Iminophosphorane complexes of rhodium(I) and X-ray crystal structure of [Rh(COD)Cl(Et_3P=N-*p*-tolyl)]

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Abstract

New rhodium(I)–iminophosphorane complexes [$RhL_2Cl(R_3P{=}NR')$], in which the iminophosphorane ligand is coordinating as a two electron donor, have been prepared by bridge splitting reactions in benzene or chloroform between $[RhL_2Cl]_2$ (L = CO, L_2 = COD) and the parent iminophosphoranes $R_3P{=}NR'$ (**1**). In solution an equilibrium is established between the product [$RhL_2Cl(R_3P{=}NR')$] and its constituting compounds. This equilibrium lies completely to the product side for L = CO, whereas for L_2 = COD it is dependent on the substituents on N and P, the temperature and the molar ratio Rh:$R_3P{=}NR'$. The molecular structure of [Rh(COD)Cl(Et_3P=N-*p*-tolyl)] (**3a**) has been determined by means of X-ray crystallography. Complex **3a** crystallizes in space group $P2_1/a$ with $a = 23.134(4)$, $b = 10.946(2)$, $c = 8.686(2)$ Å and $\beta = 90.12(2)°$, and the structure was refined to $R = 0.036$ by using 6363 independent reflections. The structure of **3a** consists of a square planar rhodium complex in which the iminophosphorane is coordinated via the lone pair on nitrogen. Important dimensions are d(Rh–N) = 2.142(3) Å, d(N–P) = 1.608(3) Å and ∠(Rh–N–P) = 121.0°.

Introduction

The coordination properties of iminophosphoranes (general structure A, B) have received ample attention during the last decades. In several studies it was shown that these compounds can act as one, two or four electron donors [1]. Iminophosphoranes of type B usually coordinate as two electron donors to the metal atom through the free electron pair on nitrogen. Examples include complexes with main group metals [2] and both early and late transition metals [3–5]. Only in one case an iminophosphorane of type B has been shown to act as a four electron donor, i.e. in $Mo_2(CO)_6(HN{=}PPh_3)_3$ each P=N ligand bridges via N between the two Mo atoms [6].

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There is a current interest in rhodium(I) complexes containing (chelating) iminophosphorane ligands [5d,g,h,7,8]. As we have been particularly interested in the organometallic chemistry of late transition metals such as Rh and Ir involving the new bidentate $[R'N{=}PPh_2CH_2]^-$ and terdentate $[(R'N{=}PPh_2)_2CH]^-$ anions [8], it was deemed of interest to try to obtain insight into the coordination properties and behaviour of the parent iminophosphoranes $R_3P{=}NR'$ towards Rh complexes. We have chosen the dimeric complexes $[RhL_2Cl]_2$ (L = CO, L_2 = COD) as the starting Rh compounds because these have been shown to be good starting materials for studies of the coordination behaviour of several monodentate ligands [9] and for the sake of obtaining compounds and data comparable to those in the series containing the anionic ligands [8].

It is known that ligands which are predominant σ-donors, such as amines [10] and phosphinesulfides [11], give exclusively complexes of the type $[RhL_2ClL']$, whereas with ligands having both σ-donating and π-accepting properties (phosphines,

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arsines, isonitriles) also other complexes may be formed, e.g. $[RhL_2L'_2]Cl$, $[RhLL'_2Cl]$, $[RhLL'Cl]_2$ or $[RhL'_4]Cl$ [12–14]. In this paper it will be shown that $[RhL_2Cl]_2$ reacts with several iminophosphoranes with different substituents on nitrogen and phosphorus to give complexes of the type $[RhL_2Cl(R_3P{=}NR')]$ exclusively, in equilibrium with its constituting compounds. The influence of several reaction parameters on this equilibrium is discussed. Furthermore, the molecular structure of [Rh(COD)Cl(Et_3P=N-*p*-tolyl)] as obtained from an X-ray crystal structure determination will be reported.

Experimental

All reactions were performed in an atmosphere of purified nitrogen. The solvents were carefully dried and distilled prior to use, unless stated otherwise. $[Rh(COD)Cl]_2$ [15a] and $[Rh(CO)_2Cl]_2$ [15b] were synthesized using literature procedures. The iminophosphoranes **1a–1i**, **1k** and **1m** were synthesized from the appropriate phosphines and arylazides using the Staudinger reaction [16], whereas Ph_3P=N-t-Bu (**1j**) was synthesized from Ph_3P and t-$BuNH_2$ [17] and Ph_3P=NH (**1l**) from Ph_3P=N-$SiMe_3$ (**1k**) and iPrOH [18]. The numbering of all compounds is shown in eqn. (1). ^1H and ^{31}P NMR spectra were obtained on a Bruker AC100 spectrometer. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Field desorption (FD) mass spectra were obtained on a Varian MAT-711 spectrometer, and were performed by the Institute for Mass Spectroscopy of the University of Amsterdam. Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, ITC/TNO, Zeist, The Netherlands.

*Synthesis of $[Rh(CO)_2Cl(R_3P{=}NR')]$ (**2a–m**)*

To 235 mg of $[Rh(CO)_2Cl]_2$ (0.60 mmol) in 8 ml benzene at room temperature was added exactly 2.0 equivalents of the iminophosphorane ligand **1a–m** in 12 ml benzene. The solution was stirred until complete conversion was achieved (as evidenced by IR spectroscopy). Then the solvent was removed *in vacuo* and the residue was washed with hexane or pentane, and dried *in vacuo*, giving **2a–m** in 60–90% yield.

FD mass: Found (calc.): **2a**: 416(416.678); **2d**: 499 (499.739); **2e**: 561 (561.810); **2f**: 577 (577.809); **2i**: 398 (=L: M=398.402); **2k**: 543 (543.868); **2l**: 471 (471.685); **2m**: 399.736.

Anal. for **2d**: Found: C, 52.78; H, 4.07; N, 2.77; P, 6.87. Calc.: C, 52.88; H, 4.03; N, 2.80; P, 6.20%. **2i**: Found: C, 51.97; H, 3.38; N, 4.56; O, 9.99. Calc.: C, 52.68; H, 3.23; N, 4.73; O, 10.80%.

*Reaction of $[Rh(COD)Cl]_2$ with $R_3P{=}NR'$ (**1a–m**)*

About 10 mg of $[Rh(COD)Cl]_2$ was mixed with exactly 2 molar equivalents of the ligand $R_3P{=}NR'$ (**1a–m**). Subsequently the mixture was dissolved in *c.* 0.4 ml $CDCl_3$. ^1H and ^{31}P NMR spectra of this solution were recorded at 295, 213, 233, 253, 273 and 295 K. The measurements were stopped when at 295 K (first measurement) equilibrium (1) was shifted to the right (>98% of [Rh(COD)Cl-($R_3P{=}NR'$)] in the ^1H NMR spectrum) or at 213 K to the left. Reactant to product ratios (Rh(COD)Cl:Rh(COD)Cl($R_3P{=}NR'$)) were determined by integration of the olefinic COD proton signals in the ^1H NMR spectra (see Table 2). When similar reactions are performed in a benzene-d_6 solution the reactant to product ratios are of the same order of magnitude as found for $CDCl_3$ solution.

Experiments with other Rh:$R_3P{=}NR'$ ratios were performed in a similar way as described for the 1:1 reaction with the ligands **1a**, **1e** and **1i**.

*Synthesis of $[Rh(COD)Cl(R_3P{=}NR')]$ (**3a–e, 3l**)*

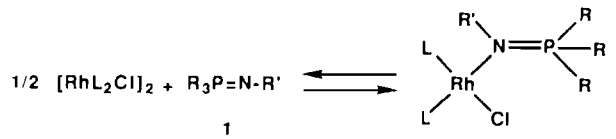
In a typical experiment 0.608 mmol $R_3P{=}NR'$ in 6 ml C_6H_6 or CH_2Cl_2 was added to 150 mg $[Rh(COD)Cl]_2$ (0.304 mmol) in 4 ml C_6H_6 or CH_2Cl_2 at room temperature. After stirring for 1 h the solvent was evaporated *in vacuo*. Compounds **3a–d** and **3l** could be isolated in *c.* 90% yield by washing the residue with Et_2O and pentane and drying *in vacuo*. Compound **3e** was isolated by dissolving a mixture of 150 mg $[Rh(COD)Cl]_2$ (0.304 mmol) and 445 mg **1e** (1.212 mmol) in 10 ml CH_2Cl_2 and cooling the solution to 253 K. Subsequent filtration of the precipitate and washing with pentane gave **3e** in 55% yield. Orange crystals of **3a**, suitable for crystal structure determination, were obtained by slow diffusion of pentane into a solution of **3a** in CH_2Cl_2 at room temperature.

FD mass: Found (calc.): **3a**: 223 (=$C_{13}H_{22}NP$, **1a**), 469 (469.842); **3b**: 181 (=$C_{10}H_{16}NP$, **1b**), 427 (427.761); **3c**: 243 (=$C_{15}H_{18}NP$, **1c**), 492 (=$[Rh(COD)Cl]_2$); **3d**: 305 (=$C_{20}H_{20}NP$, **1d**), 492 (=$[Rh(COD)Cl]_2$); **3e**: 367 (=$C_{25}H_{22}NP$, **1e**), 492 (=$[Rh(COD)Cl]_2$); **3l**: 277 (=$C_{18}H_{16}NP$, **1l**), 523 (523.849).

Anal. for **3a**: Found: C, 53.56; H, 7.47; N, 3.09; P, 6.60. Calc.: C, 53.68; H, 7.29; N, 2.98; P, 6.59%. **3e**: Found: C, 63.76; H, 5.73; N, 2.43; P, 4.77. Calc.: C, 64.56; H, 5.58; N, 2.28; P, 5.04%.

*Synthesis of $[Rh(COD)Cl(R_3P{=}NH)]$ (**3l**, **3n**)*

A mixture of 144 mg $[Rh(COD)Cl]_2$ (0.29 mmol) and 0.58 mmol $R_3P{=}N{-}SiMe_3$ (**1k**, **1m**) (Rh:$R_3P{=}NR'$ = 1:1) was dissolved in commercial $CHCl_3$. After stirring for 1 day (**3l**) or 13 days (**3m**)



(1)

Compound	a	b	c	d	e	f	g
R_3	Et_3	Me_3	Me_2Ph	$MePh_2$	PPh_3	Ph_3	Ph_3
R'	C_6H_4-CH_3-4	C_6H_4-CH_3-4	C_6H_4-CH_3-4	C_6H_4-CH_3-4	C_6H_4-CH_3-4	C_6H_4-OCH_3-4	C_6H_5
	h	**i**	**j**	**k**	**l**	**m**	**n**
R_3	Ph_3	Ph_3	Ph_3	Ph_3	Ph_3	Et_3	Et_3
R'	C_6H_4-Cl-4	C_6H_4-NO_3-4	t-Bu	$SiMe_3$	H	$SiMe_3$	H

the solvent was removed *in vacuo*. The residue was washed with Et_2O (2×) and pentane, and dried *in vacuo* giving **3l** or **3n** in 91 and 97% yield, respectively.

FD mass: Found (calc.): **3l**: 277 (=$C_{18}H_{16}NP$, **1l**), 492 (=[Rh(COD)Cl]$_2$), 523 (523.849); **3n**: 379 (379.717), 492 (=[Rh(COD)Cl]$_2$).

X-ray Structure Determination of [Rh(COD)Cl(Et$_3$P=N-p-tolyl)] (3a)

A crystal with approximate dimensions 0.18×0.18×0.25 mm was used for the crystal structure determination of **3a**. The crystal was monoclinic, space group $P2_1/a$. The unit cell had the dimensions $a=23.134(4), b=10.946(2), c=8.686(2)$ Å, $\beta=90.12°$, $V=2200(2)$ Å^3, $Z=4$, $D_{calc}=1.42$ g cm^{-3}. A total of 6363 reflections was measured within the range $-32\leqslant h\leqslant 32$, $0\leqslant k\leqslant 15$, $0\leqslant l\leqslant 12$ ($1.1\leqslant\theta\leqslant 30°$) on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda=$ 0.7107 Å). Of these, 2326 reflections were below the $2.5\sigma(I)$ level and were treated as unobserved.

The structure was solved by means of the heavy atom method, Rh and Cl having been determined from an E^2-Patterson synthesis. Refinement proceeded through block-diagonal least-squares calculations, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, which were located in a ΔF synthesis. Unit weights were employed. An empirical absorption correction (DIFABS) [19] was applied and the anomalous dispersion of Rh, Cl and P was taken into account. The final R value for the 4037 observed reflections was 0.036. The programs used were from XRAY76 [20] and the scattering factors were taken from Cromer and Mann [21].

Results

Synthesis of [RhL$_2$Cl(R$_3$P=NR')]

The iminophosphoranes R$_3$P=NR' (**1a–m**) react with the dimeric rhodium(I) complexes [Rh(COD)Cl]$_2$ and [Rh(CO)$_2$Cl]$_2$ in a bridge splitting reaction (eqn. (1)). According to ^{1}H and ^{31}P NMR an equilibrium exists between the coordination compound [RhL$_2$Cl(R$_3$P=NR')] (L=CO, L$_2$= COD) and the reactants, the position of which is dependent on the coligands L, the substituents on both P and N, the molar ratio of the reactants and the reaction temperature, as will be elaborated below.

For L=CO and a molar ratio R$_3$P=NR':Rh = 1:1 the equilibrium shown in eqn. (1) lies completely to the right at room temperature and the complexes **2a–m** can be isolated in pure form. When the reaction was performed in benzene these compounds could be obtained in good yield, whereas in chlorinated solvents ($CHCl_3$, CH_2Cl_2) extensive decomposition took place, as evidenced by an immediate blackening (Rh(0)) of the reaction mixture upon addition of the ligand to [Rh(CO)$_2$Cl]$_2$. The isolated, orange or yellow compounds **2a–m** are thermally stable for several months when stored under a nitrogen atmosphere, whereas in solution slow decomposition is observed*. Selected spectroscopic data for complexes **2a–m** (^{31}P NMR and IR) are given in Table 1.

The reaction between [Rh(COD)Cl]$_2$ and **1a–m** to give the complexes [Rh(COD)Cl(R$_3$P=NR')] (**3a–m**) was followed by means of ^{1}H and ^{31}P NMR. It was shown that for L$_2$=COD the equilibrium in eqn. (1) is strongly dependent on the substituents on P and N, and the temperature (Table 2). Whereas all complexes of general formula [Rh(CO)$_2$Cl-(R$_3$P=NR')] could readily be obtained as isolable compounds, the COD complexes could only be isolated in a few cases, at room temperature (**3a–d**, **3l**) or at 253 K (**2e**). Complexes **3l** and **3n** (R'=H)

*The stability decreases with an increasing number of alkyl substituents on phosphorus; e.g. for **2b** *c.* 10% decomposition is observed after 24 h, whereas for **2e** no decomposition is observed after 1 week in CH_2Cl_2.

TABLE 1. Selected ^{31}P NMR and IR data of the complexes $[Rh(CO)_2Cl(R_3P{=}NR')]$ (**2a–m**)

Compound no.	R_3	R′	^{31}P NMR[a] $\delta(P)$	IR		
				$\nu(P{-}N)$[b]	$\nu(CO)$[b]	$\nu(CO)$[c]
2a	Et_3	C_6H_4-CH_3-4	51.2	1237	2068; 1994	2075; 1996
2b	Me_3	C_6H_4-CH_3-4	35.9	[d]	[d]	2076; 1998
2c	$PhMe_2$	C_6H_4-CH_3-4	31.8	[d]	[d]	2075; 1996
2d	Ph_2Me	C_6H_4-CH_3-4	29.8	1261	2065; 1995	2075; 1999
2e	Ph_3	C_6H_4-CH_3-4	29.8(4.1)[e]	1245	2065; 1991	2073; 1995
2f	Ph_3	C_6H_4-OCH_3-4	29.5	1230	2066; 1993	2074; 1996
2g	Ph_3	Ph	29.1(4.8)	1242	2072; 1995	2073; 1991
2h	Ph_3	C_6H_4-Cl-4	29.7	1240	2072; 1982	2075; 1995
2i	Ph_3	C_6H_4-NO_2-4	30.9	1262	2074; 1993	2078; 2000
2j	Ph_3	t-Bu	31.1	1191	2061; 1986	2071; 1993
2k	Ph_3	$SiMe_3$	30.8[f]	1117	2059; 1990	2071; 1995
2l	Ph_3	H	37.8[f]	[d]	[d]	2072; 1995
2m	Et_3	$SiMe_3$	50.3	1119	2070; 1999	2073; 1995

[a]Measured at 40.5 MHz in $CDCl_3$ at room temperature; chemical shift values in ppm relative to 85% H_3PO_4; $^2J(Rh,P)$ in Hz in parentheses. [b]KBr pellet. [c]CH_2Cl_2. [d]Not determined. [e]Solvent CD_2Cl_2. [f]Solvent C_6D_6.

TABLE 2. Ratios of compounds **1**:**3** according to eqn. (1) starting from a 1:2 molar ratio of dimer $[Rh(COD)Cl]_2$ and $R_3P{=}NR'$ (**1**); selected ^1H[a], ^{31}P NMR[b] and IR[c] data for the complexes $[Rh(COD)Cl(R_3P{=}NR')]$ (**3a–n**)

Compound no.	R_3	R′	T (K)	Rh:RhL[d]	^1H NMR $\delta(=CH)$	^{31}P NMR $\delta(P)$[f]	IR $\nu(P{-}N)$
3a	Et_3	C_6H_4-CH_3-4	295	0:1	4.24; 3.40	47.3	1246
3b	Me_3	C_6H_4-CH_3-4[g]	295	0:1	4.73; 3.61	29.7	1258
3c	$PhMe_2$	C_6H_4-CH_3-4	295	1:3	4.36; 3.59	28.6	1238
3d	Ph_2Me	C_6H_4-CH_3-4	213	1:9.6	4.47; 3.60	27.4(3.4)	1261
			295	1:1.1	4.46; 3.59	26.4(3.0)	
3e	Ph_3	C_6H_4-CH_3-4	213	1:3.3	4.10; 3.49	22.9	1245
			295	1:0.3	[h]; 3.53	23.6	
3f	Ph_3	C_6H_4-OCH_3-4	233	1:3.9	4.10; 3.46	22.9	[i]
			295	1:0.2	[h]; 3.45	23.8	
3g	Ph_3	Ph	213	1:3.8	4.17; 3.44	23.3(2.9)	[i]
			273	1:0.3	[h]; 3.50	23.8	
3h	Ph_3	C_6H_4-Cl-4	213	1:2.6	4.20; 3.44	24.1(2.3)	[i]
			273	1:0.2	[h]; 3.46	24.6(3.9)	
3i	Ph_3	C_6H_4-NO_2-4	213	1:0.2	[h]; 3.53	26.9(2.3)	[i]
			295	1:0			
3j	Ph_3	t-Bu	233	1:0.3	4.10; 3.80	31.2	[i]
			295	1:0			
3k	Ph_3	$SiMe_3$	213	1:0			
3l	Ph_3	H	295	0:1	4.28; 3.37	33.4(4.4)	1108
3m	Et_3	$SiMe_3$[g]	295	1:0			
3n	Et_3	H	295	0:1	4.10; 3.51	57.2	1047

[a]Recorded at 100.16 MHz in $CDCl_3$; chemical shift values in ppm relative to TMS. [b]Recorded at 40.5 MHz in $CDCl_3$; chemical shift values in ppm relative to 85% H_3PO_4; coupling constants in Hz. [c]KBr pellet, wave numbers in cm^{-1}. [d]Determined from the relative area of the olefinic COD signals of $[Rh(COD)Cl]_2$(=Rh) and $[Rh(COD)Cl(R_3P{=}NR')]$(=RhL) in the ^1H NMR spectra. Experimental error <5%; for **3e**, **3f**, **3j** and **3n** the error is estimated to be 5–10% due to overlap of the product signal with the $[Rh(COD)Cl]_2$ olefinic signal at 4.10 ppm. [e]Broad signals. $^2J(Rh,P)$ in parentheses. [g]Solvent C_6D_6. [h]Obscured by olefinic signal of $[Rh(COD)Cl]_2$. [i]Not measured.

could be obtained from the reaction of $[Rh(COD)Cl]_2$ with the *N*-trimethylsilyl substituted iminophosphoranes **1k** and **1m**, respectively, via hydrolysis of the N–Si bond using unpurified commercial chloroform as the solvent.

The isolated complexes **3** are thermally stable at room temperature in moist air for several months. However, complex **3b** (R=Me, R′=*p*-tolyl) decomposes into unidentified products both in the solid state (complete decomposition within 1 week under

a nitrogen atmosphere at room temperature) and in solution (complete decomposition in 2 h in C_6D_6 at room temperature).

Spectroscopic data of [$RhL_2Cl(R_3P{=}NR')$]

In the ^1H NMR spectra of the reaction mixture containing compounds **3** (Table 2) two signals are observed for the olefinic COD protons, in agreement with a structure with C_s symmetry. In the spectra a broad signal is also observed for the olefinic COD protons of $[Rh(COD)Cl]_2$ at 4.1 ppm in $CDCl_3$. This fact and the observation that the ^1H NMR signals are slightly broadened indicate that exchange reactions between $[Rh(COD)Cl]_2$, the iminophosphorane **1** and complex **3** occur. In the ^{31}P NMR spectra one signal is found for complexes **2** or **3**, which shows no or only a small coupling with the ^{103}Rh nucleus (Tables 1 and 2, respectively). Upon coordination of the iminophosphoranes **1** to Rh(I) a high frequency shift of *c.* 25 ppm for complexes **2** and *c.* 20 ppm for **3** is observed. Only for **1j** (R = Ph, R' = t-Bu) and **1l** (R = Ph, R' = H) much higher (*c.* 41 ppm) and lower (*c.* 10 ppm) coordination shifts, respectively, towards high frequency are found. All shift values fall within the range usually found for coordination complexes of iminophosphoranes [5f,h,7,22] and the observed high frequency shift as compared to the parent iminophosphoranes must be attributed to a shift of electron density from the phosphorus atom to the metal centre.

In the IR spectra (KBr pellets) of the isolated complexes (Tables 1 and 2) a large band is observed in the region 1050–1260 cm^{-1} that can be attributed to ν(P=N), i.e. a shift of 50–150 cm^{-1} to lower wavenumber is observed upon coordination of the iminophosphorane to Rh. These values correspond well to those found for other complexes containing iminophosphorane ligands and are in agreement with a structure in which the ligand acts as a two electron donor [1b, 3–5]. The observation of two strong bands in the carbonyl region of the IR spectra of compounds **2** confirms their C_s symmetry.

The results obtained in the reaction of $[Rh(COD)Cl]_2$ with **1a–m** clearly indicate that the coordination capacity of iminophosphoranes depends on the character of its substituents on both P and N. Clearly, the affinity of iminophosphoranes towards Rh(I) is enhanced by substituting the aryl groups on P by alkyl substituents; i.e **1a/b > 1c > 1d > 1e**. Upon changing the substituent on nitrogen, both electronic and steric factors appear to affect the coordination capacity of iminophosphoranes. Increasing the donor capacity of N, e.g. **1f > 1e ≈ 1g > 1h > 1i**, shifts eqn. (1) to the right hand side*. Iminophosphoranes with bulky substituents such as t-Bu (**1j**) or $SiMe_3$ (**1k**, **1m**) on nitrogen show, due to their steric bulk, a much lower affinity towards Rh(I) than for example **1l** (R' = H) or **1e** (R' = *p*-tolyl), hence the equilibrium in eqn. (1) is shifted towards the left.

When the reactions of $[RhL_2Cl]_2$ with **1h**, **1j** or **1k** are performed with a molar ratio $R_3P{=}NR'$:Rh higher than 1:1 no other reactions or products than those depicted in eqn. (1) are found. It is known that reactions, e.g. disproportionation or substitution reactions, occur for other monodentate ligands (*vide supra*), but in the IR as well as in the ^1H and ^{31}P NMR spectra of the present reaction mixtures only sharp signals that can be attributed to $[RhL_2Cl]_2$, **1** and **2** or **3** are found. Hence, contrary to what has been observed for, e.g. phosphines [12, 13b] or phosphinesulfides [11], these Rh–iminophosphorane complexes do not undergo exchange reactions with free iminophosphorane ligand on the NMR timescale.

*Solid state structure of [Rh(COD)Cl($Et_3P{=}N$-p-tolyl)] (**3a**)*

The structure of **3a** has been determined in order to obtain accurate geometric parameters for one of our new Rh(I)–iminophosphorane complexes, which is particularly useful for comparison of, for example, bond distances in organometallic complexes containing the $[R'N{=}PPh_2CH_2^-]$ and $[(R'N{=}PPh_2)_2CH^-]$ ligands [8].

The structure of **3a** and the adopted numbering scheme are given in Fig. 1. Selected bond distances and angles involving the non-hydrogen atoms in **3a** are listed in Table 3. The molecular structure of **3a** consists of the neutral [Rh(COD)Cl($Et_3P{=}N$-*p*-tolyl)] entity in which the rhodium is surrounded by the chloride atom, the two olefinic bonds of the cyclooctadiene ligand (with M1 and M2 being the midpoints of C1–C2 and C5–C6 respectively) and the nitrogen atom of the iminophosphorane ligand. The coordination geometry around the rhodium atom is square planar, all distortions from the least-squares plane defined by Rh, M1, M2, N and Cl being less than 0.025 Å.

The *p*-tolyl-imino-triethylphosphorane ligand is coordinated as a two electron donor via the lone pair on nitrogen. This is demonstrated by the angles

*Although a higher product to reactant ratio is observed for **1g** than for **1e** in contrast with what would be expected on the basis of their donor capacity, the values are the same within the experimental error for this particular complex. The expected value of the [Rh(COD)Cl]: [Rh(COD)Cl($R_3P{=}NR'$)] ratio is 1:3.8 (for **1e**) based on the known donor capacity of **1e** [27b].

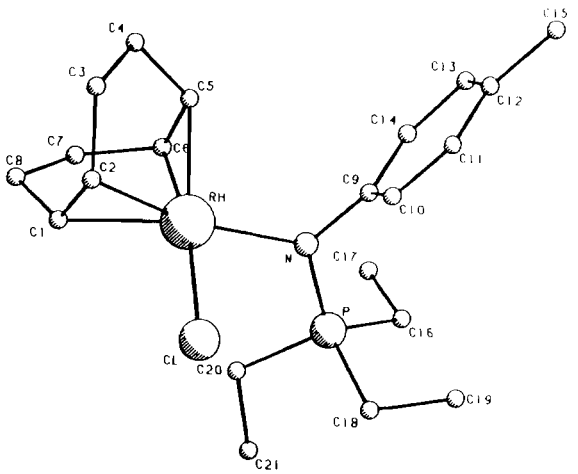


Fig. 1. Pluto drawing and adopted numbering scheme for the non-hydrogen atoms of [Rh(COD)Cl(Et_3P=N-*p*-tolyl)] (**3a**).

around nitrogen, which are between 115.6 and 121.0°, showing sp^2 hybridization of the nitrogen atom, and the P–N bond distance of 1.608(3) Å. This distance is indicative of a bond order higher than one for the P–N bond, with π_p–π_d interaction between nitrogen and phosphorus, and falls within the range found for other complexes with iminophosphoranes of type A or B, e.g. 1.64(2) Å in $[Ir(NO)(HNC_8H_{14}N{=}PPh_3)(PPh_3)]^+$ [5f], 1.57–1.63(3) Å in $Mo_2(CO)_6(HNPPh_3)_3$ [6], 1.57(1) Å in $[CdI_2(HN{=}PPh_3)_2]_2$ [5c], 1.630(8) Å in $ReCl_3(NO)(N{=}PPh_3)(O{=}PPh_3)$ [23] or 1.571(5) Å in $RuCl_3(NPEt_2Ph)(PEt_2Ph)$ [24]. The Rh–N bond distance of 2.142(3) Å and the Rh–Cl distance of 2.388(1) Å are normal values for this type of rhodium(I) compounds [8a, 25, 26].

The COD ligand is coordinated in its standard boat conformation. There is no significant difference between the two olefinic bonds (1.395(6) and 1.394(6) Å), and also the distances between Rh and the midpoints of the olefinic bonds (2.013(6) Å (*trans* to Cl) and 1.986(7) Å (*trans* to N)) are equal within experimental error.

Discussion

The formation of only one single product of the type $[RhL_2Cl(R_3P{=}NR')]$ in the reaction of $[RhL_2Cl]_2$ with **1** clearly demonstrates the predominant σ-donor character of iminophosphoranes, exhibiting only minor π-acceptor properties [10–14]. This is in line with MO calculations and experiments in which it was shown that the HOMO of iminophosphoranes is mainly located on the nitrogen atom [3d, 27]. The HOMO is strongly influenced by the introduction of electron-accepting or -donating substituents on P and N. Substituting an alkyl group by a phenyl group on phosphorus delocalizes the HOMO, thereby lowering the σ-donating capacity of the iminophosphorane. Also the introduction of π-accepting substituents on the N-aryl group (e.g. NO_2) diminishes the σ-donating capacity by stabilization of resonance structures D or E [27b]. On the other hand, electron donating R″ groups (OCH_3, CH_3) destabilize the HOMO of the iminophosphoranes, and resonance structure B or C will be most favourable.

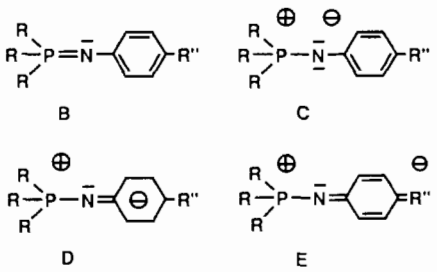
The electronic influences explain the dependence of the coordinating ability of iminophosphoranes towards Rh(I) as a function of the substituents on P and N as measured for the reactions of **1a–1n** with $[Rh(COD)Cl]_2$, i.e. for R = Me, Et or R′ = C_6H_4-OCH_3-4, for instance, the equilibrium in eqn. (1) lies on the right hand side due to the enhanced σ-donating capacity of these iminophosphoranes compared to those with e.g. R = Ph or R′ = C_6H_4Cl.

TABLE 3. Selected interatomic bond distances (Å) and angles (°) of [Rh(COD)Cl(Et_3P=N-C_6H_4-CH_3-4)] (**3a**) with standard deviations in parentheses[a]

Rh–M1	2.013(6)	C1–C2	1.395(6)	P–C16	1.803(4)	C16–C17	1.523(7)
Rh–M2	1.986(7)	C5–C6	1.394(6)	P–C18	1.824(4)	C18–C19	1.506(7)
Rh–Cl	2.388(1)	N–C9	1.425(4)	P–C20	1.797(4)	C20–C21	1.548(7)
Rh–N	2.142(3)	N–P	1.608(3)				

M1–Rh–M2	87.7(3)	Rh–N–C9	115.6(3)	C16–P–C18	105.9(3)
M1–Rh–N	177.7(2)	Rh–N–P	121.0(2)	C16–P–C20	107.8(3)
M1–Rh–Cl	90.8(2)	C9–N–P	119.9(2)	C18–P–C20	106.3(3)
M2–Rh–N	90.2(2)	N–P–C16	112.1(3)	P–C16–C17	114.5(4)
M2–Rh–Cl	178.1(2)	N–P–C18	117.0(2)	P–C18–C19	116.4(4)
N–Rh–Cl	91.3(1)	N–P–C20	107.3(2)	P–C20–C21	114.3(4)

[a]M1 is the midpoint of C1–C2, M2 is the midpoint of C5–C6.



B C D E

Gross variation of the substituent on N, i.e. aryl, H, $SiMe_3$ or t-Bu, affects both the electronic and steric properties of the iminophosphorane ligands. Therefore it is difficult to establish the factors that determine the coordinating capacity of these ligands. From the experiments with $[Rh(COD)Cl]_2$ it is clear that for R′=H this capacity is high, whereas for the bulky t-Bu and $SiMe_3$ groups the coordinating ability is low. The large difference in coordinating ability between **1j** (R′=t-Bu) and **1l** (R′=H) must completely be attributed to steric factors, since the difference in σ-donor capacity between **1j** and **1l** is only small [3d]. As the difference in steric properties between the t-Bu and $SiMe_3$ groups is only minor, the small difference in coordinating capacity between **1k** and **1l** can be attributed to electronic factors; the lowering of the σ-donating capacity of the iminophosphorane ligand **1k** compared to **1l** is most probably caused by π_p–π_d interactions between N and Si in **1k**. This phenomenon is well known to occur in iminophosphoranes [3d].

The uniform low affinity of iminophosphoranes towards $[Rh(COD)Cl]_2$ shows that these ligands are only moderate σ-donors [4e, g]. This is in line with other experiments in which it was shown that the donor/acceptor properties of these compounds lie between those of the related phosphinylides and phosphinesulfides: $R_3P{=}CR'_2 > R_3P{=}NR' > R_3P{=}S$ [3d]. In fact, in the reaction of $[Rh(COD)Cl]_2$ with phosphinesulfides it was found that these ligands were able to induce bridge splitting reactions only when at least two methyl substituents were present on the P atom [11].

The observations that in the reaction of $[Rh(CO)_2Cl]_2$ with the iminophosphoranes **1** the equilibrium (eqn. (1)) lies completely to the right, whereas for $[Rh(COD)Cl]_2$ this equilibrium is shifted to the left for corresponding iminophosphoranes, can be explained by the higher stabilizing effect of the CO ligands on the N to Rh σ-donation in the Rh–iminophosphorane complexes $[RhL_2Cl(R_3P{=}NR')]$, owing to the higher π-backbonding capacity of the CO ligands in **2** as compared to the COD ligand in **3**. The intrinsic coordinating ability of iminophosphoranes is only weak compared to conventional ligands, which is in line with the observations that these ligands can easily be exchanged for other ligands such as phosphines, arsines or bipyridine [5a, d].

The results clearly demonstrate that iminophosphoranes are capable of bridge splitting reactions with $[RhL_2Cl]_2$. In the resulting complexes of the type $[RhL_2Cl(R_2MeP{=}NR')]$, i.e. containing at least one methyl substituent on P, activation of the methyl group by the Rh(I) centre is in principle possible. However, it has been shown [8c] that activation of the methyl group in $[RhL_2Cl(Ph_2MeP{=}N\text{-}p\text{-}tolyl)]$ was not successful, even at elevated temperature or in the presence of bases.

Supplementary material

Tables with all bond distances and angles of **3a**, and with fractional coordinates and thermal parameters of **3a** can be obtained from the authors on request.

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