isolated compounds like the intermediate (5) from the reactions of (1) with CH_2ClCN and $[OMe_3][BF_4]$. From the former reaction the dicationic rhodium(III) complex $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2(CH_2CN)_2]^{2+}$ (6) was obtained as the tetraphenylborate salt; this is a yellow solid, sparingly soluble in chlorinated solvents such as $CHCl_3$ or CH_2Cl_2, soluble in acetone, and stable in the solid and in solution. The i.r. spectrum at the carbon atom; in fact the methylenic carbon of CH_2ClCN has a higher positive charge than the carbon atom in CH_3I. The relatively higher stability of $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2(CH_2CN)_2]Cl_2$ as compared to (5) can be related to the stabilising effect on the metal–carbon σ bond of the electron-withdrawing CN group.[26-28]

The dicationic complex $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Me_2]^{2+}$, (7), in which the methyl groups are directly

bonded to the rhodium atoms, was isolated as hexafluorophosphate or tetraphenylborate salts, by treating (1) with $[OMe_3][PF_6]$ in dichloromethane solution. Conductivity data indicate that (7) is a 1 : 2 electrolyte in acetone solution. Apart from the shift to higher wavenumbers in the carbonyl stretching frequency and for the bands characteristic of the anion present, the infrared spectrum of (7) closely resembles that of (1). The resonance of the methyl groups bonded to rhodium(III) atoms is observed as a doublet of doublets centred at τ 8.94; also, the magnitude of the J(H–Rh) and J(H–P) couplings can be compared very favourably with that reported [5,7,29-31] for mononuclear cyclopentadienylmethylrhodium(III) complexes or rhodium(III) complexes containing a $Rh–CH_3$ bond.

Attempts to induce methyl transfer to co-ordinated CO by adding PPh_3 to a dichloromethane solution of (7) were unsuccessful and the unreacted ionic complex could be completely recovered from the solution.

The reactivity of (1) towards the various reagents considered implies Lewis-base character of the rhodium atoms. The formation of $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2(HgCl_2)_2]$, (8), in the reaction of (1) with $HgCl_2$ further confirms such a character for each rhodium atom. In forming the adduct (8) it is necessary to use exactly equimolar amounts of the reagents because the purification of the product is very difficult. Compound (8) is an air-stable yellow solid that is quite insoluble in the common organic solvents; it was characterised by elemental analysis and the i.r. spectrum which shows a strong ν(CO) band at 2 040 cm^{-1} and a broad one at 245 cm^{-1} due to the Hg–Cl stretching vibration.[32,33] The very low solubility does not allow reliable n.m.r. data.

The chemical behaviour of the binuclear complex (1) is comparable to that of the mononuclear cyclopentadienylcarbonylphosphinerhodium(I) complexes. This is reasonable if we consider compound (1) as being formed by two $Rh(\eta\text{-}C_5H_5)(CO)PPh_2CH_2CH_2$ moieties bound through the carbon chain of the chelate.

The various transformations carried out on (1) are summarised in the Scheme.

EXPERIMENTAL

The starting materials $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ [34] and 1,4-bis(diphenylphosphino)butane [15] were prepared by literature methods. 1,4-Bis(diphenylphosphino)butane was a Strem product. 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 ^1H n.m.r. spectra. Conductivity measurements were made with a WTW LBR conductivity meter. Molecular weight was determined with a Knauer vapour pressure osmometer. 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 ^1H n.m.r. data of the prepared compounds are reported in Table 4.

[μ-1,4-Bis(diphenylphosphino)butane]-dicarbonylbis(η-cyclopentadienyl)dirhodium(I), (1).—A benzene solution (150 cm^3) containing $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ (obtained in pentane from 0.52 g of $[\{Rh(CO)_2Cl\}_2]$ and an excess of $Tl[C_5H_5]$) and 1,4-bis(diphenylphosphino)butane (1.71 g) was heated under reflux until the i.r. spectrum showed disappearance of the ν(CO) of the starting material (about 7 h). The solution was concentrated and transferred to a benzene-packed column of silica. Elution with benzene gave a yellow fraction which, after evaporation of the solvent at reduced pressure and crystallisation from benzene–hexane, gave the product as orange crystals (yield 0.34 g, 38%).

Further elution with methanol gave a fraction which held a product which does not contain the co-ordinated cyclopentadienyl ligand (see Results and Discussion section).

[μ-1,4-Bis(diphenylphosphino)butane]-bis(η-cyclopentadienyl)dinitrosyldirhodium Hexafluorophosphate, (2).—Nitrosonium hexafluorophosphate (0.08 g, 0.45 mmol) was added to a stirred solution of (1) (0.18 g, 0.22 mmol) in dry benzene (8 cm^3) and anhydrous methanol (8 cm^3). The solution changed rapidly from yellow to brown-yellow. After about 10 min the solvent was evaporated and the crude product was crystallised several times from dichloromethane–hexane. The solvent was removed and the product obtained as a yellow solid.

Reactions of (1) *with Halogens*.—A solution of chlorine in diethyl ether was added dropwise to a stirred solution of (1) in the same solvent. The orange solid $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Cl_2]Cl_2$ was obtained, collected, washed several times with pentane, and dried. Similarly, addition of bromine or iodine to (1) gave $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2Br_2]Br_2$ and $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2I_2][I_3]_2$.

The tetraphenylborate salts $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2X_2][BPh_4]_2$ (X = Cl, Br, or I) were prepared by adding $Na[BPh_4]$ dissolved in methanol to a solution of the corresponding halide salt in the same solvent.

Diacetyl-[μ-1,4-bis(diphenylphosphino)butane]-bis(η-cyclopentadienyl)di-iododirhodium(III), (4).—A mixture of (1) (0.22 g, 0.26 mmol) and MeI (3 cm^3) was stirred, at room temperature, for 30 min. During this time the solution became red. The excess of MeI was partially removed by rotary evaporation under reduced pressure and, on adding hexane, the product was obtained as a red-brown solid. This was crystallised from dichloromethane–hexane, collected, washed several times with hexane, and dried.

[μ-1,4-Bis(diphenylphosphino)butane]-dicarbonylbis(cyanomethyl)bis(η-cyclopentadienyl)dirhodium(III) *Tetraphenylborate*, (6).—A mixture of (1) (0.12 g, 0.14 mmol) and CH_2ClCN (2 cm^3) was vigorously stirred at room temperature for *ca.* 3 h. An intractable red oil was obtained on evaporation of the solvent. This was dissolved in methanol and by adding $Na[BPh_4]$ in the same solvent a yellow solid was formed. The product was collected on Buchner funnel, washed several times with hexane, and dried.

[μ-1,4-Bis(diphenylphosphino)butane]-dicarbonylbis(η-cyclopentadienyl)dimethyldirhodium(III) *Hexafluorophosphate*, (7).—A dichloromethane solution of $[OMe_3][PF_6]$ was added dropwise to a stirred solution of (1) in the same solvent. The reaction was again monitored by i.r. spectroscopy and was allowed to proceed until the ν(CO) peak of the starting complex had completely disappeared (*ca.* 20 min). The solution was filtered and concentrated and, on adding hexane, a yellow solid was formed. The solvent was removed and the residue washed with pentane and dried.

The corresponding tetraphenylborate salt was prepared by adding $Na[BPh_4]$ dissolved in methanol to a solution of the hexafluorophosphate salt in the same solvent.

[μ-1,4-Bis(diphenylphosphino)butane]-dicarbonylbis(η-cyclopentadienyl)bis(dichloromercury)dirhodium, (8).—Mercury(II) chloride (0.105 g, 0.39 mmol) in acetone (4 cm^3) was added to a solution of (1) (0.16, 0.195 mmol) in the same solvent (5 cm^3). A rapid reaction occurred and a yellow solid was formed. The solvent was removed and the residue washed with diethyl ether and dried.

X-Ray Data Collection and Structure Solution.—Orange crystals of $[Rh_2(\mu\text{-dppb})(\eta\text{-}C_5H_5)_2(CO)_2]$ suitable for *X*-ray diffraction were obtained by slowly cooling a benzene–hexane solution. All diffraction measurements were performed on a Siemens-Stoe four-circle diffractometer by using graphite-monochromated Mo-K_α radiation. Twenty reflections for θ 10—15° were located by a random search procedure and subsequently centred. These reflections were used as a basis for the indexing. The cell constants and the orientation matrix that were obtained were refined by a least-squares fit. The crystals were found to be triclinic with unit cell dimensions $a = 7.650(2)$, $b = 9.323(3)$, $c = 13.253(3)$ Å, $\alpha = 106.1(1)$, $\beta = 100.1(1)$, $\gamma = 93.4(1)°$, $U = 888$ Å^3, $F(000)$ 414, $Z = 1$, and $D_c = 1.46$ g cm^{-3}, λ(Mo-K_α) = 0.7107 Å.

For space group $P1$ no symmetry is imposed on the structure but for $P\bar{1}$ the dimeric molecule must be centrosymmetric. $P\bar{1}$ was assumed and was confirmed by successful structure solution and refinement.

Intensities were collected at room temperature for all independent reflections in a range $3 < \theta < 25°$. An θ—ω scan was used with a 0.5 count at each of 120 steps of 0.01° for each reflection and a 30-s background count at each end of the scan range. No reflections were sufficiently intense to require the insertion of attenuators into the beam. Three standard reflections measured after approximately 60 data reflections showed only random fluctuations. Of the 3 033 measured independent reflections 2 022 with $I > 3\sigma(I)$ were used for structure solution and refinement. The data were corrected for Lorentz and polarisation effects but since the linear absorption coefficient is 9.45 cm^{-1}, no absorption correction was applied. The heavy-atom positions were obtained from a three-dimensional Patterson function. The structure was refined in space group $P\bar{1}$ to convergence by using anisotropic thermal parameters for all the non-hydrogen atoms except the benzene ring carbon atoms. Hydrogen-atom contributions were used as fixed atoms in calculated positions [d(C–H) = 0.95 Å and $B_{iso.}$ = 5.0 Å^2].

The discrepancy index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ had a final value of 0.051. A final difference map revealed peaks of about 0.8 e Å^{-3} near the metal positions but was otherwise featureless. A list of observed and calculated structure factors and thermal parameters is available as Supplementary Publication No. SUP 23027 (16 pp.).*

Atomic scattering factors were taken from Cromer and Waber's [35] (A) tabulation for all atoms except hydrogen for which the values of Stewart [36] were used. Anomalous dispersion terms [37] for Rh, P, and Cl were included in F_c.

The calculations were carried out on the CYBER 76 computer of the 'Centro di Calcolo Interuniversitario; Italia Nord Orientale' with the 'SHELX 76' system [38] of programs.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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