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PYRAZOLATE BRIDGED DINUCLEAR RHODIUM COMPLEXES. X-RAY STRUCTURE OF $[Rh(Pz)(CO)P(OPh)_3]_2$

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Summary

The synthesis and properties of complexes of general formulae $[Rh(Pz)(CO)L]_2$ (Pz = pyrazolate ion, L = phosphorus donor ligand), $[Rh(Pz)(\text{diolefin})]_2$ and $[Rh(Pz)(C_2H_4)_2]_2$ are reported. The crystal structure of the novel complex $[Rh(Pz)(CO)P(OPh)_3]_2$ has been determined by X-ray methods. The crystals are triclinic, space group P_1, with $Z = 2$ in a unit cell of dimensions a 14.061(10), b 17.140(13), c 9.937(7) Å, α 102.19(7), β 10.9.55(8), γ 75.14(8)°. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.058$ for 2514 independent observed reflections. The structure consists of discrete dimeric complexes in which each rhodium is in nearly square-planar arrangement, being bonded to a carbon atom of a carbonyl group, to a phosphorus of a triphenylphosphite ligand and to two nitrogen atoms of pyrazolate ligands bridging the metal atoms. The dihedral angle between the two square planes of 86.2° gives a bent configuration to the molecule in which the carbonyls and the phosphite ligands are in a *trans* arrangement.

Introduction

The coordination chemistry of organometallic rhodium(I) derivatives with polypyrazolylborates have been investigated [1—6]. In contrast, the coordination chemistry of the pyrazolate ion (Pz^-) has been less studied. The dinuclear derivative $[Rh(Pz)(CO)_2]_2$ and some related complexes of the type $[Rh(Me_2Pz)L_2]_2$ (L = CO; L_2 = 1,5-cyclooctadiene (COD)) have been described previously [3,7], and some pyrazolate bridged heterodinuclear complexes have been recently reported by Bonati et al. [8,9].

In this paper we describe a new family of dinuclear monocarbonyl deriva-

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tives of the type $[Rh(Pz)(CO)L]_2$, along with some related complexes of the type $[Rh(Pz)(diolefin)]_2$ and $[Rh(Pz)(C_2H_4)_2]_2$. The structure of the dinuclear complex $[Rh(Pz)(CO)P(OPh)_3]_2$, which is of the first type, has been determined by X-ray methods.

Results and discussion.

Olefin complexes

Following our studies on the reactions of cationic rhodium(I) diolefin complexes [10—14], we have observed that reaction of $[Rh(COD)(bipy)]^+$ or $[Rh(COD)(PPh_3)_2]^+$ with sodium pyrazolate leads to the formation of the neutral complex $[Rh(Pz)(COD)]_2$.

A more direct method of preparing $[Rh(Pz)(diolefin)]_2$ complexes in high yields involves the reaction of $[RhCl (diolefin)]_2$ [15—17] with sodium pyrazolate, according to equation 1:

$$\tfrac{1}{2}[RhCl(diolefin)]_2 + NaPz \rightarrow \tfrac{1}{2}[Rh(Pz)(diolefin)]_2 + NaCl \qquad (1)$$

(diolefin = 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD) and tetrafluorobenzobarrelene (TFB))

The synthesis of $[Rh(Pz)(C_2H_4)_2]_2$ from $[RhCl(C_2H_4)_2]_2$ [18] was carried out by reaction 1, but the presence of NaOH was found necessary to produce high yields of the red compound.

Alternative routes to $[Rh(Pz)(diolefin)]_2$ complexes were provided by the following reactions:

$$\tfrac{1}{2}[RhCl(diolefin)]_2 + HNEt_3Pz \rightarrow \tfrac{1}{2}[Rh(Pz)(diolefin)]_2 + HNEt_3Cl \qquad (2)$$

$$[Rh(acac)(diolefin)] + HPz \rightarrow \tfrac{1}{2}[Rh(Pz)(diolefin)]_2 + Hacac \qquad (3)$$

The $[Rh(Pz)(diolefin)]_2$ complexes (see Table 1) were isolated as stable yellow microcrystalline solids, and show decomposition points above 210°C. Molecular weight measurements on some of these complexes show that they are dimeric in chloroform. The infrared spectra of the complexes show vibrations due to the pyrazolate group and the coordinated diolefin.

Attempts to cleave the pyrazolate bridges by reaction of $[Rh(Pz)(COD)]_2$ with an stoichiometric amount of triphenylphosphine in refluxing dichloromethane for 1 h were unsuccessful. It is noteworthy that the reaction of $[RhCl(COD)PPh_3]$ [15] with sodium pyrazolate affords the binuclear $[Rh(Pz)(COD)]_2$. No reaction was observed when $[Rh(Pz)(COD)]_2$ was treated with thallium cyclopentadienide or triphenylphosphite. All these results indicate a marked stability of the pyrazolate bridges in these binuclear rhodium complexes.

Carbonyl complexes

Bubbling carbon monoxide at atmospheric pressure through a dichloromethane solution of the $[Rh(Pz)(diolefin)]_2$ complexes for a few minutes gave a intermediate (presumably $[Rh(Pz)(CO)_2]_2$ [3]) which was not isolated as a solid. Addition of a phosphorus donor ligand to the solution led to evolution of

TABLE 1

ANALYTICAL DATA FOR THE COMPOUNDS

Complex	Analysis (found (calcd.) (%))			Mol. wt. ($CHCl_3$) (found (calcd.))	Yield (%)
	C	H	N		
$[Rh(Pz)(COD)]_2$	47.27	5.46	9.65	552	96
	(47.33)	(5.42)	(10.03)	(558)	
$[Rh(Pz)(NBD)]_2$	46.05	4.37	9.96	—	88
	(45.82)	(4.23)	(10.69)		
$[Rh(Pz)(TFB)]_2$	45.69	2.25	6.51	856	90
	(45.48)	(2.29)	(7.07)	(792)	
$[Rh(Pz)(C_2H_4)_2]_2$	37.15	4.95	11.75	—	70
	(37.19)	(4.90)	(12.39)		
$[Rh(Pz)(CO)P(OPh)_3]_2$	52.25	3.49	5.04	1020	82
	(51.99)	(3.57)	(5.51)	(1017)	
$[Rh(Pz)(CO)P(p\text{-}ClC_6H_4)_3]_2$	46.86	3.27	4.50	—	77
	(46.88)	(2.68)	(4.99)		
$[Rh(Pz)(CO)PPh_3]_2$	57.25	4.05	5.91	869	80
	(57.28)	(3.93)	(6.07)	(923)	
$[Rh(Pz)(CO)P(p\text{-}MeC_6H_4)_3]_2$	59.85	4.97	5.53	—	79
	(59.77)	(4.82)	(5.57)		
$[Rh(Pz)(CO)P(p\text{-}MeOC_6H_4)_3]_2$	54.08	4.36	5.22	—	80
	(54.56)	(4.39)	(5.09)		
$[Rh(Pz)(CO)_2]_2$	26.95	1.46	12.94	—	83
	(26.57)	(1.34)	(12.40)		

carbon monoxide and formation of complexes of the type $[Rh(Pz)(CO)L]_2$, according to equation 4:

$$\tfrac{1}{2}[Rh(Pz)(diolefin)]_2 + CO + L \rightarrow \tfrac{1}{2}[Rh(Pz)(CO)L]_2 + diolefin \tag{4}$$

The complexes were isolated as yellow microcrystalline solids for L = $P(OPh)_3$, $P(p\text{-}ClC_6H_4)_3$, PPh_3, $P(p\text{-}MeC_6H_4)_3$ and $P(p\text{-}MeOC_6H_4)_3$. Table 1 gives the analytical data for the new complexes. The infrared spectra in the solid state show the presence of the pyrazolate group, the ancillary phosphorus donor ligand and carbonyl groups. One $\nu(CO)$ band is observed (2020 cm^{-1}) for the $[Rh(Pz)(CO)P(OPh)_3]_2$, in agreement with the *trans* structure revealed by the X-ray determination (see next section). Two bands are observed for $[Rh(Pz)(CO)P(p\text{-}ClC_6H_4)_3]_2$ (1981 and 1988(sh) cm^{-1}) $[Rh(Pz)(CO)P(p\text{-}MeC_6H_4)_3]_2$ (1970 and 1980 cm^{-1}) complexes, but only one band (1986 cm^{-1}) is found for the $[Rh(Pz)(CO)PPh_3]_2$ complex, and three bands (1967, 1976 and 1981(sh) cm^{-1}) for the $[Rh(Pz)(CO)P(p\text{-}MeOC_6H_4)_3]_2$ complex, probably due to solid state effects, as previously observed in related complexes [19]. As expected, the $\nu(CO)$ absorptions are shifted toward lower energies when the basicity of the phosphorus donor increases, due to the increase of the back-donation from the rhodium atom to the coordinated carbonyl group.

An alternative route to $[Rh(Pz)(CO)PPh_3]_2$ involves the reaction of $[Rh(acac)(CO)PPh_3]$ [20] with pyrazole, according to equation 5:

$$[Rh(acac)(CO)PPh_3] + HPz \rightarrow \tfrac{1}{2}[Rh(Pz)(CO)PPh_3]_2 + Hacac \tag{5}$$

The proposed intermediate $[Rh(Pz)(CO)_2]_2$ can be easily prepared according to the equation 6:

$\frac{1}{2}[RhCl(CO)_2]_2 + HNEt_3Pz \rightarrow \frac{1}{2}[Rh(Pz)(CO)_2]_2 + HNEt_3Cl$ (6)

Crystal structure of the complex [Rh(Pz)(CO)P(OPh)₃]₂

The crystal structure consists of discrete dimeric *trans*-di-μ-pyrazolato dicarbonyl bis(triphenylphosphite)dirhodium(I) complexes. A view of the dimer with the atomic numbering is shown in Fig. 1; selected bond distances and angles are given in Table 2.

Each rhodium atom is in an approximately square-planar arrangement, and is bound to a carbon atom of a carbonyl, a phosphorus atom of a triphenylphosphite and two nitrogen atoms of two pyrazolate (Pz) ligands. Each Pz bridges the two Rh atoms so a double Pz bridge joins them in a dimer. Both square-planar arrangements are imperfect, the displacements of Rh(1), P(1), C(1), N(1), N(3) and of Rh(2), P(2), C(2), N(2), N(4) atoms from the mean planes passing through them being —0.02, —0.01, 0.09, 0.01, —0.08 and —0.02, 0.01, —0.01, 0.07, —0.05 Å, respectively. The dihedral angle between the two square planes of 86.2 gives a bent configuration to the complex, where the CO and phosphite ligands are in *trans*. The intramolecular Rh(1)—Rh(2) distance of 3.568 Å excludes significant metal—metal interactions.

The Rh—C bonds (Rh(1)—C(1) 1.84 Å and Rh(2)—C(2) 1.82 Å) are quite regular and the carbonyls are terminal as expected (Rh(1)—C(1)—O(1) 178° and Rh(2)—C(2)—O(2) 176°). The Rh—P bonds to the triphenylphosphite ligands (Rh(1)—P(1) 2.188 Å and Rh(2)—P(2) 2.191 Å) are longer than in the double-square planar, but unsymmetrical, complex with the same ligand, $Rh_2(COD)Cl_2[P(OPh)_3]_2$ [21] (COD = 1,5-cyclooctadiene, 2.138 and 2.146 Å) and closer to those found in analogous complexes $[RhCl(CO)(PMe_2Ph)]_2$ [22] (2.220 and

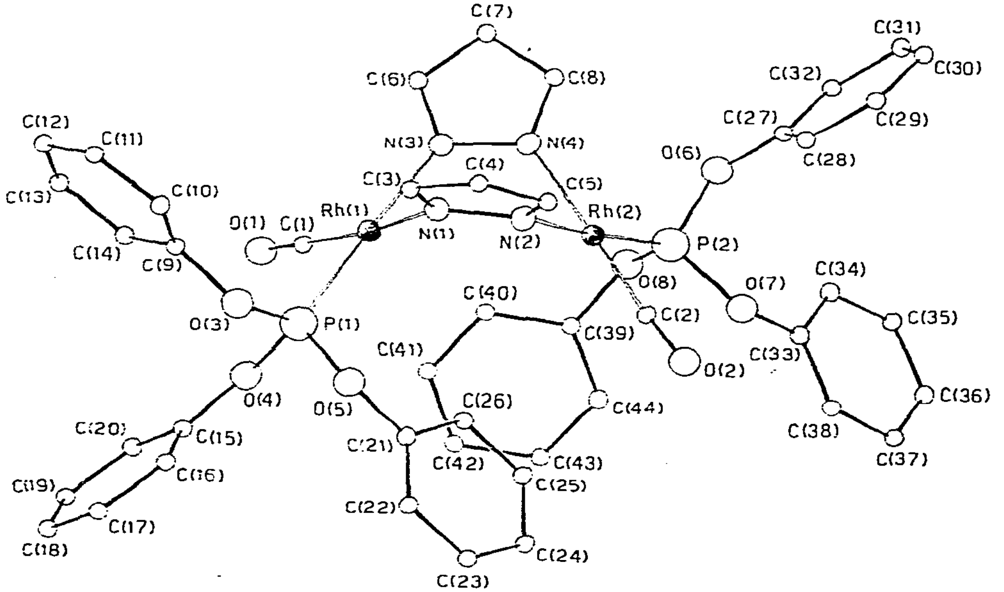

Fig. 1. View of the molecular shape of the complex $[Rh(Pz)(CO)P(OPh)_3]_2$ with the atomic numbering scheme.

TABLE 2

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

(a) in the Rh coordination sphere			
Rh(1)—P(1)	2.188(6)	Rh(2)—P(2)	2.191(6)
Rh(1)—N(1)	2.08(1)	Rh(2)—N(2)	2.07(1)
Rh(1)—N(3)	2.11(1)	Rh(2)—N(4)	2.09(1)
Rh(1)—C(1)	1.84(2)	Rh(2)—C(2)	1.82(2)
P(1)—Rh(1)—N(1)	90.8(4)	P(2)—Rh(2)—N(2)	176.3(4)
P(1)—Rh(1)—N(3)	177.3(5)	P(2)—Rh(2)—N(4)	90.5(4)
P(1)—Rh(1)—C(1)	89.5(7)	P(2)—Rh(2)—C(2)	91.0(7)
N(1)—Rh(1)—N(3)	87.0(6)	N(2)—Rh(2)—N(4)	88.2(6)
N(1)—Rh(1)—C(1)	175.6(7)	N(2)—Rh(2)—C(2)	90.3(8)
N(3)—Rh(1)—C(1)	92.8(8)	N(4)—Rh(2)—C(2)	178.5(8)
(b) in the carbonyls			
O(1)—C(1)	1.14(3)	O(2)—C(2)	1.14(3)
Rh(1)—C(1)—O(1)	178(2)	Rh—C(2)—O(2)	176(2)
(c) in the pyrazolyl ligands			
N(1)—N(2)	1.38(2)	N(3)—N(4)	1.39(2)
N(1)—C(3)	1.37(2)	N(3)—C(6)	1.33(2)
N(2)—C(5)	1.37(2)	N(4)—C(8)	1.33(2)
C(3)—C(4)	1.39(2)	C(6)—C(7)	1.38(2)
C(4)—C(5)	1.40(2)	C(7)—C(8)	1.38(2)
N(2)—N(1)—C(3)	109(1)	N(4)—N(3)—C(6)	108(1)
N(2)—N(1)—Rh(1)	122(1)	N(4)—N(3)—Rh(1)	121(1)
C(3)—N(1)—Rh(1)	130(1)	C(6)—N(3)—Rh(1)	130(1)
C(5)—N(2)—Rh(2)	131(1)	C(8)—N(4)—Rh(2)	133(1)
C(5)—N(2)—N(1)	107(1)	C(8)—N(4)—N(3)	106(1)
Rh(2)—N(2)—N(1)	121(1)	Rh(2)—N(4)—N(3)	121(1)
C(4)—C(3)—N(1)	109(2)	C(7)—C(6)—N(3)	110(2)
C(5)—C(4)—C(3)	105(2)	C(8)—C(7)—C(6)	105(2)
N(2)—C(5)—C(4)	110(2)	N(4)—C(8)—C(7)	111(2)
(d) in the $P(OPh)_3$) ligands			
P(1)—O(3)	1.60(1)	P(2)—O(6)	1.59(1)
P(1)—O(4)	1.60(1)	P(2)—O(7)	1.60(1)
P(1)—O(5)	1.59(1)	P(2)—O(8)	1.61(1)
O(3)—C(9)	1.39(2)	O(6)—C(27)	1.37(2)
O(4)—C(15)	1.40(2)	O(7)—C(33)	1.40(2)
O(5)—C(21)	1.43(2)	O(8)—C(39)	1.40(2)
C(9)—O(3)—P(1)	124.6(9)	C(27)—O(6)—P(2)	126.7(9)
C(15)—O(4)—P(1)	128.1(9)	C(33)—O(7)—P(2)	130.3(10)
C(21)—O(5)—P(1)	123.7(9)	C(39)—O(8)—P(2)	121.2(10)
O(3)—P(1)—Rh(1)	119.2(5)	O(6)—P(2)—Rh(2)	119.5(5)
O(4)—P(1)—Rh(1)	112.4(6)	O(7)—P(2)—Rh(2)	112.4(5)
O(5)—P(1)—Rh(1)	118.3(5)	O(8)—P(2)—Rh(2)	119.8(5)

2.230 Å) and $[Rh(SPh)(CO)(PMe_3)]_2$ [19] (2.256 and 2.257 Å) with substituted phosphine ligands. The Rh—N bonds are close (Rh(1)—N(1) 2.08, Rh(2)—N(2) 2.07, Rh(1)—N(3) 2.11 and Rh(2)—N(4) 2.09 Å] each Pz ligand acting as a nearly symmetrical bridge. As these nitrogen atoms are in *trans* to the CO or $P(OPh)_3$ ligands, no relevant difference in *trans* influence is observed for these ligands. The two Pz ligands are perfectly planar and nearly perpendicular to each other (the angle formed by the two rings being of 80.6°). The N(1), N(2), C(3), C(4), C(5), Rh(1), Rh(2) atoms are displaced from the plane passing through the first five atoms of —0.002, 0.003, 0, 0.004, —0.006,

—0.072 and 0.245 Å, the N(3), N(4), C(6), C(7), C(8), Rh(1), Rh(2) from the plane passing through the other Pz ring of 0.005, —0.002, —0.012, 0.012, —0.004, 0.315 and 0.063 Å.

Some interesting features in the present complex require comment. It is the third dimeric bridged rhodium(I) complex with CO's and phosphorus-containing ligands for which a crystal structure has been reported. In both the previously reported solids $[RhCl(CO)(PMe_2Ph)]_2$ [22] and $[Rh(SPh)(CO)(PMe_3)]_2$ [19], the CO and phosphine ligands are in *cis* dispositions, though the presence of the *trans* isomer has been revealed in solution; our complex represents the first solid *trans* isomer.

The α dihedral angle of 86.2° in the present complex is the smallest found for double-square planar dinuclear complexes. Values for this angle ranging from 113.0° in $[Rh(SPh)(CO)(PMe_3)]_2$ [19] to 180° in $[Rh(COD)Cl]_2$ [23] have been reported and are compared in ref. 19. In all the previously reported complexes chlorine atoms or sulphur atoms from thiophenolate ligands act as rather flexible bridges between the metal atoms, so that the α angle can assume different values; in the present complex the Pz ligand bridges the Rh atoms through two different atoms; the rigidity of the ligand, forced to coordinate to the metals in a square-planar fashion, leads to an α value close to 90° for the bent configuration.

In all previously reported complexes with bent configuration, a rather short intramolecular Rh—Rh distance, ranging from 3.02 to 3.17 Å, has been found, attributable to a weak metal—metal interaction, but in $[Rh(COD)Cl]_2$ [23], where the α angle is of 180°, this distance is of 3.50 Å. In our complex the bent configuration is accompanied by a very long intramolecular Rh—Rh distance of 3.568 Å.

Since the previous structure determinations ruled out the need for intermolecular metal—metal bonds to account for the bent configuration, postulated by Dahl et al. in discussing the structure of $[RhCl(CO)_2]_2$ [24], the results of the present structure determination confirm that the bent configuration does not require the presence of intramolecular metal—metal interactions.

Experimental

Reactions were carried out at room temperature under air unless otherwise specified. Solvents were distilled before use. C, H, N analysis were performed with a Perkin—Elmer 240 microanalyzer. IR spectra were recorded on a Perkin—Elmer 599 spectrophotometer using Nujol mulls between NaCl plates. Abscissa expansion was carried out in the carbonyl region. Melting points were determined on a Büchi apparatus. Molecular weights were measured with a Perkin—Elmer 115 osmometer.

Reaction of $[Rh(COD)(bipy)]^+$ or $[Rh(COD)(PPh_3)_2]^+$ with sodium pyrazolate

Upon addition of sodium pyrazolate (0.009 g, 0.1 mmol) in methanol (5 ml) to a solution of either $[Rh(COD)(bipy)]ClO_4$ or $[Rh(COD)(PPh_3)_2]ClO_4$ (0.1 mmol) in acetone (10 ml), $[Rh(Pz)(COD)]_2$ separated as a yellow solid. The solid was filtered off, washed with cold methanol, and dried under vacuum.

Preparation of [Rh(Pz)(diolefin)]$_2$ complexes

The compounds in which the diolefin was 1,5-cyclooctadiene, 2,5-norbornadiene, or tetrafluorobenzobarrelene were prepared by the three general routes described below for the case where the diolefin was 1,5-cyclooctadiene.

(i) To a suspension of [RhCl(COD)]$_2$ (0.025 g, 0.05 mmol) in methanol (10 ml), sodium pyrazolate (0.009 g, 0.1 mmol) in methanol/water (5/1 ml) was added dropwise. The starting material dissolved when a half of the sodium pyrazolate solution is added and when the addition was complete the product [Rh(Pz)(COD)]$_2$ precipitated almost quantitatively. It was filtered off, washed with methanol, and air-dried.

(ii) The reaction was carried out as above but the solution of sodium pyrazolate was replaced by a mixture of pyrazole (0.0068 g, 0.1 mmol) and triethylamine (15 μl) in methanol (5 ml).

(iii) On addition of pyrazole (0.0068 g, 0.1 mmol) in acetone (5 ml) to a solution of [Rh(acac)(COD)] (0.031 g, 0.1 mmol) in acetone (10 ml), [Rh(Pz)(COD)]$_2$ separated as a yellow solid. The solution was evaporated under vacuum and methanol was added to complete the precipitation. The solid was filtered off, washed with methanol, and air-dried.

Reaction of [RhCl(COD)PPh$_3$] with sodium pyrazolate

To a suspension of [RhCl(COD)PPh$_3$] (0.030 g, 0.049 mmol) in methanol (10 ml) a solution of sodium pyrazolate (0.0045 g, 0.05 mmol) in methanol/water (3/1 ml) was added. Solid [Rh(Pz)(COD)]$_2$ separated immediately and was filtered off, washed with methanol, and air-dried.

Preparation of [Rh(Pz)(C$_2$H$_4$)$_2$]$_2$

To a suspension of [RhCl(C$_2$H$_4$)$_2$]$_2$ [18] (0.030 g, 0.076 mmol) in deoxygenated methanol (5 ml) a mixture of pyrazole (0.010 g, 0.15 mmol) and sodium hydroxide (1.3 mmol) in methanol (1 ml) and water (1.3 ml) was added dropwise, giving a red solid. The mixture was stirred for 45 min and then the solid was filtered off, washed with a small volume of methanol/water 1/1. The crude product was dissolved in deoxygenated acetone and filtered through Celite. Addition of methanol/water 1/1 to the filtrate caused the precipitation of the pure compound, which was filtered off, washed with methanol/water 1/1, and dried under vacuum.

Preparation of the complexes [Rh(Pz)(CO)(PR$_3$)]$_2$

The general method used making these compounds in which PR$_3$ = P(OPh)$_3$, P(*p*-ClC$_6$H$_4$)$_3$, PPh$_3$ P(*p*-MeC$_6$H$_4$)$_3$ or P(*p*-MeOC$_6$H$_4$)$_3$ is illustrated by the case of [Rh(Pz)(CO)(PPh$_3$)]$_2$. The others were prepared similarly.

Carbon monoxide was bubbled through a solution of [Rh(Pz)(COD)]$_2$ (0.026 g. 0.05 mmol) in dichloromethane (15 ml) for 10 min to give a pale yellow solution of the dicarbonyl complex [Rh(Pz)(CO)$_2$]$_2$ [3]. Addition of solid triphenylphosphine (0.026 g, 0.1 mmol) caused evolution of carbon monoxide and the colour intensified. The solution was evaporated under vacuum and hexane was added. The solid which separated out was filtered off, washed with hexane, and air dried.

An alternative route to the title complexes lies in the reaction of [Rh(acac)(CO)(PPh$_3$)] (20) (0.1 mmol) in acetone/dichloromethane 2/1 (15 ml) with solid pyrazole (0.1 mmol). The solution was evaporated to ca. 2 ml and methanol was added to precipitate the product.

Preparation of [Rh(Pz)(CO)$_2$]$_2$

To a methanol solution of [RhCl(CO)$_2$]$_2$ (0.030 g, 0.077 mmol) was added a solution of HNEt$_3$Pz (0.0105 g, 0.154 mmol) in methanol/water (1/1). [Rh(Pz)(CO)$_2$]$_2$ separated immediately. The yellow solid was filtered off, washed with methanol/water (1/1), and dried under vacuum, ν(CO) (cyclohexane): 2022, 2079 and 2090 cm^{-1}.

X-Ray data collection

A thin yellow crystal of the complex [Rh(Pz)(CO)P(OPh)$_3$]$_2$ with dimensions of ca. 0.06 × 0.20 × 0.20 mm was used for the data collection. Preliminary cell parameters were first determined from rotation and Weissenberg photographs and then refined from a least-squares procedure of θ values for 16 reflections accurately measured by single-crystal diffractometry. The more significant crystal data are as follows: $C_{44}H_{36}N_4O_8P_2Rh_2$, M = 1016.55, triclinic, a 14.061(10), b 17.140(13), c 9.937(7) Å, α 102.19(7), β 109.55(8), γ 75.14(8)°, V 2161(3) Å^3, $Z = 2$, d_{calc}. 1.563 g/cm^3, μ(Mo-K_α) 8.79 cm^{-1}; space group $P1$ (from structure determination).

Intensity data were collected at room temperature using a Siemens AED automated single-crystal diffractometer with the Niobium-filtered Mo-K_α radiation and the θ—2θ scan technique. The intensities of 5774 independent reflections were measured with θ in the range 3—23° and 2514, having $I > 2\sigma(I)$, were employed in the analysis. A standard reflection was periodically measured after every 20 reflections to check the stability of the sample and of the instrument. The intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied because of the very low value of μr. The first absolute scale and the mean temperature factor were determined by Wilson's method.

Structure determination and refinement

The structure was solved by the heavy-atom technique; the refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [25] with initially isotropic and then anisotropic thermal parameters for the Rh, P, O and C atoms but those of the phenyl rings, which were treated as rigid groups of D_{6h} [(d(C—C) 1.395 Å) symmetry. The hydrogen atoms were placed in their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The final conventional R factor was 0.058 for the observed reflections only. The atomic scattering factors used (corrected for the anomalous dispersion of Rh and P) were taken from the International Tables [26]. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$. Unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$

TABLE 3

FRACTIONAL ATOMIC COORDINATES (X10^{4}) FOR THE NON HYDROGEN ATOMS WITH e.s.d.'s IN PARENTHESES

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Rh(1)	2048(1)	3184(1)	3132(2)	C(15)	2726(11)	5605(6)	5667(14)
Rh(2)	2907(1)	1205(1)	4230(2)	C(16)	3673(11)	5800(6)	5867(14)
P(1)	2997(4)	4101(3)	4173(6)	C(17)	3825(11)	6592(6)	6421(14)
P(2)	2078(4)	692(3)	5233(5)	C(18)	3030(11)	7189(6)	6775(14)
O(1)	205(11)	4404(9)	3574(18)	C(19)	2084(11)	6995(6)	6576(14)
O(2)	4846(11)	802(9)	6558(17)	C(20)	1932(11)	6203(6)	6022(14)
O(3)	3437(9)	4478(7)	3213(13)	C(21)	4327(9)	3555(7)	6564(10)
O(4)	2440(9)	4854(7)	5076(13)	C(22)	5187(9)	3770(7)	7648(10)
O(5)	4125(8)	3819(7)	5209(13)	C(23)	5490(9)	3491(7)	8979(10)
O(6)	1422(8)	25(6)	4298(13)	C(24)	4933(9)	2997(7)	9228(10)
O(7)	2821(9)	293(7)	6630(13)	C(25)	4074(9)	2782(7)	8144(10)
O(8)	1111(9)	1257(7)	5713(14)	C(26)	3771(9)	3061(7)	6812(10)
N(1)	3299(10)	2363(8)	2644(16)	C(27)	1800(9)	−764(6)	3796(13)
N(2)	3683(11)	1627(8)	3178(16)	C(28)	2798(9)	−1036(6)	3682(13)
N(3)	1195(11)	2259(8)	2166(17)	C(29)	3132(9)	−1853(6)	3191(13)
N(4)	1568(11)	1472(8)	2531(16)	C(30)	2469(9)	−2398(6)	2815(13)
C(1)	911(16)	3936(12)	3427(20)	C(31)	1471(9)	−2125(6)	2929(13)
C(2)	4093(17)	986(11)	5693(23)	C(32)	1137(9)	−1309(6)	3420(13)
C(3)	3894(14)	2431(11)	1849(19)	C(33)	2592(11)	−45(8)	7619(14)
C(4)	4673(14)	1738(11)	1861(22)	C(34)	1741(11)	−405(8)	7275(14)
C(5)	4524(14)	1253(12)	2710(22)	C(35)	1607(11)	−780(8)	8298(14)
C(6)	357(15)	2248(13)	1038(22)	C(36)	2325(11)	−795(8)	9664(14)
C(7)	177(18)	1468(13)	610(25)	C(37)	3176(11)	−435(8)	10007(14)
C(8)	942(16)	1014(12)	1587(23)	C(38)	3309(11)	−60(8)	8985(14)
C(9)	2841(9)	4810(7)	1955(11)	C(39)	1186(10)	2008(6)	6581(14)
C(10)	3313(9)	4694(7)	877(11)	C(40)	873(10)	2703(6)	5898(14)
C(11)	2802(9)	5064(7)	−366(11)	C(41)	857(10)	3472(6)	6717(14)
C(12)	1819(9)	5550(7)	−530(11)	C(42)	1155(10)	3547(6)	8218(14)
C(13)	1347(9)	5666(7)	548(11)	C(43)	1469(10)	2851(6)	8901(14)
C(14)	1858(9)	5296(7)	1790(11)	C(44)	1484(10)	2082(6)	8082(14)

TABLE 4

CALCULATED FRACTIONAL COORDINATES (X10^{4}) FOR THE HYDROGEN ATOMS

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
H(3)	3778	2943	1297	H(24)	5167	2782	10259
H(4)	5264	1605	1329	H(25)	3643	2400	8335
H(5)	5002	668	2961	H(26)	3106	2894	5973
H(6)	−114	2774	531	H(28)	3311	−614	3974
H(7)	−429	1259	−291	H(29)	3904	−2064	3102
H(8)	1022	370	1585	H(30)	2728	−3030	2436
H(10)	4074	4318	1004	H(31)	957	−2546	2637
H(11)	3167	4974	−1201	H(32)	365	−1099	3509
H(12)	1423	5836	−1492	H(34)	1186	−394	6217
H(13)	586	6042	421	H(35)	948	−1085	8032
H(14)	1493	5386	−1492	H(36)	2222	−1058	10456
H(16)	4289	5338	5593	H(37)	3732	−447	11064
H(17)	4558	6743	6576	H(38)	3968	219	9251
H(18)	3148	7802	7204	H(40)	643	2645	4736
H(19)	1469	7458	6851	H(41)	614	4010	6188
H(20)	1199	6053	5868	H(42)	1143	4143	8852
H(22)	5618	4152	7456	H(43)	1700	2908	10063
H(23)	6156	3657	9818	H(44)	1726	1544	8610

TABLE 5

ANISOTROPIC THERMAL PARAMETERS (X10^4) WITH e.s.d.'s IN PARENTHESES IN THE FORM: $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	403(10)	381(9)	599(13)	147(9)	141(9)	−38(7)
Rh(2)	421(10)	362(9)	562(12)	139(8)	150(8)	−67(7)
P(1)	479(31)	410(29)	603(35)	105(25)	167(28)	−81(23)
P(2)	444(30)	414(28)	584(34)	159(25)	206(26)	−63(23)
O(1)	492(89)	805(106)	1223(145)	48(97)	319(92)	148(77)
O(2)	540(92)	793(107)	1069(133)	443(96)	−48(88)	−28(78)
O(3)	481(79)	609(86)	559(90)	151(70)	148(68)	−119(65)
O(4)	505(78)	626(85)	705(93)	−2(72)	226(70)	−177(65)
O(5)	368(70)	685(84)	577(83)	174(68)	129(62)	−117(60)
O(6)	471(76)	333(67)	703(92)	60(62)	125(68)	−124(56)
O(7)	487(76)	734(89)	642(89)	364(72)	101(66)	−139(66)
O(8)	563(81)	412(72)	897(105)	144(70)	276(75)	−11(61)
N(1)	505(94)	414(91)	809(117)	151(82)	329(87)	−103(72)
N(2)	527(97)	310(82)	719(109)	79(76)	214(84)	−190(70)
N(3)	487(98)	356(91)	719(116)	115(80)	123(92)	−149(73)
N(4)	541(99)	353(88)	651(110)	171(81)	214(87)	−30(75)
C(1)	657(151)	694(137)	519(127)	138(107)	148(114)	−283(118)
C(2)	624(148)	530(121)	700(159)	132(111)	246(128)	−63(105)
C(3)	637(127)	554(127)	516(124)	133(98)	301(104)	−207(103)
C(4)	663(131)	408(114)	966(169)	−8(111)	554(125)	38(96)
C(5)	600(131)	686(137)	847(161)	218(118)	500(123)	−115(105)
C(6)	462(124)	865(154)	579(145)	212(116)	24(113)	−307(107)
C(7)	924(180)	755(157)	922(173)	316(139)	177(145)	−437(139)
C(8)	638(143)	636(139)	698(154)	41(122)	−41(122)	−323(119)

with respect to $|F_o|$. Final atomic coordinates for non-hydrogen atoms and for hydrogen atoms (in the calculated positions) are given in Tables 3 and 4 respectively. The anisotropic thermal parameters and isotropic thermal parameters for the phenyl ring carbon atoms are given in Tables 5 and 6, respectively. A list of observed and calculated structure factors is available from the authors on request.

Calculations were performed on the CYBER 7600 computer of the Centro di Calcolo Electtronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

TABLE 6

ISOTROPIC THERMAL PARAMETERS (X10^4) WITH e.s.d.'s IN PARENTHESES FOR THE PHENYL CARBONS

C(9)	521(48)	C(18)	915(74)	C(27)	434(44)	C(36)	1012(81)
C(10)	607(56)	C(19)	1088(86)	C(28)	618(54)	C(37)	995(79)
C(11)	752(64)	C(20)	782(65)	C(29)	851(69)	C(38)	807(67)
C(12)	877(71)	C(21)	469(46)	C(30)	821(65)	C(39)	534(50)
C(13)	758(64)	C(22)	606(53)	C(31)	730(61)	C(40)	785(66)
C(14)	650(55)	C(23)	665(57)	C(32)	651(56)	C(41)	953(78)
C(15)	540(50)	C(24)	701(59)	C(33)	597(53)	C(42)	712(63)
C(16)	693(59)	C(25)	693(59)	C(34)	725(62)	C(43)	772(63)
C(17)	795(65)	C(26)	599(53)	C(35)	788(66)	C(44)	706(60)

References

1 S. Trofimenko, Chem. Rev., 72 (1972) 497.
2 D.J. Sullivan and F.J. Lalor, J. Organometal. Chem., 65 (1974) C47.
3 N.F. Borkett and M.I. Bruce, J. Organometal. Chem., 65 (1974) C51.
4 R.B. King and A. Bond, J. Organometal. Chem., 73 (1974) 115.
5 F. Bonati, G. Minghetti and G. Banditelli, J. Organometal. Chem., 87 (1975) 365.
6 H.C. Clark and S. Goel, J. Organometal. Chem., 165 (1979) 383.
7 S. Trofimenko, Inorg. Chem., 10 (1971) 1372.
8 F. Bonati and H.C. Clark, Can. J. Chem., 57 (1979) 483.
9 A.L. Bandini, G. Banditelli, G. Minghetti and F. Bonati, Can. J. Chem., 57 (1979) 3237.
10 L.A. Oro, E. Pinilla and M.L. Tenajas, J. Organometal. Chem., 148 (1978) 81.
11 R. Usón, L.A. Oro, M.A. Garralda, M.C. Claver and P. Lahuerta, Transition Met. Chem., 4 (1979) 55.
12 R. Usón, L.A. Oro, J. Artigas and R. Sariego, J. Organometal. Chem., 179 (1979) 65.
13 R. Usón, L.A. Oro, M. Valderrama and C. Claver, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 577.
14 L.A. Oro, J.V. Heras, K.A. Ostoja-Startzewski, P.S. Pregosin, A. Manrique and M. Royo, Transition Met. Chem., in press.
15 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
16 E.W. Abel. M.A. Bennet and G. Wilkinson, J. Chem. Soc., (1959) 3178.
17 D.M. Roe and A.G. Massey, J. Organometal. Chem., 28 (1971) 273.
18 R. Cramer, Inorg. Chem., 1 (1962) 722.
19 J.J. Bonnet. P. Kalck and R. Poiblanc. Inorg. Chem., 16 (1977) 1514.
20 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 3156.
21 J. Coetzer and G. Gafner, Acta Cryst. B, 26 (1979) 985.
22 J.J. Bonnet, Y. Jeannin, P. Kalck, A. Maisonnat and R. Poiblanc, Inorg. Chem., 14 (1975) 743.
23 J.A. Ibers and R.G. Snyder, Acta Cryst., 15 (1962) 923.
24 L.F. Dahl, C. Martell and D.J. Wampler. J. Amer. Chem. Soc., 83 (1961) 1761.
25 G.M. Sheldrick, System of Computing Programs, University of Cambridge, 1976.
26 International Tables of X-Ray Crystallography. Vol. IV, Kynoch Press, Birmingham, 1974.