

^{31}P -NMR and X-ray studies of new rhodium(I) β -ketoiminato complexes $\text{Rh}(\text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2)(\text{CO})(\text{PZ}_3)$ where $\text{PZ}_3 = \text{PPh}_3$, PCy_3 , $\text{P}(\text{OPh})_3$ or $\text{P}(\text{NC}_4\text{H}_4)_3$

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Abstract

The substitution of the CO ligand in rhodium(I) β -ketoiminato complexes $\text{Rh}(\text{R}_1\{\text{O,N}\}\text{R}_2)(\text{CO})_2$ ($\{\text{O,N}\} = \text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2$; $\text{R}_1, \text{R}_2 = \text{CF}_3, \text{Me}, \text{CMe}_3$ in several combinations) by phosphorus ligands PZ_3 ($\text{PZ}_3 = \text{PCy}_3, \text{PPh}_3, \text{P}(\text{OPh})_3, \text{P}(\text{NC}_4\text{H}_4)_3$) leads to $\text{Rh}(\text{R}_1\{\text{O,N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes characterised by $^{31}\text{P}\{^1\text{H}\}$ -NMR and X-ray methods. The stronger σ -donor PZ_3 ligands ($\text{PZ}_3 = \text{PCy}_3, \text{PPh}_3$) substitute almost exclusively the CO group *trans* to N, forming P-*trans*-to-N isomers. The complexes $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{Me})(\text{CO})(\text{PCy}_3)$ (**II**), $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)$ (**III**), $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{Me})(\text{CO})(\text{PPh}_3)$ (**IV**) and $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ (**V**) are of a square-planar geometry with a slight tetrahedral distortion around the rhodium atom in **II**, **III** and **V**. The Rh–P(PCy_3) bonds are slightly longer than the Rh–P(PPh_3) bonds. The reaction of stoichiometric amounts of the less basic $\text{P}(\text{OPh})_3$ or $\text{P}(\text{NC}_4\text{H}_4)_3$ ligands leads to the formation of both isomers of the $\text{Rh}(\text{R}_1\{\text{O,N}\}\text{R}_2)(\text{CO})(\text{P}(\text{OPh})_3)$ or $\text{Rh}(\text{R}_1\{\text{O,N}\}\text{R}_2)(\text{CO})(\text{P}(\text{NC}_4\text{H}_4)_3)$ complex in comparable yields. The Rh–P($\text{P}(\text{OPh})_3$) distance (2.195(2) Å) in the isomer of that complex with $\text{P}(\text{OPh})_3$ coordinated *trans* to N (**VI**) is ca. 0.04 Å longer than in the isomer of that complex with $\text{P}(\text{OPh})_3$ coordinated *trans* to O (**VII**). The CO substitution in $\text{Rh}(\text{R}_1\{\text{O,N}\}\text{R}_2)(\text{CO})_2$ by PZ_3 ligands ($\text{PPh}_3, \text{PCy}_3, \text{P}(\text{OPh})_3$) causes the shortening of the Rh–C(CO) bond by ca. 0.04 Å compared to $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{Me})(\text{CO})_2$ (**I**), making difficult the coordination of another PZ_3 ligand, especially one with stronger σ -donor properties. The more π -acceptor $\text{P}(\text{OPh})_3$ ligands form bis-phosphito complexes and $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)\{\text{P}(\text{OPh})_3\}_2$ (**VIII**) exhibits inequivalence of the two $\text{P}(\text{OPh})_3$ ligands in solution (^{31}P -NMR) as well as in solid form (X-ray). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium(I) complexes; β -Ketoiminato complexes; X-ray; Substitution reaction

1. Introduction

Rhodium(I) dicarbonyl complexes of the formula $\text{Rh}(\text{LL})(\text{CO})_2$ with chelating monoanionic ligands LL^- coordinated to rhodium via $\{\text{O,O}\}$, $\{\text{O,N}\}$ or $\{\text{O,S}\}$ donor atoms represent a group of compounds that has been recently intensively studied [1–7] as catalyst precursors in hydroformylation, isomerisation and hydrogenation of olefins as well as model compounds in

studies of the key stages of catalytic cycles. Dicarbonyl complexes of the $\text{Rh}(\text{LL})(\text{CO})_2$ -type react with phosphorus ligands forming $\text{Rh}(\text{LL})(\text{CO})(\text{PZ}_3)$ complexes [8]. Furthermore, stronger π -acceptor ligands like $\text{P}(\text{OPh})_3$ or $\text{P}(\text{NC}_4\text{H}_4)_3$ substitute both the CO groups, forming $\text{Rh}(\text{LL})(\text{PZ}_3)_2$ complexes [9–13]. Kinetic studies have shown that the σ -donor/ π -acceptor properties of PZ_3 ligand determine the CO substitution rate, which increases as the π -acceptor properties of PZ_3 increase [14]. The values of the first oxidation potential of $\text{Rh}(\text{acac})(\text{CO})(\text{PZ}_3)$ complexes increase with the increase of the net electron donor properties of PZ_3 estimated electrochemically [15]. The typical coordina-

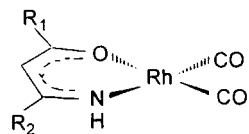
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tion number for these complexes is four, but some examples of pentacoordinate complexes, $\text{Rh}(\text{LL})(\text{CO})\text{-(PZ}_3)_2$, are also reported [1,16,17].

The reaction of triphenylphosphine with dicarbonyl complexes containing unsymmetrical β -diketonate ligands leads to the formation of two isomers of an $\text{Rh}(\text{LL})(\text{CO})(\text{PPh}_3)$ -type complex, but in most cases only one isomer was isolated in the solid form [18–22]. The only example of both isomers structurally characterised has been reported for $\text{Rh}[\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{C}_6\text{H}_5](\text{CO})(\text{PPh}_3)$ [23]. It was concluded from X-ray studies that the main factor determining the isomer formation is the *trans* influence of the donor atoms in the chelating ligand (LL), and the carbonyl group *trans* to the donor atom with the stronger *trans* influence is substituted [18,24–26]. In some complexes the opposite substitution reaction has also been observed and this was explained by the steric hindrance of a bulky substituent, e.g. CMe_3 in the β -diketonato group [20]. Contrary to the X-ray studies of solids, the analyses of complexes in solution confirmed the presence of comparable amounts of both isomeric forms of $\text{Rh}\{\text{O},\text{O}\}(\text{CO})(\text{PPh}_3)$ [9,27–30]. The preferable coordination of PPh_3 -*trans*-to-N has been NMR- and X-ray-confirmed for some rhodium(I) complexes, e.g. $\text{Rh}(\text{oxine})(\text{CO})(\text{PPh}_3)$ [31,32], $\text{Rh}(\text{oxine})(\text{CO})(\text{P}(\text{OPh})_3)$ [14,33] and $\text{Rh}(\text{Me}\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PPh}_3)$ [34].

The main goal of the studies presented in this paper was to elucidate the isomer formation during the substitution of CO with a variety of phosphorus ligands PZ_3 ($\text{PZ}_3 = \text{PCy}_3, \text{PPh}_3, \text{P}(\text{OPh})_3, \text{P}(\text{NC}_4\text{H}_4)_3$) in $\text{Rh}(\text{R}_1\text{-}\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ complexes, where $\text{R}_1\{\text{O},\text{N}\}\text{R}_2$ is a β -ketoiminato ligand, $\text{R}_1\text{C}(\text{O})\text{CHC}(\text{NH})\text{R}_2$.



$\text{R}_1 = \text{CF}_3; \text{R}_2 = \text{Me}$ or CMe_3

$\text{R}_1 = \text{Me}$ or $\text{CMe}_3; \text{R}_2 = \text{CF}_3$

All the dicarbonyl complexes selected for the studies in this paper belong to a family of compounds described in the early 1990s [35–37]. Among phosphorus donor ligands only triphenylphosphine was involved in previous NMR studies that confirmed its preferable *trans* coordination to N [38–41].

2. Results and discussion

2.1. $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ -type complexes

The IR spectra of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ complexes showed that the position of the different substituents R_1 and R_2 has practically no influence on the values of the $\nu(\text{CO})$ frequencies, whether in solid form or in solution (Table 1). The $\nu(\text{CO})$ frequencies of the complexes under study are located in between the values observed previously for their analogues with $\text{R}_1 = \text{R}_2 = \text{Me}$ (2074, 2002 cm^{-1}) and $\text{R}_1 = \text{R}_2 = \text{CF}_3$ (2092, 2026 cm^{-1}) in hexane solution [38]. In the analogous series of $\text{Rh}(\text{I})$ β -diketonato complexes of the $\text{Rh}(\text{R}_1\{\text{O},\text{O}\}\text{R}_2)(\text{CO})_2$ -type, the corresponding changes in the $\nu(\text{CO})$ frequencies caused by the presence of electronegative CF_3 substituents in the chelating ligand also span a range of about 20 cm^{-1} [42].

The inequivalence of the two CO groups in those complexes is consistent with the different values of $^1J(\text{RhC})$, (ca. 65 Hz for the C *trans* to N and ca. 72 Hz for the C *trans* to O, respectively; Table 1) and is in agreement with the generally accepted Fermi contact model of spin–spin coupling [43]. In the ^{13}C -NMR spectra of all the dicarbonyl complexes the $^1J(\text{RhC})$ value for the carbon *trans* to O is higher than that for the carbon *trans* to N by ca. 6–8 Hz. The inequivalence of the carbonyl groups in $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})_2$ (**I**), has also been characterised by the difference in the C–O

Table 1

The $\nu(\text{CO})$ band position in the IR spectra and ^{13}C -NMR parameters^a of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ complexes

R_1	R_2	$\nu(\text{CO})$ (cm^{-1}) (KBr)	$\nu(\text{CO})$, (cm^{-1}) (hexane)	δ (ppm); $^1J(\text{RhC})$ (Hz) (C- <i>trans</i> -to-O)	δ (ppm); $^1J(\text{RhC})$ (Hz) (C- <i>trans</i> -to-N)	$^2J(\text{CC})$ (Hz)	$^3J(\text{CH})$ (Hz)
CF_3	Me	2005.4 2078.8	2016 2086	185.2; 72.3	184.1; 65.2	8.7	2.7
CF_3	CMe_3	1996.0 2004.4 2072.3 2082.8	2014 2085	185.4; 72.1	184.1; 66.2	9.3	2.5
CMe_3	CF_3	2005.2 2075.8	2016 2084	185.6; 71.8	184.4; 65.5	9.1	2.5
Me	CF_3	2006.0 2075.5	2015 2082	185.3; 71.7	184.2; 65.6	8.5	2.4

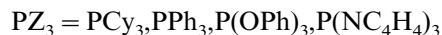
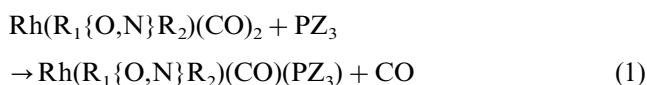
^a In chloroform solutions.

stretching force constant values, 17.24 and 16.66×10^2 N m^{-1} [35], with the lower value assumed to correspond to the CO group *trans* to O.

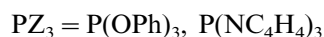
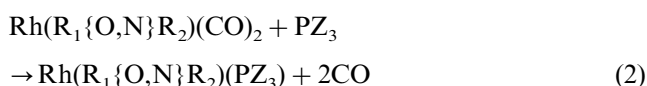
It is pertinent to note that in the ^{13}C -NMR spectra of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ with $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{CF}_3$ and $\text{R}_1 = \text{CF}_3$, $\text{R}_2 = \text{Me}$ the resonances of the carbonyl carbons *cis* to N are split due to coupling to the NH proton, with $^3J(\text{CH}) \cong 2.5$ Hz [40] (Table 1).

2.2. CO substitution in $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ complexes by PZ_3 ligands

The reactions of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ complexes with stoichiometric amounts of a phosphorus ligand PZ_3 were carried out in benzene and/or acetone solutions, and in all cases monocarbonyl complexes, $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$, were formed:



If higher concentrations of PZ_3 ($[\text{PZ}_3]:[\text{Rh}] > 1$) are applied, the next carbonyl ligand may be substituted, and $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{PZ}_3)_2$ complexes are formed for $\text{PZ}_3 = \text{P(OPh)}_3$ and $\text{P}(\text{NC}_4\text{H}_4)_3$, but not for PPh_3 or PCy_3 :



One of the products of reaction (2), $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)\{\text{P(OPh)}_3\}_2$ (**VIII**), was also characterised by X-ray studies (Fig. 7, Table 10).

Phosphorus ligands selected for these studies demonstrate different σ -donor/ π -acceptor properties that affect the $\nu(\text{CO})$ band position in the IR spectra of the $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes. For $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PZ}_3)$ complexes, the $\nu(\text{CO})$ frequencies (cm^{-1}) change in the following order of increasing π -acceptor properties of the PZ_3 ligand:

	PCy_3	PPh_3	P(OPh)_3	$\text{P}(\text{NC}_4\text{H}_4)_3$
$\nu(\text{CO})$ (cm^{-1})	1946	<1973	<2001	<2006

A similar relation was obtained for the $\nu(\text{CO})$ frequencies (cm^{-1}) complexes of the form $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PZ}_3)$:

	PCy_3	PPh_3	P(OPh)_3	$\text{P}(\text{NC}_4\text{H}_4)_3$
$\nu(\text{CO})$ (cm^{-1})	1956	<1971	<1992, 2009	<2002

In the spectrum of $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{P(OPh)}_3)$, the frequency at 1992 cm^{-1} has been tentatively assigned to the isomer with the carbonyl group *trans* to O (complex **VI**) and the one at 2009 cm^{-1} to **VII**.

The parameters of the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes obtained in solution by treating a dicarbonyl complex $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ with one equivalent of the corresponding phosphorus ligand are collected in Table 2. For those cases in which the reaction product was a mixture of both isomers, the NMR parameters were assigned according to the finding that $^1J(\text{Rh}-\text{P})$ correlates with the *trans* influence of the group located *trans* to P [39,44]. Consequently, the higher values of the $^1J(\text{Rh}-\text{P})$ coupling constants were assigned to phosphorus ligands coordinated *trans* to oxygen [9]. The lower values of the $^1J(\text{Rh}-\text{P})$ coupling constants were assigned to phosphorus atoms bound *trans* to nitrogen. In the series of complexes under study the $^1J(\text{Rh}-\text{P})$ values for isomers containing the PZ_3 ligand coordinated *trans* to N decrease in the order $\text{PCy}_3 < \text{PPh}_3 < \text{P}(\text{NC}_4\text{H}_4)_3 < \text{P(OPh)}_3$, in line with the increase of the π -acceptor properties of the phosphorus ligands.

The data collected in Table 2 corroborate the conclusion that the formation of isomers is dependent on the σ -donor/ π -acceptor properties of the phosphorus ligand. Stronger σ -donors like PCy_3 or PPh_3 replace almost exclusively the CO ligand in the position *trans* to nitrogen. The reaction products, $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PCy}_3)$ -type complexes, exist in solution as only one isomer, with the PCy_3 ligand *trans* to nitrogen, regardless of temperature changes (from $+40$ to -40°C) or kind of solvent used (acetone, benzene, toluene). Solutions of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PPh}_3)$ -type complexes contain small amounts (ca. 10%) of isomers with PPh_3 coordinated to rhodium in the position *trans* to oxygen (*P-trans-to-O*) and ca. 90% of isomers in which PPh_3 coordinates to rhodium in the position *trans* to nitrogen (*P-trans-to-N*) (Scheme 1). A domination of isomers with *P-trans-to-N* was observed earlier for $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PPh}_3)$ complexes in chloroform [39].

A completely different course of CO substitution was found for stronger π -acceptor ligands like P(OPh)_3 or $\text{P}(\text{NC}_4\text{H}_4)_3$, and neither of the isomers is preferred in these cases (Table 2, Scheme 1). The ratio of the isomers depends, however, on the solvent used.

The complex $\text{Rh}(\text{Me}\{\text{O},\text{N}\}\text{CF}_3)(\text{CO})(\text{P(OPh)}_3)$ obtained in C_6D_6 solution in the reaction of the respective dicarbonyl complex with P(OPh)_3 exists as a mixture of two isomers, with domination of *P trans* to O isomer, (ca. 62%). After complete evaporation of C_6D_6 and dissolution of the residue in $(\text{CD}_3)_2\text{CO}$, a new mixture of the isomers was obtained containing 33% of the one with *P-trans-to-O* and 67% of that with *P-trans-to-N*. When acetone (0.2 cm^3) was added to the benzene

Table 2
 $^{31}\text{P}\{^1\text{H}\}$ -NMR parameters for $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes ^a

R_1	R_2	Solvent	Isomer	$\delta^{31}\text{P}$ (ppm) [$^1J(\text{RhP})$ (Hz)] isomer content (%) ^b			
				PCy_3	PPh_3	P(OPh)_3	$\text{P}(\text{NC}_4\text{H}_4)_3$
CF_3	Me	T	P- <i>trans</i> -to-N II	55.8 [143.7] 100 complex	45.6 [150.7] 90 complex IV	126.8 [253.0] 76	^c
			P- <i>trans</i> -to-O d		60.5 [175.3] 10	129.5 [291.0] 24	^c
	A	P- <i>trans</i> -to-N II	51.4 [141.2] 100 complex	^c	123.5 [251.3] 62	100.3 [217.4] 90	
		P- <i>trans</i> -to-O d		^c	125.0 [290.8] 38	107.5 [247.7] 10	
CF_3	CMe_3	T	P- <i>trans</i> -to-N III	56.0 [145.2] 100 complex	47.5 [151.0] 90 complex V	126.4 [255.0] 50 complex VI	104.4 [218.8] ^c 62
			P- <i>trans</i> -to-O d		59.0 [174.2] 10	129.9 [290.0] 50 complex VII	112.9 [250.3] ^c 38
	A	P- <i>trans</i> -to-N III	51.5 [144.9] 100 complex	^c	122.3 [251.3] 33 complex VI	100.1 [217.4] 77	
		P- <i>trans</i> -to-O d		^c	125.2 [287.2] 67 complex VII	108.8 [244.1] 23	
CMe_3	CF_3	T	P- <i>trans</i> -to-N d	54.9 [147.1] 100	46.6 [153.9] 80	125.7 [257.0] ^f 39	105.6 [219.9] ^c 66
			P- <i>trans</i> -to-O d		59.9 [172.8] 20	130.0 [291.0] ^f 61	112.9 [250.3] ^c 34
	A	P- <i>trans</i> -to-N d	50.6 [145.0] 100	^c	121.9 [253.1] 79	101.4 [217.4] 82	
		P- <i>trans</i> -to-O d		^c	125.9 [287.2] 21	108.7 [247.8] 18	
Me	CF_3	B	P- <i>trans</i> -to-N d	50.3 [143.6] 100	47.7 [153.0] 100	126.2 [255.6] 37	105.4 [222.0] 58
			P- <i>trans</i> -to-O d		^d	130.6 [289.9] 63	112.9 [248.0] 42
	A	P- <i>trans</i> -to-N c		^c	122.1 [254.9] 67	101.1 [219.0] 100	
		P- <i>trans</i> -to-O c		^c	125.8 [287.2] 33	^d	

^a A, acetone; B, benzene; T, toluene.

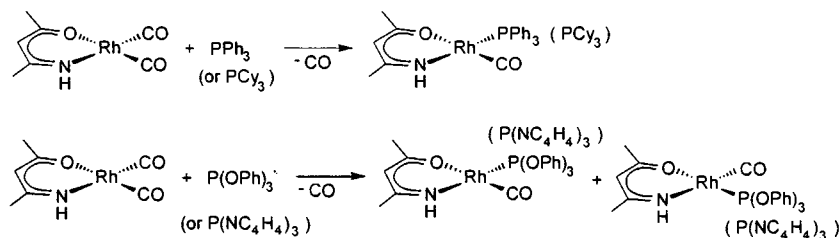
^b Calculated from ^{31}P -NMR spectra.

^c Insoluble.

^d Not detectable.

^e In benzene solution.

^f 40°C.



Scheme 1.

solution of the same complex (0.5 cm^3), the content of the P-*trans*-to-O isomer, **VII**, decreased from 62 to 50%.

2.3. Exchange of phosphorus ligands in $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes

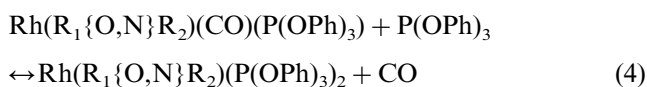
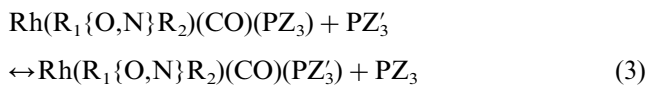
Our observations regarding the exchange of phosphorus ligands in $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PZ}_3)$ -type of complexes for equimolar amounts of the entering PZ_3 ligand and the starting complex are summarised in Table 3.

Stronger σ -donors like PCy_3 and PPh_3 replaced P(OPh)_3 in the $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{P(OPh)}_3)$ complexes (**VI** and **VII**) despite the fact that the Rh–P bond in a Rh–phosphito complex is remarkably shorter than in complexes with PPh_3 or with PCy_3 . It is important to note that the starting complex, existing in solution as a mixture of two isomers, in reaction with PPh_3 (or PCy_3) produced only one isomer of the monocarbonyl complex, nearly 100% of the P-*trans*-to-N isomer of $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)$ (**III**) or $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ (**V**), respectively (Table 3, (i) and (ii)).

The analogous isomer (*P-trans-to-N*) was also obtained in the reactions of $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{Me})(\text{CO})\text{-}(\text{P}(\text{OPh})_3)$ with PPh_3 . In both the reactions with PPh_3 as the entering ligand, another product, $\text{Rh}(\text{R}_1\{\text{O,N}\}\text{R}_2)\text{-}(\text{P}(\text{OPh})_3)_2$, was also found, independent of the PPh_3 excess used.

The substitution of coordinated PCy_3 by $\text{P}(\text{OPh})_3$ produced only 5% of $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$ (**VIII**), (Table 3, (iii)). In contrast, $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{-}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ (**V**), reacted with $\text{P}(\text{OPh})_3$ more effectively, and ca. 50% conversion of the starting complex to $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$ (**VIII**), was observed.

We propose to explain the reactions presented in Table 3 by means of Eqs. (3) and (4). In each case ((i)–(iv)), a combination of the reversible exchange of phosphorus ligands (Eq. (3)) and the subsequent irreversible replacement of CO by $\text{P}(\text{OPh})_3$ in the carbonylphosphite complex (Eq. (4)) takes place:

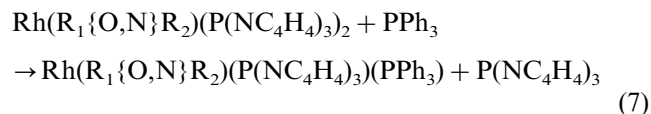
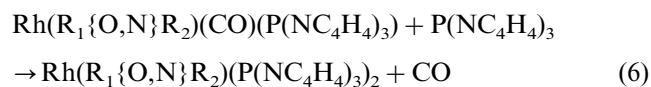
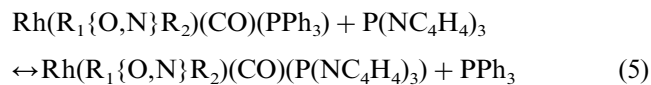


The liberated $\text{P}(\text{OPh})_3$ molecule in cases (i) and (ii) replaces the CO ligand in the starting carbonylphosphite complex, which is present in the reaction mixture in an amount depending on the position of equilibrium (3). If $\text{PZ}'_3 = \text{PCy}_3$, (i), the equilibrium (3) is almost completely shifted to the right, and hence a bis(phos-

phite) complex is not detected. If $\text{PZ}'_3 = \text{PPh}_3$, (ii), the equilibrium concentration of the carbonylphosphite complex is much greater, and a bis(phosphite) complex is formed in ca. 50%.

In cases (iii) and (iv) triphenylphosphite (PZ_3) replaces CO from the resulting carbonylphosphite complex according to the same Eq. (4). This complex is present in the equilibrium reaction mixture in a small amount in case (iii) ($\text{PZ}_3 = \text{PCy}_3$), when the equilibrium (3) is almost completely shifted to the left, and in a relatively large quantity ($\sim 50\%$) in case (iv) ($\text{PZ}_3 = \text{PPh}_3$).

In case (v) one more reaction product was detected, a mixed complex containing two different phosphorus ligands, $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{NC}_4\text{H}_4)_3)(\text{PPh}_3)$, whose analogues were surprisingly not observed in any other reaction. The formation of this product may be described by Eq. (7). Eqs. (5) and (6) are essentially similar to Eqs. (3) and (4), respectively:



Mixed complexes containing two different phosphorus ligands can be easily obtained by displacing

Table 3

The results of phosphorus ligands exchange reactions in complexes $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PZ}_3)$, according to Eqs. (3) and (4) determined by $^{31}\text{P-NMR}$

	Starting complex	Entering ligand	Complexes in the resulting reaction mixture	
(i)	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{P}(\text{OPh})_3)$ 62% <i>P-trans-to-N</i> 38% <i>P-trans-to-O</i>	PCy_3	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)$ 100% <i>P-trans-to-N</i>	100%
(ii)	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{P}(\text{OPh})_3)$ 62% <i>P-trans-to-N</i> 38% <i>P-trans-to-O</i>	PPh_3	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ 100% <i>P-trans-to-N</i> $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$	50% 50%
(iii)	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)$ 100% <i>P-trans-to-N</i>	$\text{P}(\text{OPh})_3$	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)$ 100% <i>P-trans-to-N</i> (starting complex) $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$	95% 5%
(iv)	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ 100% <i>P-trans-to-N</i>	$\text{P}(\text{OPh})_3$	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ $\sim 100\%$ <i>P-trans-to-N</i> (starting complex) $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$	50% 50%
(v)	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ 100% <i>P-trans-to-N</i>	$\text{P}(\text{NC}_4\text{H}_4)_3$	$\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ $\sim 100\%$ <i>P-trans-to-N</i> (starting complex) $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{NC}_4\text{H}_4)_3)(\text{PPh}_3)$ $\text{Rh}(\text{CF}_3\{\text{O,N}\}\text{CMe}_3)(\text{P}(\text{NC}_4\text{H}_4)_3)_2$	comparable amounts

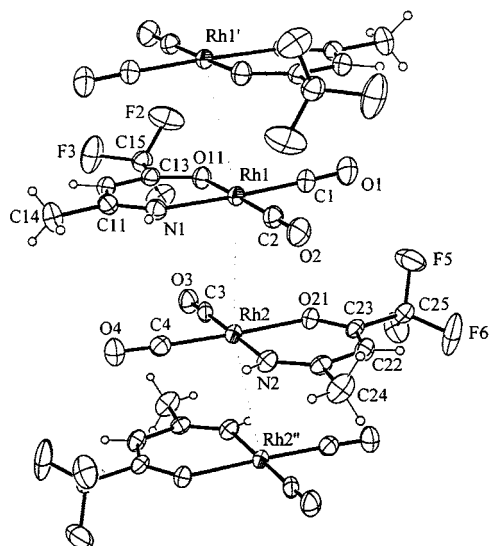


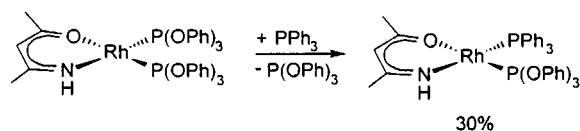
Fig. 1. The packing fragment of **I** with 50% ellipsoids. The short Rh...Rh distances of ca. 3.4 Å are marked by dotted lines. Symmetry codes: ' $-x+1, -y, -z$; " $-x+1, -y+1, -z+1$.

Table 4
Selected geometric parameters (Å, °) for $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CH}_3)(\text{CO})_2]$ (**I**)^a

Molecule 1		Molecule 2	
Rh(1)–C(2)	1.838(3)	Rh(2)–C(4)	1.847(3)
Rh(1)–C(1)	1.869(3)	Rh(2)–C(3)	1.877(3)
Rh(1)–N(1)	2.030(3)	Rh(2)–N(2)	2.038(3)
Rh(1)–O(11)	2.033(2)	Rh(2)–O(21)	2.046(2)
C(1)–O(1)	1.129(4)	C(3)–O(3)	1.131(3)
C(2)–O(2)	1.134(3)	C(4)–O(4)	1.134(4)
N(1)–C(11)	1.306(3)	N(2)–C(21)	1.295(4)
O(11)–C(13)	1.286(3)	O(21)–C(23)	1.289(3)
Rh(1)–Rh(1) # 1	3.419(2)	Rh(2)–Rh(2) # 2	3.395(2)
Rh(1)–Rh(2)	3.402(3)		
C(2)–Rh(1)–C(1)	87.85(14)	C(4)–Rh(2)–C(3)	88.75(13)
C(2)–Rh(1)–N(1)	93.35(12)	C(4)–Rh(2)–N(2)	91.78(12)
C(1)–Rh(1)–N(1)	177.74(10)	C(3)–Rh(2)–N(2)	178.55(10)
C(2)–Rh(1)–O(11)	176.02(10)	C(4)–Rh(2)–O(21)	178.08(9)
C(1)–Rh(1)–O(11)	89.42(12)	C(3)–Rh(2)–O(21)	89.96(11)
N(1)–Rh(1)–O(11)	89.47(10)	N(2)–Rh(2)–O(21)	89.54(10)
O(1)–C(1)–Rh(1)	177.7(3)	O(3)–C(3)–Rh(2)	177.8(3)
O(2)–C(2)–Rh(1)	176.9(3)	O(4)–C(4)–Rh(2)	178.5(3)

^a Symmetry transformations codes: # 1 $-x+1, -y, -z$; # 2 $-x+1, -y+1, -z+1$.

$\text{P}(\text{OPh})_3$ in $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$ (**VIII**) with triphenylphosphine. In a reaction of equimolar amounts of PPh_3 and $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$ (**VIII**) the 30% conversion of the starting rhodium complex to $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)(\text{PPh}_3)$ was observed:



The above-mentioned mixed complex was identified as the only isomer (PPh_3 -*trans*-to-N) on the basis of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The $^1J(\text{Rh}-\text{P}(\text{PPh}_3))$ coupling constant is 153.2 Hz, almost identical to $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$ (**V**), in which PPh_3 is coordinated *trans* to nitrogen. The second value of the $^1J(\text{Rh}-\text{P}(\text{P}(\text{OPh})_3))$ coupling constant is 318.3 Hz and is very close to the $^1J(\text{Rh}-\text{P})$ coupling constant in the *P-trans*-to-O isomer of the $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{P}(\text{OPh})_3)$ complex (**VI**) (Table 2). Thus, in terms of the substitution reactions the ketoiminato bis(phosphite) complex is quite similar to the dicarbonyl one. In both cases only one ligand ($\text{P}(\text{OPh})_3$ or CO , respectively), coordinated *trans* to nitrogen, is substituted by triphenylphosphine. The substitution of $\text{P}(\text{OPh})_3$ located *trans* to N in **VIII** can be related to the Rh–P distance being longer by ca. 0.04 Å compared with that *trans* to O.

It is interesting to note that PCy_3 easily substitutes triphenylphosphite in the $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{P}(\text{OPh})_3)$ complex (**VI** and **VII**) but not in $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$ (**VIII**).

Any replacement of the carbonyl group located *cis* to a strong σ -donor ligand, like PCy_3 or PPh_3 , was not observed (an effect described earlier as *cis*-symbiosis of carbonyl groups with strong σ -donor/weak π -acceptor ligands [45]).

2.4. X-ray studies

2.4.1. Structure of $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})_2]$ (**I**)

The rhodium(I) dicarbonyl complex **I** crystallises with two independent molecules of very similar geometry in an asymmetric unit. These molecules are related by an approximate centre of symmetry. The most characteristic feature of the crystal packing is that the molecules are stacked in the [001] direction forming one-dimensional chains characterised by three different Rh...Rh distances (all being about 3.4 Å), which are comparable to those found for other rhodium dicarbonyl complexes [46–48]. A fragment of the chain with the atom labelling scheme is shown in Fig. 1 and selected geometric parameters are given in Table 4.

The rhodium coordination geometry is essentially square-planar with small deviations of donor atoms from the mean plane (ca. 0.04 and 0.03 Å for molecules 1 and 2, respectively). However, analysis of the bond lengths shows that those in the coordination sphere of Rh(1) are about 3σ shorter than those in the coordination sphere of Rh(2). The Rh–O and the Rh–C distances *trans* to O in each molecule are comparable to those in $[\text{Rh}(\text{acac})(\text{CO})_2]$ [47]. In contrast, the Rh–C distances *trans* to N are ca. 0.030(3) Å longer than the Rh–C distances *trans* to O, indicating a stronger *trans* influence exerted by nitrogen compared with oxygen. It seems that the observed *trans* influence of nitrogen is

enhanced by the presence of the CF_3 substituent in the chelate ligand, because the corresponding difference of the bond lengths in $[\text{Rh}(\text{Ph}\{\text{O},\text{N}\}\text{Ph})(\text{CO})_2]$ is equal to only 0.015(5) Å [49]. The bond lengths in the chelate ring of **I** are close to the average values for different metal complexes with Schiff bases derived from β -diketones [50].

2.4.2. Structure of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PZ}_3)$ complexes **II–VII**

Crystals of phosphine- or phosphite-containing complexes **II–VII** comprise discrete molecules held together mainly by van der Waals forces. Close intermolecular contacts indicating weak interactions of the $\text{N}\cdots\text{O}$ and (or) $\text{C}\cdots\text{O}$ types (Table 8) were found in the

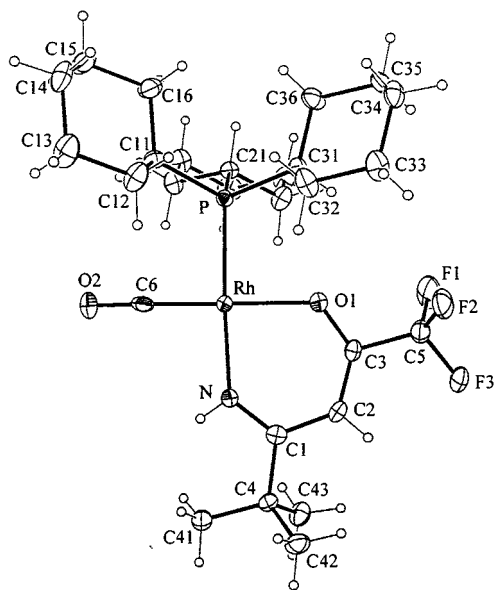


Fig. 2. Molecular structure of **III** with 50% ellipsoids.

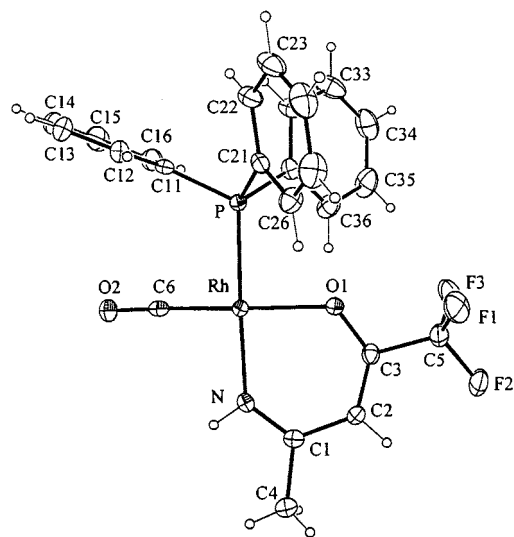


Fig. 3. Molecular structure of **IV** with 50% ellipsoids.

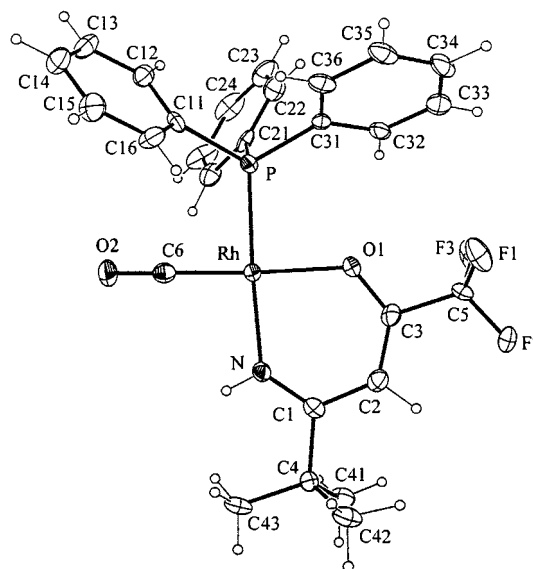


Fig. 4. Molecular structure of **V** with 50% ellipsoids.

structures of **II**, **III**, **V** and **VI**. Besides, $(\text{C})\cdots\pi$ interactions ($\text{H}\cdots\pi$ 2.9–3.1 Å) between the π -cloud of the chelate ring and the hydrogen atoms of the cyclohexyl ring (**III**), the phenyl ring (**IV**, **V**, **VI**) or the *tert*-butyl group (**VII**) were detected. They result in a nearly orthogonal arrangement of the phenyl and chelate rings, observed for **IV**, **V** and **VI**. The intermolecular interactions, although weak, determine the crystal packing, which is different for each of the six monocarbonyl compounds presented.

Views of the monocarbonyl compounds are presented in Figs. 2–6, and selected interatomic distances and angles in Tables 5–7. Due to a significant similarity between the molecular structures of **II** and **III**, only a view of **III** is presented in Fig. 2, with the numbering scheme for both the compounds. As can be seen from the figures, complexes **II–V** display a *trans* to N disposition of the phosphorous ligand. The $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{P}(\text{OPh})_3)$ complex formed two isomers, complex **VI** containing a $\text{P}(\text{OPh})_3$ ligand *trans* to N and complex **VII** having the same ligand *trans* to O. All the six complexes, **II–VII**, with expected square-planar coordination of the Rh atom, have the chelate ring, the carbonyl ligand and the P atom (from phosphorus ligand) approximately in the same plane. The most striking differences between these complexes lie in the spatial arrangements of the phosphorus ligands. The bulky PCy_3 ligand adopts almost the same spatial arrangement with respect to the flat fragment of the molecule in the two compounds **II** and **III** in spite of the different packing interactions. The significant spread in the values of the $\text{C}\text{--}\text{P}\text{--}\text{C}$ and the $\text{Rh}\text{--}\text{P}\text{--}\text{C}$ angles observed in the complexes **II** and **III** (Table 5) results from the steric interaction between the cyclohexyl rings and between the cyclohexyl rings and the

carbonyl ligand. This indicates that the size of the PCy_3 ligand exceeds the coordination site. In contrast, the smaller but also rather compact PPh_3 ligand has significantly different orientations about the Rh–P and P–C bonds in the two compounds **IV** and **V** as can be seen from a comparison of Figs. 3 and 4. However, in this case the spread in the angles about the P atom is small, which may imply no significant steric strains, and the spatial arrangement of the ligand depends mainly on intermolecular interactions. Also, the P(OPh)_3 ligand

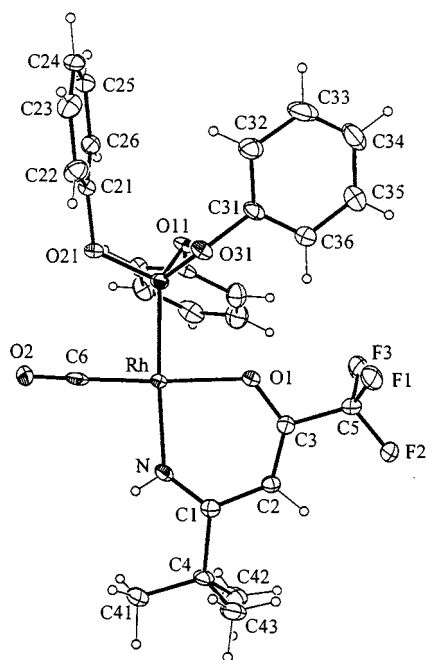


Fig. 5. Molecular structure of **VI** with 50% ellipsoids.

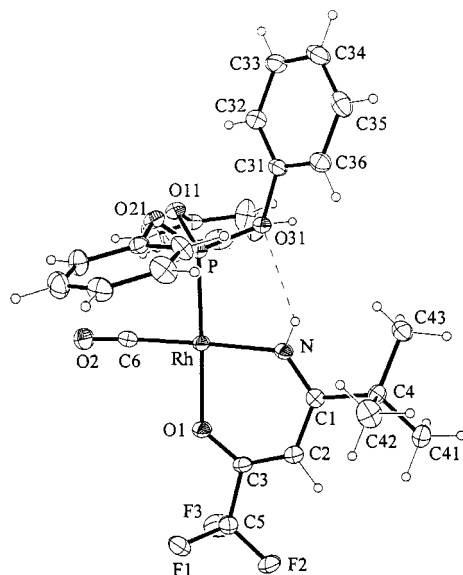


Fig. 6. Molecular structure of **VII** with 50% ellipsoids. The N–H...O hydrogen bonds are marked by a dashed line.

Table 5
Selected geometric parameters (Å, °) for $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PCy}_3)]$ (**II**) and $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)]$ (**III**)

	II	III
Rh–C(6)	1.791(3)	1.785(3)
Rh–O(1)	2.048(2)	2.042(2)
Rh–N	2.058(2)	2.052(2)
Rh–P	2.290(2)	2.2822(13)
C(6)–O(2)	1.150(3)	1.162(3)
N–C(1)	1.294(3)	1.298(3)
O(1)–C(3)	1.289(3)	1.283(3)
P–C _{av}	1.849(2)	1.852(3)
C(6)–Rh–O(1)	177.63(9)	178.44(9)
C(6)–Rh–N	93.08(9)	93.17(9)
O(1)–Rh–N	88.29(8)	87.80(7)
C(6)–Rh–P	89.26(7)	90.13(7)
O(1)–Rh–P	89.44(5)	88.98(5)
N–Rh–P	177.01(6)	175.07(6)
C(31)–P–C(21)	103.68(11)	103.36(10)
C(31)–P–C(11)	112.11(12)	111.39(11)
C(21)–P–C(11)	103.08(10)	103.97(10)
C(31)–P–Rh	111.33(8)	110.47(8)
C(21)–P–Rh	111.32(9)	110.32(8)
C(11)–P–Rh	114.49(8)	116.34(7)
O(2)–C(6)–Rh	177.4(2)	178.1(2)

Table 6
Selected geometric parameters (Å, °) for $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PPh}_3)]$ (**IV**) and $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)]$ (**V**)

	IV	V
Rh–C(6)	1.804(3)	1.803(7)
Rh–O(1)	2.045(2)	2.036(4)
Rh–N	2.045(2)	2.062(5)
Rh–P	2.2811(11)	2.277(2)
C(6)–O(2)	1.148(3)	1.151(8)
N–C(1)	1.297(3)	1.304(8)
O(1)–C(3)	1.288(3)	1.284(7)
P–C _{av}	1.828(5)	1.827(7)
C(6)–Rh–O(1)	178.68(11)	177.4(2)
C(6)–Rh–N	92.65(11)	94.7(3)
O(1)–Rh–N	87.94(9)	87.9(2)
C(6)–Rh–P	89.49(9)	88.6(2)
O(1)–Rh–P	89.91(6)	88.82(13)
N–Rh–P	177.82(7)	176.17(16)
O(2)–C(6)–Rh	177.8(2)	179.4(7)
C(11)–P–C(21)	103.52(12)	102.8(3)
C(11)–P–C(31)	103.28(12)	105.9(3)
C(21)–P–C(31)	103.82(12)	104.3(3)
C(11)–P–Rh	116.45(9)	115.3(3)
C(21)–P–Rh	113.75(9)	114.1(2)
C(31)–P–Rh	114.48(9)	113.3(2)

has different orientations with respect to the flat fragment of the molecules in two isomers, **VI** and **VII**, which indicates some rotational freedom around the Rh–P bond, similar to that observed in the case of the PPh_3 complexes. Consideration of the angles about the

Table 7
Selected geometric parameters (Å, °) for two isomers (VI and VII) of [Rh(CF₃{O,N}CMe₃)(CO){P(OPh)₃}

	VI	VII
Rh–C(6)	1.809(3)	1.849(3)
Rh–O(1)	2.035(2)	2.051(2)
Rh–N	2.056(3)	2.034(2)
Rh–P	2.195(2)	2.1535(9)
C(6)–O(2)	1.154(4)	1.131(4)
N–C(1)	1.294(4)	1.305(4)
O(1)–C(3)	1.295(3)	1.291(3)
P–O _{av}	1.605(4)	1.607(3)
O–C(Ph) _{av}	1.408(6)	1.408(3)
C(6)–Rh–O(1)	176.71(10)	89.45(10)
C(6)–Rh–N	95.04(13)	177.67(11)
O(1)–Rh–N	88.21(11)	88.33(9)
C(6)–Rh–P	88.64(11)	88.84(9)
O(1)–Rh–P	88.11(8)	178.28(6)
N–Rh–P	176.30(7)	93.37(7)
C(1)–N–Rh	130.8(2)	130.3(2)
O(31)–P–O(21)	101.90(11)	104.02(11)
O(31)–P–O(11)	99.16(10)	105.70(10)
O(21)–P–O(11)	104.48(11)	92.26(10)
O(31)–P–Rh	117.16(8)	110.79(8)
O(21)–P–Rh	114.44(10)	121.97(8)
O(11)–P–Rh	117.35(9)	119.50(8)
C(11)–O(11)–P	122.0(2)	120.7(2)
C(21)–O(21)–P	121.9(2)	123.2(2)
C(31)–O(31)–P	126.1(2)	128.4(2)

P atom (Table 7) reveals that the variation of these angles in VI is comparable to that in the PPh₃ complexes (IV, V), while in VII these angles are distorted even more than those in the PCy₃ complexes (II, III).

Table 8
Intra- and intermolecular hydrogen-like bonds^{a,b}

Compound	D–H···O	<i>d</i> (D–H) (Å)	<i>d</i> (H···A) (Å)	<i>d</i> (D···A) (Å)	∠(DHA) (°)
II	N–H(1)···O(2) # 1	0.91(3)	2.30(3)	3.172(3)	162(2)
	C(31)–H(31)···O(1)	1.00	2.51	3.022(3)	112
III	C(42)–H(44)···O(2) # 2	0.95(3)	2.52(3)	3.369(4)	148(2)
	C(31)–H(31)···O(1)	1.00	2.42	3.038(3)	119
IV	C(35)–H(35)···O(2) # 3	0.95	2.63	3.503(4)	153
	C(36)–H(36)···O(1)	0.95	2.46	3.144(3)	129
	C(26)–H(26)···O(1)	0.95	2.54	3.271(4)	133
V	C(41)–H(41)···O(2) # 4	1.02(8)	2.70(7)	3.217(10)	112(5)
VI	N–H(1)···O(2) # 5	0.77(3)	2.64(3)	3.187(4)	130(3)
	C(25)–H(25)···O(2) # 6	0.95	2.61	3.464(4)	150
	C(36)–H(36)···O(1)	0.95	2.52	3.365(4)	148
VII	N–H(1)···O(31)	0.82(3)	2.32(3)	2.909(3)	130(3)
	N(1)–H(1)···O(11)	0.91(7)	2.23(7)	2.982(6)	139(6)
VIII	N(2)–H(2)···O(31)	1.07(6)	2.36(6)	3.038(6)	120(4)
	C(412)–H(412)···O(3)	0.95	2.78	3.317(8)	117
	C(412)–H(412)···O(42)	0.95	2.77	3.354(8)	121
	C(212)–H(212)···O(1)	0.95	2.63	3.255(7)	124
	C(212)–H(212)···O(22)	0.95	2.70	3.307(8)	122

^a Symmetry codes: # 1 $-x, -y, -z$; # 2 $-x+3/2, y-1/2, -z+3/2$; # 3 $x+1/2, -y, z$; # 4 $2-x, 1/2+y, -z$; # 5 $-x+1, -y+1, -z+1$; # 6 $2-x, 2-y, -z$.

^b D, donor atom (N or C, respectively).

This may suggest that a binding site *cis* to the N atom is more sterically hindered. It also seems that intramolecular hydrogen interactions of the C–H···O-type (in VI) and the N–H···O-type (in VII), both of which involve the phosphite ligand (Table 8), affect to a large degree the conformations observed for the P(OPh)₃ ligand. Furthermore, because hydrogen interactions may be expected to occur in a transition state involved in the substitution reactions, one might expect that the formation of N–H···O intramolecular bonding would enhance the stability of the isomer with the P(OPh)₃ ligand *cis* to N, while in the case of the PPh₃ or PCy₃ ligands the potentially attractive C–H···O interaction would enhance the stability of the isomer with the P ligand *trans* to N.

Despite the different distortions discussed above, the bond distances in the phosphorous ligands are normal and the average of the three C(O)–P–C(O) angles regularly decreases in the order PCy₃ > PPh₃ > P(OPh)₃ (ca. 106.3, 104.0 and 101.2°, respectively), while the average of the three Rh–P–C(O) angles (112.4, 114.6 and 116.9°) increases in the order PCy₃ < PPh₃ < P(OPh)₃.

It is interesting that the different steric properties of the phosphorus ligands have almost no effect on the coordination geometry around rhodium and the geometries of the β-ketoiminate ligands. The distances and angles of the two ketoiminate ligands in all the complexes are very similar to each other and to the parameters found for the dicarbonyl complex I. A slight distortion of the coordination geometry about the Rh atom in II, III and V can be seen from the *trans* N–Rh–P and O–Rh–C angles, some of which are devi-

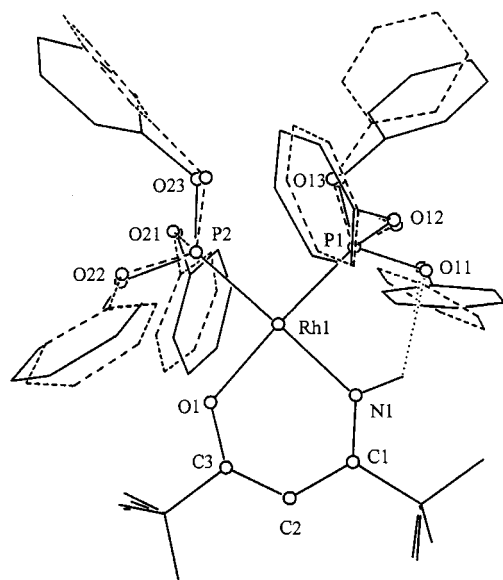


Fig. 7. Superposition of the two independent molecules of **VIII** with the numbering scheme for one molecule. The N–H···O hydrogen bonds are marked by dotted lines.

ated from linearity by at least 5° . Another major distortion is the N–Rh–C6 angle in **II–VI** and the N–Rh–P angle in **VII**, in each case greater than 90° , which indicates a weak steric interaction between the hydrogen bonded to N and the adjacent ligand. It appears that this repulsing interaction, together with the steric hindrances of each specific phosphorus ligand, can affect the process of isomer formation and can be responsible for the behaviour of the monocarbonyl complexes, studied here, during the substitution reactions.

Some trends can be noted if one focuses on the lengths of the bonds formed by rhodium (Table 9).

A comparison of the Rh–P bonds in the series of monocarbonyl complexes with the phosphorus ligand positioned *trans* to N shows that only the Rh–P bond in complex **VI** differs significantly from those in phosphine complexes (**II–V**), being ca. 0.1 \AA shorter. Variations on the order of 0.01 \AA found in the Rh–P distances for the five phosphine complexes presented in Table 9 are only slightly greater ($4\text{--}6\sigma$) than experimental error; nevertheless, the Rh–P distance tends to be greater for the PCy_3 than for the PPh_3 complexes. The Rh–P bonding distances are consistent with the decreasing order of the π -acceptor properties of the phosphorus ligands: $\text{P(OPh)}_3 > \text{PPh}_3 > \text{PCy}_3$. In addition, the fact that the Rh–P distance is similar in the PCy_3 and the PPh_3 complexes suggests domination of electronic rather than steric properties of ligands.

The Rh–C distances show only slight variations for complexes in which the carbonyl group is *trans* to O, and the mean value of $1.799(8) \text{ \AA}$ is the same as that found for the analogous PPh_3 complexes with O,O-chelate ligands [24] but is significantly shorter than the

mean value of $1.842(8) \text{ \AA}$ found for the two independent carbonyl groups (*trans* to O) in the dicarbonyl complex **I**. The shortening of the Rh–C distance after the substitution of one carbonyl group with the phosphorus ligand enhances carbonyl π -back bonding as expected, taking into account the higher π -acceptor character of the CO compared with phosphines and phosphites.

The Rh–O and Rh–N distances show no significant variations within the series of monosubstituted complexes, but their average values, $2.042(5)$ and $2.053(7) \text{ \AA}$, respectively, indicate that the Rh–N distance tends to be longer than the Rh–O distance within this series and is longer than the Rh–N distances (av. $2.034(6) \text{ \AA}$) in **I**. It is pertinent to note that these bond distances may be affected by intra- and intermolecular hydrogen interactions. However, it should also be noted that the Rh–N distances *trans* to P found in other similar complexes with N,O-bidentate ligands, e.g. $[\text{Rh}(\text{oxine})(\text{CO})(\text{PZ}_3)]$ ($\text{Z} = \text{Ph}$ [32], OPh [14]) and $[\text{Rh}(\text{LL})(\text{CO})(\text{PPh}_3)]$ where LL is 2-picolinate [52], are within the $2.088(6)\text{--}2.098(2) \text{ \AA}$ range.

The most striking differences of Rh–ligand distances were found in two isomeric phosphite complexes **VI** and **VII**. Both Rh–P distances and Rh–C distances are ca. 0.04 \AA longer when they are *trans* to N than when they are *trans* to O. Also, the Rh–O and Rh–N distances differ in these two isomeric complexes, in each case the bonds *trans* to the P(OPh)_3 ligand being ca. 0.02 \AA longer than those *trans* to the carbonyl. The correlation between the Rh–P and Rh–C bonds and the σ -donor/ π -acceptor properties of the donor atom *trans* to PPh_3 has been shown previously for $[\text{Rh}(\text{LL})(\text{CO})(\text{PPh}_3)]$ complexes, where LL denotes different bidentate ligands [14,24,53].

2.4.3. Structure of $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)\{\text{P(OPh)}_3\}_2]$ (**VIII**)

The unit cell of the diphosphite complex **VIII** contains two independent molecules, different slightly in their molecular conformation (see Fig. 7). The bond distances and angles are given in Table 10. Generally, the two P(OPh)_3 ligands exhibit the same features as the corresponding groups in **VI** and **VII**; the average O–P–O and Rh–P–O angles for each of the four phosphite ligands in **VIII** (ca. 99.6 and 117° , respectively) are similar to those in **VI** and **VII**; the spread of these angle values is significantly greater for P(OPh)_3 ligands *trans* to O than for those *trans* to N; the N–H···O hydrogen bonding involves one of the phosphite oxygens in each molecule. It is worth noticing that the cone angles, calculated for the P(OPh)_3 ligand from the molecular structures of **VI**, **VII** and **VIII**, are all ca. 145° , which value is significantly greater than Tolman's minimised value of 128° [51]. In **VIII**, the steric hindrance of two phosphite ligands, *cis* to each other,

Table 9
Bond distances (Å) around rhodium in complexes **I–VIII** and in $[\text{Rh}(\text{Me}(\text{O},\text{N})\text{Me}(\text{CO})(\text{PPh}_3)_3)]$ [34]

Compound	Rh–P <i>trans</i> to N	Rh–P <i>trans</i> to O	Rh–C <i>trans</i> to O	Rh–C <i>trans</i> to O	Rh–C <i>trans</i> to N	Rh–O <i>trans</i> to C	Rh–O <i>trans</i> to P	Rh–N <i>trans</i> to C	Rh–N <i>trans</i> to P
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CH}_3)(\text{CO})_2]$ ^a I			1.842(8)		1.873(6)				
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CH}_3)(\text{CO})(\text{PCy}_3)]$ II	2.290(2)		1.791(3)					2.034(6)	2.058(2)
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)]$ III	2.8222(13)		1.785(3)						2.052(2)
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CH}_3)(\text{CO})(\text{PPh}_3)]$ IV	2.2811(11)		1.804(3)						2.045(2)
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)]$ V	2.277(2)		1.803(7)						2.062(5)
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CH}_3)(\text{CO})(\text{PPh}_3)]$ V [34]	2.2751(13)		1.801(8)						2.045(9)
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}]$ VI	2.195(2)		1.809(3)						2.056(3)
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}]$ VII		2.1535(9)			1.849(3)			2.051(2)	
$[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)\{\text{P}(\text{O}^i\text{Pr})_3\}_2]$ ^a VIII	2.178(2)	2.134(9)						2.058(8)	2.062(11)

^a Average values for two independent molecules.

results in obtuse P–Rh–P angles and in distortions of the coordination spheres greater than in **VI** or **VII**. Slight variations occur in the bond distances in the two molecules of **VIII**, the most significant being that the Rh–P distance *trans* to O in one molecule is shorter by 0.012(2) Å than that in the other one. However, the Rh–P distances in each independent molecule differ considerably (by ca. 0.04–0.05 Å), once more evidencing a stronger *trans* influence exerted by the nitrogen atom than by the oxygen atom. At the same time, the Rh–O and Rh–N distances are practically equal to each other for the two molecules, but both are ca. 0.02–0.03 Å longer than those (*trans* to CO) in **I**, the difference being similar to that observed for the two isomeric complexes **VI** and **VII**. A comparison of the Rh–P distances in **VIII** with the corresponding distances in **VI** and **VII** shows that a substitution of the carbonyl ligand in the latter by the phosphite ligand results in the shortening of these bonds by ca. 0.017–0.019 Å. This may be rationalised by a gain of electron density on the metal d(π) orbitals, owing to the replacement of the CO ligand by the weaker π -acceptor P(O^{*i*}Pr)₃ ligand.

3. Experimental

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was synthesised as described in the literature [54].

Dicarbonyl complexes, $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$, were obtained according to the procedures previously described, either by a reaction of H(β -ketim) with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in the presence of BaCO₃ [8] or by exchange reactions between $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and copper(II) β -ketoimines [36]. ¹³C-enriched samples of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ were obtained by bubbling ¹³CO (~85% ¹³C) through a suspension of $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ [55] in C₆H₆.

Free β -ketoamines are not stable enough due to isomerisation and hydrolysis [56,57] and therefore were recrystallised before use. Copper(II) β -ketoiminate complexes are much more stable.

3.1. $\text{Rh}[\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{NH})\text{Me}](\text{CO})_2$ (**I**) [35,36]

Solid $\text{Cu}[\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{NH})\text{Me}]_2$ (0.24 g, 0.65 mmol) was added to a solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.194 g, 0.5 mmol) in hexane (20 ml). The suspension was stirred for 2 h at 40°C and then cooled to r.t. The reddish-brown precipitate contained copper(II) chloride; it was filtered off, and the solvent was removed under reduced pressure. The residue was dissolved in CHCl₃ and purified by column chromatography (silica gel, CHCl₃). The eluate was evaporated to dryness. Recrystallisation of the orange product from hexane followed by drying under vacuum yielded orange crystals (0.24 g, 77%). Anal. Found: C, 27.17; H, 1.52; N, 5.21; Rh, 33.08. Calc. for C₇H₅F₃NO₃Rh: C, 27.03; H,

1.62; N, 4.5; Rh, 33.15%; $^1\text{H-NMR}$ (δ ppm): 2.28 (s, CH_3), 5.73 (d, $J = 1.5$ Hz, CH), 8.1 (NH); $^{19}\text{F-NMR}$ (δ ppm): -69.93 (s, CF_3).

3.2. $\text{Rh}[\text{MeC}(\text{O})\text{CHC}(\text{NH})\text{CF}_3](\text{CO})_2$ [36]

Orange crystals were obtained as above using $\text{Cu}[\text{MeC}(\text{O})\text{CHC}(\text{NH})\text{CF}_3]_2$. Yield: 0.23 g, 74%. Anal. Found: C, 27.60; H, 1.62; N, 4.76; Rh, 33.09. Calc. for $\text{C}_7\text{H}_5\text{F}_3\text{NO}_3\text{Rh}$: C, 27.03; H, 1.62; N, 4.50; Rh, 33.15%; $^1\text{H-NMR}$ (δ ppm): 2.21 (s, CH_3), 5.64 (d, $J = 2.0$ Hz, CH), 7.35 (NH); $^{19}\text{F-NMR}$ (δ ppm): -67.77 (s, CF_3).

3.3. $\text{Rh}[\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{NH})\text{CMe}_3](\text{CO})_2$

Solid $\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{NH})\text{CMe}_3$ (0.26 g, 1.33 mmol) and excess BaCO_3 (0.8 g) were added to a solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.25 g, 0.64 mmol) in CHCl_3 (10 ml). The reaction mixture was stirred for 4 h at r.t., filtered, and evaporated to dryness under reduced pressure. Recrystallisation of crude product from hexane followed by drying under vacuum yielded dark red crystals with green dichroism (0.36 g, 79%). Anal. Found: C, 34.08; H, 3.15; N, 3.55; Rh, 29.20. Calc. for $\text{C}_{10}\text{H}_{11}\text{F}_3\text{NO}_3\text{Rh}$: C, 34.02; H, 3.14; N, 3.97; Rh, 29.14%; $^1\text{H-NMR}$ (δ ppm): 1.26 (s, CH_3), 5.92 (d, $J \sim 2.0$ Hz, CH), 8.3 (NH); $^{19}\text{F-NMR}$ (δ ppm): -69.73 (s, CF_3).

Table 10

Selected geometric parameters (\AA , $^\circ$) for $[\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)\{\text{P}(\text{OPh})_3\}_2]$ (VIII)

Molecule 1		Molecule 2	
Rh(1)–O(1)	2.052(4)	Rh(2)–O(3)	2.064(4)
Rh(1)–N(1)	2.056(5)	Rh(2)–N(2)	2.069(5)
Rh(1)–P(1)	2.140(2)	Rh(2)–P(3)	2.128(2)
Rh(1)–P(2)	2.179(2)	Rh(2)–P(4)	2.178(2)
C(1)–N(1)	1.288(8)	C(10)–N(2)	1.310(7)
O(1)–C(3)	1.298(7)	O(3)–C(30)	1.283(7)
P–O _{av}	1.613(11)	P–O _{av}	1.613(13)
O–C(Ph) _{av}	1.401(10)	O–C(Ph) _{av}	1.407(11)
O(1)–Rh(1)–N(1)	87.6(2)	O(3)–Rh(2)–N(2)	88.1(2)
O(1)–Rh(1)–P(1)	176.45(12)	O(3)–Rh(2)–P(3)	176.39(12)
N(1)–Rh(1)–P(1)	89.07(15)	N(2)–Rh(2)–P(3)	88.43(15)
O(1)–Rh(1)–P(2)	88.98(12)	O(3)–Rh(2)–P(4)	90.55(12)
N(1)–Rh(1)–P(2)	175.7(2)	N(2)–Rh(2)–P(4)	178.21(14)
P(1)–Rh(1)–P(2)	94.42(6)	P(3)–Rh(2)–P(4)	92.85(6)
O(13)–P(1)–O(12)	104.5(2)	O(33)–P(3)–O(32)	104.7(2)
O(13)–P(1)–O(11)	103.1(2)	O(33)–P(3)–O(31)	103.4(2)
O(12)–P(1)–O(11)	90.7(2)	O(31)–P(3)–O(32)	92.1(2)
O(23)–P(2)–O(22)	102.7(2)	O(43)–P(4)–O(42)	102.1(2)
O(23)–P(2)–O(21)	99.1(2)	O(43)–P(4)–O(41)	100.0(2)
O(22)–P(2)–O(21)	96.4(2)	O(42)–P(4)–O(41)	96.8(2)

3.4. $\text{Rh}[\text{CMe}_3\text{C}(\text{O})\text{CHC}(\text{NH})\text{CF}_3](\text{CO})_2$

Dark red crystals with green dichroism were obtained as above using $\text{C}(\text{CH}_3)_3\text{C}(\text{O})\text{CHC}(\text{NH})\text{CF}_3$. Yield: 0.38 g, 83%. Anal. Found: C, 34.13; H, 3.00; N, 3.25; Rh, 29.07. Calc. for $\text{C}_{10}\text{H}_{11}\text{NO}_3\text{F}_3\text{Rh}$: C, 34.02; H, 3.14; N, 3.97; Rh, 29.14%; $^1\text{H-NMR}$ (δ ppm): 1.21 (s, CH_3), 5.81 (CH), 7.8 (NH); $^{19}\text{F-NMR}$ (δ ppm): -67.71 (s, CF_3).

3.5. $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PPh}_3)$ and $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{PCy}_3)$

These complexes were obtained in reactions of equimolar amounts of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ and PPh_3 or PCy_3 , respectively, in $\text{C}_6\text{H}_5\text{CH}_3$ or C_6H_6 (0.5 cm^3). After addition of ca. 0.2 cm^3 of hexane the solution was left to crystallise in a refrigerator. Crystals suitable for X-ray analysis were obtained from these solutions. All complexes of that type were also obtained as orange-yellow microcrystalline powders in reactions of equimolar amounts of the reactants in acetone or hexane with yields of 85–95%.

The analytical and NMR data presented below for the triphenylphosphine complexes are related to mixtures of both isomers. Owing to the low intensity of the NMR signals of the *P-trans-to-O* isomer, the corresponding values of the imino proton chemical shift and the $^4J(\text{HH})$ coupling constants of NH and CH protons (ca. 2 Hz) are not reported. Proton resonances of the phenyl and cyclohexyl groups are omitted. In the $^{13}\text{C-NMR}$ spectra the resonances of carbonyl carbons are split due to coupling with ^{103}Rh (ca. 75 Hz), ^{31}P (ca. 22 Hz) and imino ^1H (ca. 1.5 Hz) nuclei.

3.6. $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PPh}_3)$

Anal. Found: C, 52.91; H, 3.76; N, 2.60; Rh, 18.77. Calc. for $\text{C}_{24}\text{H}_{20}\text{F}_3\text{NO}_2\text{RhP}$: C, 52.86; H, 3.70; N, 2.57; Rh, 18.87%. *P-trans-to-N* isomer (IV): $^1\text{H-NMR}$ (δ ppm): 2.22 (s, CH_3), 5.56 (d, $J = 1.9$ Hz, CH), 8.45 (NH); $^{19}\text{F-NMR}$ (δ ppm): -70.26 (s, CF_3); $^{13}\text{C-NMR}$ (δ ppm): 190.3 (ddd, $J = 76.4$ Hz, $J = 22.0$ Hz, $J = 1.6$ Hz, CO). *P-trans-to-O* isomer: $^1\text{H-NMR}$: 1.68 (s, CH_3), 5.74 (d, CH); $^{19}\text{F-NMR}$: -69.66 (s, CF_3); $^{13}\text{C-NMR}$ (δ ppm): 189.4(ddd, $J = 67.9$ Hz, $J = 22.6$ Hz, CO).

3.7. $\text{Rh}(\text{Me}\{\text{O},\text{N}\}\text{CF}_3)(\text{CO})(\text{PPh}_3)$

Anal. Found: C, 52.78; H, 3.56; N, 2.40; Rh, 18.72. Calc. for $\text{C}_{24}\text{H}_{20}\text{F}_3\text{NO}_2\text{RhP}$: C, 52.86; H, 3.70; N, 2.57; Rh, 18.87%. *P-trans-to-N* isomer: $^1\text{H-NMR}$ (δ ppm): 1.73 (s, CH_3), 5.42 (d, $J = 1.7$ Hz, CH), 8.27 (NH); $^{19}\text{F-NMR}$ (δ ppm): -67.86 (s, CF_3); $^{13}\text{C-NMR}$ (δ ppm): 190.4 (ddd, $J = 74.6$ Hz, $J = 22.6$ Hz, $J = 1.5$ Hz, CO). *P-trans-to-O* isomer: $^1\text{H-NMR}$: 2.24 (s, CH_3),

5.65 (d, CH); ^{19}F -NMR: -68.56 (s, CF_3); ^{13}C -NMR (δ ppm): 189.5 (dd, $J = 68.5$ Hz, $J = 22.9$ Hz, CO).

3.8. $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PPh}_3)$

Anal. Found: C, 55.61; H, 4.20; N, 2.30; Rh, 17.24. Calc. for $\text{C}_{27}\text{H}_{26}\text{F}_3\text{NO}_2\text{RhP}$: C, 55.19; H, 4.46; N, 2.39; Rh, 17.52%. *P-trans-to-N* isomer (**V**): ^1H -NMR (δ ppm): 1.26 (s, CH_3), 5.77 (d, $J = 2.0$ Hz, CH), 8.8 (NH); ^{19}F -NMR (δ ppm): -70.00 (s, CF_3); ^{13}C -NMR (δ ppm): 190.6 (ddd, $J = 75.1$ Hz, $J = 22.1$ Hz, $J = 1.6$ Hz, CO). *P-trans-to-O* isomer: ^1H -NMR: 0.74 (s, CH_3), 5.61 (d, CH); ^{19}F -NMR: -69.36 (s, CF_3); ^{13}C -NMR (δ ppm): 189.8 (dd, $J = 68.5$ Hz, $J = 22.2$ Hz, CO).

3.9. $\text{Rh}(\text{CMe}_3\{\text{O},\text{N}\}\text{CF}_3)(\text{CO})(\text{PPh}_3)$

Anal. Found: C, 55.77; H, 4.64; N, 2.16; Rh, 17.30. Calc. for $\text{C}_{27}\text{H}_{26}\text{F}_3\text{NO}_2\text{RhP}$: C, 55.19; H, 4.46; N, 2.39; Rh, 17.30%. *P-trans-to-N* isomer: ^1H -NMR (δ ppm): 0.72 (s, CH_3), 5.60 (d, $J = 2.2$ Hz, CH), 8.25 (NH); ^{19}F -NMR: (δ ppm): -67.70 (s, CF_3); ^{13}C -NMR (δ ppm): 190.4 (ddd, $J = 75.2$ Hz, $J = 22.0$ Hz, $J = 1.7$ Hz, CO). *P-trans-to-O* isomer: ^1H -NMR: 1.25 (s, CH_3), 5.72 (d, CH); ^{19}F -NMR: -68.28 (s, CF_3); ^{13}C -NMR (δ ppm): 189.4 (dd, $J = 68.3$ Hz, $J = 23.0$ Hz, CO).

3.10. $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{Me})(\text{CO})(\text{PCy}_3)$ (**II**)

Anal. Found: C, 51.42; H, 6.80; N, 2.59. Calc. for $\text{C}_{24}\text{H}_{38}\text{F}_3\text{NO}_2\text{RhP}$: C, 51.16; H, 6.80; N, 2.50%. ^1H -NMR (δ ppm): 2.17 (s, CH_3), 5.51 (d, $J = 1.7$ Hz, CH), 8.4 (NH); ^{19}F -NMR: (δ ppm): -70.09 (s, CF_3).

3.11. $\text{Rh}(\text{Me}\{\text{O},\text{N}\}\text{CF}_3)(\text{CO})(\text{PCy}_3)$

Anal. Found: C, 51.00; H, 6.13; N, 2.75. Calc. for $\text{C}_{24}\text{H}_{38}\text{NO}_2\text{F}_3\text{RhP}$: C, 51.42; H, 6.30; N, 2.50%. ^1H -NMR (δ ppm): 1.99 (s, CH_3), 5.38 (d, $J = 2.2$ Hz, CH), 8.2 (NH); ^{19}F -NMR: (δ ppm): -68.10 (s, CF_3).

3.12. $\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{CO})(\text{PCy}_3)$ (**III**)

Anal. Found: C, 53.61; H, 6.21; N, 2.31. Calc. for $\text{C}_{27}\text{H}_{44}\text{F}_3\text{NO}_2\text{RhP}$: C, 53.80; H, 6.86; N, 2.33%. ^1H -NMR (δ ppm): 1.24 (s, CH_3), 5.68 (d, $J = 2.2$ Hz, CH), 8.7 (NH); ^{19}F -NMR: (δ ppm): -69.84 (s, CF_3).

3.13. $\text{Rh}(\text{CMe}_3\{\text{O},\text{N}\}\text{CF}_3)(\text{CO})(\text{PCy}_3)$

Anal. Found: C, 53.08; H, 7.00; N, 2.29. Calc. for $\text{C}_{27}\text{H}_{44}\text{F}_3\text{NO}_2\text{RhP}$: C, 53.80; H, 6.86; N, 2.33%. ^1H -NMR (δ ppm): 1.14 (s, CH_3), 5.57 (d, $J = 2.2$ Hz, CH), 8.7 (NH); ^{19}F -NMR: (δ ppm): -67.92 (s, CF_3).

$\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{P}(\text{OPh})_3)$ and $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})(\text{P}(\text{NC}_4\text{H}_4)_3)$ complexes have not been isolated from the solutions prepared for $^{31}\text{P}\{^1\text{H}\}$ -NMR measurements by use of equimolar amounts of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ and $\text{P}(\text{OPh})_3$ or $\text{P}(\text{NC}_4\text{H}_4)_3$. Small samples for IR measurements have been obtained by solvent evaporation in vacuo. Crystals of **VI** and **VII** have been obtained by slow evaporation of CDCl_3 -MeOH solutions in a refrigerator.

$\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{P}(\text{OPh})_3)_2$ complexes have been obtained as yellow powders in reactions of $\text{Rh}(\text{R}_1\{\text{O},\text{N}\}\text{R}_2)(\text{CO})_2$ with three- to fivefold excesses of $\text{P}(\text{OPh})_3$ in hexane. The complete CO substitution was confirmed by the absence of $\nu(\text{CO})$ bands in the IR spectra and the presence of two resonances of inequivalent $\text{P}(\text{OPh})_3$ ligands in $^{31}\text{P}\{^1\text{H}\}$ -NMR. Complex **VIII** have been obtained by recrystallisation of the crude product from MeOH.

$^{31}\text{P}\{^1\text{H}\}$ -NMR data in CDCl_3 , δ (ppm) [$^1J(\text{Rh-P})$] (Hz); $^2J(\text{P-P})$ (Hz) are the following:

$\text{Rh}(\text{CF}_3\{\text{O},\text{N}\}\text{CMe}_3)(\text{P}(\text{OPh})_3)_2$ (**VIII**): 126.6 [300], 122.8 [262]; 104.

$\text{Rh}(\text{CMe}_3\{\text{O},\text{N}\}\text{CF}_3)(\text{P}(\text{OPh})_3)_2$: 124.5 [303], 121.3 [264]; 102.

$\text{Rh}(\text{Me}\{\text{O},\text{N}\}\text{CF}_3)(\text{P}(\text{OPh})_3)_2$: 125.6 [301], 121.7 [267]; 103.

The spectral (IR and NMR) parameters of the compounds under consideration were partially published previously [35,36,38,41]. IR spectra were recorded on Specord IR 75 or Nicolet Impact 400 instruments. NMR spectra (in CDCl_3) were recorded on a Bruker AM-500 instrument in a pulse mode at the following frequencies: ^1H , 500.14 MHz; ^{13}C , 125.76 MHz; ^{19}F , 470.56 MHz. The solvent CDCl_3 resonances served as internal standards for the ^1H and ^{13}C spectra ($\delta^1\text{H}$ from residual protons 7.25 ppm and $\delta^{13}\text{C}$ 77.04 ppm). The ^{19}F chemical shifts were determined with hexafluorobenzene ($\delta^{19}\text{F} - 162.9$ ppm) as an external standard. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra have been measured on a Bruker 300 (121.5 MHz for ^{31}P) with 85% H_3PO_4 as an external standard. The amounts of complexes have been calculated from the signals' intensities (integration).

3.14. X-ray measurements

Diffraction data for crystals **I-VII** were collected on a Kuma KM4 κ -geometry diffractometer (ω - 2θ scan) and for **VIII** on a Kuma KM4CCD area detector diffractometer (ω scan) [58], with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The empirical correction [59] for absorption was applied for **II**, **III**, **VI** and **VII**, while no corrections were needed for **I**, **IV**, **V** and **VII**. For **VIII**, 6952 overlapping reflections, which occur owing to the large c lattice parameter, had been removed during data reduction. The structure **IV**

Table 11
 Crystal data and structure refinement for I–VIII

Compound	I	II	III	IV	V	VI	VII	VIII
Empirical formula	C ₇ H ₅ F ₃ NO ₃ Rh	C ₂₄ H ₃₈ F ₃ NO ₂	C ₂₇ H ₄₄ F ₃ NO ₂	C ₂₄ H ₂₀ F ₃ NO ₂	C ₂₇ H ₂₆ F ₃ NO ₂	C ₂₇ H ₂₆ F ₃ NO ₅	C ₂₇ H ₂₆ F ₃ NO ₅	C ₄₄ H ₄₁ F ₃ NO ₇
Formula weight	311.03	563.43	605.51	545.29	587.37	635.37	635.37	917.63
Temperature (K)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$Pca2_1$	$P2_1$	$P\bar{1}$	$P2_1/c$	Cc
Crystal colour	Yellow–brown	Yellow	Yellow	Pale yellow	Pale yellow	Yellow	Pink-blue	Yellow
Crystal habit	Parallelepiped	Block	Plate	Block	Plate	Block	Plate	Parallelepiped
Crystal size (mm)	0.13 × 0.13 × 0.08	0.75 × 0.40 × 0.40	0.60 × 0.20 × 0.15	0.40 × 0.40 × 0.40	0.25 × 0.15 × 0.15	0.70 × 0.35 × 0.35	0.25 × 0.06 × 0.37	0.4 (sphere)
Unit cell dimensions								
<i>a</i> (Å)	7.957(5)	8.027(6)	12.348(6)	16.681(8)	11.387(9)	9.632(6)	9.388(3)	18.599(4)
<i>b</i> (Å)	11.174(6)	21.128(12)	16.643(7)	8.400(4)	8.177(8)	10.348(6)	26.043(8)	11.463(3)
<i>c</i> (Å)	12.086(6)	15.224(10)	14.487(6)	16.172(8)	13.792(13)	14.687(8)	11.351(4)	39.371(6)
α (°)	109.05(5)					99.86(5)		
β (°)	107.07(5)	100.26(6)	105.84(4)		99.87(8)	96.14(5)	107.29(3)	101.23(3)
γ (°)	92.78(5)					107.57(6)		
<i>V</i> (Å ³)	958.5(9)	2541(3)	2864(2)	2266(2)	1265(2)	1355.2(14)	2649.8(15)	8233(3)
<i>Z</i>	4	4	4	4	2	2	4	8
μ (Mo–K α) (mm ⁻¹)	1.813	0.778	0.695	0.870	0.785	0.747	0.764	0.558
Max 2θ	56	50	52	56	50	46	54	57
Reflections collected	7534	4466	5664	5500	3976	3453	5847	25 434
Reflections observed	2806	3648	4194	4614	2679	3080	3926	11 162
Completeness to θ_{\max}	0.96	0.964	0.963	1.00	0.998	0.910	0.97	0.908
Data/parameters	4440/311	4466/309	5664/360	5488/309	3866/349	3453/387	5730/355	12 351/1058
R^a (F , $F^2 > 2\sigma$)	0.0222	0.0233	0.0242	0.0236	0.0307	0.0226	0.0269	0.0456
R_w^b (F^2 , all data)	0.0647	0.0667	0.0678	0.0642	0.0882	0.0661	0.0813	0.0962
Goodness-of-fit on F^2	0.987	1.061	1.042	1.046	1.041	1.060	1.034	1.085
Weights a/b^c	0.0347/0.114	0.0354/1.459	0.0343/0.766	0.0407/0.000	0.0494/0.000	0.0448/0.602	0.0434/1.326	0.0136/52.29
Flack parameter	–	–	–	–0.03(2)	–0.02(4)	–	–	0.00(2)

$$^a R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$^b R_w = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$$

$$^c w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } P = [\max(0 \text{ or } F_o^2) + 2F_o^2]/3$$

is isomorphous to that found [34] for the similar compound, Rh(Me{O,N}Me)(CO)(PPh₃). The other structures were solved using direct methods with SHELXS97 [60] and refined by the full-matrix least-squares method on all the F^2 data using SHELXL97 [60]. The hydrogen atoms of the phosphorus ligands were included in the geometrical positions and refined as the riding model.

The hydrogen atoms of the chelate ligands were found from difference Fourier maps and refined. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were given isotropic thermal parameters equivalent to 1.2 times those of the atom to which they are attached. Crystal and refinement data for all the crystals are compiled in Table 11.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 154496–154503 for **I–VIII**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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