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THREE-COORDINATE $RhX[P(C_6H_{11})_3]_2$, THEIR REACTIONS WITH N_2 AND O_2, AND THE *trans*-INFLUENCE IN $RhX[P(C_6H_{11})_3]_2L$ (X = anionic, L = neutral ligand)

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Summary

Three-coordinate $RhX(PCy_3)_2$ complexes (X = F, Cl, Br, I; Cy = cyclohexyl) have been prepared from rhodium(I) cyclooctene compounds. $RhCl(PCy_3)_2$ is in equilibrium with its dimer. The complexes $RhX(PCy_3)_2$ (X = Cl, Br, I) form the adducts $RhX(PCy_3)_2(N_2)$ with dinitrogen, the times for N_2-fixation being 4 days, 3 hours and 15 minutes respectively. The three-coordinate complexes form four-coordinate dioxygen adducts $RhX(PCy_3)_2(O_2)$ which have unusually high $\nu(O{=}O)$ at about 990 cm^{-1}. This high frequency is attributed to the four-coordination, which is exceptional for dioxygen complexes. From $RhF(PCy_3)_2$ carbonyl, ethene, and diphenylacetylene complexes $RhX(PCy_3)_2L$ (X = F, Cl, Br, I, N_3, NCO, NCS; L = CO, C_2H_4, C_2Ph_2) (X = CN, NO_3, acetate; L = CO) have been prepared. The *trans*-influence of the anionic ligands on the infrared frequencies of the neutral ligands is discussed in terms of the different π-bonding properties of the X- and L-ligands.

Introduction

Rhodium(I)—phosphine complexes catalyse a great variety of organic reactions. A three-coordinate species of the type $RhCl(PR_3)_2$ has often been invoked as an intermediate in catalytic processes [1—4], but evidence for such three-coordinate complexes is lacking [4]. Although a three-coordinate rhodium(I)—carborane complex $Rh(carborane)(PPh_3)_2$ was proposed [5], a crystal structure determination showed that such a complex contained a chelating carborane with a rhodium—carbon bond and a Rh—H—B bridge bond [6].

We have studied the chemistry of rhodium complexes containing the bulky ligand tricyclohexylphosphine (PCy_3), which can stabilise unusual coordination numbers and valence states of rhodium [7—11]. In a preliminary note [7] we suggested the existence of the three-coordinate complex $RhCl(PCy_3)_2$, prepared from $[RhCl(C_8H_{14})_2]_2$ [12] (C_8H_{14} = cyclooctene) and PCy_3. This complex formed $RCl(PCy_3)_2(N_2)$ [7] with molecular nitrogen and $RhCl(PCy_3)_2(O_2)$ with molecular oxygen. The latter complex had an infrared band at 993 cm^{-1} [7], an unusual frequency for an O_2-ligand vibration [13]. The synthesis of $[RhF(C_8H_{14})_2]_n$ [8] made it possible to prepare similar (pseudo)halobis(tricyclohexylphosphine)rhodium(I) complexes and to study their reaction with nitrogen and oxygen, as well as with carbon monoxide, ethylene and diphenylacetylene. A full account of these reactions is given below.

Experimental

Infrared spectra were measured on a Perkin—Elmer 283 spectrophotometer (4000—200 cm^{-1}), equipped with a digital frequency counter.

Fourier transform ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL 100 spectrometer at 100 and 40.5 MHz respectively. Air-sensitive compounds were sampled for ^{31}P NMR under helium in 12 mm sample tubes which were subsequently vacuum sealed. C, H and N analyses were carried out at the microanalytical department of this university; other analyses and molecular weight determinations by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany; the analytical results are given in Table 1. Reactions were carried out with analytical grade reagents and under argon unless otherwise stated. $[RhCl(C_8H_{14})_2]_2$ and $[RhF(C_8H_{14})_2]_n$ were prepared as described in ref. 12 and ref. 8, respectively.

$[RhX(PCy_3)(C_8H_{14})]_n$ (X = F, Cl, Br, I)

91 mg (0.31 mmol) PCy_3 is stirred for 30 min with 109 mg $[RhF(C_8H_{14})_2]_n$ or 116 mg (0.155 mmol) $[RhCl(C_8H_{14})_2]_2$ in 10 ml acetone. For the bromo and iodo complexes, 25 mg LiBr or NaI is added to the fluoro complex and the mixture is stirred for another 30 min. The complexes $[RhX(PCy_3)(C_8H_{14})]_n$ are isolated by filtration, washed with acetone, and dried under vacuum.

$RhX(PCy_3)_2$ (X = F, Cl, Br, I)

(a) 182 mg PCy_3 and 109 mg $[RhF(C_8H_{14})_2]_n$ or 116 mg $[RhCl(C_8H_{14})_2]_2$ are stirred for 30 min in 10 ml benzene. For X = Br or X = I, 25 mg LiBr or NaI is added to the fluoro complex and the mixture is stirred for another 15 min, whereupon the inorganic salts are removed by filtration. Acetone (X = F, Cl) or hexane (X = Br, I) is added and the formed precipitate (X = F: red; X = Cl, Br, I: lilac) is collected on a filter, washed with acetone (X = F, Cl) or hexane (X = Br, I).

(b) $RhCl(PCy_3)_2$ may also be prepared by stirring the required equivalents of $[RhCl(C_8H_{14})_2]_2$ and PCy_3 in acetone for 30 min or in hexane for 4 h. The reaction of $[RhF(C_8H_{14})_2]_n$ and PCy_3 in acetone or hexane gives $[RhF(PCy_3)(C_8H_{14})]_n$; $RhF(PCy_3)_2$ is not formed. When acetone is used in the preparation of $RhBr(PCy_3)_2$ or $RhI(PCy_3)_2$, large percentages of $RhX(PCy_3)_2(CO)$ (X = Br, I) are formed, probably by decarbonylation of CH_3OH present in the acetone. Solid $RhX(PCy_3)_2$ (X = F, Cl, Br, I) is immediately decomposed on contact with air. The complexes degrade slowly even under an inert atmosphere. In solution,

TABLE 1

ANALYTICAL DATA Found (calcd.) (%)

Compound	C	H	Others	
$[RhF(C_8H_{14})(PCy_3)]_2$	59.5 (60.9)	9.45 (9.24)		
$[RhCl(C_8H_{14})(PCy_3)]_2$	59.2 (59.9)	9.42 (8.96)		
$RhCl(PCy_3)_2$	59.7 (61.8)	9.29 (9.52)	P: 7.71 (8.86)	Cl: 4.39 (5.07)
$RhBr(PCy_3)_2$	55.0 (58.1)	8.60 (8.95)	P: 8.96 (8.33)	Br: 11.98 (10.74)
$RhI(PCy_3)_2$	53.4 (54.7)	8.43 (8.41)	P: 7.05 (8.33)	I: 14.47 (16.04)
$RhCl(PCy_3)_2(N_2)$	59.5 (59.5)	9.31 (9.14)	N: 3.06 (3.85)	
$RhBr(PCy_3)_2(N_2)$	56.6 (56.0)	8.93 (8.62)	N: 2.68 (3.62)	
$RhI(PCy_3)_2(N_2)$	53.4 (52.8)	8.30 (8.13)	N: 2.96 (3.42)	
$RhCl(PCy_3)_2(O_2)$	59.9 (59.1)	9.16 (9.10)		
$RhBr(PCy_3)_2(O_2)$	58.9 (55.7)	9.06 (8.58)		
$RhI(PCy_3)_2(O_2)$	49.2 (5.26)	7.57 (8.09)		
$RhF(PCy_3)_2(CO)$	60.6 (62.5)	9.14 (9.36)		
$RhI(PCy_3)_2(CO)$	56.0 (54.3)	8.47 (8.13)		
$Rh(N_3)(PCy_3)_2(CO)$	59.1 (60.6)	8.67 (9.07)	N: 5.25 (5.72)	
$Rh(NCS)(PCy_3)_2(CO)$	61.8 (60.9)	9.29 (8.87)	N: 1.63 (1.87)	
$Rh(NO_3)(PCy_3)_2(CO)$	56.8 (58.9)	8.47 (8.83)	N: 1.90 (1.86)	
$Rh(CH_3COO)(PCy_3)_2(CO)$	61.5 (62.4)	9.30 (9.26)		
$RhF(PCy_3)_2(C_2H_4)$	62.8 (64.2)	9.68 (9.93)		
$RhCl(PCy_3)_2(C_2H_4)$	63.0 (62.8)	9.62 (9.70)		
$RhBr(PCy_3)_2(C_2H_4)$	58.7 (59.1)	9.38 (9.14)		
$RhI(PCy_3)_2(C_2H_4)$	57.2 (55.8)	9.21 (8.62)		
$Rh(N_3)(PCy_3)_2(C_2H_4)$	60.8 (62.2)	9.14 (9.61)	N: 5.26 (5.72)	
$Rh(NCO)(PCy_3)_2(C_2H_4)$	60.5 (63.8)	9.31 (9.62)	N: 1.55 (1.91)	
$RhF(PCy_3)_2(C_2Ph_2)$	68.0 (69.7)	8.87 (9.00)		
$RhCl(PCy_3)_2(C_2Ph_2)$	67.7 (68.5)	8.20 (8.80)		
$RhBr(PCy_3)_2(C_2Ph_2)$	65.8 (65.1)	8.47 (8.41)		
$RhI(PCy_3)_2(C_2Ph_2)$	62.3 (61.9)	8.19 (8.00)		
$Rh(NCS)(PCy_3)_2(C_2Ph_2)$	66.1 (68.1)	8.62 (8.51)	N: 1.59 (1.56)	

the decomposition products are, among others, $RhX_2(PCy_3)_2$ (X = Cl, Br) [10] and $RhHX_2(PCy_3)_2$ (X = Cl, Br, I) [10].

$RhX(PCy_3)_2(N_2)$ (X = Cl, Br, I)

$RhX(PCy_3)_2$ in benzene (about 150 mg in 10 ml) is stirred at room temperature under 1 atm. of nitrogen until the original colour has disappeared. Acetone is added, the precipitate is filtered off, washed with acetone, and dried under vacuum. $RhCl(PCy_3)_2$, either isolated from acetone and dissolved in benzene, or prepared in situ in benzene, needs 4 to 5 days for the reaction with N_2; $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$, both prepared in situ, need about 3 h and 15 min respectively, for this reaction. $RhF(PCy_3)_2$ gives no addition product with N_2 even after one month. A suspension of $RhCl(PCy_3)_2$ in acetone or hexane does not react with N_2, whereas suspensions of $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ do. $RhX(PCy_3)_2(N_2)$ is contaminated with $RhX(PCy_3)_2(CO)$, $RhHX_2(PCy_3)_2$ [10] (X = Cl, Br, I) and $RhX_2(PCy_3)_2$ [10] (X = Cl, Br). The contaminants may be responsible for the pale green (X = Cl, Br) or orange (X = I) colour of samples of $RhX(PCy_3)_2(N_2)$.

$RhX(PCy_3)_2(O_2)$ (X = Cl, Br, I, N_3), $RhCl(PCy_3)_2(^{18}O_2)$

A benzene solution of $RhF(PCy_3)_2$ is stirred with NaX (X = Br, I, N_3) for about 30 min. The inorganic salts are removed by filtration. The resulting solution, or a solution of $RhCl(PCy_3)_2$ (about 150 mg in 10 ml benzene), is exposed to a small amount of O_2, and gently stirred for a few minutes. Acetone is added and the precipitate is filtered off, washed with acetone, and dried under vacuum. $^{18}O_2$ was allowed to react with about 15 mg $RhCl(PCy_3)_2$ in 2 ml benzene, and $RhCl(PCy_3)_2(^{18}O_2)$ was isolated by vacuum evaporation of the solvent. $RhF(PCy_3)_2$ reacted quickly with O_2 giving $OPCy_3$. $RhX(PCy_3)_2(O_2)$ is blue-green (X = Cl, Br, N_3) or dark red (X = I).

General procedure for the preparation of $RhX(PCy_3)_2L$ (L = CO, C_2H_4, C_2Ph_2; X = various anionic ligands)

(a) A benzene solution of $RhF(PCy_3)_2$ is stirred with NaX for several hours. The inorganic salts were filtered off. To the filtrate (or to a solution of $RhF(PCy_3)_2$ or $RhCl(PCy_3)_2$) is added CO, C_2H_4 or tolane. Ethanol is added (L = CO) or the solution is concentrated to a small volume and acetone is added (L = C_2H_4, tolane). The precipitate is filtered off, washed with ethanol (L = CO) or acetone (L = C_2H_4, tolane), and dried under vacuum.

(b) $RhF(PCy_3)_2L$ (L = CO, C_2H_4 or tolane) is stirred with NaX in benzene for several hours. The inorganic salts are filtered off, and the products isolated as in (a).

(c) $RhF(PCy_3)_2L$ (L = CO, C_2H_4, tolane) is stirred with NaX in acetone for several hours. The precipitate is filtered off, washed with water and acetone, and dried under vacuum.

Results and discussion

Fluororhodium(I) complexes

Fluoro complexes of platinum group metals in low valence states are relatively rare. This has been rationalised in terms of a thermodynamically unfavourable "hard base"—"soft acid" combination [14]. Recently a series of palladium(II) and platinum(II) fluoro complexes has been reported [14]. $IrF(PPh_3)_2(CO)$ has been known for some time [15,16] and addition complexes of this compound with π-acidic ligands have been described [16,17]. The only fluororhodium(I) complex known until recently was $RhF(PPh_3)_2(CO)$ [15]. We recently described the preparation of $[RhF(C_8H_{14})_2]_n$ [8]. By cyclooctene displacement a variety of fluororhodium complexes may be made from this complex, and in this way we prepared the fluoro analogue of Wilkinson's catalyst, $RhF(PPh_3)_3$ [8].

Just as with $[RhCl(C_8H_{14})_2]_2$ [7], PCy_3 displaces cyclooctene from $[RhF(C_8H_{14})_2]_n$, forming in a first step $[RhF(PCy_3)(C_8H_{14})]_n$ and in a second step $RhF(PCy_3)_2$. The ^{31}P NMR spectrum and the three-coordination of the latter compound are discussed below. In contrast with $RhCl(PCy_3)_2$, the fluoro complex does not react with molecular nitrogen. With oxygen $RhF(PCy_3)_2$ forms $OPCy_3$ in solution and in the solid state.

Addition complexes of $RhF(PCy_3)_2$ with CO, C_2H_4 and C_2Ph_2 have been prepared. They show ν(Rh—F) at 470, 421 and 462 cm^{-1} (Table 4). $RhF(PCy_3)_2(CO)$ has in the ^{31}P NMR spectrum ^1J(Rh—P) 131 Hz and ^2J(F—P) 20 Hz, comparable with the values of $RhF(PPh_3)_2(CO)$ (Table 2).

All the fluoro complexes have a labile fluoro ligand, which is displaceable by several other coordinating anions. This metathesis is fast in a benzene—water two layer system, but the work-up is easier, when the reaction is carried out in benzene with a suspension of a sodium salt, or in acetone. A summary of reactions is given in Scheme 1.

SCHEME 1

Survey of reactions

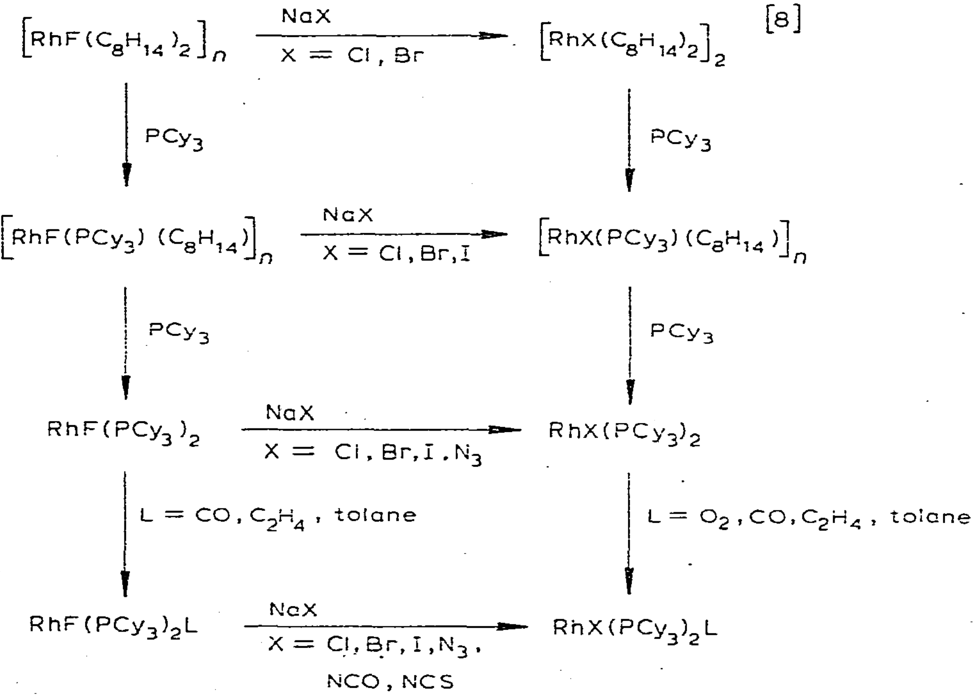


TABLE 2

^{31}P NMR DATA FOR SOME RHODIUM PHOSPHINE COMPLEXES

Solvent C_6D_6, internal reference PCy_3. δ(ppm) calculated with respect to trimethylphosphate (δ(PCy_3) −7.1 ppm)

Compound	δ(ppm)	^1J(Rh—P) (Hz)	^2J(F—P) (Hz)
PCy_3	−7.1		
$OPCy_3$	−44.3		
$RhF(PCy_3)_2$	−55.0	206.0	165.0
$RhI(PCy_3)_2$	−46.1	207.0	
$RhBr(PCy_3)_2$	−45.8	210.0	
$RhCl(PCy_3)_2$	−45.9	209.9	
$RhCl(PCy_3)_2(C_8H_{14})$	−11.2	104.0	
$[RhCl(PCy_3)_2]_2$	−44.4	193.8	
$[RhCl(P(p\text{-}Tol)_3)_2]_2$ [a]		196	
$[RhCl(PCy_3)(C_8H_{14})]_2$	−45.1	182.9	
$RhBr(PCy_3)$(norbornadiene)	−28.4	160.8	
$RhHCl_2(PCy_3)_2$ [b]	−32.0	96.2	
$RhCl(PCy_3)_2(O_2)$	−21.0	106.3	
$RhCl(PCy_3)_2(CO)$	−11.9	119.9	
$RhF(PCy_3)_2(CO)$	−10.6	131.0	20.0
$RhF(PPh_3)_2(CO)$ [c]		136	22.0

[a] Ref. 4. [b] Ref. 11. [c] Ref. 14.

Three-coordinate complexes

The compounds $RhX(PCy_3)_2$ (X = F, Cl, Br, I) decompose slowly under an inert atmosphere. Their structures have been derived from ^{31}P NMR data. $RhF(PCy_3)_2$ shows a pair of doublets, with ^1J(Rh—P) 206 Hz and ^2J(F—P) 165 Hz (Table 2). In addition, resonances due to $OPCy_3$ and to excess added PCy_3 are present. The pair-of-doublets pattern excludes a dimer or oligomer with fluorine bridges. A fourth coordination place may be occupied, however, by a solvent molecule (benzene) or a C—H bond interaction of a cyclohexyl group with the metal. In Table 3 are given the ranges of known values of rhodium—phosphorus and fluorine—phosphorus coupling constants for rhodium complexes and for d^8-fluoro complexes with triaryl- or trialkyl-phosphines as function of the coordination number and relative ligand position. In $RhF(PCy_3)_2$, the ^2J(F—P) value of 165 Hz is much too large to have the two PCy_3 ligands in a 90° *cis* position to the fluorine, and two equivalent PCy_3 ligands cannot occupy the single *trans* position to the fluorine (see Tables 2 and 3). These facts strongly suggest trigonal three-coordination of $RhF(PCy_3)_2$ (Fig. 1), without a solvent molecule or any other coordinating group present as a fourth ligand. The three-coordination is further supported by the large ^1J(Rh—P) value of 206 Hz, larger

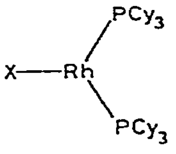


Fig. 1.

TABLE 3

^{31}P NMR DATA AND COORDINATION NUMBER

Range of ^{31}P NMR coupling constants of rhodium complexes and of d^8-fluoro complexes with alkyl- or aryl-phosphines as function of coordination number and relative ligand position. Data from this work and from ref. 4, 11, 14, 18—20

	^1J(Rh—P)			^2J(F—P)
	6-coord.	5-coord.	4-coord.	
PR_3 *trans* to PR_3	80—100	95—110	104—153	
PR_3 *trans* to L, L≠PR_3	103—130	145	160—196	
F *trans* to PR_3				139—160
F *cis* to PR_3				20—39

than any previously found value for rhodium(I) triaryl- or trialkyl-phosphine complexes. The value of the ^1J coupling constant is directly related to the *s*-character of the orbital of the metal used in the bonding to phosphorus. This *s*-character is determined both by the coordination number and by the relative positions of the ligands. From Table 3, one can see that a value of 206 Hz is reasonable for a three-coordinate species, if one takes into account that in a trigonal geometry the valence angles at the rhodium are neither 90° nor 180°, but somewhere in between.

The major resonances of $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ are a doublet with ^1J(Rh—P) of 210 and 207 Hz, respectively, in addition to minor resonances, attributed to free PCy_3 (added in excess), $OPCy_3$ and $RhHX_2(PCy_3)_2$ (X = Br, I). The ^1J values of $RhBr(PCy_3)_2$ and $RhI(PCy_3)_2$ are close to that of $RhF(PCy_3)_2$, which means that the bromo and the iodo complex are probably also three-coordinate. The spectra of $RhCl(PCy_3)_2$ are dependent on the conditions of sampling. In addition to the main resonances, resonances from added free PCy_3, $OPCy_3$, $RhHCl_2(PCy_3)_2$, and sometimes $RhCl(PCy_3)_2(O_2)$ are present. In concentrated solution the main resonances are a slightly broadened doublet with ^1J(Rh—P) 193.8 Hz. In dilute solutions an additional doublet with ^1J(Rh—P) 209.9 Hz is present, and both doublets are broadened. A solution of $[RhCl(C_8H_{14})_2]_2$ and PCy_3 shows a doublet with ^1J(Rh—P) 104.0 Hz, and a more concentrated solution shows this doublet and also a doublet with ^1J 193.8 Hz. In the presence of cyclooctene the main resonance is the doublet with the coupling constant of 104 Hz; we therefore ascribe this to $RhCl(PCy_3)_2(C_8H_{14})$. The doublet with coupling constant 209.9 Hz may be ascribed to the monomeric three-coordinate $RhCl(PCy_3)_2$, similar to $RhX(PCy_3)_2$ (X = F, Br, I), and the doublet with *J* 193.8 Hz to the dimeric $[RhCl(PCy_3)_2]_2$, in view of its concentration dependance and by comparison with the ^1J(Rh—P) of $[RhCl(P(p\text{-}Tol)_3)_2]_2$ of 196 Hz [4]. The observations can be explained by assuming the following equilibria:

$$\underset{(193.8\ \text{Hz})}{\tfrac{1}{2}[RhCl(PCy_3)_2]_2} \rightleftharpoons \underset{(209.9\ \text{Hz})}{RhCl(PCy_3)_2} \rightleftharpoons \underset{(104.0\ \text{Hz})}{RhCl(PCy_3)_2(C_8H_{14})}$$

In the presence of cyclooctene, the equilibrium lies to the right; in concentrated solutions the equilibrium shifts to the left. In fact, "$RhCl(PCy_3)_2$" is the least soluble of the series $RhX(PCy_3)_2$ (X = F, Cl, Br, I), and concentrated solutions for X = Cl can only be obtained by evaporating cyclooctene from a solution prepared in situ. In this way supersaturated solutions are obtained, from which $[RhCl(PCy_3)_2]_n$ precipitates after a short time. In the far infrared the precipitate shows only a broad Rh—Cl band at 275 cm^{-1}, which does not permit definitive conclusions about its formulation as a dimer in the solid state. The presence of two PCy_3 ligands in a *cis* configuration is unfavourable on steric grounds, but has a precedent in the pseudo-square planar $[Pt(allyl)(PCy_3)_2]^+$ [21].

Three-coordination is very rare in d^8-metal chemistry. The sp^2-hybridisation in trigonal geometry is unfavourable for d^8, because an empty d-orbital lies near the region of filled d-orbitals (in ideal trigonal geometry the d^8-complex should be paramagnetic with two unpaired electrons). In addition, trigonal geometry leads to relatively weak σ-bonding [22]. It is therefore expected that in the free energy of formation of a four-coordinate adduct the enthalpy contribution will generally far exceed the opposing entropy contribution. However, steric hindrance turns out to be effective in stabilizing this d^8-three-coordination.

That $RhCl(PCy_3)_2$ is in equilibrium with its dimer and with its cyclooctene adduct indicates that only small free energy differences are involved in the underlying systems. For the bromo and iodo complexes, the apparent absence of the analogous equilibria may be caused by the larger covalent radius of the anionic ligand, and thus increased steric hindrance; in the fluoro complex it may be caused by a weaker metal—fluoro bond and a more positive metal center.

Dinitrogen coordination

Of the three-coordinate complexes $RhX(PCy_3)_2$, the chloro, the bromo and the iodo complex add molecular nitrogen at room temperature and 1 atm of nitrogen. The reaction times of nitrogen addition are:

$RhF(PCy_3)_2 + N_2$ no reaction

$RhCl(PCy_3)_2 + N_2 \xrightarrow{\text{4 to 5 days}} RhCl(PCy_3)_2(N_2)$

$RhBr(PCy_3)_2 + N_2 \xrightarrow{3h} RhBr(PCy_3)_2(N_2)$

$RhI(PCy_3)_2 + N_2 \xrightarrow{\text{15 min}} RhI(PCy_3)_2(N_2)$

The differences in rate of addition may be caused by increasing electron density on the rhodium in the order $F < Cl < Br < I$, facilitating the nucleophilic attack on the nitrogen [32]. In addition, the rate of the chloro complex may be influenced by the monomer—dimer equilibrium. Whether the P—Rh—P angle differs among the four complexes and whether this influences the rates is not known.

The complexes show $\nu(N{\equiv}N)$ near 2100 cm^{-1}, and $\nu(Rh{-}N)$ near 460 cm^{-1} (Table 4). The most probable structure is square planar with *trans*-phosphines (Fig. 2). The complexes can be stored over long periods at room temperature under nitrogen. Carbon monoxide displaces N_2 from the complexes, while O_2 displaces N_2 slowly from the chloro complex, but more rapidly from the iodo complex. Ethylene displaces N_2 from the iodo complex, but not from the chloro complex.

$RhCl(PCy_3)_2$ was the first rhodium compound reported to react spontaneously with nitrogen [7]. The only other case is an unidentified complex with phenyl-5(5H)-dibenzophosphole (DBP) [23]. The resulting dinitrogen containing com-

TABLE 4

INFRARED DATA OF DINITROGEN AND DIOXYGEN COMPLEXES (cm^{-1})

in CsI, (a) Same values in benzene

Compound	$\nu(N_2)/\nu(O_2)$	ν(Rh—N)	Others
$RhCl(PCy_3)(N_2)$	2100vs (a)	470s	317 ν(Rh—Cl)
$RhBr(PCy_3)_2(N_2)$	2103vs (a)	462m	
$RhI(PCy_3)_2(N_2)$	2108vs (a)	440s	
$RhCl(PCy_3)_2(O_2)$	993m		328m ν(Rh—Cl)
$RhBr(PCy_3)_2(O_2)$	991m		
$RhI(PCy_3)_2(O_2)$	986m		
$Rh(N_3)(PCy_3)_2(O_2)$	989m		2053s (N_3)
$RhCl(PCy_3)_2(^{18}O_2)$	943w		328m ν(Rh—Cl)

plex has been formulated tentatively but probably incorrectly as a six-coordinate rhodium(I) complex $Rh(BH_3CN)(N_2)(CO)(DBP)_3$.

The only other known rhodium—dinitrogen complex $RhCl(PPh_3)_2(N_2)$ [24] was prepared indirectly by the reaction:

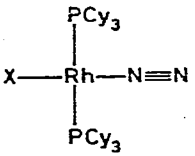
$$RhL_n(CO) + RC(O)N_3 \rightarrow RhL_n(N_2) + RC(O)NCO$$

The same reaction was used to prepare a series of iridium(I)—dinitrogen complexes [25].

Four-coordinate dioxygen complexes

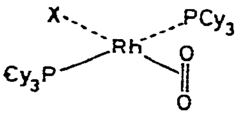
In solution the reaction of $RhX(PCy_3)_2$ with O_2 gives rather stable dioxygen adducts $RhX(PCy_3)_2(O_2)$, except for $RhF(PCy_3)_2$, which forms $OPCy_3$.

The ^{31}P NMR spectrum of $RhCl(PCy_3)_2(O_2)$ shows a ^1J(Rh—P) coupling constant of 106.3 Hz (Table 2), in the range of four-coordinate $RhCl(PCy_3)_2L$ complexes, where L is a side-on coordinating ligand [11]. $RhCl(PCy_3)_2(O_2)$ has a single ν(Rh—Cl) at 328 cm^{-1}, which gives further support for a monomeric four-coordinate structure with side-on coordinated dioxygen (Fig. 3). The complex shows $\nu(^{16}O_2)$ at 993 cm^{-1} and $\nu(^{18}O_2)$ in an $^{18}O_2$ enriched sample at 943 cm^{-1}. The other dioxygen complexes $RhX(PCy_3)_2(O_2)$ (X = Br, I, N_3) have $\nu(O_2)$ at about 990 cm^{-1}. This is an unusual position for the stretching vibration frequency of coordinated O_2. Several reviews of dioxygen complexes have appeared [13,26—28] and a division based on infrared data lists superoxo complexes ($\nu(O_2)$ ranging from 1075 to 1195 cm^{-1}) and peroxo complexes ($\nu(O_2)$ ranging from 790 to 932 cm^{-1}) [13]. The range of h^2-dioxygen complexes runs from 800 to



X = Cl, Br, I

Fig. 2.



X = Cl, Br, I, N_3

Fig. 3.

932 cm^{-1} [13] and the range of h^2-dioxygen—rhodium complexes from 833 to 890 cm^{-1} (data from [28]). The $RhX(PCy_3)_2(O_2)$ complexes have $\nu(O_2)$ significantly outside these ranges. The value of 990 cm^{-1} can, however, be explained on the basis of the four-coordination in the complexes.

The known d^{10}- and d^8-metal complexes with side-on dioxygen, which have well-defined structures are trigonal or trigonal bipyramidal [27,28]; the $RhX(PCy_3)_2(O_2)$ apparently are the first d^8-square planar dioxygen complexes. For d^6- d^8- and d^{10}-metal alkyne and alkene complexes a division into class S (square planar and octahedral) and class T (trigonal and trigonal bipyramidal) complexes has been given [29], corresponding to relatively weak and relatively strong π-backbonding. This division is supported by the infrared data for alkyne complexes [30] and tetrafluoroethylene complexes [31] for which the stretching vibration frequencies of the coordinated multiple bond in the four-coordinate complexes lies significantly above the range of frequencies of the five-coordinate complexes. So weak π-backbonding in the four-coordinate complexes $RhX(PCy_3)_2(O_2)$ may explain the O_2 stretching vibration frequency of 990 cm^{-1}, which is unusually high compared with the dioxygen complexes of trigonal or trigonal bipyramidal geometry.

Trans-Influence in $RhX(PCy_3)_2L$ (X = anionic, L = neutral ligand)

We have examined in some detail the *trans*-influence of a series of anionic ligands on the infrared properties of carbon monoxide, ethene and diphenylacetylene (tolane) in addition to those of dinitrogen and dioxygen. The complexes were prepared from $RhF(PCy_3)_2$. The expected structures of the complexes are given in Fig. 4—6, and infrared spectroscopic data are given in Table 5. Attempts to prepare complexes $RhX(PCy_3)_2(O_2)$ with X = F, NCO, CN or NCS were unsuccessful. Also $Rh(CN)(PCy_3)_2L$ could not be prepared for $L = C_2H_4$ and C_2Ph_2. The ethene, tolane and O_2 series have no precedent in the chemistry of four-coordinate complexes of rhodium(I) and iridium(I).

In Table 6 the AB ligand stretching frequencies of the AB molecules ($AB = N_2$, CO, $H_2C{=}CH_2$, $PhC{=}CPh$, O_2) are given as a measure of the metal—(π-acid) interaction. For the ethene complexes, the sums of the vibrations near 1200 and near 1500 cm^{-1} (the coupled $\nu(C{=}C)$ and $\delta(C—H)$ vibrations) are given [32]. The relative precision is ± 1 cm^{-1}, for the ethene complexes ± 2 cm^{-1}. As expected, the differences are small, but in view of the invariance of the ordering of the anions as a function of $\nu(CO)$ in similar series of $MX(CO)(PR_3)_2$ complexes (M = Rh, Ir; R = alkyl or aryl) [25,33] the varying ordering of the anions as a function of $\nu(C{\equiv}C)$ is thought to be significant.

On theoretical grounds contributions to the measured IR *trans*-influence in these complexes of C_{2v} symmetry come from σ-effects as well as from π in-plane

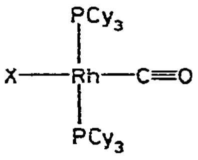


Fig. 4.

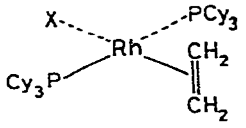


Fig. 5.

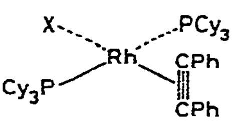


Fig. 6.

TABLE 5

INFRARED DATA FOR CARBONYL, ETHYLENE AND TOLANE COMPLEXES (cm^{-1})

in CsI (a) same value in Nujol mull

Compound	ν(CO)		δ(CO)	Others
$RhF(PCy_3)_2(CO)$	1936s		602s	470m (νRh—F) (a)
$RhCl(PCy_3)_2(CO)$	1947s		582s	305m (νRh—Cl)
$RhBr(PCy_3)_2(CO)$	1947s		574s	
$RhI(PCy_3)_2(CO)$	1948s		564s	
$Rh(N_3)(PCy_3)_2(CO)$	1950s		591s	2067s (N_3)
$Rh(NCO)(PCy_3)_2(CO)$	1950s		592s	2218s (NCO)
$Rh(NCS)(PCy_3)_2(CO)$	1961s		596s	2096s, 836m (SCN)
$Rh(CN)(PCy_3)_2(CO)$	1964s		585s	1945s (CN)
$Rh(NO_3)(PCy_3)_2(CO)$	1953s		593s	1472m, 1288s (NO_3)
$Rh(CH_3COO)(PCy_3)_2(CO)$	1943s		595s	1622s, 1367s (ac)
	$\delta(CH_2)$	ν(C=C)	ν(CH)	Others
$RhF(PCy_3)_2(C_2H_4)$	1500w	1200m	940m	421m ν(Rh—F) (a)
$RhCl(PCy_3)_2(C_2H_4)$	1511w	1208m	942m	294m ν(Rh—Cl)
$RhBr(PCy_3)_2(C_2H_4)$	1513w	1215m	947m	
$RhI(PCy_3)_2(C_2H_4)$	1512w	1209m	936m	
$Rh(N_3)(PCy_3)_2(C_2H_4)$	1510w	1209m	940m	2064s (N_3)
$Rh(NCO)(PCy_3)_2(C_2H_4)$	1510w	1209m	941m	2215s (NCO)
$Rh(NCS)(PCy_3)_2(C_2H_4)$	1514w	1213m	948m	2085s, 826m (NCS)
	ν(C=C)	$\nu_{as}(Rh—C_2)$		Others
$RhF(PCy_3)_2(C_2(C_2Ph_2)$	1868m	585m		462m ν(Rh—F) (a)
$RhCl(PCy_3)_2(C_2Ph_2)$	1860m	573m		315m ν(Rh—Cl)
$RhBr(PCy_3)_2(C_2Ph_2)$	1860m	574m		
$RhI(PCy_3)_2(C_2Ph_2)$	1846m	570m		
$Rh(N_3)(PCy_3)_2(C_2Ph_2)$	1856m	570m		2058s (N_3)
$Rh(NCO)(PCy_3)_2(C_2Ph_2)$	1865m			2217s (NCO)
$Rh(NCS)(PCy_3)_2(C_2Ph_2)$	1878m			2080s, 832m (NCS)

TABLE 6

INFLUENCE OF ANIONIC LIGAND X ON THE ν(AB) FREQUENCIES (cm^{-1}) IN $RhX(PCy_3)_2(AB)$ COMPLEXES (AB = N_2, CO, $H_2C{=}CH_2$, $PhC{\equiv}CPh$, O_2)

relative precision ± 1 cm^{-1}, for ethene ± 2 cm^{-1}

X	AB				
	N_2	CO	C_2H_4 [a]	C_2Ph_2	O_2
F		1936	2700	1868	
Cl	2100	1947	2719	1860	993
Br	2103	1947	2728	1860	991
I	2108	1948	2721	1846	986
N_3		1950	2719	1856	989
NCO		1950	2719	1865	
NCS		1961	2727	1878	
CN		1964			

[a] For C_2H_4, the sum of the coupled ν(C=C) and δ(C—H) is given [32].

and π out-of-plane effects. A dominant σ-contribution to the measured *trans*-influence should lead to a similar X-ligand order, and especially a similar position of fluorine, for the ethene and tolane complexes, as these molecules are effected in the same way be σ-bonding. This is found not to be so and we therefore postulate an important π-contribution to the observed *trans*-influence.

The L-ligands differ in their ligand-to-metal π-orbitals: all five possess an empty π-orbital perpendicular to the square plane, the π-orbital in the square plane is empty for N_2 and CO, "non-existing" for ethene, and filled for tolane and O_2. Apparently, the infrared frequencies of the L-ligands discriminate between the different π-bonding properties of the X-ligands by virtue of their own π-bonding requirements, resulting in different IR *trans*-influence series.

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