

Reactions of bis(iminophosphoranyl)methanes with chloro-bridged rhodium or iridium dimers giving complexes in which the ligand is coordinated either as a σ -N, σ -N' or as a σ -N, σ -C chelate. X-ray crystal structure of the σ -N, σ -N' Rh(I) complex
 $[\text{Rh}\{(4\text{-CH}_3\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$

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Abstract

Bridge splitting reactions of $[\text{ML}_2\text{Cl}]_2$ ($\text{M}=\text{Rh}, \text{Ir}$; $\text{L}_2=\text{COD}, \text{NBD}$; $\text{L}=\text{CO}$) with bis-iminophosphoranylmethanes $\text{CH}_2(\text{PPh}_2=\text{NR})_2$ (bipm, **I**) lead to Rh(I) and Ir(I) complexes with N,N' as well as N,C bidentate coordinated bipm: $[\text{ML}_2\{(4\text{-R}'\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2)_2\text{CH}_2\}]^+\text{X}^-$ (**II**) and $[\text{ML}_2\{(4\text{-R}'\text{-C}_6\text{H}_4\text{-NH-PPh}_2)\text{CH}(\text{PPh}_2=\text{N-C}_6\text{H}_4\text{-R}'\text{-4})\}]^+\text{X}^-$ (**III**; $\text{R}'=\text{CH}_3, \text{NO}_2, \text{OCH}_3$; $\text{X}=\text{Cl}, \text{MCl}_2\text{L}_2, \text{BF}_4, \text{PF}_6$). The ratio **II**:**III** depends on the metal, the bipm ligand **I**, the solvent and the presence of silver(I) or sodium salts. In the N,C coordinated bipm, a tautomeric 1,3-H shift from carbon to the pendant nitrogen atom has taken place. The X-ray crystal structure of $[\text{Rh}\{(4\text{-CH}_3\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$ has been solved. Space group $P2_1/c$, monoclinic, $a=21.832(9)$, $b=22.349(6)$, $c=12.001(6)$ Å, $\beta=100.28(3)^\circ$, $Z=4$. Refinement of 4071 observed reflections converged to $R=0.087$. The structure comprises a distorted square planar Rh(I) environment where the coordination positions are taken by COD and the two nitrogen atoms of the bipm ligand. The six-membered Rh-N=P-C-P=N-Rh metallacycle has a distorted boat conformation. Synthesis and spectroscopic data of the pure complexes **II** and **III** are described. The formation of the complexes and the influence of the reaction parameters on the ratio **II**:**III** are discussed.

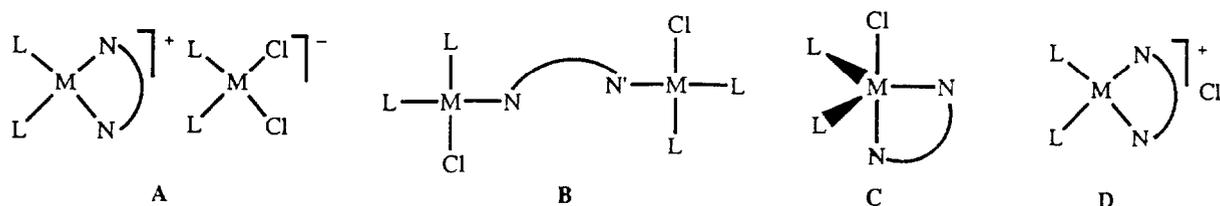
Introduction

The bridge splitting reactions of the binuclear complexes $[\text{ML}_2\text{Cl}]_2$ ($\text{M}=\text{Rh}, \text{Ir}$; $\text{L}_2=\text{COD}, \text{NBD}$; $\text{L}=\text{CO}$) with potential $\text{N}\wedge\text{N}$ bidentate coordinating ligands, i.e. for example diazabutadiene [1], 2,2'-bipyridine [2], 1,10-phenanthroline [2, 3], pyridine-2-carboxaldehyde-*N*-imines [4], etc. [5], yield different products depending on the metal to ligand ratio, the coligands L_2 and the steric and electronic properties of the $\text{N}\wedge\text{N}$ ligand. When the metal compound and ligand are applied in a 2:1 stoichiometry the ionic product $[\text{ML}_2(\text{N}\wedge\text{N})][\text{ML}_2\text{Cl}_2]$ (**A**) is usually formed. However with diazabutadiene a binuclear species was shown to exist (**B**) [1a, d, f].

Upon reaction of the metal and the ligand in a ratio 1:1 both five coordinate $[\text{ML}_2\text{Cl}(\text{N}\wedge\text{N})]$ (**C**) and four coordinate ionic complex $[\text{ML}_2(\text{N}\wedge\text{N})]\text{Cl}$ (**D**) may be formed. Crystalline solids of $[\text{ML}_2(\text{N}\wedge\text{N})]^+\text{X}^-$ can often be obtained by exchange of chloride with bulky anions X^- such as ClO_4^- , PF_6^- or BPh_4^- . This type of complex can also be obtained in the reaction of the dimer $[\text{ML}_2\text{Cl}]_2$ with the appropriate silver salts and subsequent addition of the $\text{N}\wedge\text{N}$ ligand.

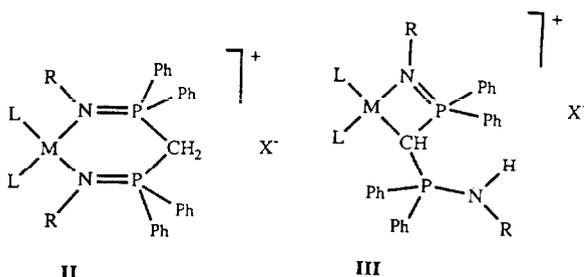
There is a current appreciation of the synthesis and chemistry of complexes of late transition metals which contain an iminophosphorane group, since this combination of a reactive metal species and a polarized ligand has been shown to give rise to interesting chemistry [6]. The bis(iminophosphoranyl)-methane ligand $\text{CH}_2(\text{PR}_2=\text{NR}')_2$ may react with

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transition metal compounds to give complexes similar to the ones mentioned above for $N \wedge N$ ligands, i.e. σ -N, σ -N' bidentate coordination. However, as a result of the combination of a polarized ligand and an electron-rich metal centre, also other reactions such as C-H activation or a metal-induced hydrogen shift may occur, giving rise to, for example, a σ -N, σ -C coordinated bis(iminophosphoranyl)methanide ligand.

In a preliminary communication it has been shown [6] that in the reaction of $[RhL_2Cl]_2$ ($L = CO$, $L_2 = COD$) with the potential bidentate coordinating bis(iminophosphoranyl)methane ligand $CH_2(PPh_2 = N-p\text{-tolyl})_2$ (**Ia**) not only the expected σ -N, σ -N' coordination mode is found (**II**), but also a complex in which the ligand has adopted a σ -N, σ -C coordination mode (**III**). This alternative coordination mode is a result of the ability of one of the methylene protons of $CH_2(PPh_2 = NR')$ to migrate to either of the terminal N atoms [7]. In this way the formation of a Rh to C(sp^3) bond that is stabilized by internal coordination of an iminophosphorane group has been achieved.



In this paper we will describe the reactions of $[ML_2Cl]_2$ ($M = Rh, Ir$; $L_2 = COD, NBD$; $L = CO$) with $CH_2(PPh_2 = N-C_6H_4-R'-4)_2$ (**Ia**: $R' = CH_3$; **Ib**: $R' = OCH_3$; **Ic**: $R' = NO_2$) to give the new organo-rhodium and -iridium complexes in which the ligand can be coordinated in either a σ -N, σ -N' (**II**) or a σ -N, σ -C (**III**) chelating mode. The σ -N, σ -C coordination mode has been published in a preliminary communication [6] and the σ -N, σ -N' coordination mode of **Ia**, as established by means of an X-ray structure determination of $[Rh\{p\text{-tolyl-N=PPh}_2\}_2CH_2\}(COD)] \cdot PF_6$, will be presented here. Moreover, the influence of the ratio of reactants, the type of complex $[ML_2Cl]_2$,

the coligands L, the ligand I and the reaction conditions on the product formation will be discussed.

Experimental

All reactions were performed in an atmosphere of purified nitrogen, using standard Schlenk techniques. The solvents were carefully dried and distilled prior to use. $[Rh(COD)Cl]_2$ [7], $[Rh(NBD)Cl]_2$ [8], $[Rh(CO)_2Cl]_2$ [9], $[Ir(COD)Cl]_2$ [10] and the bis(iminophosphoranyl)methanes $CH_2(PPh_2 = N-C_6H_4-R')_2$ (**Ia**: $R' = CH_3$; **Ib**: $R' = OCH_3$; **Ic**: $R' = NO_2$) [7, 11] were synthesized by literature procedures. 1H NMR spectra were obtained on Bruker WM250 and AC100 spectrometers. ^{31}P NMR spectra were recorded on Bruker AC100 and WP80 spectrometers. ^{19}F NMR spectra were obtained on a Bruker AC100 spectrometer. Chemical shift values are in ppm relative to Me_4Si for 1H NMR spectra, to 85% H_3PO_4 for ^{31}P NMR spectra and to $CFCl_3$ for ^{19}F NMR spectra, adopting the sign convention that shifts to high frequency are positive. IR spectra (KBr pellets) were recorded with a Perkin-Elmer 283 spectrophotometer. Field desorption (FD) mass spectra were obtained on a Varian MAT711 double focussing mass 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.

Reaction of $[ML_2Cl]_2$ with $CH_2(PPh_2 = N-C_6H_4-R'-4)_2$ (**Ia-c**)

Method 1, general procedure

To a solution of c. 200 mg $[ML_2Cl]_2$ in 10 ml CH_2Cl_2 or benzene a solution of exactly 2 molar equivalents of I (i.e. M:I = 1:1) in 10 ml CH_2Cl_2 or benzene was added at room temperature. After stirring for 2 h at room temperature the mixture was filtered and the volume was reduced to c. 20%. After addition of diethyl ether the precipitate was filtered off and washed twice with c. 5 ml diethyl

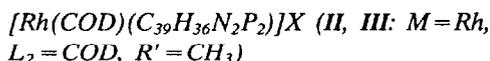
ether. The residue contained **II** and **III**. The filtrate contained **I** and small quantities of **II** and **III**.

Method 2: reaction in the presence of sodium salts

A solution of *c.* 150 mg $[\text{ML}_2\text{Cl}]_2$ and 10 equivalents NaX ($\text{X} = \text{PF}_6, \text{CF}_3\text{COO}, \text{BF}_4$) in 10 ml CH_2Cl_2 was stirred for 30 min at room temperature. Subsequently 2 equivalents of **I** in 8 ml CH_2Cl_2 were added and the mixture was stirred for 2 h at room temperature. After filtration the solvent was removed *in vacuo* giving **II** and **III** in 80–90% yield.

Method 3: reaction in the presence of silver salts

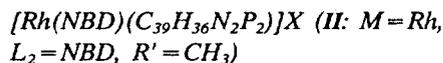
To a solution of *c.* 150 mg $[\text{RhL}_2\text{Cl}]_2$ ($\text{L}_2 = \text{COD}, \text{NBD}$) in 10 ml CH_2Cl_2 two equivalents of AgX ($\text{X} = \text{BF}_4, \text{PF}_2\text{O}_2$) were added at room temperature. After stirring for 30 min the mixture was filtered and 2 equivalents of **Ia** in 8 ml CH_2Cl_2 were added. After 20 min the solvent was evaporated *in vacuo*. The residue was washed with diethyl ether and dried *in vacuo* giving **III** in 95% yield.



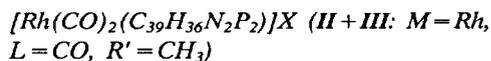
$\text{X} = \text{Cl}$ or $[\text{Rh}(\text{COD})\text{Cl}_2]$, synthesis method 1: $\text{Cl}:[\text{Rh}(\text{COD})\text{Cl}_2] \approx 3:2$. ^1H (CD_2Cl_2): 4.05 ppm ($=[\text{Rh}(\text{COD})\text{Cl}_2]$). FD mass found $m/z = 805, 804$ (M^+ , $(M-H)^+$ respectively). *Anal.* Found: C, 64.48; H, 5.60; N, 3.18. Calc. for $\text{C}_{47}\text{H}_{48}\text{N}_2\text{P}_2\text{Rh} \cdot \text{Cl} : \text{C}_{47}\text{H}_{48}\text{N}_2\text{P}_2\text{Rh} \cdot \text{C}_8\text{H}_{12}\text{Cl}_2\text{Rh} = 3:1$, C, 64.15; H, 5.60; N, 2.98%. Crystals of $[\text{Rh}(p\text{-tolyl-N}=\text{PPh}_2\text{-CH-PPh}_2\text{-NH-}p\text{-tolyl})(\text{COD})][\text{Rh}(\text{COD})\text{Cl}_2]$ (**III**, $M = \text{Rh}$, $L_2 = \text{COD}$, $R' = \text{CH}_3$, $\text{X} = [\text{Rh}(\text{COD})\text{Cl}_2]$) suitable for X-ray structure determination were obtained by slow evaporation of a solution of **II** and **III** in a $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) mixture [6a].

$\text{X} = \text{PF}_6$, synthesis method 2: ^{31}P (CD_2Cl_2): -141.9 (septet; $^1\text{J}(\text{P},\text{F}) = 713$ Hz; PF_6); ^{19}F (CDCl_3): -72.7 (d, $^1\text{J}(\text{P},\text{F}) = 713$ Hz; PF_6). FD mass found: $m/z = 805$ (M^+). Crystals of $[\text{Rh}\{(p\text{-tolyl-N}=\text{PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$ (**II**, $M = \text{Rh}$, $L_2 = \text{COD}$, $R' = \text{CH}_3$, $\text{X} = \text{PF}_6$) suitable for X-ray structure determination were obtained by slow evaporation of a solution of **II** in a mixture of $\text{C}_6\text{H}_6/\text{CH}_2\text{Cl}_2$ (10:1) at room temperature. The orange crystals contained according to ^1H NMR, elemental analysis and X-ray structure determination, 1.5 equivalent C_6H_6 . *Anal.* Found: C, 64.92; H, 5.78; N, 2.54. Calc. for $\text{C}_{47}\text{H}_{48}\text{F}_6\text{N}_2\text{P}_3\text{Rh} \cdot 1.5\text{C}_6\text{H}_6$: C, 64.80; H, 5.54; N, 2.70%.

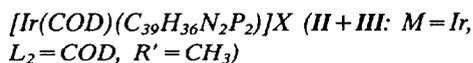
$\text{X} = \text{PF}_2\text{O}_2$, synthesis method 3: ^{31}P (CD_2Cl_2): -13.4 (t, $^1\text{J}(\text{P},\text{F}) = 958$ Hz; PF_2O_2). *Anal.* Found: C, 62.30; H, 5.42; N, 3.10; P, 9.47. Calc. for $\text{C}_{47}\text{H}_{48}\text{F}_2\text{N}_2\text{O}_2\text{P}_3\text{Rh}$: C, 62.26; H, 5.34; N, 3.09; P, 10.25%.



$\text{X} = \text{BF}_4$, synthesis method 3: FD mass found 789 (M^+). *Anal.* Found: C, 63.20; H, 5.20; N, 3.21. Calc. for $\text{C}_{46}\text{H}_{44}\text{BF}_4\text{N}_2\text{P}_2\text{Rh}$: C, 63.03; H, 5.06; N, 3.20%.

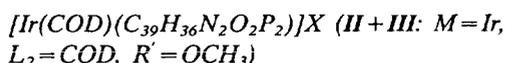


$\text{X} = \text{Cl}/[\text{Rh}(\text{CO})_2\text{Cl}_2]$, synthesis method 1: $\text{Cl}:[\text{Rh}(\text{CO})_2\text{Cl}_2] \approx 7:1$. FD mass found ($[M-H]^+$). *Anal.* Found: C, 60.90; H, 4.80; N, 3.37; O, 4.08. Calc. for $\text{C}_{41}\text{H}_{36}\text{N}_2\text{O}_2\text{P}_2\text{Rh} \cdot \text{Cl} : \text{C}_{46}\text{H}_{44}\text{BF}_4\text{N}_2\text{P}_2\text{Rh} \cdot \text{C}_2\text{Cl}_2\text{O}_2\text{Rh} = 7:1$: C, 60.91; H, 4.46; N, 3.44; O, 4.43%.



$\text{X} = \text{CF}_3\text{COO}$, synthesis method 2: ^{19}F (tol-d8): -74.7 ppm (CF_3COO). *Anal.* Found: C, 57.91; H, 4.79; N, 2.88; P, 6.02. Calc. for $\text{C}_{49}\text{H}_{48}\text{F}_3\text{IrN}_2\text{O}_2\text{P}_2$: C, 58.38; H, 4.80; N, 2.78; P, 6.15%.

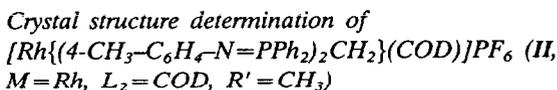
$\text{X} = \text{PF}_6$, synthesis method 2: ^{31}P (CDCl_3): -144.2 (sept, $^1\text{J}(\text{P},\text{F}) = 713$ Hz; PF_6). *Anal.* Found: C, 54.25; H, 4.66; N, 2.69; P, 9.71. Calc. for $\text{C}_{47}\text{H}_{48}\text{F}_6\text{IrN}_2\text{P}_3$: C, 54.28; H, 4.65; N, 2.69; P, 8.93%.



$\text{X} = \text{Cl}/[\text{Ir}(\text{COD})\text{Cl}_2]$, synthesis method 1: $\text{Cl}:[\text{Ir}(\text{COD})\text{Cl}_2] \approx 3:1$. *Anal.* Found: C, 55.89; H, 4.86; N, 2.97; P, 6.07. Calc. for $\text{C}_{47}\text{H}_{48}\text{IrN}_2\text{O}_2\text{P}_2 \cdot \text{Cl} : \text{C}_{47}\text{H}_{48}\text{IrN}_2\text{O}_2\text{P}_2 \cdot \text{C}_8\text{H}_{12}\text{Cl}_2\text{Ir} = 3:1$: C, 56.24; H, 4.91; N, 2.68; P, 5.92%.

NMR experiments

Mixtures of *c.* 0.03 mmol $[\text{ML}_2\text{Cl}]_2$ and 0.06 mmol **Ia**, **Ib** or **Ic** were dissolved in 0.4 ml CD_2Cl_2 or C_6D_6 . Subsequently the reaction was monitored by taking ^{31}P NMR spectra of the reaction mixture. The approximate product ratio was determined by integration of the corresponding signals. Exact determination of this product ratio was precluded because of integration errors due to the broadening of the signals which was a result of several exchange reactions. A summary of the results is listed in Table 1.



A crystal with approximate dimensions $0.15 \times 0.15 \times 0.30$ mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated $\text{Mo K}\alpha$ radiation. 10 338 intensities ($1.1 < \theta < 25^\circ$) were measured within the

TABLE 1. Reaction parameters and product ratio II:III:I^a of the reaction between [ML₂Cl]₂ and CH₂(PPh₂=N-C₆H₄-R'-4)₂ (Ia-c)

M	L ₂ ^b	R'	M:Ln	Solvent ^c	t (h) ^d	Additives	II:III:I ^e
Rh	COD	CH ₃	1:1	bz	0.25		1:1.9:1.7
Rh	COD	CH ₃	1:1	bz	2		1:1.8:1.7
Rh	COD	CH ₃	1:1	bz	48		1:1.4:1.5 ^f
Rh	COD	CH ₃	1:1	bz	120		1:1.0:1.5 ^g
Rh	COD	CH ₃	1:1	dic	2		1:1.5:1.6
Rh	COD	CH ₃	1:1	thf	2		1:3.4:2.1
Rh	COD	CH ₃	1:0.5	bz	2		1:5.1:0.9
Rh	COD	CH ₃	1:1	bz	2	Et ₃ N ^h	1:2.1:0.7
Rh	COD	CH ₃	1:1	dic	2	NaBF ₄	1:1.0:-
Rh	COD	CH ₃	1:1	dic	2	NaPF ₆	1:4.0:-
Rh	COD	CH ₃	1:1	dic	0.1 ⁱ	AgBF ₄	1:-:-
Rh	COD	CH ₃	1:1	dic	1 ⁱ	AgPF ₂ O ₂	1:6.0:-
Rh	COD	OCH ₃	1:1	bz	2		1:1.0:0.9
Rh	COD	NO ₂	1:1	chl	16		-:-:1
Rh	NBD	CH ₃	1:1	dic	2		1:0.2:-
Rh	NBD	CH ₃	1:1	dic	3	NaPF ₆	1:-:-
Rh	NBD	CH ₃	1:1	dic	1 ⁱ	AgBF ₄	1:-:-
Rh	(CO) ₂	CH ₃	1:1	dic	2		1:5:0.1
Rh	(CO) ₂	CH ₃	1:1	dic	3	Et ₃ N ^h	1:3:-
Rh	(CO) ₂	CH ₃	1:1	dic	2	NaPF ₆	1:0.9:-
Ir	COD	CH ₃	1:1	bz	0.3		1:1.7:-
Ir	COD	CH ₃	1:1	dic	0.3		1:8.5:-
Ir	COD	CH ₃	1:1	dic	16		1:1.4:- ^g
Ir	COD	CH ₃	1:1.5	dic	0.3		1:5:-
Ir	COD	CH ₃	1:2.3	dic	0.3		1:1.3:0.5
Ir	COD	CH ₃	1:4	dic	0.3		1:2:0.8
Ir	COD	CH ₃	1:1	dic	0.3	Et ₃ N ^h	1:1:-
Ir	COD	CH ₃	1:1	dic	0.5	NaPF ₆	1:1:-
Ir	COD	CH ₃	1:1	dic	0.5	NaO ₂ CCF ₃	1:0.2:-
Ir	COD	OCH ₃	1:1	dic	0.3		1:1.7:0.3
Ir	COD	NO ₂	1:1	thf	0.3		-:-:1

^aProduct ratios were determined by integration of the ³¹P NMR signals; the product ratio values given in this Table represent equilibrium values, which has been checked by taking a ³¹P NMR spectrum after c. 24 h. Observed differences in values are mainly a result of decomposition reactions and integration errors (<5%), due to the broadening of the signals. ^bCOD=1,5-cyclooctadiene; NBD=norbornadiene. ^cdic=CH₂Cl₂ or CD₂Cl₂; bz=C₆H₆ or C₆D₆; thf=tetrahydrofuran; chl=CDCl₃. ^dTime between dissolution of the reactants and the start of the ³¹P NMR measurements. Duration of measurements c. 30 min. ^eDecomposition products less than 15%, horizontal bar means not observed. ^fDecomposition products c. 30%. ^gDecomposition products c. 40%. ^h2 Equivalents. ⁱReaction time after filtration of AgCl and addition of L. ^jNo signal observed, probably due to severe broadening.

range $-25 \leq h \leq 25$, $0 \leq k \leq 26$, $0 \leq l \leq 14$. Of these, 6267 were below the $2.5\sigma(I)$ level and were treated as unobserved. The structure was solved using the symbolic-addition program system SIMPEL [12] which yielded the positions of the Rh and P atoms and part of the rest of the structure. The structure was completed by means of subsequent fourier syntheses from which it appeared that the PF₆ was disordered and that 1.5 molecule of benzene was present in the asymmetric unit. One molecule (C321-C326) is in a general position and the remaining half molecule (C311-C313) represents a benzene molecule centered at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

Refinement proceeded through block-diagonal least-squares calculations employing unit weights. Since no satisfactory description of the disorder could be given a single PF₆ group was introduced separately and refined isotropically. An empirical absorption correction [13] was used and an extinction correction was applied. The anomalous dispersion of Rh and P was taken into account. The final *R* value was 0.087 for the 4071 observed reflections (*R*_w=0.106). Crystal data and numerical details of the structure determination are given in Table 2.

The programs used, apart from SIMPEL, were from XTAY76 [14]. The scattering factors were taken from Cromer and Mann [15].

TABLE 2. Crystal data and details of the structure determination of $[\text{Rh}\{(4\text{-CH}_3\text{-C}_6\text{H}_4\text{-N=PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$ (**II**, $\text{M}=\text{Rh}$, $\text{L}_2=\text{COD}$, $\text{R}'=\text{CH}_3$)

<i>Crystal data</i>	
Formula	$\text{C}_{27}\text{H}_{48}\text{N}_2\text{P}_2\text{Rh}\cdot\text{PF}_6\cdot 1.5\text{C}_6\text{H}_6$
Molecular weight	1067.90
Space group	$P2_1/c$
Crystal system	monoclinic
a (Å)	21.832(9)
b (Å)	22.349(6)
c (Å)	12.001(6)
β (°)	100.28(3)
V (Å ³)	5762(4)
Z	4
D_x (g cm ⁻³)	1.28
μ (Mo $K\alpha$) (cm ⁻¹)	4.2
Crystal size approx. (mm)	0.15 × 0.15 × 0.30
<i>Data collection</i>	
Radiation (Å)	Mo $K\alpha$, 0.71069
T (K)	293
Data set	$-25 \leq h \leq 25$, $0 \leq k \leq 26$, $0 \leq l \leq 14$
Total unique reflections	10338
Observed data ($I > 2.5 \sigma(I)$)	4071
<i>Refinement</i>	
Weighting scheme	unit weights
Final R values	
R	0.087
R_w	0.106

Results

Synthesis of the complexes

The reactions of the bis(iminophosphoranyl)methane ligands $\text{CH}_2(\text{PPh}_2=\text{N}-\text{C}_6\text{H}_4-\text{R}'-4)_2$ (**Ia**: $\text{R}'=\text{CH}_3$; **Ib**: $\text{R}'=\text{OCH}_3$; **Ic**: $\text{R}'=\text{NO}_2$) with the chloro bridged dimers $[\text{ML}_2\text{Cl}]_2$ ($\text{M}=\text{Rh}$: $\text{L}_2=\text{COD}$, NBD , $\text{L}=\text{CO}$; $\text{M}=\text{Ir}$: $\text{L}_2=\text{COD}$) are shown in Scheme 1. In these reactions generally a mixture of two types of complexes is formed, i.e. complexes in which the ligand is coordinated in a $\sigma\text{-N}, \sigma\text{-N}'$ chelating mode, forming a six membered metallacycle (**II**), and complexes in which the ligand has adopted a $\sigma\text{-N}, \sigma\text{-C}$ coordination mode, giving a four membered ring (**III**). In the latter a net migration of a hydrogen atom from the central methylene carbon to either of the terminal nitrogen atoms has occurred.

In solution several equilibrium reactions take place depending on the metal to ligand ratio, the metal, the coligands, the coreactant and the ligand used. Furthermore during the reactions some decomposition takes place into *inter alia* $[\text{Ph}_2\text{MeP}-\text{NH}-\text{C}_6\text{H}_4-\text{R}'-4]^+$, i.e. ligand splitting possibly caused by hydrogen transfer reactions was observed.

Because of the similar properties of **II** and **III**, the pure form of either of these complexes could be obtained only in a few favorable cases. Product separation of **II** and **III** using column chromatography was not successful. However, for instance, pure **II** could be obtained in the reaction of $[\text{RhL}_2\text{Cl}]_2$ ($\text{L}_2=\text{COD}$, NBD) with silver salts and subsequent reaction with **Ia**, whereas pure **III** ($\text{M}=\text{Rh}$, $\text{L}_2=\text{COD}$, $\text{R}'=\text{CH}_3$, $\text{X}=[\text{Rh}(\text{COD})\text{Cl}_2]$) or **II** ($\text{M}=\text{Rh}$, $\text{L}_2=\text{COD}$, $\text{R}'=\text{CH}_3$, $\text{X}=\text{PF}_6$) could be obtained by selective crystallization from the crude reaction mixtures. Interconversion between isomers **II** and **III** does not occur, as the pure compounds **II** and **III** are stereochemically integer. Also, the composition of any mixture of **II** and **III** ($\text{X}=\text{PF}_6$, BF_4 , PF_2O_2 or CF_3COO) remains constant (in the absence of free **I**).

The products, formed in the reaction of $[\text{ML}_2\text{Cl}]_2$ with **Ia-c**, have been analysed by ¹H and ³¹P NMR, IR (Table 5). FD mass spectroscopy, elemental analysis and X-ray crystal structure determinations of $[\text{Rh}\{(p\text{-tolyl-N=PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$ (**II**) and $[\text{Rh}(p\text{-tolyl-N=PPh}_2\text{-CH-PPh}_2\text{-NH-}p\text{-tolyl})\text{-}(\text{COD})][\text{Rh}(\text{COD})\text{Cl}_2]$ (**III**) [**6a**]. ¹H and ³¹P NMR data of characteristic cationic species are given in Tables 4 and 5, respectively. The differences in chemical shift data upon variation of the anion **X** are not significant and hence the data will not be given separately for each compound. Additional data (NMR data of anionic species, FD-MS and elemental analyses) are given in 'Experimental'.

Furthermore, the influence of several reaction parameters on the product formation in the reaction of $[\text{ML}_2\text{Cl}]_2$ with **Ia-c** has been investigated, i.e. (i) the metal to ligand ratio, (ii) the starting complex $[\text{ML}_2\text{Cl}]_2$, (iii) the coreactants, (iv) the ligand and (v) the reaction conditions (temperature, reaction time, solvent). The approximate ratio **II:III:I** has been determined by ³¹P NMR on the reaction mixture in NMR tubes or on samples taken from the reaction mixture. Exact determination of the product ratio **II:III** by use of ³¹P NMR was hampered by broadening of the signals, due to intermolecular exchange reactions between **II** or **III** and free **I**. A summary of the results as a function of several reaction parameters is given in Table 1.

Solid state structures of **II** and **III**

The X-ray structures of both $[\text{Rh}\{(p\text{-tolyl-N=PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$ (**II**) and $[\text{Rh}(p\text{-tolyl-N=PPh}_2\text{-CH-PPh}_2\text{-NH-}p\text{-tolyl})\text{-}(\text{COD})][\text{Rh}(\text{COD})\text{Cl}_2]$ (**III**) have been determined. The structure of the latter has been discussed in a preliminary communication [**6a**].

Although a detailed discussion of the structure of $[\text{Rh}\{(p\text{-tolyl-N=PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$ (**II**) is not

warranted due to the large R value and uncertainty in bond lengths and angles, the main features of the molecular structure of **II** will be briefly addressed. The structure of **II** ($M = \text{Rh}$, $L_2 = \text{COD}$, $R' = \text{CH}_3$, $X = \text{PF}_6$) consists of a discrete cation–anion pair and 1.5 benzene molecules, in agreement with the analytical and spectroscopic data. The structure of the cationic part and the adopted numbering scheme are shown in Fig. 1. Selected bond distances and angles are given in Table 3.

The cationic part of **II** is the square planar four coordinate rhodium complex $[\text{Rh}\{(p\text{-tolyl-N}=\text{PPh}_2)_2\text{CH}_2\}(\text{COD})]^+$ with the coordination positions around Rh taken by the two nitrogen atoms N1 and N2 of the chelating bis(iminophosphoranyl)methane ligand and by the two olefinic bonds of the COD ligand (with M1 and M2 being the midpoints of C1–C2 and C5–C6, respectively). The square planar coordination geometry is considerably distorted as indicated by the deviations of N1, N2, M1 and M2 from the least-squares plane defined by these atoms and Rh ($-0.08, 0.10, -0.08, 0.10 \text{ \AA}$). The Rh–N bond distances of 2.144(9) and 2.17(1) \AA are long but fall within the range usually found for comparable complexes [5b, 16], e.g. 2.061(5) and 2.119(4) \AA in

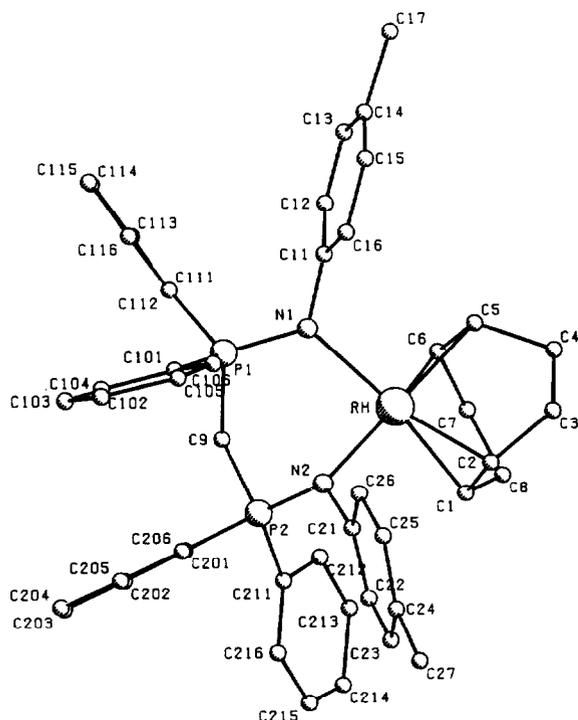


Fig. 1. The molecular structure of the cationic part of $[\text{Rh}\{(4\text{-CH}_3\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2)_2\text{CH}_2\}(\text{COD})]\text{PF}_6$.

$[\text{Rh}(\text{COD})(\text{pyrrol-2-carbaldehyd-(S)-1-phenylethyl-imine})]$ [5b] or 2.142(3) \AA in $[\text{Rh}(\text{COD})\text{Cl}(\text{Et}_3\text{P}=\text{N}-p\text{-tolyl})]$ [16d]. The Rh–olefin bond distances are normal as indicated by the Rh–M distances of 2.021 and 2.048 \AA [16, 17]. The angle between the olefinic bonds and the coordination plane deviate considerably from the ideal 90° (86.1 and 80.9°). The COD ligand has a distorted boat conformation, which is shown in Fig. 2. These distortions within the molecule can most probably be ascribed to both steric and packing effects.

Within the bis(iminophosphoranyl)methane ligand all data point to a coordination mode which is best described by the coordination of two separate iminophosphorane entities to the Rh atom which are coupled by a methylene group. Both P=N bonds (1.59(1) and 1.61(1) \AA) are a little longer than in the free ligand **Ia** (1.568(2) and 1.566(2) \AA) [7], which are normal bond distances upon coordination of an iminophosphorane ligand [18]). The P–C9 bond lengths of 1.85(1) and 1.81(1) \AA indicate that these are normal single P–C bonds [7, 19]. The six-membered metallacycle has a distorted boat conformation (Fig. 2).

The anionic part of the molecule is a distorted PF_6 ion, indicated by the P3–F1 bond distance of 1.61(2) \AA with a mean P3–Fx bond length value of 1.50 \AA ($x=2-6$).

The main features of the structure of the cationic part of **III** (Fig. 3) [6a], i.e. $[\text{Rh}(p\text{-tolyl-N}=\text{PPh}_2\text{-CH-PPh}_2\text{-NH-}p\text{-tolyl})(\text{COD})]$, are the four membered Rh–N–P–C metallacycle and the newly formed N1b–Hb bond (1.30 \AA). Carbon atom C9b is chiral, both enantiomers are present in the unit cell. In this complex a Rh–C(sp^3) bond is present (2.21(1) \AA) which is stabilized by internal coordination of an iminophosphorane moiety, with a P–N bond length of 1.613(8) \AA and a Rh–N2b bond distance of 2.081(8) \AA . The structure of the four-membered ring is closely related to the analogous metallacycles in other complexes containing a mono- or bis(iminophosphoranyl)methanide ligand, i.e. $[\text{Rh}(\text{COD})(\text{CH}_2\text{PPh}_2=\text{N-}p\text{-tolyl})]$ [17d] or $[\text{Ir}(\text{COD})\{\text{CH}(\text{PPh}_2=\text{N-}p\text{-tolyl})_2\}]$ [20], indicating that this configuration is only little influenced by the substituents on the methanide carbon atom. There is a slight but significant *trans*-influence of C9b on the Rh–M2 distance, noticeable as compared to the Rh–M1 distance. The free aminophosphonium entity is pointing away from the Rh atom with torsion angles $\text{P2b-C9b-P1b-N1b} = 83.5^\circ$ and $\text{Rh-C9b-P1b-N1b} = 173.2^\circ$. The P1b–N1b bond (1.658(10) \AA) is lengthened with respect to free **Ia** due to the presence of both a proton and a *p*-tolyl group on the nitrogen atom. The hybridization of

TABLE 3. Selected interatomic bond distances (Å) and bond angles (°) of [Rh((4-CH₃-C₆H₄-N=PPh₂)₂CH₂)(COD)]PF₆ (II) with e.s.d.s. in parentheses

Around Rh				Within COD	
Rh-N1	2.144(9)	Rh-C1	2.18(1)	C1-C2	1.46(2)
Rh-N2	2.17(1)	Rh-C2	2.12(1)	C5-C6	1.43(2)
Rh-M1	2.021	Rh-C5	2.21(1)	<Csp ² -Csp ³ >	1.56(2)
Rh-M2	2.048	Rh-C6	2.13(1)	<Csp ³ -Csp ³ >	1.54(2)
Within L				Within anion	
N1-C11	1.44(1)	N2-C21	1.44(1)	P3-F1	1.61(2)
N1-P1	1.59(1)	N2-P2	1.61(1)	P3-F2	1.50(2)
P1-C9	1.85(1)	P2-C9	1.81(1)	P3-F3	1.48(2)
P1-C101	1.83(1)	P2-C201	1.78(1)	P3-F4	1.48(2)
P1-C111	1.79(1)	P2-C211	1.81(1)	P3-F5	1.50(2)
				P3-F6	1.54(2)
Around Rh				Within COD	
N1-Rh-N2	88.3(5)	N2-Rh-M1	91.7(3)	<Csp ³ -Csp ² -Csp ² >	124(1)
N1-Rh-M1	177.6(4)	N2-Rh-M2	172.4(3)	<Csp ² -Csp ³ -Csp ³ >	112(1)
N1-Rh-M2	91.2(3)	M1-Rh-M2	89.0(4)		
Within L					
P1-N1-C11	119.1(10)	N1-P1-C9	107.6(8)	N2-P2-C9	107.8(8)
P1-N1-Rh	120.6(6)	N1-P1-C101	117.5(8)	N2-P2-C201	113.1(8)
Rh-N1-C11	120.3(8)	N1-P1-C111	112.6(8)	N2-P2-C211	117.8(7)
P2-N2-C21	119.1(9)	C9-P1-C101	106.1(9)	C9-P2-C201	106.4(8)
P2-N2-Rh	114.1(6)	C9-P1-C111	107.1(8)	C9-P2-C211	105.6(8)
Rh-N2-C21	119.3(8)	C101-P1-C111	105.2(9)	C201-P2-C211	107.8(8)
P1-C9-P2	112.7(8)				
Within anion					
F1-P3-F2	94(1)	F2-P3-F3	90(2)	Fe-P3-F5	172(1)
F1-P3-F3	97(2)	F2-P3-F4	175(1)	F3-P3-F6	86(2)
F1-P3-F4	83(1)	F2-P3-F5	95(2)	F4-P3-F5	89(2)
F1-P3-F5	77(1)	F2-P3-F6	88(1)	F4-P3-F6	95(2)
F1-P3-F6	176.5(9)	F3-P3-F4	86(2)	F5-P3-F6	100(2)

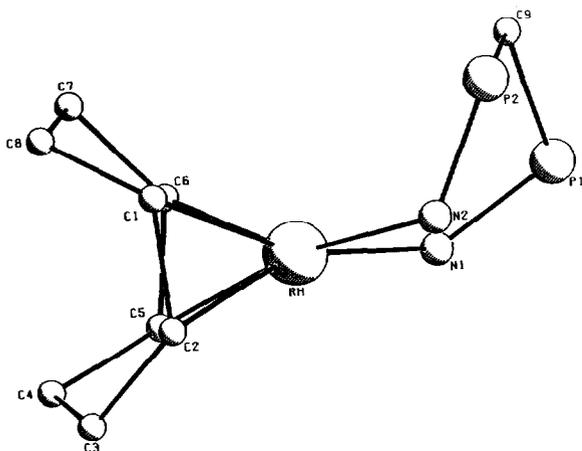


Fig. 2. Part of the structure of Fig. 1, showing the boat conformation of the ligands.

N1b deviates from sp² (sum of angles around N1b amounts to 350(2)°). However, the bond order between P1b and N1b will be larger than unity.

Spectroscopic characterization of complexes II and III

NMR spectroscopy

¹H and ³¹P NMR data for the cationic complexes II and III are given in Tables 4 and 5, respectively. The differences in NMR data upon variation of the anion X are small, so the data are given only for each of the cationic species.

In the ¹H NMR spectra of the complexes II a triplet is found for the methylene hydrogen atoms at about 4.2 ppm. This signal is found at a slightly higher frequency compared to the value for the free ligand I (3.7 ppm) [7] indicating a small deshielding of these protons upon coordination of the bis(iminophosphoranyl)methane ligand. A single resonance is found for the olefinic COD hydrogen atoms and in the ³¹P NMR spectra only one signal is found for complex II. Thus the complexes II have in solution on average at least C_{2v} symmetry in agreement with a σ-N,σ-N' coordination mode.

In the ¹H NMR spectra of complexes III the methine proton is found as a doublet of doublets

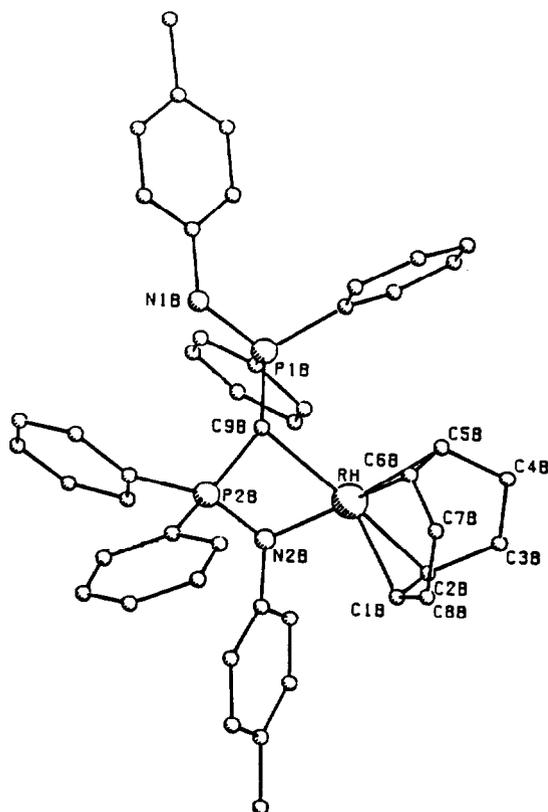


Fig. 3. The molecular structure of the cation of $[\text{Rh}(4\text{-CH}_3\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2\text{-CH-PPH}_2\text{-NH-C}_6\text{H}_4\text{-CH}_3\text{-4})(\text{COD})]^+$ $[\text{Rh}(\text{COD})\text{Cl}_2]^-$ from ref. 6a.

due to coupling with the two different P atoms. In the complexes containing rhodium additional $^2J(\text{Rh}, \text{H})$ coupling of *c.* 2 Hz is found, indicating the presence of a Rh–C bond [17c, d, 21]. The δ value of the methine proton is sensitive to the ligand in *trans* position and the metal, high frequency shifts being observed when COD is substituted by CO and when Rh is substituted by Ir. Furthermore, the chemical shift values are shifted to higher frequencies with respect to the mono-iminophosphoranylmethanide complexes $[\text{M}(\text{CH}_2\text{PPh}_2=\text{N-}i\text{-p-tolyl})\text{L}_2]$ [17d] as a result of the deshielding effect of the aminophosphonium entity. The N–H signals are found at high frequencies as a doublet due to $^2J(\text{P}, \text{H})$. Two resonances are found for the olefinic COD hydrogen atoms at 3.51 and 4.15 ppm for $\text{M}=\text{Rh}$, $\text{R}'=\text{CH}_3$ and at 3.25 and 4.18 ppm for $\text{M}=\text{Ir}$, $\text{R}'=\text{CH}_3$.

In the ^{31}P NMR spectra of the cationic complexes **III** two resonances are found. The signals in the region 34–39 ppm are attributed to the aminophosphonium P atom based on the observation that only marginal differences in chemical shift are encountered when M and/or L are varied and also on the observed small $^2J(\text{Rh}, \text{P})$ in the complexes con-

taining rhodium. The other signals show a larger variation upon changing M and L (chemical shifts from 27.9 to 42.5 ppm) which runs parallel to the variation found for the analogous mono-iminophosphoranylmethanide complexes [17d]. Also the $^2J(\text{Rh}, \text{P})$ of *c.* 16 Hz for **III** is close to the values of about 18 Hz observed for similar compounds [17d].

IR spectroscopy

Selected IR data (KBr) are given in Table 5. For the complexes **II** a strong signal is found for $\nu(\text{P}=\text{N})$ in the region $1230\text{--}1260\text{ cm}^{-1}$, i.e. a normal low frequency shift of $60\text{--}90\text{ cm}^{-1}$ is found upon coordination of the bis(iminophosphoranyl)methane ligand [16d, 22]. For $\text{M}=\text{Rh}$, $\text{L}=\text{CO}$, $\text{R}'=\text{CH}_3$ two strong signals are found for $\nu(\text{CO})$ at 2077 and 2012 cm^{-1} . In complexes **III** $\nu(\text{P}=\text{N})$ is found at *c.* 1280 cm^{-1} , i.e. a value close to those normally observed for complexes containing the iminophosphoranylmethanide ligand [17d, 20], pointing to the presence of the four-membered M–N–P–C ring. For $[\text{Rh}(4\text{-CH}_3\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2\text{-CH-PPH}_2\text{-NH-C}_6\text{H}_4\text{-CH}_3\text{-4})(\text{CO})_2]^+$ $\nu(\text{CO})$ are found at 2059 and 1980 cm^{-1} , in agreement with C_s symmetry and a mutual *cis* geometry of the CO ligands and are close to the values of the related mono-iminophosphoranylmethanide complexes [17d]. The resonances at *c.* 960 cm^{-1} can be assigned to $\nu(\text{P}-\text{N})$ of the $\text{R}_3\text{P}-\text{NHR}'$ group [7, 23].

FD mass spectroscopy

In the field desorption (FD) mass spectra of the reaction products only signals are found that must be attributed to the cationic parts of complexes **II** and/or **III**. Interestingly, for complex **II** a signal is found that can be assigned to the parent ion M^+ , whereas for complex **III** a signal is observed at $[\text{M}-\text{H}]^+$, i.e. **III** loses a hydrogen atom during the measurement. For the complexes containing Ir, isotope patterns are found which are in agreement with the natural abundance of the isotopes ^{191}Ir and ^{193}Ir (37 and 63%). The values given in 'Experimental' account for the highest observed peaks.

Reaction of $[\text{ML}_2\text{Cl}]_2$ with $\text{CH}_2(\text{PPh}_2=\text{N-C}_6\text{H}_4\text{-R}')_2$

In the following section the reactions of $[\text{ML}_2\text{Cl}]_2$ with $\text{CH}_2(\text{PPh}_2=\text{N-C}_6\text{H}_4\text{-R}')_2$ (Scheme 1) as a function of several reaction parameters will be described. In general the ligand is $(\text{CH}_2(\text{PPh}_2=\text{N-C}_6\text{H}_4\text{-CH}_3\text{-4}))_2$ (**Ia**). $[\text{ML}_2\text{Cl}]_2$ and the ligand have been mixed in a 1:2 molar ratio ($\text{M}:\text{I}=1:1$), unless stated otherwise. For convenience the $\sigma\text{-N}, \sigma\text{-N}'$ and the $\sigma\text{-N}, \sigma\text{-C}$ coordinated bis(iminophosphoranyl)methanes will be indicated as $\text{N}\wedge\text{N}$ and $\text{N}\wedge\text{C}$,

TABLE 4. ¹H NMR data of the cationic complexes **II** and **III**^a

Compound (M,L ₂)	δ(CH ₂) ^b	δ(CH ₃)	δ(aryl) ^c	δ(Ph)	δ(NH) ^b	δ(=CH) (diene) ^d	δ(CH ₂) (diene) ^d
II (Rh,COD)	4.22(t,11.6)	2.13	6.27(d,8.1) 6.72(d,8.1)	7.27–7.84(m)		3.37	1.5–1.7 2.3–2.4
II (Rh,NBD)	4.18(t,12.2)	2.10	6.26(d,8.2) 6.71(d,8.2)	7.0–7.9(m)		2.91	1.01 ^e
II (Rh,(CO) ₂)	4.27(t,12.4)	2.23	6.90(d,8.5) 7.01(d,8.5)	7.3–8.1(m)			
II (Ir,COD)	^f	2.16	6.08(d,7.3) 6.69(d,7.3)	7.2–8.4(m)		3.77	1.1–1.4 1.7–2.1
III (Rh,COD) ^g	3.85(ddd,18.8; 3.5) ^h	1.82 1.94	6.19(d,7.4) 6.51(d,7.5) 6.60(d,7.4) ^f	6.9–7.4(m) 8.0–8.5(m)	10.70(d,6.2)	3.51 4.15	1.1–1.4 2.0–2.5
III (Rh,(CO) ₂) ⁱ	4.56(ddd,16.6; 3.5) ⁱ	1.81 1.97	^f	6.5–7.5(m) 7.7–8.7(m)	8.64(d,4.9)		
III (Ir,COD) ^k	5.36(dd,20.6; 3.9)	1.80 1.96	6.37(d,8.0) 6.49(d,8.5) 6.63(d,8.0) ^f	6.75–7.40(m) 7.74–7.95(m) 8.24–8.55(m)	11.90(d,6.3)	3.25 4.18	1.5–1.9 2.1–2.5

^aMeasured at 100 MHz at room temperature; chemical shift values in ppm relative to TMS, coupling constants in Hz, solvent CD₂Cl₂; d=doublet, t=triplet, dd=doublet of doublets, ddd=doublet of double doublets, m=multiplet; R'=CH₃. ^b²J(P,H) in parentheses. ^c³J(H,H) in parentheses. ^dBroad signals. ^eδ(-CH, NBD)=3.55 ppm. ^fObscured. ^gSolvent CDCl₃. ^h²J(Rh,H)=1.8 Hz. ⁱSolvent C₆D₆. ^j²J(Rh,H)=2.0 Hz. ^kSolvent tol-d₈.

TABLE 5. ³¹P NMR^a and IR^b data of the cationic complexes **II** and **III**

Compound (M,L ₂ ,R')	³¹ P NMR			IR		
	δ(P)	² J(P,P)	² J(Rh,P)	ν(P=N)	ν(P-N)	ν(CO)
II (Rh,COD,CH ₃)	25.7(d)		0.8	1256 1238		
II (Rh,NBD,CH ₃)	24.3			1247		
II (Rh,(CO) ₂ ,CH ₃)	25.9			1231		2077 2012
II (Ir,COD,CH ₃)	25.8			1263		
II (Ir,COD,OCH ₃) ^c	26.4			^d		
III (Rh,COD,CH ₃)	27.9(dd) 34.1(dd)	4.4 4.4	16.2 3.8	1284	949	
III (Rh,(CO) ₂ ,CH ₃)	38.7(dd) 42.5(dd)	3.9 3.9	6.8 16.6	1283	949	2059 1980
III (Ir,COD,CH ₃) ^c	36.8(d) 41.5(d)	4.9 4.9		1279	959	
III (Ir,COD,OCH ₃)	37.0(d) 41.9(d)	4.9 4.9		^d	^d	

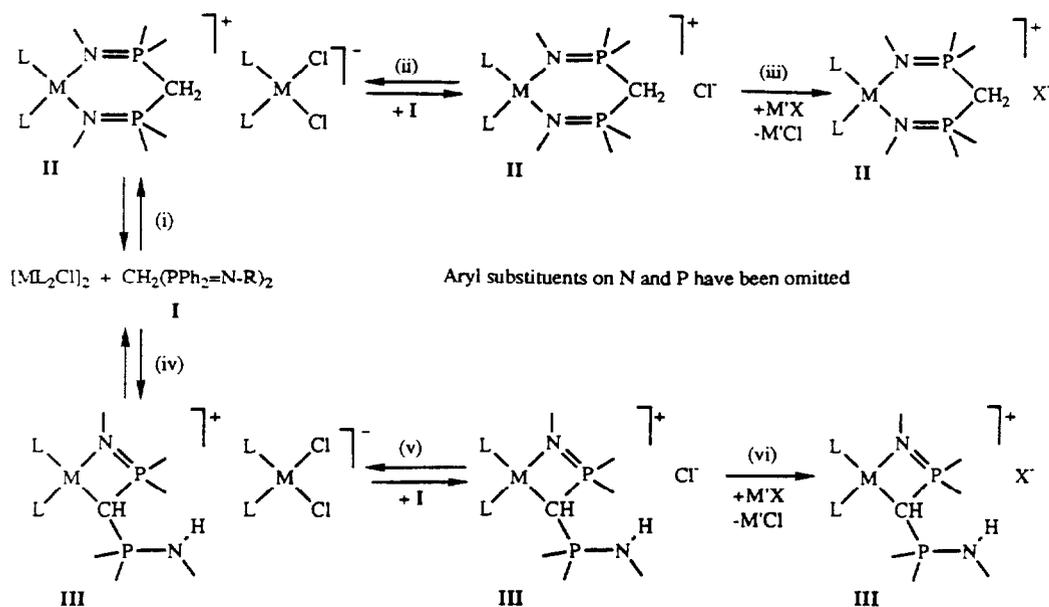
^aMeasured at 32.4 or 40.5 MHz at room temperature; chemical shift values in ppm relative to 85% H₃PO₄, coupling constants in Hz; solvent: CD₂Cl₂; d=doublet, dd=doublet of doublets. ^bKBr pellets. ^cSolvent: CDCl₃. ^dNot determined.

respectively. A summary of the results of these reactions is given in Table 1.

Metal to ligand ratio (M:I)

When [Rh(COD)Cl]₂ and **Ia** are mixed in a M:Ia ratio of 1:1 equilibria (ii) and (v) play a predominant role. In solution the presence of the cationic species **II** and **III** and of free **Ia** is shown by their (broad)

signals in the ³¹P NMR spectra at room temperature. From the molar ratio of the products **Ia**, **II** and **III** it can be deduced that both [Rh(COD)Cl₂]⁻ and Cl⁻ should be present as the anions in **II** and **III**. The presence of [Rh(COD)Cl₂]⁻ is supported by the observation of a signal at 4.05 ppm in the ¹H NMR spectrum which is close to the 4.08 ppm for the olefinic protons of AsPh₄[Rh(COD)Cl₂] in CD₂Cl₂



Scheme 1.

[1h, 24]. The approximate equal quantities of **Ia** and **III** suggest that **III** is mainly present as $[\text{Rh}(\text{N}\wedge\text{C})(\text{COD})][\text{Rh}(\text{COD})\text{Cl}_2]$, i.e. equilibrium (v) lies largely on the left hand side. This is corroborated by the fact that from a mixture of **II** and **III** in CH_2Cl_2 /hexane crystals of $[\text{Rh}(\text{N}\wedge\text{C})(\text{COD})][\text{Rh}(\text{COD})\text{Cl}_2]$ are formed exclusively [6a].

With $\text{M}=\text{Rh}$, $\text{L}_2=\text{NBD}$ and $\text{M}:\text{Ia}=1:1$ equilibria (ii) and (v) lie both mainly to the right hand side as indicated by the presence of only little free **Ia** (<2%) in the ^{31}P NMR spectra. For $\text{M}=\text{Rh}$ and $\text{L}=\text{CO}$ likewise only a small amount of free ligand is observed (^{31}P NMR) and in the IR spectra of the reaction mixture (CH_2Cl_2) no signals were found in the carbonyl region that could be assigned to $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ (1994 and 2070 cm^{-1}) [25], although these signals could be obscured by the signals of $[\text{Rh}(\text{N}\wedge\text{C})(\text{CO})_2]^+$ at 1980 and 2059 cm^{-1} . Elemental analysis of the crude reaction product showed that indeed chloride is the predominant anion. Also for $\text{M}=\text{Ir}$, $\text{L}_2=\text{COD}$ and $\text{M}:\text{Ia}=1:1$ equilibria (ii) and (v) lie largely to the right hand side since in the ^{31}P NMR spectra no signals of free **I** could be observed. However, the broadening of the signals for **II** and **III** in these spectra indicates that some exchange occurs, implying that some free **I** must be present in the reaction mixture, since it participates in reactions (ii) and (v) and in ligand exchange reactions (*vide infra*).

Increasing the metal to ligand ratio from 1:1 to 2:1 shifts equilibria (ii) and (v) to the left and

equilibria (i) and (iv) play a predominant role. In the reactions of $[\text{M}(\text{COD})\text{Cl}_2]$ with **Ia** broad signals of **II**, **III** and **Ia** are found in the ^{31}P NMR spectra, showing that exchange takes place and that the equilibria (i) and (iv) lie not completely to the right hand side. In both reactions the **II**:**III** ratio is smaller than in the $\text{M}:\text{I}=1:1$ reaction, indicating that formation of **III** is more favourable at lower ligand concentrations.

At $\text{M}:\text{Ia}$ ratios smaller than 1:1 fast exchange between the complexes **II** and **III** and free **Ia** occurs as evidenced by broadening of the signals of the complexes **II** and **III** and of the ligand **Ia** in the ^{31}P NMR spectra. These exchange reactions are largely influenced by the concentration of both the complex and the ligand and by the type of starting complex $[\text{ML}_2\text{Cl}_2]$ used. With a small excess **Ia** (i.e. $\text{M}:\text{Ia}\approx 1:1.05$) mainly exchange between **III** and **Ia** is observed. During this reaction the ratio **II**:**III** is hardly influenced. However at higher ligand concentrations (1:1.5–1:4) relatively more **II** is formed and exchange of **Ia** with both **II** and **III** is observed.

The observed dynamic behaviour can be explained by a mechanism involving an association equilibrium of complex **III** with free **Ia** (Scheme 2) giving rise to five coordinate complexes (eq. (vii)). Interchange will occur via Berry pseudorotations. A similar isomerization process through a five coordinate intermediate was proposed for $[\text{Rh}(\text{diene})(\text{O}\wedge\text{S})]$ ($\text{O}\wedge\text{S}=\text{monothio-}\beta\text{-diketonate}$) [26] and $[\text{Rh}(\text{diene})-(\text{N}\wedge\text{N})]$ ($\text{N}\wedge\text{N}=\text{pyridine-2-carboxaldehyde-N-}$

imine) [1h] or via intramolecular attack in the complexes $[M\{(4-R'-C_6H_4-N=PPh_2)_2CH\}L_2]$ [20] or $[M(COD)(tripod)]$ ($M = Rh, Ir$; tripod = $CH(PPh_2)_3$) [27].

At higher ligand concentrations (i.e. lower M:Ia ratio) not only equilibrium (vii) occurs but also equilibria (ix), (x) and (viii) take place. This means that at higher ligand concentration exchange reactions of **II** with **Ia** (eq. (ix)) occur and that interconversion between **II** and **III** is observed (eq. (viii) and (x)).

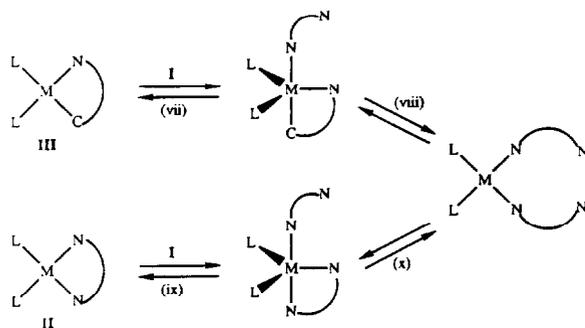
Dimer $[ML_2Cl]_2$

The product formation is influenced to an appreciable extent by variation of the starting complex $[ML_2Cl]_2$. When using ligand **Ia**, the product ratio **II:III** for $M = Rh$ increases from 1:5 via 1:1.5 to 1:0.2, when going from $L_2 = (CO)_2$ via COD to NBD. The formation of **III** is also favoured with respect to **II** when Rh is replaced by Ir ($L_2 = COD$). As mentioned above also the equilibria (ii) and (v) are influenced by variation of both L_2 and M. The exact influence of steric and electronic factors on the product formation is difficult to establish since the product ratio **II:III** is dependent amongst other things on: (a) the stability of the products formed, (b) the equilibrium constants for (i), (ii), (iv) and (v) in Scheme 1, (c) the M-Cl bond strength in the chloro bridged dimers $[ML_2Cl]_2$.

Coreactants

Addition of the base Et_3N to the reaction mixture of $[ML_2Cl]_2$ and **Ia** gives a small increase in the **II:III** ratio and a lower concentration of free ligand. Thus addition of Et_3N causes the equilibria (ii) and (v) to shift to the right, most probably due to a stabilizing effect on the final anion-cation complexes (i.e. a solvation effect).

When the reactions of $[ML_2Cl]_2$ with **Ia** are performed in the presence of 10 equivalents of NaX ($X = PF_6, BF_4$ or CF_3COO) only products of the type $[M(N \wedge N)L_2]X$ or $[M(N \wedge C)L_2]X$ are formed,



Scheme 2. $N \wedge N$ and $N \wedge C$ are $\sigma-N, \sigma-N'$ or $\sigma-N, \sigma-C$ coordinated ligand **I**, respectively.

i.e. the equilibria (ii) and (v) are completely shifted to the right and chloride has been completely substituted by the anion X. However, also the product ratio **II:III** is influenced by the introduction of X. This is best illustrated for $M = Ir$, $L_2 = COD$ with **Ia** in CH_2Cl_2 . Without sodium salts the **II:III** ratio is 1:8.5, with $NaPF_6$ 1:1 and with $NaOCCF_3$ 1:0.2. These results can be explained by assuming that not only does interchange of Cl with X occur (eqs. (iii) and (vi)) but that the presence of X also has influence on the reversible bridge splitting reactions (i) and (iv) or on the equilibria (ii) and (v), for example via exchange of $[ML_2Cl]_2^-$ with X^- . When the chloride in $[RhL_2Cl]_2$ ($L_2 = COD, NBD$) is abstracted first in a reaction with $AgBF_4$ and **Ia** is subsequently added, only products of the type $[Rh(N \wedge N)L_2]BF_4$ (**II**) are formed. However when $AgPF_2O_2$ is used instead, both **II** and **III** are formed, indicating that association of the anion with the complex has impact on the relative amounts of final products.

Ligand $CH_2(PPh_2=N-C_6H_4-R')_2$

A few experiments were performed in order to investigate the influence of the nucleophilicity of the N atom of the ligand **I** on the product formation. To this end ^{31}P NMR spectra were taken of the reaction mixtures of $[M(COD)Cl]_2$ ($M = Rh, Ir$) with **Ib** ($R' = OCH_3$) or **Ic** ($R' = NO_2$). No attempts were made to isolate the complexes formed and hence these complexes have not been fully characterized.

Replacement of $R' = CH_3$ by OCH_3 has only little influence on the relative amounts of the final products: for both $M = Rh$ and Ir an increase in the **II:III** product ratio and a change in the concentration of free ligand is observed. However for $R' = NO_2$ the differences are more pronounced: with $[M(COD)Cl]_2$ ($M = Rh, Ir$) no signals were found in the ^{31}P NMR spectra that can be attributed to either **II** or **III**. This shows that the nitrogen atom in **Ic** is not nucleophilic enough, due to the strong electron withdrawing capacity of the NO_2 substituent, to give bridge splitting reactions and/or the resulting $N \wedge N$ or $N \wedge C$ complexes are not stable with respect to decomposition to starting compounds. Similar results were obtained in other reactions of Rh or Ir complexes with iminophosphoranes, in which it was shown that a *p*-nitrophenyl substituted N atom showed a much lower affinity towards the metal atom compared to a *p*-tolyl substituted N atom [16d, 17d, 20].

Reaction conditions

Variation of the reaction conditions, such as the solvent (C_6H_6, CH_2Cl_2, THF), reaction temperature, reaction time or the sequence of reactant addition (**M** to **Ia**, **Ia** to **M** or mixing the reactants before dissolution) has only little effect on the final product

distribution. When long reaction times are employed (> 4 h) decomposition reactions are observed, i.e. formation of $\text{Ph}_2\text{PMe-NH-C}_6\text{H}_4\text{-R}'\text{-4}$, $\text{Ph}_2\text{P(Me)=O}$ and $\text{Ph}_2\text{P(=O)-NH-C}_6\text{H}_4\text{-R}'\text{-4}$ as a result of hydrogen migration reactions and/or the introduction of small quantities of oxygen or water in the reaction vessel was observed [11c, 28].

Discussion

In the reaction of $[\text{ML}_2\text{Cl}]_2$ with $\text{CH}_2(\text{PPh}_2=\text{N-C}_6\text{H}_4\text{-R}'\text{-4})_2$ (**I**) products similar to those usually found in the bridge splitting reactions of $[\text{ML}_2\text{Cl}]_2$ with bidentate ligands $\text{X} \wedge \text{Y}$ [1-5], i.e. at high metal to ligand ratios complexes of the type $[\text{ML}_2(\text{X} \wedge \text{Y})][\text{ML}_2\text{Cl}_2]$ (**A**) are formed, whereas reaction at higher ligand concentration gives rise to the anion-cation complexes $[\text{ML}_2(\text{X} \wedge \text{Y})]\text{Cl}$ (**D**). Exchange of the Cl anion can be accomplished by reaction with sodium salts NaX ($\text{X} = \text{PF}_6, \text{PF}_2\text{O}_2, \text{BF}_4, \text{CF}_3\text{OO}$) (Scheme 1).

However, product formation in the reaction with **I** is very complex as a result of concomitant formation of two different types of cationic species, i.e. complexes in which the bis(iminophosphoranyl)methane ligand is coordinated in a $\sigma\text{-N}, \sigma\text{-N}'$ mode (**II**) and complexes in which the ligand has adopted a $\sigma\text{-N}, \sigma\text{-C}$ coordination mode (**III**). Moreover, since the formation of both the cationic and the anionic species are influenced in different ways by the reaction parameters, exact determination of the equilibrium constants as a function of these reaction parameters is very difficult. This is *inter alia* demonstrated by the influence of the metal to ligand ratio on the product formation. At high M:I ratios complexes of type **A** with the bis(iminophosphoranyl)methane ligand in its $\sigma\text{-N}, \sigma\text{-C}$ coordination mode (**III**) are preferred, whereas increasing the ligand concentration leads not only to the formation of complexes of the type **D**, but also relatively more **II** is formed. This suggests that reaction of **I** with the dimer $[\text{ML}_2\text{Cl}]_2$ gives preferably **III** whereas with the anion $[\text{ML}_2\text{Cl}_2]^-$ predominantly **II** is formed. Furthermore, at high ligand concentration the product ratio **II:III** may be influenced by interconversion between **II** and **III** according to Scheme 2.

The complexity of the product formation as a function of several reaction parameters is also well demonstrated by the influence of sodium salts (NaX). If X would give interchange reactions with chloride only, one would expect the ratio **II:III** to be independent on the addition of these salts and the anion used. However, from the results (Table 1) it

is clear that the ratio **II:III** is determined to a large extent by whether or not NaX is present and by the type of anion.

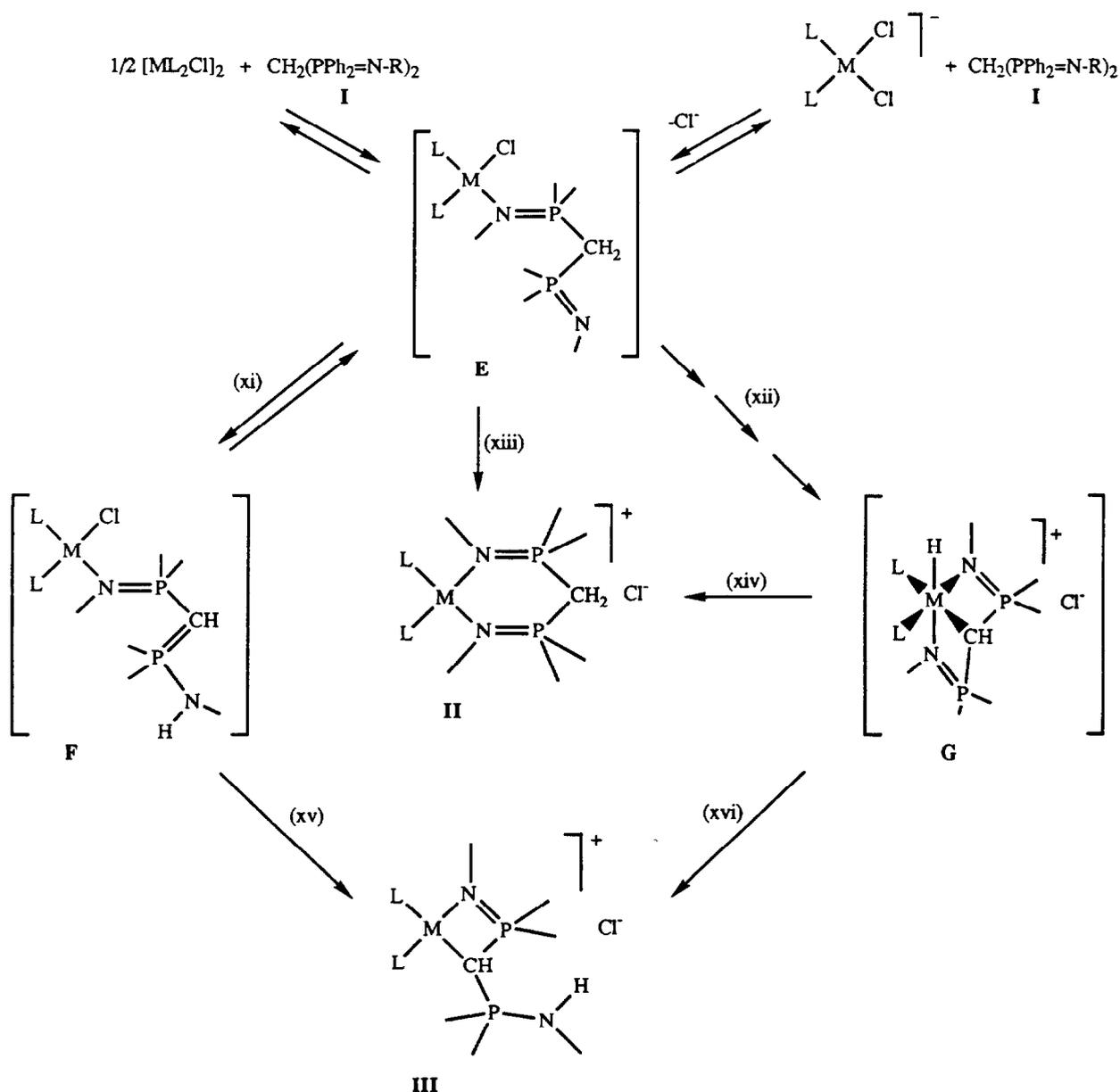
From the results in Table 1 and the discussion above it can be inferred that Scheme 1 represents a simplified picture of the reactions between $[\text{ML}_2\text{Cl}]_2$ and $\text{CH}_2(\text{PPh}_2=\text{N-R})_2$ and that other reactions may occur as well.

Several routes may be followed for the formation of both **II** and **III** in the reaction of either $[\text{ML}_2\text{Cl}]_2$ or $[\text{ML}_2\text{Cl}_2]^-$ with **I**, of which the most probable ones are depicted in Scheme 3. The first step in the formation of **II** and **III** is coordination of **I** via an N atom giving intermediate **E** in which the ligand is monodentate coordinated. Complex **II** can be formed from **E** via substitution of chloride by the free iminophosphorane N atom according to (xiii). Formation of **III** may be explained by a tautomeric equilibrium (xi), in which a methylene hydrogen migrates to the uncoordinated N atom giving intermediate **F**, followed by coordination of the ylide C atom to the metal (xv).

Alternatively **II** and **III** may be formed via cyclometallation of the methylene group in **E**, followed by dissociation of chloride and coordination of the pendant N atom to the metal centre, giving the intermediate **M(III)-hydride** complex **G** (xii). Successive reductive elimination of N-H according to (xvi) gives **III**, whereas reductive elimination of C-H according to (xiv) yields **II**. These reductive eliminations should take place irreversibly as otherwise interconversions between **II** and **III** would be conceivable whereas such interconversions do not take place (*vide supra*).

The tautomeric equilibrium (xi) between **E** and **F** would be closely related to those of the well known 1,3-diketones or bis(methylenephosphoranyl)methanes. Whereas such an equilibrium is not observed for free bis(iminophosphoranyl)methanes [7], coordination of one iminophosphorane entity may influence the acidity of the methylene group in such a way that equilibrium (xi) shifts towards tautomer **F**, in which the charge on the ylide carbanion is stabilized by the polarized coordinated iminophosphorane substituent. Schmidbauer *et al.* [29] have shown in a study on the tautomerization reactions of several related ylide compounds, that substituents which are capable of stabilizing the charge on ylide carbanions shift the tautomeric equilibrium towards tautomers which are related to **F**.

In general the difference in acidity between methylene or aminophosphonium groups is quite large [30]. However, in **E** and **F** this difference is reduced as a result of the coordination of one of the iminophosphorane groups to the metal giving rise to



Scheme 3. Aryl substituents on N and P have been omitted.

an extra polarization within the P-N entity, raising the acidity of the connected methylene group, favouring the tautomeric form of I. This would explain the large difference in product formation upon variation of the coligands L: with the strongly π -accepting carbonyl ligands the polarization in the P-N entity would be strongest, thus favouring formation of **III**.

The formation of **II** and **III** via intermediate **G** is in line with other reactions in which an initial oxidative addition to a rhodium(I) or iridium(I) centre is succeeded by hydrogen transfer reactions [5, 31c, 32]. Moreover, intermediate **G** has previously been observed in the reaction of the bis-

(iminophosphoranyl)methanide complexes $[M\{(4-CH_3-C_6H_4-N=PPh_2)_2CH\}L_2]$ ($M = Rh, Ir$; $L_2 = (CO)_2, COD$) with 1 equivalent HCl [20]. This reaction yielded both **II** and **III** in ratios **II:III** of 1:4 ($M = Rh, L_2 = COD$), 1:6 ($M = Rh, L = CO$) and 1:1 ($M = Ir, L_2 = COD$). Although these product ratios differ from those found in the reactions of $[ML_2Cl]_2$ with **Ia** (1:1.5, 1:5 and 1:8.5, respectively), formation of the intermediate complex **G** during the reaction of $[ML_2Cl]_2$ with **I** seems a reasonable alternative. In this respect we recall that both reactions were performed under different reaction conditions and it has been shown that the product ratio **II:III** is

strongly dependent on several reaction parameters (Table 1).

Both reaction pathways depicted in Scheme 3 may account for the formation of II and III.

Conclusions

It has been shown that pure compounds of the type $[\text{ML}_2\{(4\text{-R}'\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2)_2\text{CH}_2\}]^+\text{X}^-$ (II) and $[\text{ML}_2(4\text{-R}'\text{-C}_6\text{H}_4\text{-N}=\text{PPh}_2\text{-CH-PPh}_2\text{-NH-C}_6\text{H}_4\text{-R}'\text{-4})]^+\text{X}^-$ (III) have been obtained in the reaction of $[\text{ML}_2\text{Cl}]_2$ with $\text{CH}_2(\text{PPh}_2=\text{N-C}_6\text{H}_4\text{-R}'\text{-4})_2$ (I) only in a few favourable cases whereas generally mixtures of II and III are formed. The product ratio II:III is influenced by several reaction parameters, such as ratio of reactants, the type of reactants and the reaction conditions, in a way that is not fully understood on the basis of the data yet available.

Supplementary material

Full details concerning the crystal structure determination can be obtained from the authors on request.

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