

Synthesis, structure and NMR spectroscopy of some rhodium(III) cyclometallated Schiff's base complexes derived from 2-benzylidene-3-methylpyridines. Crystal structure of $[\text{RhHI}\{2\text{-}(3\text{-nitrobenzylidene})\text{-}3\text{-methylpyridine}\}(\text{PPh}_3)_2]$

A. Albinati*

Istituto di Chimica Farmaceutica, Università di Milano, I-20131 Milano (Italy)

C. Arz and P.S. Pregosin*

Laboratorium für Anorganische Chemie, ETH-Z, Universitätstrasse 6, CH-8092 Zürich (Switzerland)

(Received April 21st, 1987)

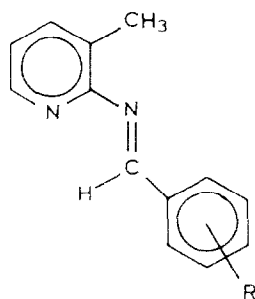
Abstract

The Schiff's base derived from 2-amino, 3-methylpyridine and an aryl aldehyde reacts with either $\text{RhCl}(\text{PPh}_3)_3$ or $[\text{Rh}(\mu\text{-Cl})(\text{cyclooctene})_2]_2$ in the presence of four equivalents of L (L = PPh_3 , $\text{P}(4\text{-ClC}_6\text{H}_4)_3$, $\text{P}(\text{cyclohexyl})_3$, AsPh_3 , SbPh_3) to give a Rh^{III} cyclometallated complex (**2**), in which the imine C–H bond has oxidatively added to the metal. The complexes **2** react with reagents such as Br^- , CN^- , CH_3I , $\text{C}\equiv\text{NR}$ (R = cyclohexyl, t-butyl), $\text{P}(\text{OCH}_3)_3$, CO, to give substitution products (**3**), in which the Cl has been replaced. The complexes **2** and **3**, as well as some few Ir^{III} analogs (**4**), have been isolated and characterized using ^1H , ^{31}P , and (occasionally) ^{13}C NMR spectroscopy.

The crystal structure of the complex $\text{RhHI}\{2\text{-}(3\text{-nitrobenzylidene})\text{-}3\text{-methylpyridine}\}(\text{PPh}_3)_2$ (**3b**) has been determined by X-ray diffraction. The complex shows a distorted octahedral structure with the following bond distances (Å) and angles (°): Rh–I, 2.771(2); Rh–N(1), 2.15(1); Rh–C(7'), 1.98(2); Rh–P(1), 2.326(5); Rh–P(2) 2.332(5); P–Rh–P, 159.7(2), N(1)–Rh–C(7'), 78.5(6). In the light of the NMR and X-ray data, it is suggested that the $-\text{C}(\text{R})=\text{N}-$ moiety exerts a large *trans* influence.

Introduction

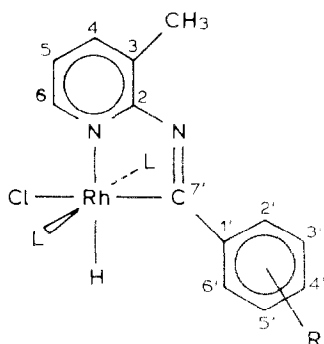
Our interest in cyclometallation reactions in which aldehyde [1] and imine [2] C–H bonds are attacked lead us to consider some of the chemistry associated with the imines **1**, derived from 2-amino-3-methylpyridine. Compound **1** has been shown



(R = a variety of substituents)

(1)

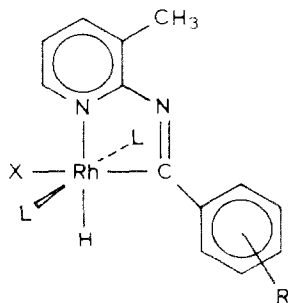
by Suggs and co-workers [3] to react smoothly with $\text{RhCl}(\text{PPh}_3)_3$ to afford Rh^{III} complexes of type 2. We report here (i) the synthesis and characterisation of an



(2)

	L	R
a	PPh_3	2- NO_2
b	PPh_3	3- NO_2
c	$\text{P}(4\text{-ClC}_6\text{H}_4)_3$	3- NO_2
d	AsPh_3	3- NO_2
e	PPh_3	4- NO_2
f	Pcy_3	4- NO_2
g	PPh_3	4-Br
h	PPh_3	2-OH
i	PPh_3	2- CH_3
j	PPh_3	2-OH , 3- OCH_3
k	SbPh_3	2-OH

extensive variety of the complexes 2, with different R and L combinations, (ii) their reactions with reagents such as Br^- , CN^- , CH_3I , CO , $\text{P}(\text{OMe})_3$, isonitriles and nitriles, and (iii) the molecular structure of the iodo complex 3b.



(3)

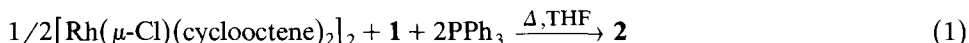
(L = PPh_3)

	R	X
a	4- NO_2	Br
b	3- NO_2	I
c	4- NO_2	I
d	2- CH_3	^{13}CN
e	3- NO_2	$\text{C}\equiv\text{N}(\text{cyclohexyl})$
f	3- NO_2	$\text{C}\equiv\text{N}(\text{Bu}^t)$
g	3- NO_2	$\text{P}(\text{OCH}_3)_3$
h	2-OH	$\text{P}(\text{OCH}_3)_3$
i	2-OH	CO
j	3- NO_2	PhCN
k	2- CH_3	PhCN
l	3- NO_2	acetone

Results and discussion

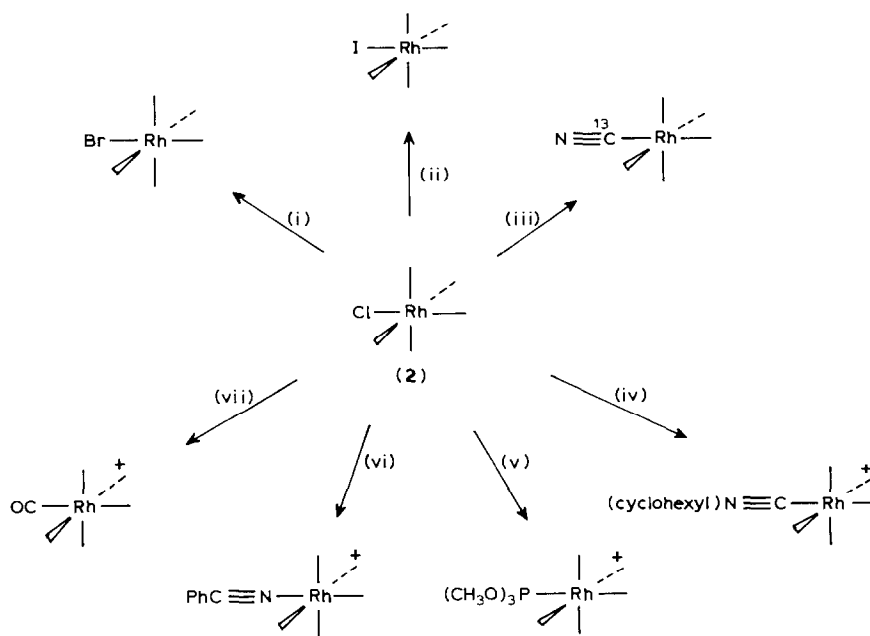
Preparative studies

Complexes of type **2** may be prepared either by: (i) refluxing equimolar amounts of **1** with $\text{RhCl}(\text{PPh}_3)_3$ in THF for 0.5 h, as previously suggested [3], or (ii) by refluxing a solution of one equivalent of the dimer $[\text{Rh}(\mu\text{-Cl})(\text{cyclooctene})_2]_2$, two equivalents of **1**, and four equivalents of tertiary phosphine in THF for 1 h; this reaction is depicted in eq. 1.



The second approach is superior in that it is more general (AsPh_3 , SbPh_3 , or others may be substituted for PPh_3 , see below), it avoids waste of one equivalent of phosphine (or arsine...), and it is not necessary to prepare RhClL_3 ($\text{L} = \text{PR}_3$, AsPh_3 ...) in a previous step. Complexes of type **2** with L ligands, $\text{P}(4\text{-ClC}_6\text{H}_4)_3$, Pcy_3 (cy = cyclohexyl), AsPh_3 and SbPh_3 were all obtained in good to excellent yields using the cyclooctene rhodium dimer route (eq. 1).

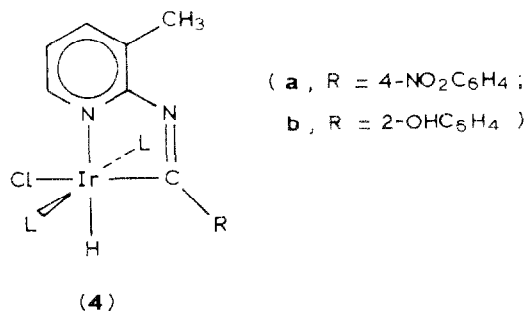
The chloride ligand may be replaced by a variety of negative and neutral ligands as shown in Scheme 1. A cationic acetone complex **3** was prepared as its BF_4 salt ($\nu(\text{CO})$ 1671 cm^{-1} in CH_2Cl_2 solution, $\delta(\text{CH}_3)_2\text{CO}$ 2.09 ppm) by an in situ reaction of the chloride analog with AgBF_4 in acetone, and was isolated by precipitation with hexane. Cations were also available by reaction of **2** with NH_4PF_6 . A complex which we tentatively consider to arise from substitution of Cl^-



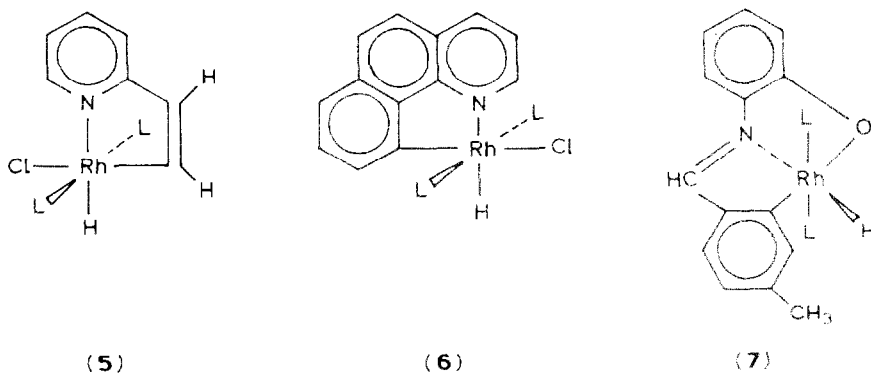
Scheme 1. (i) LiBr in acetone; (ii) MeI in THF; (iii) K^{13}CN in THF; (iv) $\text{C}\equiv\text{N}(\text{cyclohexyl})$ in CH_2Cl_2 ; (v) $\text{P}(\text{OCH}_3)_3$ in CH_2Cl_2 ; (vi) NH_4PF_6 , PhCN in MeOH ; (vii) from the benzonitrile analog with CO , in THF.

by CF_3SO_3^- was obtained by treating **2e** with excess $\text{CF}_3\text{SO}_3\text{H}$ in acetone. The product shows a hydride resonance at $\delta -11.42$ ppm, $^2J(\text{P,H})$ 13.3 Hz, and a ^{31}P signal at δ 28.7 ppm, $^1J(\text{Rh,P})$ 101 Hz, and the occurrence of this reaction raises the question of the relative stability of the Rh-C(imine) bond. Whether the reagent was $\text{CF}_3\text{SO}_3\text{H}$, CO, $\text{C}\equiv\text{N}(\text{cyclohexyl})$, $\text{P}(\text{OMe})_3$ or $^{13}\text{CN}^-$ we found no evidence for reaction of the M-C moiety at room temperature. We assume that this relative robustness arises from the following factors: (a) complexes **2** are octahedral d^6 species, whose reactions may be relatively slow [4]; (b) the molecule has a carbon ligand which is part of a chelate ring and so may not undergo insertion reactions as readily as a monodentate carbon ligand; and (c) in some cases carbon ligands attached to electron withdrawing groups insert relatively slowly [5].

Two iridium(III) complexes of type **4** were also prepared from $[\text{Ir}(\mu\text{-Cl})(\text{cyclooctene})_2]_2$. We include these as they provide further evidence for the generality of the

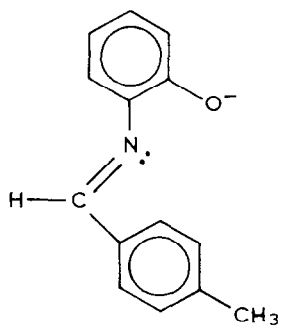


oxidative addition although this reaction type is quite common for iridium [6]. In the course of these studies we also prepared **5-7** with L = PPh_3 in all three



complexes. Compound **5** is formed from the reaction of $\text{RhCl}(\text{PPh}_3)_3$ with 2-vinylpyridine in THF, whereas **6** was obtained from a reaction analogous to that shown in eq. 1, but with benzoquinoline as ligand. These complexes are interesting in that they presumably arise, via a route similar to that which affords **2**, i.e., coordination of a nitrogen ligand followed by oxidative addition. We note that a complex related to **5** (with Cl instead of H) has been reported [7].

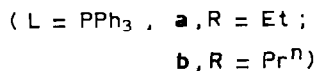
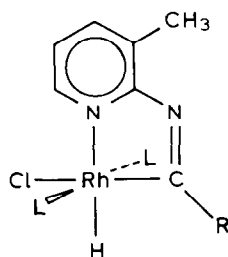
Derivative **7** is formed from ligand **8**, again by reaction with the rhodium dimer and PPh_3 in THF, and is analogous to the benzoquinoline example in that the



(8)

rhodium has added to a proximate aromatic C–H, but not analogous to **2** in that the oxidative addition does not take place at the imine. We do not know in which sequence the N and O atoms coordinate. Cyclometallations for **5–7** and related compounds have been documented previously [7–9].

Finally, we mention two complexes related to **2** which differ in that aliphatic aldehydes (as their amins) were used to afford **9**.



(9)

NMR spectroscopy

Except for **3b** and **3e**, the complexes were characterized by NMR (¹H, ³¹P and ¹³C), IR and microanalytical methods (see Tables 1–4).

The ¹H NMR spectra for the rhodium complexes show a hydride resonance between δ –10.61 and –13.20 ppm. The two iridium compounds have hydride signals at slightly lower frequency (**4a**, δ –14.60, **4b**, –14.91 ppm). Amongst the rhodium derivatives the highest field hydride resonances were found for the neutral Pcy₃ (**2f**) and SbPh₃ (**2k**) complexes, the P(OCH₃)₃ cations **3g** and **3h** and the cyano complex **3d**. The complexes **2** show splitting of the hydride resonance by two equivalent ³¹P spins and the ¹⁰³Rh. As both of these spin–spin couplings are frequently in the range 10–16 Hz, the hydride multiplet often appears as a pseudo quartet; however, higher resolution studies usually reveal the expected doublet of triplets.

Interestingly, those rhodium complexes with the highest field hydride resonance tend to have the signal from H(6), the proton adjacent to the pyridine nitrogen, at lowest field. The pyridine methyl group resonates at δ 2.34–2.89 ppm except for the P(OCH₃)₃ derivatives **4a**, **4b**, for which it appears at 1.88 and 1.75, respectively.

Table 1
 ^1H NMR parameters for the complexes

Com- pound	H(5)	H(6)	CH ₃	H(2')	H(3')	H(4')	H(5')	H(6')	Hydride	$^1J(\text{Rh}-\text{H})$
2a	6.46	8.24	2.34		7.95	6.98	6.77	7.24	-11.41	14.0
2b	6.70	8.60	2.56	8.39		7.96	6.84	7.69	-11.23	13.8
2c	6.81	8.58	2.58	8.46		7.90	6.99	7.47	-11.42	13.5
2d	6.77	8.87	2.55	8.42		8.03	6.86	7.73	-11.88	9.4
2e	6.63	8.54	2.55	7.52	7.77		7.77	7.52	-11.21	13.7
2f	7.06	9.39	2.63	8.20	8.80		8.80	8.20	-12.78	14.3
2g	6.61	8.45	2.50	7.52	6.81		6.81	7.52	-11.27	13.3
2h ^b	6.77	8.64	2.37		6.28	7.93	6.16	^a	-11.35	12.4
2i ^c	6.56	7.99	2.46		^a	6.81	6.59	7.96	-11.26	13.6
2j ^d	6.79	8.66	2.39			6.44	6.09	7.60	-11.37	13.4
2k ^e		9.12	2.34		6.50	^a	6.36	8.32	-12.22	4.6
3a ^f	6.70	8.68	2.56	7.50	7.80		7.80	7.50	-11.44	13.5
3b	6.78	8.98	2.58	8.49		7.96	6.87	7.75	-11.80	12.4
3c	6.71	8.93	2.59	7.56	7.81		7.81	7.56	-11.79	12.8
3d ^g	6.31	8.00	2.49		6.60	^a	6.80	7.88	-12.23	10.5
3e	6.89	8.59	2.40	8.44		7.92	7.02	7.80	-11.78	14.9
3f ^h	6.83	8.59	2.56	8.42		7.91	6.97	7.87	-11.44	13.9
3g ⁱ	^a	9.65	1.88	9.11		8.01	^a	7.74	-12.58	14.6
3h ^j	^a	10.40	1.75		6.49	6.96	6.15	7.97	-13.07	11.0
3i ^k	7.25	9.40	2.89		6.63	7.05	6.34	7.90	-10.61	14.5
3j	6.94	9.10	2.34	8.68		8.08	7.04	7.82	-11.26	14.2
3k ^l	6.61	7.89	2.64		^a	6.89	6.74	^a	-11.21	15.7
3l	^a	9.26	2.29	8.98	^a	4.42	^a	7.99	-10.83	14.8
4a	6.58	8.35	2.57	7.51	7.85		7.85	7.51	-14.60	
4b ^m	6.64	8.50	2.42		6.34	6.80	6.10	7.90	-14.91	
8a ⁿ	7.16	9.12	2.21						-11.44	15.7
8b ^o	6.51	8.52	2.44						-12.10	12.5

^a CDCl₃ solutions. Chemical shifts in ppm are ± 0.01 . Coupling constants are in Hz, ± 0.5 . H(4) is frequently under the PPh₃, AsPh₃, SbPh₃... resonances. Where it is resolved it appears at ca. δ 7.35–7.66. ^b OH at δ 15.76. ^c CH₃ at δ 1.91, complex with AsPh₃ instead of PPh₃ has hydride δ -12.03, $^2J(\text{P},\text{H})$ 7.3. ^d OH at δ 16.41, OCH₃ at 3.70, complex with AsPh₃ instead of PPh₃ has hydride δ -12.02, $^2J(\text{P},\text{H})$ 8.6. ^e OH at δ 16.05. ^f Complex with 3-NO₂ instead of 4-NO₂ has hydride δ -11.43, $^2J(\text{P},\text{H})$ 13.1. ^g CH₃ at 2.02. 2-OH instead of 2-CH₃ had hydride δ -12.43, $^2J(\text{P},\text{H})$ 10.6. OH at δ 15.82. With AsPh₃ (instead of PPh₃) and 3-NO₂, hydride δ -13.20, $^2J(\text{P},\text{H})$ 9.7. ^h Bu^t at δ 1.52. ⁱ OCH₃ at δ 3.15. ^j OCH₃ at δ 2.99, OH at δ 16.14. ^k OH at δ 14.43. ^l CH₃ at δ 2.07. ^m OH at δ 17.10. ⁿ CH₂ at δ 2.15, $^3J(\text{H},\text{H})$ 6.6, CH₃ at δ 0.86. ^o CH₂ (next to imine) at δ 1.86, $^3J(\text{H},\text{H})$ ca. 7.5, CH₂ at δ 0.92, CH₃ at δ 0.10, $^3J(\text{H},\text{H})$ 7.5.

The PPh₃ rhodium complexes show a ³¹P signal in the range δ 28–35 ppm with $^1J(^{103}\text{Rh}, ^{31}\text{P})$ 103–118 Hz, in keeping with the literature [10]. Although these ³¹P data are not revealing, the $^1J(^{103}\text{Rh}, ^{31}\text{P})$ values for the coordinated P(OCH₃)₃, in **3g** and **3h**, 104 and 109 Hz, respectively, are relatively small. The anion *trans*-Rh(CF₃CO₂)₄{P(OCH₃)₃}₂⁻ [11] has a one-bond coupling of 132.5 Hz, but the cations Rh(cp){P(OCH₃)₃}₃²⁺ [12] and RhH(cp)(CO){P(OCH₃)₃}⁺ [13] have much larger $^1J(^{103}\text{Rh}, ^{31}\text{P})$ values of 200 and 195 Hz, respectively. Consequently, it would seem that the iminoyl carbon exerts a substantial NMR *trans* influence, and we return to this subject later in the discussion of the structure of **3b**.

The complexes **2** and **3** are only moderately soluble, and so we have not obtained many ¹³C spectra; however, some ¹³C(7') data for a few complexes are shown in

Table 2
 ^{31}P NMR data ^a for the complexes

Complex	$\delta(^{31}\text{P})$	$^1J(^{103}\text{Rh}, ^{31}\text{P})$
2a	32.47	114.1
2b	30.57	113.0
2c	29.16	115.0
2e	30.63	114.5
2f	23.00	105.3
2h	30.69	112.5
2i	34.39	117.7
2j	30.71	112.5
3a	29.91	114.4
3b	28.17	114.4
3c	28.22	113.6
3d	38.18	109.4
3e ^b	33.66	102.6
3g ^c	32.96	104.1
3h ^d	34.36	110.7
3i	31.82	97.7
3j	33.32	109.8
3k	34.67	114.0
3l	34.11	114.4
4a	2.70	
4b	2.43	
5	39.92	117.0
6	37.42	115
7	39.32	118.6
8a	32.63	121.7
8b	32.55	121.4

^a δ rel. to ext. H_3PO_4 , ± 0.05 ppm. J in Hz, ± 1.5 Hz, CDCl_3 solutions when not specified. ^b Analogous 4- NO_2 complex has δ 33.71, $^1J(\text{Rh},\text{P})$ 105.3 Hz. ^c δ $\text{P}(\text{OCH}_3)_3$ 118.84, $^1J(\text{Rh},\text{P})$ 133.7 Hz, $^2J(\text{P},\text{P})$ 43.7 Hz. ^d δ $\text{P}(\text{OCH}_3)_3$ 94.47, $^1J(\text{Rh},\text{P})$ 120.0 Hz, $^2J(\text{P},\text{P})$ 43.0 Hz.

Table 3, along with those for **5**. The signals for $\text{C}(7')$ are all at δ 225–252 ppm, whereas the uncomplexed imine $\text{C}(7')$ signal is found at δ 160–170 ppm [2]. This low-field position for **2** and **3** is suggestive of carbene-like properties; however, the

Table 3
 Some ^{13}C data ^a for $\text{C}(7')$

Complex	$\delta(\text{C}(7'))$	$^1J(\text{Rh},\text{C})$	$^2J(\text{P},\text{C})$
2e	225.16	34	8
3e ^b	227.48	27	9
3h	252.00	25	11 (to PPh_3) 47 (to $\text{P}(\text{OCH}_3)_3$)
3d ^c	248.08	28	9
5 ^d	178.15	31	12

^a δ in ppm, J in Hz. ^b For the 4- NO_2 and not the 3- NO_2 derivative. ^c For the 2-OH and not the 2- CH_3 derivative. $\delta(^{13}\text{CN})$ 142.64, $^1J(\text{Rh},\text{CN})$ 33, $^2J(\text{P},\text{CN})$ 17, $^2J(\text{C}(7'),\text{CN})$ 28. The complex **3d** has $\delta(^{13}\text{CN})$ 141.57, $^1J(\text{Rh},\text{C})$ 34, $^2J(\text{P},\text{CN})$ 17. ^d For the metallated carbon.

Table 4
Microanalytical data

Complex	Found (calc) (%)		
	C	H	N
2a	65.15 (65.09)	4.93 (4.57)	4.06 (4.65)
2b	65.10 (65.09)	5.05 (4.57)	4.20 (4.65)
2c	52.93 (52.98)	3.19 (3.18)	3.70 (3.78)
2d	58.92 (59.32)	4.40 (4.17)	4.11 (4.24)
2e	64.96 (65.09)	5.08 (4.57)	4.20 (4.65)
2j	66.27 (66.34)	4.68 (4.90)	2.85 (3.09)
2g	62.96 (62.74)	4.92 (4.41)	2.68 (2.99)
2h	66.76 (67.25)	5.28 (4.84)	2.94 (3.20)
2k	55.60 (55.69)	4.09 (4.01)	2.78 (2.65)
3a	62.09 (62.04)	4.93 (4.36)	5.02 (4.43)
3c	59.01 (59.11)	4.39 (4.15)	3.90 (4.22)
3h	62.58 (62.50)	4.90 (5.14)	2.60 (2.80)
3k	62.87 (63.05)	4.55 (4.55)	3.89 (3.87)
3i	59.29 (59.30)	4.37 (4.18)	2.69 (2.77)
4a	59.60 (59.24)	4.23 (4.16)	4.21 (4.23)
8a	66.62 (66.64)	5.43 (5.22)	3.36 (3.45)

higher field value for the metallated carbon in **5**, δ 178.15 ppm is more informative. Although this resonance is still at very low field, relative to the analogous ^{13}C signal in the free ligand, such a shift is not unusual for a cyclometallated sp^2 carbon [15]. Moreover, our cyclometallation-induced low-field shift is reminiscent of other low-field shifts observed where a chelating atom is incorporated in a five-membered ring [16], and so we now view these unusual iminoyl ^{13}C chemical shifts in terms of a ring effect and not carbene-like character.

A separate report concerned with the ^{103}Rh NMR characteristics of **3** has appeared [14], and these data will not be discussed further.

X-Ray structure of 3b

The structure of the iodo complex, **3b**, reveals the expected distorted octahedral geometry. Whereas the I–Rh–C(7') angle is $174.8(4)^\circ$, slightly less than 180° , the I–Rh–N(1) angle is $98.1(4)^\circ$, suggesting that the five-membered ring with its small

bite angle, $\text{N}(1)\text{-Rh-C}(7')$, $78.5(6)^\circ$, leads to distortions from the ideal values. The P-Rh-P angle of $159.7(2)^\circ$ reveals these three atoms to be far from linear; however, this is relatively common for hydride complexes [17] and reflects a low energy structural distortion in which the relatively large PPh_3 ligands bend towards the small hydride ligand. We note that the angles $\text{P}(1)\text{-Rh-N}(1)$ and $\text{P}(2)\text{-Rh-N}(1)$, $99.0(4)$, $101.3(4)^\circ$, respectively, show that the phosphine ligands bend away from the cyclometallated chelate ligand toward the hydride ligand.

The Rh-P distances at $2.326(5)$ and $2.332(5)$ Å are normal for octahedral complexes of Rh^{III} , but the Rh-I separation, $2.771(2)$ Å is relatively long. $\text{Rh}(\text{cp})\text{I}(\text{COCH}_3)\text{P}$ ($\text{P} = \text{Ph}_2\text{PNHCH}(\text{CH}_3)\text{Ph}$) has a Rh-I distance of $2.691(1)$ Å [18] and the five-coordinate $\text{RhI}_2(\text{CH}_3)(\text{PPh}_3)_2$ has Rh-I bond lengths of $2.635(1)$ Å [19]. We assume the relatively long Rh-I bond in **3b** stems from its position *trans* to the iminoyl carbon. A strong *trans* influence for this carbon ligand would be in keeping both with our chemistry (in that we find that **2** readily undergoes substitution reactions in which the Cl is displaced) and the ^{31}P NMR spectroscopy discussed above.

The $\text{Rh-C}(7')$ distance at $1.98(2)$ Å is about what one would expect for a covalent Rh-C bond [20]; however, as suitable model complexes are rare we cannot judge whether this bond separation merits further comment.

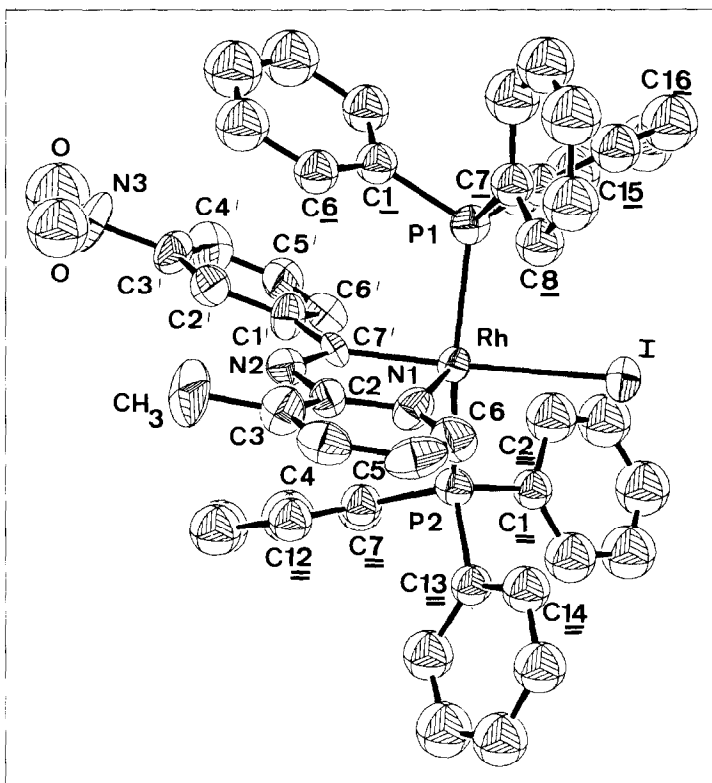


Fig. 1. ORTEP view of **3b**. Numbers underlined once, e.g. C1, or twice, e.g. C1, refer to aromatic carbons of P(1), or P(2), respectively

Table 5. Selected bond distances (Å), bond angles (°) and torsion angles for **3b**. The corresponding values for **3e** are listed for comparison in square brackets

Rh–I	2.771(2)		Rh–C(7′)–C(1′)	128.9(7)	
Rh–N(1)	2.15(1)	[2.19(4)]	Rh–C(7′)–N(2)	117.6(9)	
Rh–C(7′)	1.98(2)	[2.03(2)]	Rh–N(1)–C(2)	109.4(9)	
Rh–P(1)	2.326(5)	[2.341(5)]	Rh–N(1)–C(6)	131.7(7)	
Rh–P(2)	2.332(5)	[2.336(5)]	I–Rh–C(7′)	174.8(4)	
P–C ^a	1.83(3)		P(1)–Rh–P(2)	159.7(2)	[166.7(4)]
N(1)–C(6)	1.34(2)		I–Rh–N(1)	98.1(4)	
N(1)–C(2)	1.35(2)		N(1)–Rh–C(7′)	78.5(6)	[75.8(6)]
C(2)–N(2)	1.38(2)	[1.43(3)]	P(1)–Rh–I	90.0(1)	
C(7′)–N(2)	1.35(2)	[1.29(3)]	P(1)–Rh–N(1)	99.0(4)	[97.7(4)]
C(7′)–C(1′)	1.45(2)	[1.53(2)]	P(1)–Rh–C(7′)	94.4(4)	[93.4(5)]
C(3)–C(8)	1.47(3)	[1.46(3)]	P(2)–Rh–I	87.3(1)	
C(3′)–N(3)	1.46(3)		P(2)–Rh–N(1)	101.3(4)	[96.5(4)]
O(1)–N(3)	1.17(2)		P(2)–Rh–C(7′)	89.5(5)	[89.1(5)]
O(2)–N(3)	1.20(3)		N(1)–C(2)–C(3)	122.2(1.1)	
C(2)–C(3)	1.43(2)		N(1)–C(2)–N(2)	119.4(1.1)	[116.4(1.3)]
C(3)–C(4)	1.34(3)		C(2)–N(2)–C(7′)	114.7(1.1)	[115.8(1.3)]
C(4)–C(5)	1.45(3)		N(2)–C(7′)–C(1′)	113.5(1.2)	[115.3(1.3)]
C(5)–C(6)	1.41(3)		N(2)–C(2)–C(3)	118.3(1.1)	
C(1′)–C(6′)	1.44(2)		C(7′)–C(1′)–C(6′)	120.3(1.1)	
C(1′)–C(2′)	1.41(3)		C(7′)–C(1′)–C(2′)	120.4(1.2)	
C(5′)–C(6′)	1.42(3)		C(2)–C(3)–C(8)	122.0(1.2)	
C(4′)–C(5′)	1.36(3)		C(4)–C(3)–C(8)	118.8(1.4)	
C(3′)–C(4′)	1.43(3)		N(3)–C(3′)–C(2′)	119.2(1.3)	
C(2′)–C(3′)	1.39(3)		N(3)–C(3′)–C(4′)	118.4(1.4)	
			O(1)–N(3)–O(2)	121.4(1.6)	
Rh–N(1)–C(2)–N(2)	–6.2		C(2)–N(2)–C(7′)–C(1′)	178.5	
Rh–C(7′)–N(2)–C(2)	0.4		N(2)–C(7′)–C(1′)–C(6′)	165.5	
Rh–C(7′)–C(1′)–C(6′)	–16.7		C(2′)–C(3′)–N(3)–O(1)	177.9	
I–Rh–N(1)–C(2)	–171.4		N(2)–C(2)–C(3)–C(8)	3.2	
N(1)–C(2)–N(2)–C(7′)	4.2		C(3)–C(2)–N(2)–C(7′)	–174.6	

^a Average value; the e.s.d. on the mean is given by $\sigma = [(\sum x_i - x)^2 / n - 1]^{1/2}$. ^b e.s.d.'s on torsion angles in the range (1.1–1.8°).

The C(2)–N(2) separation of 1.38(2) Å seems reasonable for a double bond, and we note that the imine nitrogen is 2.85(1) Å from the metal, thereby excluding any significant interaction of this atom with rhodium.

We have recently determined the structure of the isonitrile compound **3e** [21] and it is instructive to compare this with that of **3b** (see Table 5 and Figs. 1 and 2). This molecule possesses a distorted octahedral coordination geometry with bond angles C(7′)–Rh–C≡N 177.7(6) and P(1)–Rh–P(2) 166.7(4)°. The remaining valence angles are all relatively close to 90°, with the exception of that for the cyclometalated chelate ring, 75.8(6)°. It seems that the primary structural difference between **3b** and **3e** relates to the angle subtended by the two phosphines, which is some 7° larger for **3e** than for **3b**. It is not immediately obvious why this should be, and we note only that the cyclohexyl of the isonitrile is > 4 Å from the rhodium, whereas the I is < 3 Å from the metal. There are no crystallographically significant differences between analogous bond lengths (see Table 5). The isonitrile is linear Rh–C(≡N)–N(4) 177.0(8)°, and the C≡N separation, 1.17(3) Å, is consistent with

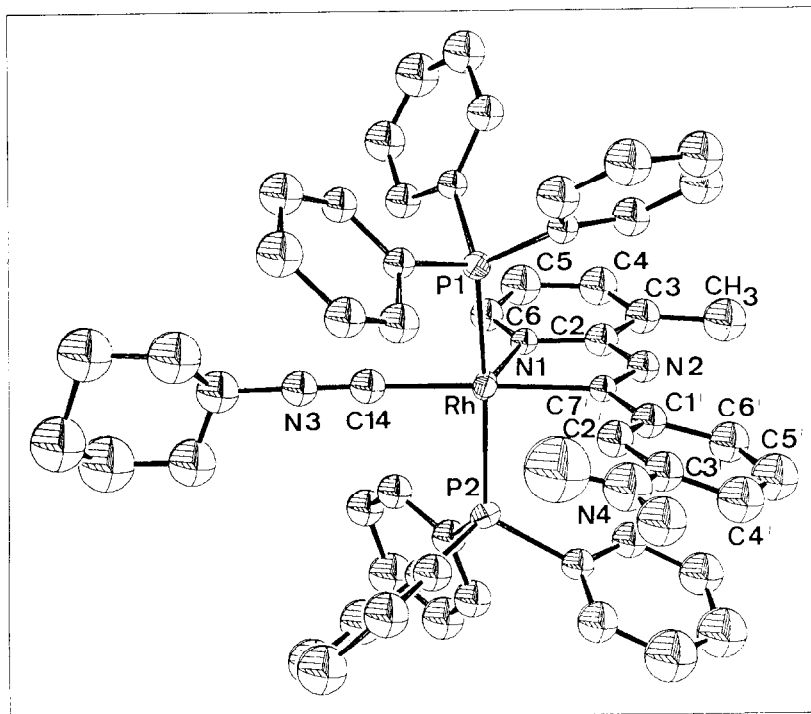


Fig. 2. ORTEP view of **3e**.

the expected triple bond. Interestingly, the rhodium–carbon (isonitrile) separation of 2.03(2) Å is relatively long, despite the experimental uncertainty. On the basis of covalent radii of ca. 1.25 Å and 0.58 Å for rhodium and carbon, respectively [20], this separation would be expected to be ca. 1.85 Å. We attribute the observed value, once again, to the substantial *trans* influence of our iminoyl carbon.

It would seem that species such as **2** and **3** have a rich synthetic and structural chemistry, and further work in this area is in progress.

Experimental

^1H , ^{31}P and ^{13}C spectra were recorded with a Bruker WM-250 NMR spectrometer as CDCl_3 solutions. IR spectra were recorded as either KBr or RbI disks using either a Perkin–Elmer 1430 or 883 infrared spectrophotometer. Analyses were performed by the microanalytical laboratory of the ETH Zürich.

The Schiff's base compounds were prepared by condensing 2-amino-3-methylpyridine with the appropriate aldehyde. The phosphines were commercially available, as was AsPh_3 and SbPh_3 .

The complexes **2** were prepared either by reaction with $\text{RhCl}(\text{PPh}_3)_3$ or with $[\text{RhCl}(\text{cyclooctene})_2]_2$. Two typical preparations are described below.

Preparation of **2j**

A solution of Wilkinson's catalyst (300 mg, 0.32 mmol) and 2- $\{\text{N}=\text{CH}(2\text{-OH}, 3\text{-OCH}_3\text{C}_6\text{H}_3)\}$ -3-methylpyridine (82 mg, 0.32 mmol) in ca. 20 ml of THF was

refluxed for 1 h. Addition of n-hexane led to precipitation of the product, which was filtered off. Yield: 273 mg (94%).

Preparation of 2e

A solution of $[\text{Rh}(\mu\text{-Cl})(\text{cyclooctene})_2]_2$ (200 mg, 0.28 mmol), 2-($\text{N}=\text{CH}(4\text{-NO}_2\text{C}_6\text{H}_4)$)-3-methylpyridine (135 mg, 0.56 mmol), and triphenylphosphine (293 mg, 1.12 mmol) in ca. 20 ml of THF was refluxed for 1 h. Addition of n-hexane induced precipitation of the product, which was filtered off. Yield: 380 mg (75%).

Analytical data are shown in Table 1.

Subsequent experiments revealed that it is not necessary to reflux the mixtures, since the reaction with aryl phosphines proceeds fairly rapidly at room temperature.

Preparation of 3a

A solution of **2e** (150 mg, 0.17 mmol) in acetone was treated with a ca. 5-fold excess of LiBr for 20 h at room temperature. Filtration through Celite was followed by removal of the solvent under reduced pressure. The crude product was recrystallized from CH_2Cl_2 /hexane. Yield: 135 mg (82%).

The same product was obtained in 93% yield starting from $\text{RhBr}(\text{PPh}_3)_3$ as described above for the synthesis of **2j**.

Preparation of 3c

Reaction of **2e** (250 mg, 0.28 mmol) in ca. 20 ml THF with 2 ml MeI for 20 h gave a dark red solution. Addition of hexane induced precipitation of the product as an orange powder. Yield: 192 mg (68%).

Preparation of 3h

A solution of **2h** (100 mg, 0.11 mmol) in ca. 20 ml CH_2Cl_2 was treated with ca. 2 ml of neat $\text{P}(\text{OCH}_3)_3$. Stirring at room temperature for 25 h was followed by filtration through Celite. Addition of low boiling petroleum ether induced precipitation of the product as a yellow powder. Yield: 83 mg (73%).

The isonitrile complex **3e** was prepared similarly by use of ca. 2 ml of neat cyclohexyl isonitrile.

Preparation of 3k

A solution of **2i** (350 mg, 0.40 mmol), NH_4PF_6 (98 mg, 0.60 mmol), and 2 ml benzonitrile in degassed MeOH was stirred at room temperature for 3 h. The resulting white suspension was filtered and the solid collected. Yield: 306 mg (70%).

Preparation of 3i

2h was used to prepare a benzonitrile analog as described for **3k** above. A solution of this benzonitrile complex (200 mg, 0.18 mmol) in 20 ml THF was treated with CO gas for 4 h. The resulting red solution was treated with hexane, which induced precipitation of the cationic orange product as its PF_6 salt. Yield: 135 mg (72%).

Preparation of 3d

2i was used to prepare a benzonitrile analog, as described for **3k** above. A suspension of this benzonitrile complex (130 mg, 0.12 mmol) and K^{13}CN (15.6 mg,

0.24 mmol) in ca. 20 ml degassed THF was stirred at room temperature for 20 h. Addition of hexane induced precipitation of the product as a yellow powder. Yield: 87 mg (83%).

Preparations of **2d**, **2h**, **2c** and **2f**

The triphenylarsine complex, **2d**, the triphenylstibene complex **2h**, the P(4-ClC₆H₄)₃ analog **2c**, and the P(cyclohexyl)₃ compound **2f** were all prepared in the way described for **2e**, i.e. via [Rh(μ -Cl)(cyclooctene)₂]₂.

Yield: from 336 mg of dimer 1150 mg (83%) of **2d**
 from 130 mg of dimer 275 mg (72%) of **2k**
 from 330 mg of dimer 900 mg (88%) of **2c**
 from 120 mg of dimer 250 mg (82%) of **2f**.

Preparation of **4a**

A mixture of [Ir(μ -Cl)Cl(cyclooctene)₂]₂ (180 mg, 0.20 mmol), the Schiff's base (97 mg, 0.40 mmol), PPh₃ (211 mg, 0.80 mmol) and ca. 20 ml THF was refluxed for 1 h. Addition of hexane induced precipitation of the product as a dark yellow powder. Yield: 325 mg (83%).

Complex **5** was prepared from 2-vinylpyridine and RhCl(PPh₃)₃ as described for **2j**, above. Yield: 72%; ¹H NMR δ (ppm): -12.68 (dxt, hydride, ¹J(Rh,H) 14.9, ²J(P,H) 10.9 Hz); 5.99 (d, H(7), ³J(H(7),H(8)) 6.9 Hz), 7.57 (dxd, H(8), ³J(H(7),H(8)) 6.9 Hz). Found: C, 66.44; H, 4.77; N, 1.79. C₄₃H₃₇ClNP₂Rh calc: C, 67.24; H, 4.86; N, 1.82%.

Complex **6** was obtained from benzoquinoline and [Rh(μ -Cl)(cyclooctene)₂]₂ as described for **2c**. Yield: 73%. ¹H NMR, δ (ppm): -13.09 (dxt, hydride, ¹J(Rh,H) 15.3, ²J(P,H) 12.1 Hz).

Complex **7** was prepared from the analogous phenolate, rhodium dimer and PPh₃ as for **2j**. Yield: 79%. ¹H NMR (acetone-*d*₆) δ (ppm): -10.64 (hydride, ¹J(Rh,H) 13.1, ²J(P,H) 13.3 Hz). Found: C, 70.72; H, 5.11; N, 1.51. C₅₀H₄₂NOP₂Rh calc: C, 71.69; H, 5.05; N, 1.67%.

The cationic complexes **3e**, **3f**, **3g**, **3h** were prepared as chloride salts; the **3i**, **3j**, **3k** derivatives as PF₆ salts and the acetone cationic complex **3l** as its BF₄ salt. The PF₆ salts showed a ³¹P resonance at δ ca. -144.68 to -147.72 ppm with ¹J(P,F) 711-712 Hz.

X-Ray structure determination

Crystals suitable for X-ray diffraction were obtained via recrystallization from CH₂Cl₂/hexane (the crude solid contains THF) and are air stable.

A prismatic crystal was chosen for the data collection and mounted on a glass fiber at a random orientation. A Nonius CAD4 diffractometer was used both for the space group and cell constants determination and for the data collection. Cell constant values were obtained by least-squares fit of 25 high-angle reflections (11.0 $\leq \theta \leq$ 15.0) using the CAD4 centering routines [22]. Cell parameters, experimental conditions, and other crystallographic details are listed in Table 6. Data were collected at variable scan speed to obtain a constant statistical precision of the measured intensities. Three standard reflections (1 $\bar{7}$ $\bar{3}$, 1 7 $\bar{3}$, $\bar{1}$ $\bar{7}$ 3) were used to check the stability of the crystal and of the experimental conditions and measured every hour; no significant variation was detected. The crystal orientation was

Table 6

Crystallographic parameters and experimental data ^a for the X-ray diffraction study of **3b**·THF

Formula	RhIP ₂ N ₃ O ₃ C ₃₃ H ₄₉
Mol. weight	1068.76
Crystal dim. (mm)	0.35 × 0.20 × 0.17
Cryst. system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	15.157(7)
<i>b</i> (Å)	16.596(3)
<i>c</i> (Å)	18.830(5)
β (°)	91.97(3)
<i>V</i> (Å ³)	4733.88
<i>Z</i>	4
ρ (calc) (g cm ⁻³)	1.499
μ (cm ⁻¹)	5.2
Radiation	Mo- <i>K</i> α
	(graphite-monochromated, λ 0.71069 Å)
Measd. refl.	$\pm h, +k, +l$
θ range (°)	2.3 $\leq \theta \leq$ 22.0
Scan type	$\omega/2\theta$
Max. scan speed (° min ⁻¹)	20.2
Scan width (°)	1.2 + 0.35 tan θ
Max. counting time (s)	55
Prescan rejection limit	0.5 (2 σ)
Prescan acceptance limit	0.03 (33 σ)
Bkgd. time	0.5 × scan time
horiz. receiving aperture (mm)	1.95 + tan θ
vert. receiving aperture (mm)	4.0
No. of independent data	4379
No. of observed data	3274
	($F_0 \geq 2.5\sigma(F_0)$)
<i>R</i> ^b	0.070
<i>R</i> _w ^c	0.090

^a Data collected at r.t. ^b $R = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$. ^c $R_w = [\Sigma_w(|F_0| - |F_c|)]^2 / \Sigma_w F_0^2]^{1/2}$.

checked by measuring three standards (1 5 9, 1 $\bar{7}$ $\bar{3}$, 3 5 $\bar{7}$) every 300 reflections. Data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied using azimuthal (ψ) scans of 5 reflections at high χ angles and increasing θ values: 5 0 $\bar{2}$, 7 0 $\bar{2}$, 8 0 $\bar{2}$, 10 0 $\bar{4}$, 14 0 $\bar{4}$; transmission factors were in the range 0.97–0.99; calculations were performed using the data reduction programs of the CAD4-SDP package [22]. Reduced data were considered as observed if $F_0 \geq 2.5\sigma(F_0)$ while an $F_0 = 0.0$ was given to those reflections having negative net intensities.

The structure was solved by a combined use of Patterson and Fourier methods and refined by block-diagonal least-squares using anisotropic temperature factors for all atoms except the phosphine-carbon atoms, which were treated as isotropic. The real part of the anomalous dispersion was taken into account [23], and scattering factors were taken from Ref. 23. A Cruickshank weighting scheme [24] was used throughout the refinement. Upon convergence a Fourier difference map showed the presence of a highly disordered THF molecule. The refinement of the THF parameters gave unsatisfactory results, so only the contribution of the four

Table 7. Final atomic coordinates for **3b**·THF

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Rh(1)	0.26326(9)	0.07117(8)	0.32025(7)
I	0.24935(9)	0.20931(8)	0.23797(7)
P(1)	0.41505(32)	0.06986(30)	0.30598(25)
P(2)	0.11312(33)	0.05084(28)	0.29537(27)
N(1)	0.26071(92)	0.12732(85)	0.42301(74)
N(2)	0.25888(88)	-0.01026(84)	0.45458(73)
N(3)	0.20748(140)	-0.30875(93)	0.44156(103)
O(1)	0.20473(210)	-0.37690(103)	0.42588(129)
O(2)	0.19246(155)	-0.28692(115)	0.50054(94)
C(2)	0.25419(113)	0.07011(97)	0.47349(84)
C(3)	0.24075(128)	0.08958(113)	0.54639(96)
C(4)	0.23655(133)	0.16742(137)	0.56575(108)
C(5)	0.24380(133)	0.23003(131)	0.51285(118)
C(6)	0.25758(132)	0.20464(118)	0.44240(104)
C(1')	0.26651(117)	-0.10843(101)	0.36552(91)
C(6')	0.29240(125)	-0.13324(114)	0.29600(96)
C(5')	0.29070(144)	-0.21607(124)	0.27662(108)
C(4')	0.26081(152)	-0.27204(142)	0.32263(122)
C(3')	0.23514(127)	-0.24724(117)	0.39192(106)
C(2')	0.23995(122)	-0.16716(119)	0.41426(103)
C(7')	0.26404(100)	-0.02381(95)	0.38387(81)
C(15)	0.22731(155)	0.02683(148)	0.60043(108)
C(1)P(1)	0.48670(119)	0.14706(112)	0.34945(97)
C(2)P(1)	0.45292(140)	0.22611(132)	0.35893(114)
C(3)P(1)	0.51141(151)	0.28325(140)	0.39118(122)
C(4)P(1)	0.59392(158)	0.26734(149)	0.41589(128)
C(5)P(1)	0.62373(167)	0.18765(155)	0.40732(136)
C(6)P(1)	0.57360(149)	0.12443(136)	0.37572(120)
C(7)P(1)	0.44468(116)	0.07956(107)	0.21219(94)
C(8)P(1)	0.38984(162)	0.04156(152)	0.15750(131)
C(9)P(1)	0.41226(169)	0.04492(158)	0.08657(139)
C(10)P(1)	0.48959(171)	0.08863(161)	0.06984(142)
C(11)P(1)	0.53804(167)	0.12295(157)	0.11768(135)
C(12)P(1)	0.51919(159)	0.11896(149)	0.19234(128)
C(13)P(1)	0.46614(123)	-0.02312(116)	0.33534(99)
C(14)P(1)	0.46840(128)	-0.04246(120)	0.40669(103)
C(15)P(1)	0.50679(152)	-0.11537(145)	0.43318(127)
C(16)P(1)	0.54378(177)	-0.16899(168)	0.38023(141)
C(17)P(1)	0.54574(162)	-0.15092(153)	0.31007(128)
C(18)P(1)	0.50895(142)	-0.07599(132)	0.28643(115)
C(1)P(2)	0.03094(123)	0.12636(116)	0.32120(100)
C(2)P(2)	-0.06129(158)	0.10652(152)	0.31131(129)
C(3)P(2)	-0.12356(162)	0.16462(155)	0.33269(131)
C(4)P(2)	-0.09813(168)	0.23089(158)	0.36267(138)
C(5)P(2)	-0.01091(157)	0.25475(150)	0.37453(126)
C(6)P(2)	0.06084(139)	0.19888(127)	0.35203(111)
C(7)P(2)	0.09601(127)	0.04096(118)	0.19780(102)
C(8)P(2)	0.04391(144)	0.09610(136)	0.16159(117)
C(9)P(2)	0.03971(167)	0.08641(156)	0.08260(136)
C(10)P(2)	0.09121(182)	0.03001(171)	0.05335(149)
C(11)P(2)	0.13759(172)	-0.02375(161)	0.09111(140)
C(12)P(2)	0.13881(145)	-0.02098(137)	0.16464(119)
C(13)P(2)	0.06430(125)	-0.03884(116)	0.33446(102)
C(14)P(2)	0.05543(127)	-0.04104(120)	0.40721(104)
C(15)P(2)	0.01724(151)	-0.10737(142)	0.43897(124)
C(16)P(2)	-0.01144(162)	-0.17125(154)	0.39863(131)
C(17)P(2)	-0.00475(178)	-0.17201(170)	0.32879(143)
C(18)P(2)	0.03412(134)	-0.10148(127)	0.29281(109)

highest peaks in the Fourier difference was retained (interatomic distances in the range 1.3–1.8 Å) and included in the calculations together with the contribution of the hydrogen atoms fixed in their idealized positions (C–H 0.95 Å) but not refined. Final atomic coordinates are listed in Table 7. An extended list of bond lengths and angles, a list of thermal parameters and a table of values of F_{obs} and F_{calc} may be obtained from the authors.

Acknowledgements

We thank the Swiss National Science Foundation for support for C.A., and the Johnson Matthey Research Centre, England, for the loan of RhCl_3 .

References

- 1 A. Albinati, C.G. Anklin, G. Ganazzoli, H. Rüegg and P.S. Pregosin, *Inorg. Chem.*, 26 (1987) 503; C.G. Anklin and P.S. Pregosin, *J. Organomet. Chem.*, 243 (1983) 101 and references therein.
- 2 A. Albinati, C. Arz and P.S. Pregosin, *Inorg. Chem.*, 26 (1987) 508.
- 3 J.W. Suggs, *J. Am. Chem. Soc.*, 101 (1979) 489; J.W. Suggs, *J. Am. Chem. Soc.*, 100 (1978) 640.
- 4 J.D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole, California 1985.
- 5 G.K. Anderson and R.J. Cross, *Acc. Chem. Res.*, 17 (1984) 67.
- 6 J.F. van Baar, K. Vrieze and D.J. Stufkens, *J. Organomet. Chem.*, 97 (1979) 461; *ibid.*, 85 (1975) 249; J.F. van Baar, J.M. Klerks, P. Overbosch, D.J. Stufkens and K. Vrieze, *J. Organomet. Chem.*, 112 (1976) 95.
- 7 R.J. Foot and B.T. Heaton, *J. Chem. Soc., Dalton Trans.*, (1979) 295.
- 8 (a) M. Nonoyama, *Bull. Chem. Soc. Jpn.*, 47 (1974) 767; (b) see also I. Omae, *Chem. Revs.*, 79 (1979) 287 and references therein.
- 9 J. Dehand and M. Pfeffer, *Coord. Chem. Revs.*, 18 (1976) 327.
- 10 P.S. Pregosin and R.W. Kunz, *NMR Basic Principles and Progress*, Springer Verlag, Berlin, 1979, Vol. 16.
- 11 J. Telser and R.S. Drago, *Inorg. Chem.*, 25 (1986) 2989.
- 12 S.J. Thompson, C. White and P.M. Maitlis, *J. Organomet. Chem.*, 136 (1977) 87.
- 13 T.J. Bitterwolf, *Inorg. Chim. Acta*, 122 (1986) L5.
- 14 C. Arz, P.S. Pregosin and C. Anklin, *Magn. Res. Chem.*, 25 (1987) 158.
- 15 B.E. Mann and B.F. Taylor, *¹³C NMR Data for Organometallic Compounds* Academic Press, London, 1981.
- 16 P.E. Garrou, *Chem. Rev.*, 81 (1981) 229.
- 17 M. Kretschmer, P.S. Pregosin, A. Albinati and A. Togni, *J. Organomet. Chem.*, 281 (1985) 365; A. Albinati, H. Lehner and L.M. Venanzi, *Inorg. Chem.*, 24 (1985) 1483; H. Lehner, D. Matt, A. Togni, R. Thouvenot, L.M. Venanzi and A. Albinati, *Inorg. Chem.*, 23 (1984) 4254.
- 18 S. Quin, A. Shaver and V.W. Day, *J. Amer. Chem. Soc.*, 104 (1982) 1096.
- 19 A.R. Siedle, R.A. Newmark and L.H. Pignolet, *Organometallics*, 3 (1984) 855.
- 20 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1960.
- 21 A. Albinati, C. Arz and P.S. Pregosin, *Inorg. Chim. Acta*, 128 (1987) L5.
- 22 Enraf-Nonius Structure Determination Package, SDP; Enraf-Nonius, Delft (1980).
- 23 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham (1974) vol. IV.
- 24 D.W.J. Cruickshank in A. Ahmed (Ed.), *Computing Methods in Crystallography* Munksgaard, Copenhagen, 1972.