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# A rhodium(I) complex containing a mixed donor ' $P_2N'$ tridentate ligand

Note

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#### Abstract

The reaction of 2-(diphenylphosphino)-*N*-[2-(diphenylphosphino)benzylidene]benzeneamine (PNCHP) with 0.5 equivalents of [{RhCl(1,5-cyclooctadiene)}<sub>2</sub>] affords the extremely, air-sensitive compound, [RhCl(PNCHP- $\kappa^3 P, N, P$ )]. This reacts with carbon monoxide to afford [RhCl(CO)(PNCHP- $\kappa^3 P, N, P$ )] which rearranges in dichloromethane solution to [Rh(CO)(PNCHP- $\kappa^3 P, N, P$ )]Cl·HCl. The single crystal structure of [Rh(CO)(PNCHP- $\kappa^3 P, N, P$ )]Cl·HCl shows the Rh to be in a square planar environment with the HCl molecule held via hydrogen bonding in the lattice. NMR experiments show the coordinated chloride in [RhCl(PNCHP- $\kappa^3 P, N, P$ )] can be substituted with tetrahydrofuran, acetonitrile or triphenylphosphine and the complex undergoes oxidative addition with dichloromethane to yield [Rh(CH<sub>2</sub>Cl)Cl<sub>2</sub>(PNCHP- $\kappa^3 P, N, P$ )].

Keywords: Crystal structure; Rhodium; Phosphorus-nitrogen donor

#### 1. Introduction

A major aspect of the chemistry of rhodium(I) is the formation of tertiary phosphine complexes [1]. Of these, complexes of the type [RhXL<sub>3</sub>], inspired by Wilkinson's compound, where L is a neutral ligand and X can be virtually any uninegative ion, are the most populous class. All are 16 electron compounds and are formally coordinatively unsaturated [2]. Five-coordinate rhodium(I) species are commonly produced by addition of neutral ligands to the four-coordinate species [3]. They are also the intermediates in substitution reactions of square planar rhodium(I) complexes, which are often rapid and proceed by an associative pathway [4].

Generally, the rhodium(I) chemistry of polydentate ligands is similar to the monodentate case discussed

above. In addition, polydentate ligands have been shown to: (i) Offer a more predictable coordination number and stoichiometry, as the chelate effect minimises the tendency of one or more phosphine groups to be displaced during a chemical reaction. (ii) Increase the basicity of the rhodium atom. (iii) Allow more control on the stereochemistry of the complexes. (iv) Impart detailed structural and bonding information in the form of metal-phosphorus and phosphorus-phosphorus coupling constants [5,6].

Most of the rhodium(I) square planar complexes undergo oxidative addition reactions yielding octahedral rhodium(III) complexes [7]. The most common of these are the [RhX<sub>3</sub>L<sub>3</sub>] species, where meridional isomers are normally the rule [8]. The oxidative addition of carbon halides to low valent metal complexes is of paramount interest. It is a key step in a number of industrially important catalytic processes, such as, carbonylation of methanol to acetic acid, cross coupling and carbonylation reactions. It has been found that for oxidative additions of carbon halide substrates to complexes of rhodium(I) (and iridium(I)), the additions are generally

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enhanced by increasing the electron density on the metal atom. The activation of dichloromethane requires relatively strong donor ligands, for example, the ligand *bis*-(dimethylphosphino)ethane in the complex [Rh{Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>}]Cl [9,10]. Coordination of ligands with three or four nitrogen donor atoms to rhodium(I) also gives strong nucleophilic species that can activate dichloromethane [9]. Whilst the arylphosphine moieties of the PNCHP ligand (Scheme 1) are less basic than the alkylphosphine ligands employed to activate carbon halides, the nitrogen donor in combination with the chelating abilities of the ligand should increase the basicity of the rhodium atom.

In this study, we have synthesised a Wilkinson's compound analogue with a 'ClNP<sub>2</sub>' donor set using the mixed donor multidentate ligand, 2-(diphenylphosphino)-*N*-[2-(diphenylphosphino)benzylidene]benzeneamine (PNCHP) [11], and report a preliminary investigation into its reactivity.



Scheme 1. The PNCHP ligand.

#### 2. Results and discussion

# 2.1. Synthesis and reactivity of $[RhCl(PNCHP-\kappa^{3}P, N, P)]$ (1)

Scheme 2 depicts the synthesis and reactions of the rhodium(I) complex, [RhCl(PNCHP- $\kappa^{3}P, N, P$ )] (1). All syntheses and manipulations were carried out under argon due to the air-sensitive nature of the parent compound 1 and most of the reaction products. The dark-green ( $\lambda_{max} = 651$  nm,  $\varepsilon_{max} = 2500$  M<sup>-1</sup>cm<sup>-1</sup>,  $Rh{\rightarrow}\pi^*_{imine}$ charge transfer band) complex [RhCl(PNCHP- $\kappa^{3}P, N, P$ )] (1) is prepared by reacting two equivalents of the PNCHP ligand with the chlorobridged dimer [{Rh(COD)Cl}2], in benzene. By contrast, the reaction of PNHCH<sub>2</sub>P, which has the imine functional group reduced to a secondary amine, with [{Rh(COD)Cl}<sub>2</sub>], gives rise to the five-coordinate  $[Rh(COD)(PNHCH_2P-\kappa^3P, N, P)]Cl$  [12]. In the reduced-ligand complex, the PNHCH<sub>2</sub>P ligand adopts a facial geometry, unlike PNCHP which prefers a meridional geometry [11]. A solution (e.g., benzene) of 1 changes from dark-green to a rust colour within seconds when exposed to air. The colour change also occurs in the solid state but is slower. <sup>31</sup>P NMR spectroscopy shows the reaction is complex, with the formation of many products, but mass spectrometry suggests one is



Scheme 2. Reactivity of [RhCl(PNCHP- $\kappa^3 P, N, P$ )] (1). <sup>a</sup>Cl ligands in 7 maybe *cis*.

[RhCl(PNCHP- $\kappa^{3}P, N, P$ )] (1) reacts with CO to give the neutral, five-coordinate, compound [RhCl(CO)-(PNCHP- $\kappa^{3}P, N, P$ )] (2), as a dark-green precipitate. The mass spectrum of 2 shows the most intense peak at m/z 680 (100%), corresponding to the loss of the chloride ion from the parent. Upon dissolution of 2 in dichloromethane, the coordinated chloride ion is lost and the orange ionic four-coordinate compound [Rh(CO)- $(PNCHP-\kappa^{3}P, N, P)$ ]Cl · HCl (3) is obtained, the identity of which was determined by an X-ray study (see Section 2.2). In the IR, the shift of the v(CO) band from 1959  $cm^{-1}$  for 2 to 2009  $cm^{-1}$  for 3 is consistent with the decrease in the coordination number of the Rh(I) atom and the formation of a cationic complex. The air-sensitivity of **3** is dramatically diminished compared to the parent complex 1, with estimated half-lives in solution (as observed by <sup>31</sup>P NMR) of several days (for 3) and several seconds (for 1).

NMR experiments show acetonitrile (MeCN) will substitute for the chloride of [RhCl(PNCHP- $\kappa^{3}P, N, P$ )] (1), with the aid of  $AgBF_4$ , to give the brown-orange, cationic complex,  $[Rh(MeCN)(PNCHP-\kappa^{3}P, N, P)]BF_{4}$ (4). The mass spectrum of 4 shows a peak at m/z 653 (100%) which corresponds to the loss of MeCN from the parent cation although the parent cation [Rh(MeCN)- $(\text{PNCHP}-\kappa^3 P, N, P)]^+$  is also observed at m/z 693 (87%). In a similar reaction, the dark-red, tetrahydrofuran (THF) adduct, [Rh(THF)(PNCHP- $\kappa^{3}P, N, P$ )]BF<sub>4</sub> (5), is prepared by reacting 1 with AgBF<sub>4</sub> in THF. The THF can be readily displaced yielding the yellow, triphenylphosphine complex,  $[Rh(PPh_3)(PNCHP-\kappa^3 P, N, P)]BF_4$ (6) which has a peak at m/z 914 (40%) in the mass spectrum corresponding to the parent cation. When 1 is dissolved in CH<sub>2</sub>Cl<sub>2</sub> a yellow oxidative-addition product is obtained which is formulated as [Rh(CH2Cl)- $Cl_2(PNCHP-\kappa^3 P, N, P)$  (7) on the basis of its mass spectrum [the observation of a peak m/z 736 (76%) assignable to the  $[M-C1]^+$  ion] and its NMR spectrum (see Section 2.3).

# 2.2. Single crystal structure of $[Rh(CO)(PNCHP-\kappa^{3}P,N,P)]Cl \cdot HCl(3)$

The X-ray crystal structure of the cation of  $[Rh(CO)(PNCHP-\kappa^3P, N, P)]Cl \cdot HCl$  (3) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The cation lies on a twofold rotational axis with Rh(1), C(100) and O(100) occupying special positions on that axis and the PNCHP ligand being disordered. The geometry of the coordination polyhedron about the rhodium atom is approximately square planar. The PNCHP ligand occupies three of the coordination sites



Fig. 1. An ORTEP diagram of the cation,  $[Rh(CO)(PNCHP-\kappa^3P, N, P)]^+$ , of complex 3 showing the numbering system used. Thermal ellipsoids are at the 50% probability level.

Table 1 Selected bond lengths and angles for complex 3 [Å and °] with estimated standard deviations in parentheses

Rh(1)-C(100)	1.802(4)	C(100)-Rh(1)-N	171.34(9)
Rh(1)–N	2.106(4)	C(100)-Rh(1)-P(1)	95.90(2)
Rh(1) - P(1)	2.2864(6)	N-Rh(1)-P(1)#1	90.05(14)
N–C(1)	1.283(6)	N-Rh(1)-P(1)	78.22(15)
N-C(36)	1.450(8)	P(1)-Rh(1)-P(1)#1	168.20(3)
C(1)-C(46)	1.439(12)		

Symmetry transformations used to generate equivalent atoms: #1, -x + 1, y, -z + 3/2.

by bonding through the two phosphorus atoms [P(1)]and P(1)#1] and the one nitrogen atom (N) with the fourth site occupied by a carbon monoxide ligand [C(100)-O(100)]. The Rh(1)-P(1) [2.2864(6) Å], Rh(1)-C(100) [1.802(4) Å], Rh(1)–N1 [2.106(4) Å] distances are similar to other rhodium(I)-monocarbonyl cations with mixed P and N donor sets [13,14]. The P(1)-Rh-P(1)#1 bond angle at  $168.20(3)^{\circ}$  shows a significant deviation from the 180° expected for an ideal square-planar geometry. The N–C(1) imine bond distance at 1.283(6) A is  $\sim 0.02$  Å longer than the value observed for the uncoordinated ligand [11b]. Apart from the expected chloride ion, the asymmetric unit also contains an HCl molecule (for details see Section 4.3) which appears to have arisen from the chlorinated solvent used for the synthesis of the compound. The HCl is held in the lattice via hydrogen bonds between the chloride and the PNCHP imine proton, H(1A), one of the aromatic hydrogens, H(15A) and as well there is a hydrogen bond between the two chloride ions (Table 2).

## 2.3. NMR spectroscopy

Proton NMR spectra showed the expected integration and peak multiplicities. The chemical shifts for the imino proton (Table 3) ranged from  $\delta$  10.25 for 3, to

D–H····A	d(D-H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	$d(\mathbf{D}\cdots\mathbf{A})$	<(DHA)
C(15)-H(15A)···Cl(1)#2	0.95	2.36	3.307(5)	172.3
$C(1)-H(1A)\cdots Cl(1)$	0.95	2.77	3.467(7)	130.9
$C(1)-H(1A)\cdots Cl(1)#1$	0.95	2.64	3.099(7)	110.0
$Cl(1)-H(1)\cdots Cl(2)$	0.93(3)	2.53(4)	3.305(6)	141(3)

Table 2 Hydrogen bonds for compound **3** [Å and °]

Symmetry transformations used to generate equivalent atoms: #1, -x + 1, y, -z + 3/2; #2, -x + 3/2, -y + 3/2, -z + 2.

Table 3 <sup>31</sup>P and <sup>1</sup>H NMR data for selected compounds<sup>a</sup>

Compound	$\delta P$		$^{2}J(\mathbf{P},\mathbf{P})$ (Hz)	$^{1}J(\operatorname{Rh},\operatorname{P})$ (Hz)		$\delta CH = N$	$^{3}J(Rh,H)$ (Hz)
	Pa	P <sub>b</sub>	-	Pa	$\mathbf{P}_{\mathrm{b}}$		
[RhCl(PNCHP)] (1)	32.0	27.1	408	142	148		
[Rh(CO)(PNCHP)]Cl·HCl (3)	44.4	31.5	283	123	127	10.25(d)	2.1
[Rh(MeCN)(PNCHP)]BF <sub>4</sub> <sup>b</sup> (4)	36.6	30.8	331	138	138	8.49(d)	3.7
[Rh(THF)(PNCHP)]BF <sub>4</sub> <sup>c</sup> (5)	33.6	29.7	338	146	148		
$[Rh(PPh_3(PNCHP)]BF_4^{c}$ (6)	44.3	32.6	296	143	138		
	47.1 <sup>d</sup>		41, 32	164			
$[Rh(CH_2Cl)Cl_2(PNCHP)]^e(7)$	40.2	27.3	505	101	103	8.78(d)	3.2

 $^{a 31}$ P NMR recorded at 109 MHz, chemical shifts are in ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>, solvent CDCl<sub>3</sub> unless stated otherwise. <sup>1</sup>H NMR recorded at 270 MHz, chemical shifts are in ppm relative to Si(CH<sub>3</sub>)<sub>4</sub>, solvent CDCl<sub>3</sub> unless stated otherwise.

<sup>b 31</sup>P data in CH<sub>3</sub>CN; <sup>1</sup>H data in C<sub>6</sub>D<sub>6</sub>; Rh-NCCH<sub>3</sub> signal at  $\delta$  2.25(s).

°In THF.

<sup>d</sup> Rh-*P*Ph<sub>3</sub>.

 $^{e_{31}}$ P data in CH<sub>2</sub>Cl<sub>2</sub>. Rh-CH<sub>2</sub>Cl signals at  $\delta$  3.85(m) and 3.46(m).

below the aromatic protons ( $\delta > 7.4$ ) for **1**. The imino proton resonance was observed as a doublet for all the compounds due to coupling with the spin 1/2, <sup>103</sup>Rh nucleus (100%), with the <sup>3</sup>*J*(Rh,H) coupling constants in the range 2–4 Hz.

The MeCN complex, **4**, displays a singlet at  $\delta$  2.25, assignable to the methyl group of the coordinated acetonitrile ligand [15]. Two signals, at  $\delta$  3.85 and 3.46, with multiple splitting, are exhibited by the complex [Rh(CH<sub>2</sub>Cl)Cl<sub>2</sub>(PNCHP- $\kappa^3 P, N, P$ )]BF<sub>4</sub> (7) – each of these have been assigned to one of the –CH<sub>2</sub>Cl protons. The observed chemical shift is similar to other Rh(III)– CH<sub>2</sub>Cl complexes [9,16], although in those cases, the methylene protons were magnetically equivalent.

The parent rhodium compound [RhCl(PNCHP- $\kappa^{3}P, N, P$ ] (1) exhibits an ABX type <sup>31</sup>P spectrum resulting from mutual coupling of the two inequivalent phosphorus nuclei ( $\delta$  32.0 and 27.1) of the PNCHP ligand, and a phosphorus coupling to the <sup>103</sup>Rh (100%) nucleus which has I = 1/2 (Table 2). The coupling constant,  ${}^{2}J(P,P)$  is 408 Hz and the coupling constants  ${}^{1}J(P,Rh)$  are 142 and 148 Hz, respectively. The coupling constants and chemical shifts are typical of other complexes with nitrogen/phosphorus donor atoms, where phosphorus atoms of the PPh<sub>2</sub> moiety are *trans* to each other [17]. For compounds 3 and 6, in which the chloride in 1 has been replaced by CO or PPh<sub>3</sub>, one of the phosphorus resonances of PNCHP has shifted by 12 ppm to higher frequency, while the other exhibits a much smaller shift. The higher frequency <sup>31</sup>P signal is

most likely caused by the phosphorus atom involved in the five-membered chelate ring due to the ring contribution ( $\Delta R$ ) effect [18,19]. The closely related complexes  $[Rh(CO)(PNHCH_2P-\kappa^3P, N, P)]^+$  and [Rh- $(PPh_3)(PNHCH_2P-\kappa^3P, N, P)]^+$ , where PNHCH\_2P is PNCHP with the imine functional group reduced to a secondary amine, have similar spectroscopic properties to the PNCHP compounds above [12]. The product 7 of the reaction between [RhCl(PNCHP- $\kappa^{3}P, N, P$ )] and CH<sub>2</sub>Cl<sub>2</sub>, displays a relatively large increase in the  ${}^{2}J(\mathbf{P},\mathbf{P})$  coupling constant and a large reduction of the  ${}^{1}J(P,Rh)$  coupling constant. This feature is indicative of a increase in the rhodium oxidation state from +1 to +3[20]. Chemical shifts and the  ${}^{2}J(P,P)$  coupling constants of the product points to the two phosphorus atoms of PNCHP coordinated in a trans arrangement with the nitrogen atom also bound.

### 3. Conclusions

The enhanced reactivity of [RhCl(PNCHP- $\kappa^3 P, N, P$ )] (1) relative to [RhCl('P<sub>3</sub>')] systems ('P<sub>3</sub>' = mono-, bi- or tridentate phosphines), can be attributed to the presence of the coordinated imino nitrogen which has the effect of increasing the nucleophilicity of the rhodium atom. Thus the complex rapidly decomposes in air and activates the halo-carbon bond of dichloromethane. A comparison of the reactivities of the 'P<sub>3</sub>' ligand complex, [RhCl(PhP(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>- $\kappa^3 P, P, P$ )] [5], and the

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'N<sub>3</sub>' ligand complex, [RhCl(2,6-(C(R<sup>1</sup>) = NR<sup>2</sup>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N- $\kappa^{3}N, N, N$ )] [9], shows the latter to react in seconds with CH<sub>2</sub>Cl<sub>2</sub> whereas the 'P<sub>3</sub>' ligand complex does not react. As expected, the 'P<sub>2</sub>N' complex, **1**, lies between these two extremes, requiring a few hours for the reaction to go to completion. Exposure to carbon monoxide allows the formation of the cation [Rh(CO)PNCHP- $\kappa^{3}P, N, P$ )]<sup>+</sup> which does not show the same high reactivity of the parent [RhCl(PNCHP- $\kappa^{3}P, N, P$ )] (1) complex, due to the carbon monoxide removing electron density from the Rh atom.

### 4. Experimental

#### 4.1. Materials and instrumentation

NMR measurements were performed on a JEOL GX270W spectrometer. IR spectra were recorded on a BIO-RAD FTS-40 instrument. UV-Vis spectra were recorded using a Shimadzu UV-310PC UV-VIS-NIR spectrometer. Mass spectra were obtained using a Varian VG70-250S double-focussing magnetic sector spectrometer by the method of liquid ion secondary mass spectroscopy (LSIMS) using m-nitrobenzyl alcohol as the matrix. Isotope abundance calculations were performed to identify the parent ion. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. All synthetic work was carried out in an argon atmosphere glove-box, unless stated otherwise. The complex  $[{RhCl(COD)}_2]$  [21] and PNCHP [11a] were prepared as previously reported. Solvents were dried by standard procedures [22].

#### 4.2. Syntheses

#### 4.2.1. $[RhCl(PNCHP-\kappa^{3}P, N, P)]$ (1)

A mixture of  $[{RhCl(COD)}_2]$  (0.239 g, 0.485 mmol) and PNCHP (0.528 g, 0.961 mmol) in ca. 10 mL of benzene was stirred at room temperature for 1 h. The resulting dark-green precipitate of 1 (0.661 g, 100%) was isolated by filtration and washed with *n*-pentane. Anal. Found: C, 64.54; H, 4.29; N, 1.86. Calc. for C<sub>37</sub>H<sub>29</sub>ClNP<sub>2</sub>Rh: C, 64.60; H, 4.25; N, 2.04%; MS: *m*/*z* 687 [M]<sup>+</sup>, 652 [M–Cl]<sup>+</sup>; UV/Vis:  $\lambda$  651 nm,  $\varepsilon_{max} = 2500$  $M^{-1}$  cm<sup>-1</sup>. When a dark-green solution of 1 (0.100 g, 0.145 mmol) dissolved in MeCN (4 mL), was combined with a solution of AgBF<sub>4</sub> (0.0283 g, 0.145 mmol) dissolved the same solvent (2 mL), a red-brown coloured solution formed instantaneously. After the solution had been stirred for 1 h, the white precipitate of AgCl was removed by filtration to give a rust coloured solution of  $[Rh(MeCN)(PNCHP-\kappa^{3}P, N, P)]BF_{4}$  (4), which was taken to dryness in vacuo. MS: m/z 693 [M]<sup>+</sup>, 652 [M-MeCN]<sup>+</sup>. The THF adduct, [Rh(THF)(PNCHP- $\kappa^{3}P, N, P$ ]BF<sub>4</sub> (5), was prepared in a similar manner

using THF as solvent. Similarly the PPh<sub>3</sub> adduct, [Rh(PPh<sub>3</sub>)(PNCHP- $\kappa^3 P$ , N, P)]BF<sub>4</sub> (6), was prepared by adding the phosphine (in a 1:1 mole ratio) to a THF solution of **5** and stirring at room temperature. After the resulting yellow solution was filtered through a plug of alumina (eluting with THF), the solvent was removed in vacuo. MS: m/z 914 [M]<sup>+</sup>, 652 [M–PPh<sub>3</sub>]<sup>+</sup>.

#### 4.2.2. $[RhCl(CO)(PNCHP-\kappa^{3}P,N,P)]$ (2)

Carbon monoxide was bubbled through a dark-green solution of **1** (0.154 g, 0.224 mmol) dissolved in 20 mL of THF for 30 min to give a dark-green precipitate. The solvent was removed in vacuo, yielding **2** (0.160 g, 79%) as dark-green microcrystals. *Anal*. Found: C, 63.10; H, 4.65; N, 1.82. Calc. for  $C_{38}H_{29}CINOP_2Rh$ : C, 63.75; H, 4.08; N, 1.96%; MS: *m/z* 680 [M–CI]<sup>+</sup>; IR (nujol) 1959 cm<sup>-1</sup> [*v*(CO)]. When compound **2** (0.030 g, 0.042 mmol) was dissolved in dichloromethane (2 mL), the green colour of the starting material slowly discharged. *n*-Hexane vapour was diffused into the resulting yellow solution to yield orange crystals of [Rh(CO)(PNCHP- $\kappa^3 P, N, P$ )]Cl·HCl (**3**) after several days. A single crystal was selected for an X-ray study. IR (CHCl<sub>3</sub>) 2009 cm<sup>-1</sup> [*v*(CO)].

### 4.2.3. $[Rh(CH_2Cl)Cl_2(PNCHP-\kappa^3P,N,P)]$ (7)

Compound 1 (0.030 g, 0.042 mmol) was dissolved in dichloromethane (2 mL) and allowed to stand until the green colour of the starting material discharged. *n*-Hexane vapour was then slowly diffused into the yellow solution resulting in the title compound as a yellow powder. *Anal.* Found: C, 55.25; H, 3.87; N, 1.65; Cl, 18.10. Calc. for  $C_{38}H_{31}Cl_3NP_2Rh \cdot ^2/_3CH_2Cl_2$ : C, 55.99; H, 3.92; N, 1.69; Cl, 18.50%; MS: *m/z* 736 [M–Cl]<sup>+</sup>.

# 4.3. Determination of the crystal structure of $[Rh(CO)(PNCHP-\kappa^3P,N,P)]Cl \cdot HCl(3)$

A single crystal of compound 3, was grown as described in the above section and attached to the ends of a glass fibre with cyanoacrylate glue. Data collection and refinement were performed as previously described [23]. The molecule lies on a twofold rotational axis with the Rh(1), C(100) and O(100) occupying special positions on that axis and the PNCHP ligand being disordered. The two phenyl rings [C(11) to C(16) and C(21)to C(26)] and the phosphorus atom P(1) transform quite well into their symmetry related positions, leading to larger, but tolerable, temperature factors for the carbon atoms and were thus refined with site occupation factors of 1. The oxygen of the CO ligand also shows an elongated parabolloid but a disordered refinement shows no significant improvement, hence the special position constraint was left in place. The phenyl-N=CH-phenyl fragment of the PNCHP ligand was refined as disordered around the C2 axis with site occupation factors (sof) of 0.5, which gave acceptable bond and temperature factors. The temperature factors of related carbon atom pairs [C(31) C(41), C(32) C(42), etc.] were constrained to be equal. The asymmetric unit contains two chlorine atoms (sof 0.5), which are also disordered around the C2 axis (pointing to the presence of lattice HCl). The atoms, Cl(1) and Cl(2), are 3.305 Å apart indicating a hydrogen bond between the two (the distance of 2.827 Å for the symmetry equivalent of Cl(2)seems too short - published Cl-H···Cl distances lie around 3.2-3.3 A). The most likely position for this hydrogen was found at the later stages of the refinement as Q3 and refined labelled H(1). This appears chemically sensible, however, due to the disorder of the chlorine atoms, this assignment has to be regarded with caution. Crystal data for  $C_{38}H_{30}Cl_2NOP_2Rh$ : M = 752.38, monoclinic, space group C2/c, a = 20.0936(1), b =19.3859(1), c = 8.9418(1) Å,  $\beta = 92.227(1)^{\circ}$ , V =3480.49(5) Å<sup>3</sup>, Z = 4, T = 200(2) K,  $D_{calc} = 1.436$  g cm<sup>-1</sup>, F = 1528,  $\mu$ (Mo K $\alpha$ ) 0.767 mm<sup>-1</sup>, 10561 reflections collected  $(2.92^\circ < 2\theta < 54.92^\circ)$ , of which 3804 were unique  $R_{int} = 0.0227$ ). Data were corrected for absorption effects;  $T_{\text{max}} = 0.8807$ ,  $T_{\text{min}} = 0.7389$ . The final  $R_1[I > 2\sigma I] = 0.0326$ ,  $wR_2[I > 2\sigma I] = 0.0887$ ,  $R_1$  $(all data) = 0.0385, wR_2 (all data) = 0.0922.$ 

#### 5. Supplementary material

CCDC 215017 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or E-mail: data\_request@ccdc.cam.ac.uk).

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