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CARBONYL COMPLEXES OF RHODIUM WITH LEWIS BASES: MOLECULAR STRUCTURE OF *cis*-CHLORODICARBONYL(TRICYCLOHEXYLPHOSPHINE OXIDE)RHODIUM(I)

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Summary

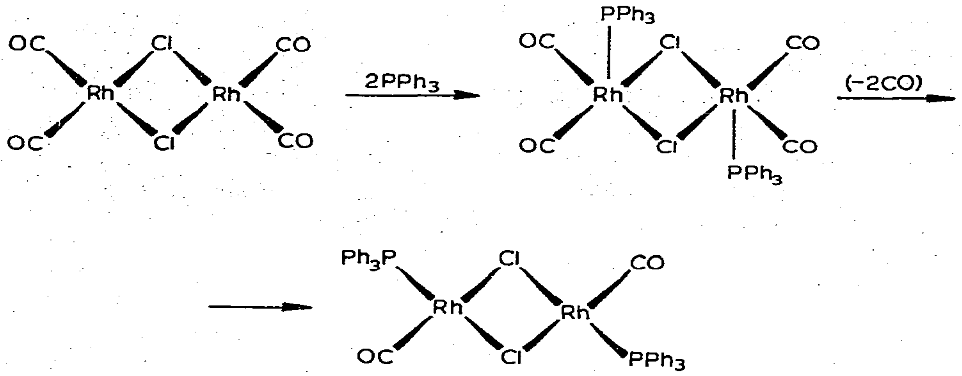
The reaction of $[RhCl(CO)_2]_2$ with tricyclohexylphosphine oxide (Cy_3PO) (Rh/Cy_3PO molar ratio 1) gives the dicarbonyl derivative, *cis*-$[RhCl(CO)_2(Cy_3PO)]$, which is stable toward loss of carbon monoxide and subsequent dimerization. An X-ray structure determination shows that the rhodium is in a square-planar *cis*-dicarbonyl configuration.

Introduction

The reaction of $[Rh(CO)_2Cl]_2$ with Lewis bases (L) is known to take different courses depending on the nature of the ligand L, on the Rh/L molar ratio used, and on the solvent. The halogen bridge in this rhodium carbonyl chloride dimer is readily split by aromatic amines [1] or enimines [2] to give mononuclear dicarbonyl complexes of the type *cis*-$[RhCl(CO)_2(\text{amine})]$. Tertiary phosphines, arsines, or stibines in excess give instead mononuclear monocarbonyl derivatives of the type *trans*-$[RhCl(CO)L_2]$ with evolution of carbon monoxide [3—5]. By use of chelating diphosphines with an excess of $[Rh(CO)_2Cl]_2$ at low temperature the complex (diphosphine)$[Rh(CO)_2Cl]_2$ could be isolated, but it appeared to be contaminated by a product having less carbon monoxide per metal atom [6]. A study of the $[Rh(CO)_2Cl]_2$—phosphine (L) system at various Rh/L molar ratios and carbon monoxide pressures [7] has established the existence of two series of complexes, viz. mononuclear complexes of formula $[RhCl(CO)_{3-n}L_n]$ ($n = 1, 2, 3$) and dinuclear complexes of formula $[Rh_2Cl_2(CO)_{4-m}L_m]$ ($m = 0$—4). In particular, the equilibria shown in eqn. 1 were detected;

$$[RhCl(CO)_2]_2 + 2PPh_3 \rightleftharpoons 2\,cis\text{-}[RhCl(CO)_2(PPh_3)] \rightleftharpoons trans\text{-}[RhCl(CO)(PPh_3)]_2 + 2CO \quad (1)$$

these involve initial halide bridge cleavage by PPh_3. On attempted isolation, each molecule of the unstable *cis*-$[RhCl(CO)_2(PPh_3)]$ loses one CO group and the coordinatively unsaturated fragments recombine eventually to the stable halide bridged monocarbonyl dinuclear derivative, *trans*-$[RhCl(CO)(PPh_3)]_2$ which had previously been formulated as *trans*-$[RhCl(CO)_2(PPh_3)]$ [8]. An alternative interpretation [9] suggests the intermediacy of the labile dimeric *cis*-$[RhCl(CO)_2(PPh_3)]_2$ (eqn. 2).



(2)

However, the system appears to be even more complicated, and the infrared spectra of reaction mixtures observed by other authors [10] agree only to a limited extent with published data.

We have examined the course of the reaction of $[RhCl(CO)_2]_2$ with tricyclohexylphosphine oxide (Cy_3PO) and describe here the molecular structure of the product, *cis*-$[RhCl(CO)_2(Cy_3PO)]$.

Experimental

1. Preparation of cis-[RhCl(CO)₂(Cy₃PO)]

$[RhCl(CO)_2]_2$ (1.87 g, 4.8 mmol) in 25 ml of dichloromethane was treated dropwise with stirring with a solution of Cy_3PO (2.84 g, 9.6 mmol) in 20 ml of dichloromethane under nitrogen. The resulting solution was concentrated on a rotary evaporator and ethyl ether was added, whereupon the product (nc.) precipitated as very pale yellow crystals. Recrystallization was from CH_2Cl_2/ether. (Found: C, 49.37, H, 6.90; Cl, 7.30. Calcd.: C, 48.94; H, 6.78; Cl, 7.22%.)

2. Crystal data

$C_{20}H_{33}O_3ClPRh$ (mol. wt. 490.8), monoclinic, a 9.368 (10), b 13.410 (8), c 18.271 (24) Å, β 100.84 (9)°, U 2254.3 Å^3, D_m 1.44 g·cm^{-3}, Z 4, D_c 1.45 g·cm^{-3}, space group $P2_1/c$ (C^5_{2h}, No. 14). For Cu-K_α radiation (λ 1.54178 Å), μ 81.5 cm^{-1}.

Accurate lattice and orientation parameters were obtained by a least-squares analysis [11] of the setting angles of 30 high-order reflections which have been carefully centered on a Siemens 'on-line' automatic four-circle diffractometer at a take-off angle of 3.8° with Ni-filtered Cu-K_α radiation and a Na(Tl)I scintillation counter.

For measurement of intensities, a crystal (dimensions 0.27 × 0.20 × 0.007 mm) was mounted such that the crystallographic a axis was parallel to the ϕ axis of the goniostat. The data were collected at room temperature with the θ—2θ scan method using a 'five value' measuring procedure. In the reciprocal space corresponding to 2θ of 100° there are 2317 non-equivalent lattice sites excluding those prohibited by the space group. Using the criterion $I \leqslant 2\sigma(I)$, 412 reflections were rejected as statistically insignificant and were treated as unobserved and omitted in the subsequent refinement procedure. Each of these reflections was assigned a threshold given by $I_{th} = 2\sigma(I)$. An experimental absorption correction was applied to the $|F_0|$ data according to the method of Huber and Kopfmann [12].

3. *Structure determination and refinement*

An unsharpened three-dimensional Patterson function was calculated which provided coordinates for the heavy atoms. The remainder of the non-hydrogen atoms were subsequently located by the successive application of least-squares refinement of the heavy atoms positional parameters followed by a difference Fourier synthesis. With all of the non-hydrogen atoms in the calculation, refinement by a block-diagonal least-squares process of positional and isotropic thermal parameters led to a conventional R factor of 0.12.

A difference Fourier map calculated at this point revealed pronounced anisotropy in the motions of the heavy atoms. Refinement was therefore continued with the introduction of anisotropic thermal parameters of the form exp $-(h^2 \cdot \beta_{11} + 2\,h \cdot k \cdot \beta_{12} + \ldots\ldots)$ for these atoms. Several more cycles of refinement led to convergence at R 0.086. A further eight cycles of positional and anisotropic thermal parameters (only the oxygen atoms of the two carbonyl groups were treated isotropically) refinement reduced the discrepancy index to the final value of 0.065.

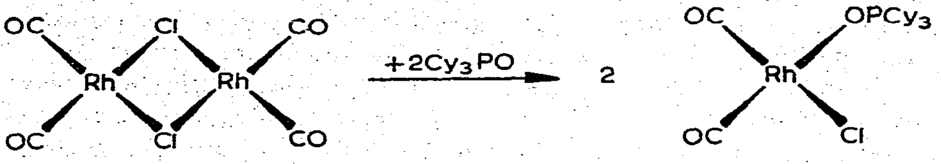
Difference Fourier syntheses revealed reasonable positions for most of the hydrogen atoms (peak heights 0.4—0.7 eÅ^{-3}) as well as some equally large features attributable to uncorrected thermal motion and probably to improper treatment of the rhodium scattering. The function minimised in the refinement was $\Sigma w \cdot (K|F_0| - |F_c|)^2$ with the weighting scheme $w^{-1} = \Sigma a_i|F_0|^i$ (i_{max} 11). The number and values of the a_i parameters were re-evaluated several times during the refinement (with a program written by two of us, D.A.C. and G.B.) so as to give approximately constant averages of $w \cdot (K|F_0| - |F_c|)^2$ for equally populated ranges of $|F_0|$. Scattering factors for neutral Rh, Cl, P, O and C were those tabulated by Cromer and Waber [13]. The scattering factors for Rh and Cl included both the real and imaginary parts of the correction for the effects of anomalous dispersion [14].

Observed and calculated structure factors from the last cycle of refinement are available from the authors. The solution and refinement of the structure were carried out using the Crystal Structure Calculations System X-Ray '70, described by J.M. Stewart, F.A. Kundell, and J.C. Baldwin at the University of Maryland, integrated by the ABSORP program of G. Kopfmann at the University of München. The calculations were carried out at the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), CDC 6600 computer.

Results and discussion

1. *Formation of cis-[RhCl(CO)$_2$(Cy$_3$PO)]*

The reaction of [RhCl(CO)$_2$]$_2$ with Cy$_3$PO in dichloromethane at room temperature (Rh/Cy$_3$PO molar ratio 1) gives the halide bridge splitting product *cis*-[RhCl(CO)$_2$(Cy$_3$PO)] in high yield:



(I)

The IR spectrum of this dicarbonyl species shows strong bands attributed to ν(CO) at 2078 and 1998 cm^{-1} (CS$_2$), ν(PO) at 1110 cm^{-1} [Nujol; ν(PO) in free Cy$_3$PO at 1154 cm^{-1}] and ν(Rh—Cl) at 315 cm^{-1} (Nujol).

Complex (I) is quite stable toward loss of carbon monoxide, resembling the analogous *cis*-dicarbonyl—amine complexes *cis*-[RhCl(CO)$_2$(amine)] [1, 2]. A dichloromethane solution under nitrogen may be stored for considerable periods without decomposition. It appears that Cy$_3$PO is not as effective in labilizing the CO group *trans* to it as are tertiary phosphines and arsines [7—9], since formation of the expected decarbonylation product, [RhCl(CO)(Cy$_3$PO)]$_2$, was not observed under our conditions [cf. the easy decarbonylation of *cis*-[RhCl(CO)$_2$(PPh$_3$)] [8] or alternatively *cis*-[RhCl(CO)$_2$(PPh$_3$)]$_2$ [9] on attempted isolation even under mild vacuum]. This behavior of the Cy$_3$PO ligand is likely to be related to its poorer π-acceptor properties and higher σ-donating ability compared with those of phosphines which stabilize the *cis*-dicarbonyl configuration.

At present we are investigating the chemical behavior of (I) toward oxidative addition, activation of small molecules, and catalytic properties.

The structure of complex (I) has been confirmed definitively by an X-ray structure determination and is described in the following section.

2. *Description of the molecular structure of cis-[RhCl(CO)$_2$(Cy$_3$PO)]*

The positional and thermal parameters obtained from the last cycle of least-squares refinement are listed in Table 1 together with their associated standard deviations as estimated from the inverse least-squares matrix. Table 2 gives a list of the molecular geometry data (the most significant interatomic distances and interbond angles, the mean coordination plane equation and the closest intermolecular approaches). The overall coordination geometry about the rhodium atom is closely square planar (the maximum deviation of metal and ligand donor atoms from the coordination plane being only 0.03 Å), with the two carbonyl ligands arranged in a *cis* configuration as predicted on the basis of the infrared spectrum of the complex. A perspective view of the molecule is given in Fig. 1.

The Rh—Cl distance of 2.322(4) Å is comparable to that found in similar Rh^{I} complexes with non-bridging chloride ligands (Table 3) and in analogous

TABLE 1

ATOMIC PARAMETERS [a]

Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)
Rh	0.2021(1)	0.1761(1)	0.1309(1)	
Cl	−0.0406(3)	0.1968(2)	0.1388(2)	
P	0.1304(3)	−0.0634(2)	0.1755(1)	
O(1)	0.2090(12)	0.3927(9)	0.1125(7)	10.34(30)
O(2)	0.5152(13)	0.1615(9)	0.1290(7)	10.83(30)
O(3)	0.1902(7)	0.0239(5)	0.1377(4)	
C(1)	0.2093(16)	0.3040(9)	0.1220(8)	
C(2)	0.3868(14)	0.1687(8)	0.1269(8)	
C(3)	0.1829(10)	−0.0578(7)	0.2759(5)	
C(4)	0.3488(11)	−0.0513(9)	0.2985(6)	
C(5)	0.3976(14)	−0.0476(10)	0.3835(6)	
C(6)	0.3272(15)	0.0476(10)	0.4130(7)	
C(7)	0.1635(15)	0.0371(10)	0.3924(6)	
C(8)	0.1113(14)	0.0364(8)	0.3072(5)	
C(9)	−0.0648(10)	−0.0652(7)	0.1527(5)	
C(10)	−0.1261(10)	−0.0530(8)	0.0686(5)	
C(11)	−0.2920(12)	−0.0319(9)	0.0569(7)	
C(12)	−0.3698(14)	−0.1152(11)	0.0907(8)	
C(13)	−0.3047(15)	−0.1297(12)	0.1736(8)	
C(14)	−0.1408(12)	−0.1522(9)	0.1842(7)	
C(15)	0.2189(11)	−0.1750(7)	0.1477(5)	
C(16)	0.1796(14)	−0.1897(8)	0.0632(6)	
C(17)	0.2755(14)	−0.2776(8)	0.0403(7)	
C(18)	0.2563(15)	−0.3693(9)	0.0805(8)	
C(19)	0.2910(16)	−0.3540(8)	0.1646(8)	
C(20)	0.1971(14)	−0.2689(8)	0.1897(7)	

ANISOTROPIC TEMPERATURE PARAMETERS (× 10^3)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	16.9(1)	3.3(1)	3.3(0)	−0.9(1)	1.2(1)	0.0(0)
Cl	17.2(4)	4.8(2)	4.4(1)	1.1(2)	0.4(2)	−0.5(1)
P	11.7(3)	2.7(1)	2.8(1)	0.2(2)	0.1(1)	0.1(1)
O(3)	15.4(10)	3.7(4)	3.9(3)	−0.9(5)	1.3(4)	−0.2(3)
C(1)	29.5(27)	3.9(7)	8.4(7)	0.2(11)	5.0(12)	1.1(6)
C(2)	22.1(22)	5.3(6)	7.5(6)	−2.4(10)	4.9(10)	−1.2(6)
C(3)	11.5(14)	5.3(7)	3.4(4)	1.1(8)	0.1(6)	−0.5(4)
C(4)	12.3(15)	9.5(10)	3.3(4)	0.0(9)	−0.7(6)	−0.9(5)
C(5)	20.9(21)	10.6(11)	3.6(4)	2.2(12)	−1.3(8)	0.3(5)
C(6)	23.4(22)	10.3(10)	4.5(5)	1.5(12)	−1.0(8)	−2.1(6)
C(7)	24.7(23)	9.7(10)	3.4(4)	4.0(12)	−1.2(8)	−1.3(6)
C(8)	25.3(22)	7.3(8)	2.6(4)	4.0(11)	−0.5(7)	−1.7(4)
C(9)	12.0(13)	4.5(6)	3.2(4)	−2.0(6)	−0.5(6)	0.5(4)
C(10)	11.7(14)	7.1(8)	2.7(3)	0.9(8)	−0.6(6)	0.1(4)
C(11)	12.9(16)	9.0(9)	5.2(5)	−0.1(10)	0.1(7)	1.7(6)
C(12)	16.2(18)	12.1(12)	5.7(6)	−2.7(12)	−1.1(9)	2.0(7)
C(13)	18.6(22)	13.9(13)	5.5(6)	−5.3(13)	0.8(13)	2.1(7)
C(14)	13.2(16)	7.4(8)	5.6(5)	−0.4(9)	0.0(7)	2.1(5)
C(15)	18.8(17)	3.2(6)	3.3(4)	1.0(8)	1.7(7)	−0.2(4)
C(16)	24.4(21)	6.2(8)	3.5(4)	4.0(10)	1.8(8)	−0.7(5)
C(17)	25.9(23)	4.7(7)	5.0(5)	2.8(10)	3.4(9)	0.0(5)
C(18)	24.2(23)	6.0(8)	6.6(6)	1.6(10)	3.7(10)	−2.1(6)
C(19)	32.2(27)	4.1(7)	5.8(6)	4.0(11)	3.3(10)	0.8(5)
C(20)	25.3(22)	4.6(7)	4.9(5)	3.1(10)	3.9(9)	0.4(5)

[a] The estimated standard deviations are in units of the last place of decimals given.

complexes of elements in the latter part of the second transition series, viz., Pd—Cl (2.33(4) Å) in [Pd(TPAS)Cl]ClO_4 [TPAS = *o*-phenylenebis[{*o*-(dimethylarsino)phenyl}arsine]] [15] and Ru—Cl [2.388(8) Å] in [$RuCl_2$ $(PPh_3)_3$] [16]. The two independent Rh—C distances of 1.72(1) and 1.75(1) Å are dif-

TABLE 2

MOLECULAR GEOMETRY

Interatomic distances and estimated standard deviations (Å)

Rh—Cl	2.322(4)	C(3)—C(4)	1.53(1)	C(12)—C(13)	1.54(2)
Rh—O(3)	2.049(7)	C(4)—C(5)	1.54(2)	C(13)—C(14)	1.54(2)
Rh—C(1)	1.725(12)	C(5)—C(6)	1.58(2)	C(14)—C(9)	1.53(2)
Rh—C(2)	1.748(14)	C(6)—C(7)	1.52(2)	C(15)—C(16)	1.53(1)
C(1)—O(1)	1.20(2)	C(7)—C(8)	1.54(1)	C(16)—C(17)	1.58(2)
C(2)—O(2)	1.20(2)	C(8)—C(3)	1.58(2)	C(17)—C(18)	1.46(2)
O(3)—P	1.52(1)	C(9)—C(10)	1.54(1)	C(18)—C(19)	1.52(2)
P—C(3)	1.81(1)	C(10)—C(11)	1.55(2)	C(19)—C(20)	1.56(2)
P—C(9)	1.80(1)	C(11)—C(12)	1.53(2)	C(20)—C(15)	1.51(2)
P—C(15)	1.83(1)				

Intramolecular angles and estimated standard deviations (°)

Cl—Rh—C(1)	86.7(5)	C(4)—C(5)—C(6)	107.9(9)
Cl—Rh—O(3)	92.9(2)	C(5)—C(6)—C(7)	108.0(10)
C(2)—Rh—C(1)	89.8(6)	C(6)—C(7)—C(8)	111.4(11)
C(2)—Rh—O(3)	90.7(4)	C(7)—C(8)—C(3)	107.1(9)
Rh—C(1)—O(1)	176.6(12)	C(8)—C(3)—C(4)	109.5(8)
Rh—C(2)—O(2)	175.6(13)	C(9)—C(10)—C(11)	109.3(9)
Rh—O(3)—P	145.5(5)	C(10)—C(11)—C(12)	110.6(9)
O(3)—P—C(3)	112.1(4)	C(11)—C(12)—C(13)	111.1(11)
O(3)—P—C(9)	110.6(4)	C(12)—C(13)—C(14)	110.5(12)
O(3)—P—C(15)	106.2(5)	C(13)—C(14)—C(9)	109.0(10)
P—C(3)—C(4)	110.1(7)	C(14)—C(9)—C(10)	110.0(8)
P—C(3)—C(8)	110.2(6)	C(15)—C(16)—C(17)	108.7(9)
P—C(9)—C(10)	113.6(7)	C(16)—C(17)—C(18)	111.3(11)
P—C(9)—C(14)	116.5(7)	C(17)—C(18)—C(19)	111.8(10)
P—C(15)—C(16)	110.5(7)	C(18)—C(19)—C(20)	111.7(10)
P—C(15)—C(20)	115.5(8)	C(19)—C(20)—C(15)	108.9(11)
C(3)—C(4)—C(5)	111.6(9)	C(20)—C(15)—C(16)	112.1(8)

Best least-squares plane

In the following equation the fractional unit-cell coordinates x, y, z refer to direct space.

Plane defined by Rh, Cl, C(1), C(2), O(3): $0.567x + 0.928y + 17.661z = 2.587$.

Distances of atoms from the plane (Å): Rh 0.0; Cl 0.02; C(1) −0.03; C(2) 0.03; O(3) −0.02; O(1) −0.12; O(2) 0.13; P 0.53.

Intermolecular distances (Å) *less than 3.7* Å

O(1)—C(18$^{\mathrm{I}}$)	3.29	O(2)—C(11$^{\mathrm{II}}$)	3.55
O(1)—C(19$^{\mathrm{I}}$)	3.57	Cl—C(16$^{\mathrm{III}}$)	3.68

Roman numerals as superscripts refer to atoms in the equivalent positions, relative to the reference molecule at x, y, z: (I), $x, 1+y, z$; (II), $1+x, y, z$; (III), $\bar{x}, \bar{y}, \bar{z}$.

ferent to an extent which is only barely significant and therefore probably not meaningful; they are significantly shorter than those reported for the compounds in Table 3 and certainly shorter than would be expected on the basis of the usual radii sum rules [17]; however, this shortening has been noted previously in three other compounds (ref. 18, 22, 28; Table 3).

The Rh—C—O geometry found in this analysis agrees well with that found in related Rh$^{\mathrm{I}}$ complexes (Table 3); thus, the carbonyl groups are bonded to the rhodium atom of the complex in an essentially linear fashion with the Rh—C—O angles equal to 176.6(12) and 175.6(13)°. The C—O distances [both 1.20(2) Å] are not significantly different from those reported for rhodium carbonyls or for most other metal complexes of carbon monoxide and the dif-

TABLE 3

Rh—Cl, Rh—C··O, Rh··C—O BOND LENGTHS AND Rh—C—O ANGLES IN SOME Rh^1 COMPLEXES

Compound	Ref.	Coordination polyhedron	Rh—Cl (Å)	Rh—C··O (Å)	Rh··C—O (Å)	Rh—C—O (Å)
$[(n\text{-}C_4H_9)_4N][RhCl_2(CO)_2]$	[22]	Square planar	2.345(6)	1.72(3)	1.19(3)	173.4
$(C_{23}H_{18}N_2)RhCl(CO)_2$	[23]	Square planar	2.335(2)	1.844(15); 1.865(15)		
cis-$[RhCl(PF_2 \cdot NEt_2)_2(PPh_3)]$	[24]	Square planar	2.375(2)			
$Rh_2[P(OPh)_3]_2(C_8H_{12})Cl_2$	[25]	Square planar	2.410(5); 2.398(5)			
$Rh(CO)_2(CH_3COCHCOCH_3)$	[18]	Square planar		1.76(2); 1.75(2)	1.21(3); 1.26(3)	174; 171
$Rh(CS)Cl(PPh_3)_2$	[26]	Square planar	2.386(3)			
$Rh_2(CO)_4Cl_2$	[27]	Square planar	2.38; 2.33	1.77; 1.85	1.21; 1.14	173; 177
$(RhC_5H_5CO)_3$	[28]	Square planar		1.75(2)	1.19(2)	175.9
$[RhClO_2(PPh_3)_2]_2$	[19]	Trigonal bipyramid	2.390(5)			
$RhCl(SbPh_3)_2C_4(CF_3)_4 \cdot CH_2Cl_2$	[29]	Trigonal bipyramid	2.381(3)			
$RhH(CO)(PPh_3)_3$	[30]	Trigonal bipyramid		1.829(28)	1.17	179
$Rh(CO)Cl(Ph_2AsCH_2AsPh_2)_2$-$Rh(CO)Cl$	[31]	Square pyramid	2.372(3)	1.797(10)	1.098(13)	177.1
$RhCl(C_4H_6)_2$	[32]	Square pyramid	2.44(1)			
$(Ph_3P)_3RhCl$; $(Ph_3P)_2C_2F_4RhCl$	[20]	Tetrahedral	2.373(8); 2.375(8)			
$RhCl(CO)SO_2(PPh_3)_2$	[33]	Tetragonal pyramid	2.355(2)	1.847(7)	1.126(7)	179.4
$RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4$	[34]	Octahedron	2.446(5)			
$(C_5H_5)_2(CO)_3Rh_2$	[35]	Binuclear with a bridging CO group		1.840(23); 1.894(20)	1.151(25); 1.105(22)	175.6; 177.0
$C_5H_5Rh(CO)(C_2F_5)I$	[36]	Octahedron		1.97(3)	1.05(4)	175.8
$[RhCl(C_8H_{12})]_2$	[37]	Dimeric molecule, square planar	2.38(1)			

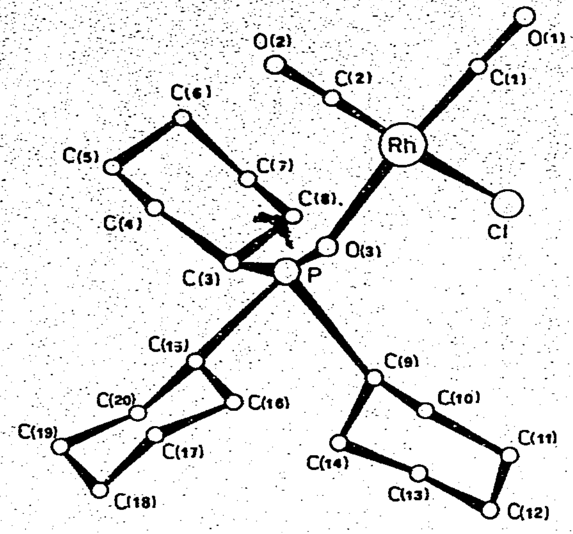


Fig. 1. A perspective view of the complex.

ferences are, in most cases, covered by the estimated standard deviations. The Rh—O distance [2.049(7) Å] appears to be normal, as judged by the usual radii sum rules, although there are few structures in the literature with which this distance can be compared [18—20].

The O—P bond length [1.52(1) Å] corresponds with that expected for considerable double bond character, being similar to that found from spectroscopic studies for the uncoordinated O—P bond (1.47 Å) [21]. The mean P—C distance is 1.82(1) Å and the tetrahedral arrangement of the phosphorus atoms is such that the O—P—C angles range from 106.2 to 112.1° and the C—P—C angles from 105.4 to 114.8°.

Finally, there are no intermolecular contacts in the crystal less than the sum of van der Waals radii (Table 2).

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