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Orthometallation reactions of rhodium compounds containing orthohaloarylphosphines

V *. Synthesis and reactivity of orthometallated rhodium(III) compounds. Crystal structure of $RhCl(CO)[P(o\text{-}ClC_6H_4)Ph_2]_2$

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Abstract

The reaction of $RhCl_3 \cdot 3H_2O$ with a 3-molar proportion of $P(o\text{-}ClC_6H_4)Ph_2$, (PCCl) at room temperature gives $RhCl(PCCl)_2$ (**1**), in high yield. Reaction of $[Rh(cot)_2Cl]_2$, (cot = cyclooctene), with PCCl, 1/2 molar ratio, also gives compound **1**. Refluxing of a solution of **1** in 96% ethanol gives $RhCl_2(PC)(\eta^2\text{-PCCl})$, $[PC = (C_6H_4)PPh_2]$ (**2**). Complex **1** reacts with CO to give $RhClCO(PCCl)_2$ (**3**). ^{31}P NMR studies reveal that **1** exhibits a fluxional behaviour in solution in the temperature range −50 to 0 °C. The low temperature spectrum is consistent with the formulation $RhCl(\eta^2\text{-PCCl})(\eta^1\text{-PCCl})$. In cyclic voltammetry complex **2** shows two two-electronic reduction processes, at −0.98 and −1.56 V. Electrochemical or chemical reduction of **2** under carbon monoxide give compound **3**. Crystal structure of **3** was solved in the $P2_1/n$ space group, $Z = 2$, with cell parameters a 9.394(2), b 17.194(4), c 10.948(2) Å, and β 111.62(2)°. The structure consists of a rhodium atom in a square planar environment with the two chlorine atoms from the phosphines orientated towards the apical positions.

Replacement of chlorine or PCCl in compound **2** has enabled isolation of several orthometallated derivatives, RhCl(hp)(PC)(PCCl) (hp 2-oxypyridinate, **4**; 6-Clhp, **5** and $6\text{-}CH_3hp$, **6**) and $RhCl_2(PC)(P\text{–}P)$ (P–P bis(diphenylphosphino)methane (dppm), **7**, and 1,2-bis(diphenylphosphino)ethane (dppe), **8**).

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* For part IV see ref. 3.

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Introduction

Many orthometallated complexes with a five-membered ring structure have been described in the literature [1]. Orthometallated complexes with a four-membered ring in P donor ligands are less common, presumably because to the higher strain in the four-membered structure means that this type of compounds is less readily formed.

The reaction of $RhCl_3 \cdot 3H_2O$ and *ortho*-haloarylphosphines such as P(*o*-BrC_6F_4)Ph_2 [2], (PCBr) or (PCCl) [3], proved to be an efficient method for preparing compounds of stoichiometry $RhClBr[(C_6F_4)PPh_2](\eta^2\text{-PCBr})$ or $RhCl_2(PC)(\eta^2\text{-PCCl})$ (**2**). The molecular structure of **2** shows a distorted octahedral coordination around the rhodium atom, with marked distortion in the bond angles involved in the four-atom metalocycle [3].

We previously suggested that the reaction of $RhCl_3 \cdot 3H_2O$ and PCBr to give $RhClBr[(C_6F_4)PPh_2](\eta^2\text{-PCBr})$ takes place via a rhodium(I) species $RhCl(PCBr)_2$ that readily undergoes intramolecular oxidative addition. The postulated intermediate compound $RhCl(PCBr)_2$, has been prepared by other routes, but not from the direct reaction of $RhCl_3$ with PCBr [2]. We have now found that $RhCl_3 \cdot 3H_2O$ reacts with the phosphine PCCl under mild conditions which allow isolation of the compound $RhCl(PCCl)_2$, which is the intermediate in the orthometallation reaction previously mentioned. The reactions of **2** with various neutral and anionic ligands are also described.

Results and discussion

Reaction of $RhCl_3 \cdot 3H_2O$ and PCCl (1/3 molar ratio) in 96% ethanol at room temperature gave the insoluble reddish-orange compound $RhCl(PCCl)_2$. Important amounts of phosphine oxide are also present in the reaction mixture, and the solution is acidic.

On the basis of the elemental analysis and ^{31}P NMR spectrum ($CDCl_3$, $-50\,^\circ C$), we formulated this compound as $RhCl(\eta^2\text{-PCCl})(\eta^1\text{-PCCl})$. The low temperature spectrum shows two doublets of doublets, centered at 47.5 ppm (^1J(Rh–P) 216 Hz) and 66.8 ppm (^1J(Rh–P) 179 Hz) (Fig. 1). The low field signal is assigned to the bidentate phosphine. The $^2J(PP')$ coupling constant is 46 Hz indicative of a cis disposition of the two P nuclei in a square planar environment.

At higher temperatures the two phosphorus environments become magnetically equivalent. At $-10\,^\circ C$ the coupling between the two phosphorus nuclei disappears, and at around $20\,^\circ C$ there is only a broad signal. This dynamic process involved can be represented by the equilibrium 1. The average signal corresponding to the fast

$$RhCl(\eta^2\text{-PCCl})(\eta^1\text{-}^{*}PCCl) \rightleftharpoons RhCl(\eta^1\text{-PCCl})(\eta^2\text{-}^{*}PCCl) \qquad (1)$$

exchange cannot be observed because **1** undergoes intramolecular oxidative addition at higher temperatures. This reaction is not observed at room temperature, but in refluxing ethanol **2** is generated in a few minutes.

Compound **1** and the analogous $RhCl(PCBr)_2$ are interesting examples of rhodium(I) species of stoichiometry $RhClL_2$ that are relatively stable in solution owing to the ability of these phosphines to act as bidentate ligands which coordinate to the rhodium via the P and the halogen atoms [2]. We have not found any

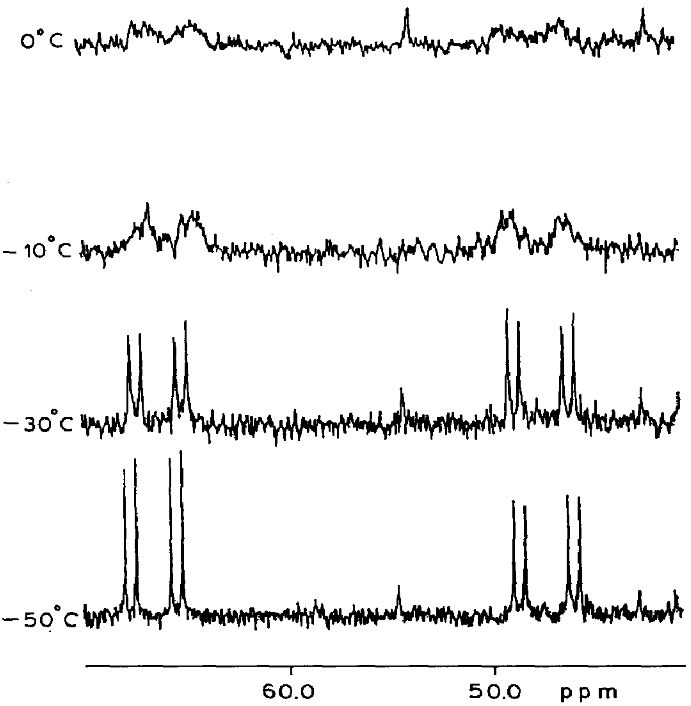

Fig. 1. ^{31}P NMR spectrum ($CDCl_3$) of compound **1** in the temperature range of −50 to 0°C. Positive shifts are downfield from aqueous 85% H_3PO_4.

spectroscopic evidence for a monomer–dimer equilibrium such as was described for similar species involving PCy_3 (Cy = cyclohexyl) [6]. In the solid state and in solution $RhCl(PCBr)_2$, is more stable than compound **1** towards oxidation by air, but it undergoes intramolecular oxidative addition more readily than compound **1**. Several factors must be responsible for the different reactivities of these two compounds, namely the relative abilities of the halogen to coordinate the rhodium atom, the different labilities of the carbon–halogen bond and the different electrophilic character of the aromatic carbon bonded to the halogen. Additional studies are necessary to establish the relative influence of these factors.

Complex **1** readily adds carbon monoxide at room temperature and one atmosphere pressure to give $RhCl(CO)(PCCl)_2$ (**3**), (ν(CO) 1970 cm^{-1}) quantitatively. This compound can also be obtained by treating $RhCl_3 \cdot 3H_2O$ with the phosphine PCCl at room temperature under a carbon monoxide atmosphere. The ^{31}P NMR spectrum of **3** consists of a doublet centred at 28 ppm (^1J(Rh–P) 132 Hz).

Compound **2** is a good substrate for substitution reactions. It readily reacts with silver oxypyridinate salts in THF to give the corresponding oxypyridinate compounds **4**–**6**. The ^{31}P NMR spectra of these compounds consist of two doublets of doublets with chemical shift and ^2J(PP′) values similar to the observed for **2** (see Table 1), indicating that the two P nuclei retain their *cis* disposition. The observed chemical shifts do not allow unambiguous structural assignments for compounds **4**–**6**. The high field shift ($\approx$ 15 ppm) of the resonance assigned to the coordinate PCCl ligand suggests that a change from η^2 to η^1 coordination mode may accompany the replacement of a chloride by an oxypyridinate ligand [7]. The high field

Table 1

^{31}P NMR spectroscopic data.

	δ(PC) * (ppm)	δ(PCCl) * (ppm)	δ(P–P) * (ppm)	$^2J(PP')$ (Hz)
1 $RhCl(PCCl)_2$		47.5(216)		46
		66.8(179)		
2 $RhCl_2(PC)(PCCl)$	−31.2(121)	44.1(130)		25
3 $RhCl(CO)(PCCl)_2$		28.3(132)		
4 RhCl(PC)(PCCl)(hp)	−40.2(106)	28.5(121)		25
5 RhCl(PC)(PCCl)(6-Clhp)	−42.9(105)	31.0(132)		26
6 $RhCl(PC)(PCCl)(6\text{-}CH_3hp)$	−43.6(107)	29.6(124)		26
7 $RhCl_2(PC)(dppm)$	P^a −50.5(74)		P^b −29.1(87)	P^a–P^b 527
			P^c −19.8(116)	P^a–P^c 18
				P^b–P^c 54
8 $RhCl_2(PC)(dppe)$	P^a −50.2(72)		P^b 39.8(103)	P^a–P^b 493
			P^c 48.1(132)	P^a–P^c 24
				P^b–P^c 12

* Positive shifts are downfield from aqueous H_3PO_4 85%. Values of $^1J(Rh–P)$, in Hz, are in parentheses.

shift observed for the phosphorus of the metallated phosphine, may be mainly due to steric effects of the bulky oxypyridinate ligands.

Replacement of the PCCl by diphosphine ligands (dppm or dppe) also occurs in compound **2**. Reaction of **2** with an equimolecular amount of dppm in chloroform at room temperature gives $RhCl_2(PC)(dppm)$ (**7**) in high yield. The reaction is complete after 2 h. The ^{31}P NMR spectrum consists of three groups of signals, centred at −50.5, −29.1, and −19.8 ppm. From the chemical shifts we conclude that all the phosphorus atoms are incorporated in four member rings [4]. The $^2J(PP')$ coupling constants indicate that two phosphorus atoms are mutually *trans*, and the third one *cis* to the other two nuclei. The high field signal is assigned to the metallated phosphine.

Reaction of **2** with dppe takes place analogously to give $RhCl_2(PC)(dppe)$ (**8**). The ^{31}P NMR spectrum also shows three groups of signals. One of these is assignable to the metallated phosphine on the basis of the chemical shift (−50.2 ppm) [4]. The other two in this case are shifted to lower field (39.8 ppm and 48.1 ppm) in accord with the presence of a five membered ring, as it could be expected for the chelating dppe. The $^2J(PP')$, coupling constants in this case indicate that two P atoms are again in a *trans* disposition and the third *cis* to the other two.

Electrochemical study

In cyclic voltammetry in THF, compound **1** is reduced irreversibly at −1.96 V, and oxidized, also irreversibly, at +0.48 V, as expected for a neutral rhodium(I) compound [5].

It is noteworthy that compound **3** in THF is oxidized in a partially reversible process at sweep rates higher than 250 mVs^{-1}, which contrasts with the total irreversibility observed for the same redox process in the case of the analogous PPh_3 complex. This can best be accounted for by assuming that in **3** the two chlorine atoms of the phosphine ligand are oriented towards the rhodium atom so giving rise

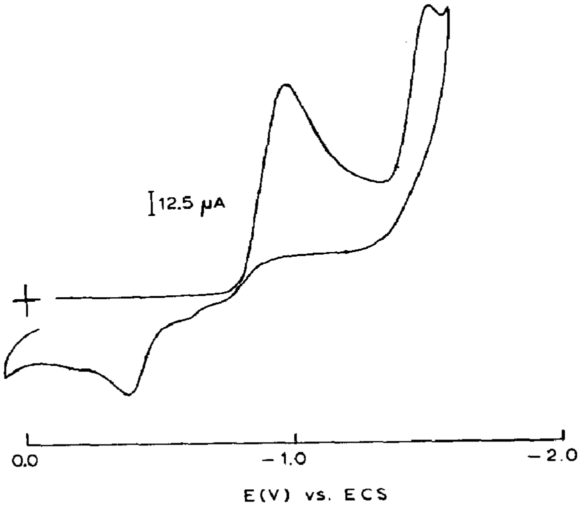

Fig. 2. Cyclic voltammogram of compound **2** in THF containing NBu_4PF_6 as supporting electrolyte. Sweep rate 0.1 V s^{-1}.

to axially-elongated octahedral coordination. Because of this the oxidized species can be stabilized in the octahedral coordination characteristic of complexes with a d^6 electronic configuration.

The electrochemical behaviour of **2** was examined by cyclic voltammetry and coulometry. In THF it shows two irreversible reduction processes of equal intensity at −0.96 and −1.56 V vs. SCE (Fig. 2). Potential controlled electrolysis at −1.0 V (0 °C, in THF) involves a consumption of approximately 2F/mol and no well defined species can be isolated after the electrolysis. The results suggest that the two peaks correspond to two two-electron reduction processes yielding a Rh^I and Rh^{-I} species, respectively

$$\mathrm{Rh^{III}} \overset{+2e^-}{-----} \mathrm{Rh^{I}} \overset{+2e^-}{-----} \mathrm{Rh^{-I}}$$

However, if a carbon monoxide atmosphere is present during the electrolysis (under the same conditions) compound **3** is obtained. The formation of this product implies that the reduction involves breaking of the Rh–C bond of the metallocycle, probably as a consequence of the excess of electron density. Chemical reduction with sodium naphthalenide and carbonylation also yields compound **3**.

Crystal and molecular structure of 3

Figure 3 shows a perspective view of the molecule with the atomic numbering scheme. Selected bond distances and bond angles are given in Table 2. A list of atomic coordinates for non-hydrogen atoms is also given in Table 3.

As expected, the coordination about the central atom is square planar. The atoms PP′C(1)Cl(2) define a plane within 0.01 Å, and the rhodium atom lies in the plane. The adjacent ligand–Rh–ligand bond angles are not far from the theoretical value of 90°.

The bond length Rh–P of 2.344(2) Å and Rh–Cl(2) of 2.430(8) Å, as well as the remaining bond lengths and angles, are in good agreement with those found in

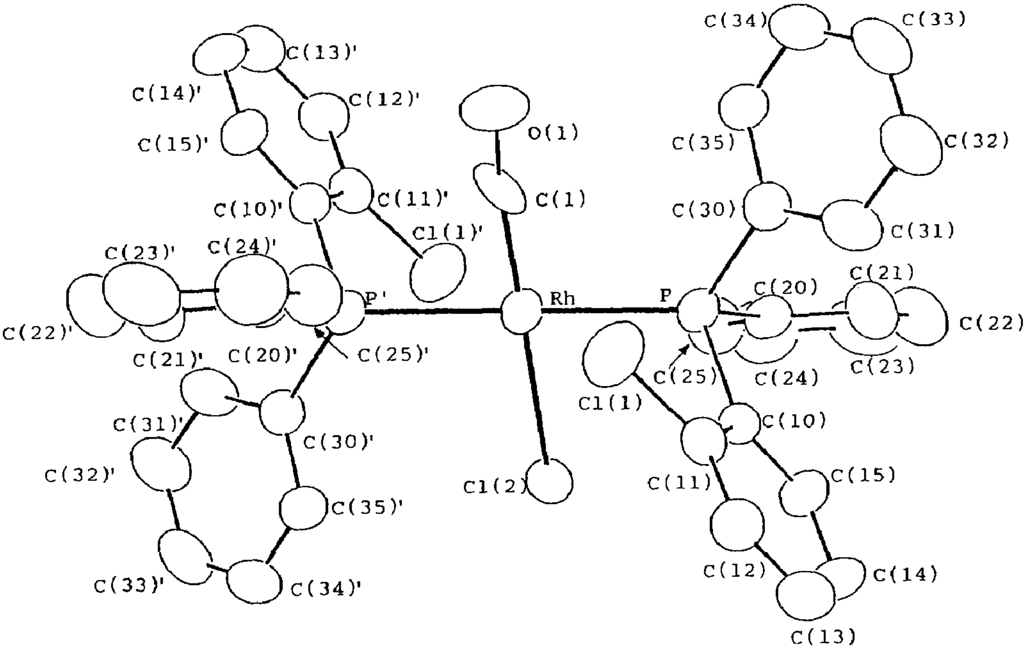

Fig. 3. ORTEP view of compound 3. Atoms labelled with a prime are related with the asymmetric unit via the transformation x', y', $z' = 1 - x$, $1 - y$, $1 - z$. For clarity the Cl and CO ligands are shown as ordered.

similar compounds [12], except perhaps, for the Rh–CO bond length (1.722(15) Å), which is a little shorter than that 1.821(5) Å found for the compound *trans*-Rh(CO)Cl$(PPh_3)_2$ [13], in which no disorder was observed. However, the apparent difference may well arise from the disorder assumed in the refinement. Other values

Table 2

Selected bond lengths (Å) and angles (deg.) in *trans*-RhCl(CO)$(PCCl)_2$

Rh–P	2.344(2)	P–Rh–Cl(2)	84.8(3)
Rh–Cl(2)	2.430(8)	P–Rh–C(1)	96.0(10)
Rh–C(1)	1.722(15)	Cl(2)–Rh–C(1)	178.8(10)
O(1)–C(1)	1.151	Rh–P–C(10)	110.7(2)
P–C(10)	1.836(6)	Rh–P–C(20)	112.5(2)
P–C(20)	1.834(7)	Rh–P–C(30)	123.4(2)
P–C(30)	1.845(7)	Rh–C(1)–O(1)	171.2(39)
Cl(1)–C(11)	1.744(7)	Cl(1)–C(11)–C(10)	120.3(5)
		Cl(1)–C(11)–C(12)	117.8(6)
		C(10)–P–C(20)	104.9(3)
		C(10)–P–C(30)	101.3(3)
		C(20)–P–C(30)	102.1(3)
		P–C(10)–C(11)	120.4(5)
		P–C(10)–C(15)	121.9(5)
		P–C(20)–C(21)	121.8(6)
		P–C(20)–C(25)	119.0(5)
		P–C(30)–C(31)	122.0(5)
		P–C(30)–C(35)	120.0(5)

Table 3

Final fractional coordinates of the non-hydrogen atoms for *trans*-RhCl(CO)(PCCl)$_2$.

	x	*y*	*z*
Rh	0.5	0.5	0.5
P	0.4918(2)	0.3882(1)	0.6197(2)
Cl(1)	0.8458(2)	0.4362(1)	0.7532(2)
Cl(2)	0.4027(15)	0.5660(6)	0.6495(13)
C(1)	0.5719(32)	0.4547(15)	0.3947(26)
O(1)	0.6307(42)	0.4187(18)	0.3380(37)
C(10)	0.5830(8)	0.4063(3)	0.7969(6)
C(11)	0.7383(8)	0.4257(4)	0.8525(6)
C(12)	0.8121(9)	0.4364(4)	0.9860(7)
C(13)	0.7303(11)	0.4305(4)	1.0673(8)
C(14)	0.5757(11)	0.4151(5)	1.0140(8)
C(15)	0.5023(8)	0.4020(4)	0.8795(7)
C(20)	0.2956(8)	0.3584(4)	0.5945(6)
C(21)	0.2650(10)	0.2911(5)	0.6483(9)
C(22)	0.1129(12)	0.2713(6)	0.6258(11)
C(23)	0.0049(13)	0.3167(7)	0.5504(11)
C(24)	0.0260(9)	0.3830(7)	0.4939(10)
C(25)	0.1736(9)	0.4040(5)	0.5145(8)
C(30)	0.5808(7)	0.2950(4)	0.6038(6)
C(31)	0.6547(10)	0.2480(4)	0.7110(8)
C(32)	0.7115(10)	0.1758(5)	0.6968(9)
C(33)	0.6961(10)	0.1513(5)	0.5745(10)
C(34)	0.6219(10)	0.1948(5)	0.4669(9)
C(35)	0.5629(9)	0.2668(5)	0.4814(7)

for similar compounds involving Ir–CO bond lengths are 1.817(8), 1.791(13), and 1.67(4) Å, for, respectively, *trans*-Ir(CO)Cl[P(*p*-tol)$_3$]$_2$ [14], *trans*-Ir(CO)Cl(PPh$_3$)$_2$ [12], and *trans*-Ir(CO)Cl[P(*o*-tol)$_3$]$_2$ [11], the last two of these exhibited the same type of disorder as we found.

The most significant feature of the structure is perhaps, the peculiar position of the two symmetry-related Cl atoms of two phosphine ligands. These atoms are respectively above and below the plane of coordination of the central atom, giving a pseudo octahedral coordination around the Rh atom.

In spite of apparently long Rh...Cl(1) distance (3.578 Å) this is about the minimum value for that interaction for the geometry concerned. The plane of the phenyl ring to which the chlorine atom is linked is almost perpendicular to the rhodium coordination plane, making the Rh–Cl(1) distance as short as possible and suggesting some interaction between these atoms. The electrochemical behaviour of the compound in solution also suggests that there is some interaction between Rh and Cl atoms, as previously discussed. For the related compound *trans*-Ir(CO)Cl[P(*o*-tol)$_3$]$_2$ [11], an apical interaction between Ir and the CH$_3$ groups of the phosphine ligands [11], (Ir...CH$_3$ distance 3.55(2) Å.) has been proposed.

Experimental

General comments

Chemical reactions were carried out under dry argon by Schlenck-line procedures. All solvents were reagent grade and were dried and distilled before use. The

$RhCl_3 \cdot 3H_2O$ was purchased from Engelhard Industries. P(*o*-ClC_6H_4)Ph_2 [8], $RhCl(COT)_2$ [9], and $[RhCl(COD)]_2$ [10] were prepared by published procedures. The ^{13}P NMR were recorded on a Bruker AC 200 spectrometer, operating at 81.015 MHz (^{31}P), with H_3PO_4 85% as external reference. The infrared spectra were recorded an a Philips-SP2000 spectrophotometer for $CHCl_3$ solutions. The electrochemical experiments were carried out in a three-electrode cell; the working and auxiliary electrodes were platinum, the reference electrode was a saturated calomel electrode electrically connected to the solution by a "salt bridge" containing a saturated solution of the supporting electrolyte and the solvent. Cyclic voltammograms were obtained with a programming function generator 305 HQ instrument connected to a 552 Amel potentiostat, and were recorded on a Rike–Denshi F-35 *x–y* recorder. The solvent was THF which had been freshly distilled from sodium benzophenone. The supporting electrolyte, Bu_4NPF_6, was recrystallized from ethanol and dried at 80 °C under vacuum for 48 h. Potential-controlled electrolysis was carried out in a three compartments cell separated by fritted glass. Working and auxiliary electrodes were a platinum mesh. The charge transferred was calculated by recording intensity versus the time and carrying out a further integration. The system was calibrated with cobaltocene.

Crystal and molecular structure of $RhCl(CO)(PCCl)_2$ *(3): experimental data*

Yellow prismatic crystals of $C_{37}H_{28}OCl_3P_2Rh$, *M* 759.5, monoclinic, *a* 9.394(2), *b* 17.194(4), *c* 10.948(2) Å, β 111.62(2)°, *V* 1643.9(8) Å^3, D_c 1.53 g cm^{-3}, *F*(000) 768, μ(Mo K_α) 8.00 cm^{-1}, λ(Mo K_α) 0.71069 Å. Although the molecule has no centre of symmetry, the structure was solved and refined in the space group $P2_1/n$ with $Z = 2$ by assumption of a pseudo-inversion center with disordered CO and Cl ligands.

Data collection. A well formed crystal of dimensions 0.14 × 0.14 × 0.35 mm, grown by slow diffusion of n-hexane into a solution of the complex in chloroform, was mounted on a diffractometer equipped with a graphite monocromator. The cell dimensions were obtained by least-squares refinement of 40 well-centered reflections. Examination of three standard reflections after each 45 minutes showed no appreciable intensity decay. 4595 reflections were measured ($3 < 2\theta < 45°$, $0 < h < 10$, $-18 < k < 18$, $-12 < l < 12$) with the variable-speed ω–2θ technique, and 1605 independent reflections with $I > 2\sigma(I)$ were used throughout the analysis. The value assigned to each *hkl* was the mean value of the intensities measured for equivalent reflections. Lorentz and polarization corrections were applied, but no allowance was made for absorption.

Space group. From systematic absences, initially the space group $P2_1/n$ was assigned. Since there are only two molecules in the unit cell the rhodium atom must lie at a center of symmetry, but the molecule has no inversion center. Careful examination of the systematic absences showed that if it is the case that all the planes have small intensities compared with the rest, there are a group of 29 (30.5% of *h*0*l*, for $h + l = 2n + 1$) with $I > 2\sigma(I)$ which, cannot strictly be considered as absent, providing evidence for lower symmetry ($P2_1$ or *Pn* space groups). However, an almost centrosymmetric distribution of electron density is expected around the rhodium atom, the only departure from such symmetry being the presence of a CO group *trans* to a Cl ligand through the center of symmetry occupied by the rhodium atom. Similar examples of disorder between coordinated halogen and carbon monoxide have been reported [11,12]. We thus decided to solve the structure in the $P2_1/n$ space group, simulating the actual configuration by assuming random disorder between chloro and carbonyl ligands.

Structure determination. The rhodium atom was fixed at 0.5,0.5,0.5 and from a Patterson synthesis the position of Cl(2) atom was determined. The remaining non-hydrogen atoms were located from successive difference electron density maps.

Structure refinement. The structure refinement was carried out by weighted full-matrix least-squares first with isotropic and then with anisotropic temperature factors. The model assumes that the Cl and CO sites were half-occupied as previously explained. Twelve hydrogen atoms were located by Fourier difference syntheses and the coordinates of the remaining two (H(22),H(35)) were calculated. All hydrogen atoms were included in the refinement with fixed isotropic thermal parameters similar to those of the C atoms to which they are bonded. At the end of the refinement it was noticed that the C–O distance was too large, and so it was fixed at 1.15 Å. Only poorly defined peaks corresponding to the chlorine atom, Cl(2), and the carbonyl group were found on a final electron density map when these three atoms, Cl(2), C(1) and O(1), were excluded.

The final R values were R 0.0477 and R_w 0.0351 (256 parameters refined). $\Sigma w(|F_o|-|F|)^2$ minimized with $w=1/(\sigma^2(F_o)+0.000163(F_o)^2)$ with $\sigma^2(F_o)$ from counting statistics. In the final difference map the residual maxima were less than 0.64 eÅ^{-3}. Some attempts were made to refine the structure in the lower symmetry space groups $P2_1$ and Pn but the results were not very different, and somewhat worse.

Atomic scattering factors and corrections for anomalous dispersion for the rhodium atom were taken from International Tables of X-ray Crystallography [15]. Solution and refinement of the structure were carried out with the SHELX-76 system [16]. The geometrical calculations were performed with XANADU [17], and molecular structure was drawn with ORTEP. Complete atomic coordinates, full lists of tables of molecular dimensions, and thermal paremeters, and lists of F_o/F_c values are available from the authors.

Synthesis of $RhCl(PCCl)_2$ (1)

Method A. $RhCl_3 \cdot 3H_2O$ (50 mg; 0.19 mmol) and PCCl (169 mg; 0.57 mmol) were stirred at room temperature in ethanol 96% (30 ml). After 45 min the red solution was reduced under vacuum to half its initial volume. The red-orange precipitate obtained was filtered off and recrystallized from $CHCl_3$/n-hexane under argon. The air-sensitive product was dried under vacuum and stored under argon (119 mg, yield 80%). Found: C, 52.6; H, 3.9. $C_{36}H_{28}Cl_3P_2Rh.CHCl_3$ calcd.: C, 52.2; H, 3.4%.

Method B. A solution of $[RhCl(COT)_2]_2$ (50 mg; 0.07 mmol) and PCCl (83 mg; 0.28 mmol) in 15 ml of 96% ethanol was stirred at room temperature for 3 h. The product was isolated as described in above (87 mg, Yield: 85%).

Preparation of $RhCl_2(PC)(PCCl)$ (2)

Compound **2** can be prepared either by direct reaction of $RhCl_3 \cdot 3H_2O$ with the phosphine, as we previously described [3], or from $RhCl(PCCl)_2$.

Thermal reaction of 1. Compound **1** (50 mg; 0.068 mmol) was refluxed in 96% ethanol (15 ml) for 2 h. The resulting yellow suspension was evaporated to dryness under vacuum and the residue was chromatographed on a columm (25 × 1.5 cm) packed with silica gel in hexane. Elution with $CHCl_3/CH_3OH$ (75/1) gave compound **2** (35 mg, yield 71%). Analysis: Found: C, 58.4; H, 4.2. $C_{36}H_{28}Cl_3P_2Rh$ calcd.: C, 59.0; H, 3.8%.

Preparation of RhClCO(PCCl)$_2$ (3)

Method A. Carbon monoxide was slowly bubbled for 4 h at room temperature through a suspension of $RhCl_3 \cdot 3H_2O$ (100 mg; 0.38 mmol) and PCCl (337 mg; 1.14 mmol) in degassed 96% ethanol (40 ml). The reaction was slow, and a carbon monoxide atmosphere was maintained for 12 h. The resulting yellow precipitate was filtered off, washed with hexane (2 × 10 ml), then dissolved with chloroform and chromatographed on a columm (25 × 1.5 cm) packed with silica gel in hexane. Elution with $CHCl_3$/hexane 2/1 gave a pale yellow band, which was evaporated to leave a yellow solid. It was recrystallized from CH_2Cl_2/n-hexane (223 mg, yield 77%). Analysis: Found: C, 55.7; H, 4.1. $C_{37}H_{28}Cl_3OP_2Rh \cdot 0.5CH_2Cl_2$ calcd.: C, 56.0; H, 3.7%.

Method B. $RhCl(PPCl)_2$ (50 mg; 0.068 mmol) was dissolved in 96% ethanol (25 ml) under argon and carbon monoxide was slowly bubbled through the solution. After 40 min a yellow solid had separated and this was filtered off and washed with hexane (2 × 10 ml). Purification by columm chromatography as described above gave **3** (41 mg, yield 79%).

Reduction of 2

Electrochemical reduction. A suspension of compound **2** (150 mg; 0.2 mmol) in 30 ml of THF was placed in the cathodic compartment of the electrolytic cell which was introduced into an ice-bath (ca. 0 ° C). The electrolysis was performed at −1.5 V and carbon monoxide was bubbled through the solution. During potential-controlled electrolysis no important colour changes were observed and, the initial suspension was transformed into yellow solution. When the current fell to 1% of the initial value, and ca. 2 F/mol had been consumed, the electrolysis was considered complete, and a new reduction peak at 2.20 V was detected. The resulting yellow solution was evaporated to dryness and the products were separated from the supporting electrolyte by extraction into toluene. The extracts were evaporated to dryness and the residue was dissolved in chloroform and chromatographed on a column (25 × 1.5 cm) packed with silica gel in hexane. Elution with chloroform/hexane 1/1 separated a pale yellow band, which was evaporated to dryness. Recrystallization from chloroform/n-hexane yielded a yellow solid, which was identified as compound **3** (46 mg, yield 35%).

Chemical reduction. A solution of sodium naphthalenide (2ml; 0.4 mmol) was added dropwise is a suspension of compound **2** (150 mg; 0.2 mmol) in 30 ml of freshly distilled THF at ca. 0 ° C (ice-bath). The mixture was stirred for 10 min to give a red solution. Carbon monoxide was bubbled through for 30 min to give a yellow solution. Work-up as described for the electrochemical reduction gave **3** (78 mg, yield 40%).

Preparation of RhČl(Hp)(PC)(PCCl) (Hp = hp, 4; Hp = 6-Clhp, 5; Hp = 6-CH$_3$hp, 6)

A mixture of compound **2** (100 mg, 0.137 mmol) and the relevant silver oxypyridinate (0.151 mmol) in 30 ml of THF was stirred vigorously. After 17 h a white precipitate was separated by filtration from the light yellow solution. The solution was concentrated under vacuum to dryness, and the pale yellow solid obtained was twice recrystallized from CH_2Cl_2/n-hexane.

Compound **4** (42 mg, yield 35%). Found: C, 59.8; H, 4.0; N, 1.7. $C_{41}H_{32}Cl_2P_2NORh \cdot 0.15CH_2Cl_2$. calcd.: C, 59.6; H, 4.4; N, 1.5%.

Compound **5** (73 mg, yield 78%). Found: C, 55.4; H, 3.6; N, 1.5. $C_{41}H_{31}Cl_3P_2NORh \cdot CH_2Cl_2$ calcd.: C, 55.9; H, 4.5; N, 1.6%.

Compound **6** (69 mg, yield 54%). Found: C, 56.6; H, 4.0; H, 1.5. $C_{42}H_{34}Cl_2P_2NORh \cdot CH_2Cl_2$ calcd.: C, 56.7; H, 3.8; N, 1.6%.

*Preparation of $RhCl_2(PC)(P\text{–}P)$, ($P\text{–}P$ = dppm, **7**; $P\text{–}P$ = dppe, **8**)*

A solution of dppm [bis(diphenylphosphino)methane] or dppe [bis(diphenylphosphino)ethane] (0.103 mmol) in 5 ml of CH_3Cl was added to a solution of compound **2** (75 mg, 0103 mmol) in CH_3Cl (25 ml). The reaction, which was monitored by ^{31}P NMR spectroscopy, was complete in 2 h. The pale yellow solution was concentrated to dryness, and the yellow solid obtained, which was washed with three portions of 10 ml of n-hexane then recrystallized from dichloromethane/n-hexane to give compound **7** (71 mg, yield 85%). Found: C, 63.2; H, 4.5. $C_{43}H_{36}Cl_2P_3Rh$ calcd.: C, 63.0; H, 4.4%.

Compound **8** was obtained in the way described for compound **7**. The product was chromatographed in a column of (25 × 1.5 cm) packed with silica gel in n-hexane. Elution with 20/1 dichloromethane/acetone gave a pale yellow band, from which a yellow solid was isolated (34 mg, yield 40%). Found: C, 63.3; H, 4.9. $C_{44}H_{38}Cl_2P_3Rh$ calcd.: C, 63.4; H, 4.6%.

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