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Stabilization of Rhodium(I)- and Iridium(I)–Alkyl Bonds by Intramolecular Coordination of an Iminophosphorane. X-ray Crystal Structure of [$Rh(CH_2PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(COD)$]

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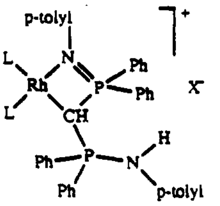
Lithium(iminophosphoranyl)methanide Li[$CH_2PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4$] (**2a**) reacts with the rhodium and iridium complexes [$ML_2Cl]_2$ (M = Rh, L_2 = COD, L = CO: M = Ir, L_2 = COD) to yield the complexes [$M(CH_2PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)L_2$] (**3a**, M = Rh, L_2 = COD; **3c**, M = Rh, L = CO; **3e**, M = Ir, L_2 = COD), in which the (iminophosphoranyl)methanide ligand is coordinated as a σ-N,σ-C chelate, forming a new four-membered metallacycle. The molecular structure of **3a** has been determined by X-ray crystallographic analysis. Compound **3a** crystallizes in space group $P2_1/n$ with a = 31.877 (3) Å, b = 12.932 (2) Å, c = 13.579 (2) Å, and β = 99.14 (1)°, and the structure was refined to R = 0.041 (R_w = 0.043) by using 10 500 independently measured reflections. The square-planar coordination around rhodium(I) involves the two olefinic bonds of COD and the N and C atoms of the σ-N,σ-C chelated (iminophosphoranyl)methanide ligand (Rh–N = 2.132 (3) Å and Rh–C_1 = 2.128 (3) Å). In the rhodium and iridium (iminophosphoranyl)methanide complexes the M–C(sp^3) bond is effectively stabilized by intramolecular coordination of an iminophosphorane group, as illustrated by their thermal stability and the inertness of **3a,c** toward small molecules such as CO and CO_2, as well as activated olefins and acetylenes. Reaction of the rhodium complexes **3a,c** with 1 equivalent of HCl gives either the σ-N-coordinated iminophosphorane complex [$Rh(4\text{-}CH_3\text{-}C_6H_4\text{-}N{=}P(CH_3)Ph_2)L_2Cl$] (**5**) or the N-protonated species [$Rh(CH_2PPh_2NH\text{-}C_6H_4\text{-}CH_3\text{-}4)L_2]Cl$ (**6**) depending on the ligand L and the applied conditions. The reaction proceeds most probably via an intermediate Rh(III) oxidative-addition product (a metal hydride was observed by IR spectroscopy) that further reacts via hydrogen migration reactions to yield **5** or **6**, i.e. with a net protonation of the C atom or the N atom, respectively, in **3**.

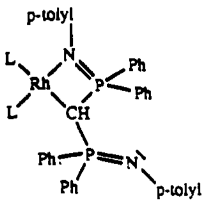
Introduction

There is a current appreciation of the synthesis and chemistry of complexes of late transition metals that 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.[1] In the course of this work we found that bis((*p*-tolylimino)diphenylphosphoranyl)methane and -methanide can coordinate in a σ-N,σ-C chelating mode toward Rh(I) (complexes I and II, respectively).[1c,d,2]



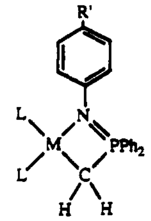
I: L=CO, L_2=COD

X=Cl, $Rh(COD)Cl_2$

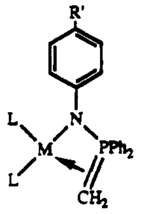


II: L=CO, L_2=COD

Thus far such four-membered M–N–P–C rings were unknown for iminophosphorane compounds, and we were interested to know whether a similar (iminophosphoranyl)methanide complex containing a secondary methanide carbon atom as in **3** or **3′** could be synthesized, i.e. substituting the pending aminophosphonium substituent as in I or the iminophosphorane substituent as in II for hydrogen.



3a: M=Rh, L_2=COD, R′=CH_3
3b: M=Rh, L_2=COD, R′=NO_2
3c: M=Rh, L=CO, R′=CH_3
3d: M=Rh, L=CO, R′=NO_2
3e: M=Ir, L_2=COD, R′=CH_3



3′

Other, related ligands of the type X–Y–Z that can adopt a similar pseudoallylic coordination geometry are well-known, i.e. for example amidino (RN–CR–NR),[3-8] triaz-

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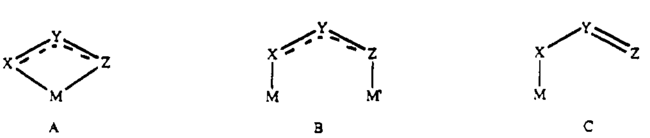
enido (RN-N-NR),[3,8,9] diimidophosphonium (RN-PR'$_2$-NR),[10-12] or phosphoniobis(methylide) (R_2C-PR'$_2$-CR_2)[13-16] compounds. It has been shown that these types of ligands usually coordinate in a chelating (A), bridging (B), or monodentate (C) coordination mode with metal atoms.



Phosphoniobis(methylide) complex ([R'$_2$P(CH$_2$)$_2$]$^-$), for example, can coordinate in a σ-C,σ-C' chelating or bridging mode with Rh(I), dependent on the substituents on P, the ligands on Rh, and the reaction temperature.[13,14,16]

In this paper the synthesis and structure of the new rhodium(I) and iridium(I) (iminophosphoranyl)methanide complexes [M(CH$_2$PPh$_2$=N-*p*-tol)L$_2$] (**3a**, M = Rh, L$_2$ = COD; **3c**, M = Rh, L = CO; **3e**, M = Ir, L$_2$ = COD; tol = tolyl) are reported. In these complexes (iminophosphoranyl)methanide acts as a σ-N,σ-C chelating ligand toward the metal atom in solution as well as in the solid state, just as has been found for the bis(iminophosphoranyl)methanide complexes I and II.[1c,2] We also report on the X-ray crystal structure of complex [Rh(CH$_2$PPh$_2$=N-*p*-tol)(COD)] (**3a**), which confirmed the molecular structure of this new type of compound and provided structural details about the four-membered metallacycle.

Furthermore, the reactivity of the Rh complexes **3a,c** toward some small molecules has been evaluated in order to assess the stability of the Rh-C and Rh-N bonds in these complexes and to probe the chemistry of molecules containing this combination of a pseudoallylic ligand and an electron-rich transition metal.

Experimental Section

All reactions were carried out in an atmosphere of purified nitrogen with the use of standard Schlenk techniques. Solvents were carefully dried and distilled prior to use. [Rh(COD)Cl]$_2$,[17] [Rh(CO)$_2$Cl]$_2$,[18] and [Ir(COD)Cl]$_2$[19] were synthesized according to literature procedures. Ph$_2$P(CH$_3$)=N-C$_6$H$_4$-R'-4 (R' = CH$_3$, NO$_2$) was synthesized from PPh$_2$CH$_3$ and 4-R'-C$_6$H$_4$-N$_3$ (R' = CH$_3$, NO$_2$) by using the Staudinger reaction.[20] [Rh(Ph$_2$P(CH$_3$)=N-C$_6$H$_4$-CH$_3$-4)ClL$_2$] (**5a**, L$_2$ = COD; **5c**, L = CO) was synthesized from Ph$_2$P(CH$_3$)=N-C$_6$H$_4$-CH$_3$-4 and [RhL$_2$Cl]$_2$.[21]

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC100 and WM250 spectrometers. ^{31}P NMR spectra were obtained on Bruker WP80 and AC100 spectrometers. ^{103}Rh NMR spectra were recorded on a Bruker AC100 spectrometer, by using indirect 2D ^{31}P,^{103}Rh{^{1}H} NMR spectroscopy.[22] Chemical shift values are in ppm relative to Si(CH$_3$)$_4$ for ^{1}H and ^{13}C spectra, to 85% H$_3$PO$_4$ for ^{31}P spectra, and to Ξ(^{103}Rh) = 3.16 MHz for ^{103}Rh spectra, adopting the sign convention that shifts to high frequency are positive. Coupling constants are in hertz. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. Field desorption (=FD) mass spectra were obtained on a Varian MAT711 double-focusing mass spectrometer, fitted with a 10-μm tungsten-wire FD-emitter containing microneedles with an average length of 30 μm, and were performed by the Institute for Mass Spectroscopy of the University of Amsterdam. Elemental analyses were carried out by the Elemental Analysis section of the Institute for Applied Chemistry, ITC/TNO, Zeist, The Netherlands.

Synthesis of [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(COD)] (3a). Li[CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4] (**2a**) was prepared by adding 11 mL of a 0.135 M BuLi solution in benzene to a stirred solution of Ph$_2$P(CH$_3$)=N-C$_6$H$_4$-CH$_3$-4 (**1a**; 458 mg, 1.5 mmol) in benzene (60 mL) at 283 K. After 2 h a solution of 370 mg of [Rh(COD)Cl]$_2$ (0.75 mmol) in 60 mL benzene was added dropwise at 283 K. Upon addition the color of the reaction mixture changed immediately to dark brown. After being stirred for 2 h at room temperature, the brown solution was evaporated to dryness. The brown residue was extracted with pentane until the initially yellow extracts were almost colorless (ca. 70 mL). The combined extracts were evaporated to dryness in vacuo, giving a yellow powder in approximately 50% yield. Orange crystals of **3a**, suitable for crystal structure determination, were formed from the pentane extracts upon standing for 10 h at 298 K under N$_2$ atmosphere. Anal. Calcd for C$_{28}$H$_{31}$NPRh: C, 65.25; H, 6.06; N, 2.72; P, 6.01. Found: C 65.16; H, 6.12; N, 2.54; P, 5.72. FD mass: found, *m*/*z* = 515 (M$^+$); calcd for C$_{28}$H$_{31}$NPRh, M_r = 515.442.

Synthesis of [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(CO)$_2$] (3c). Method 1. To a solution of 1.34 mmol of **2a** in 60 mL of benzene, which was prepared in a way similar to that described for **3a**, was slowly added 260.5 mg of [Rh(CO)$_2$Cl]^2 (0.67 mmol) in 60 mL of benzene at 283 K. After addition the reaction mixture was stirred for 2 h at 298 K. Then the dark brown solution was concentrated to ca. 2 mL, and 20 mL of pentane was added. The gray precipitate was filtered off and washed with pentane. The combined filtrate and washings were evaporated to dryness in vacuo, giving yellow **3c** in circa 40% yield. Crystallization of **3c** from pentane at 253 K under N$_2$ atmosphere gave orange crystals, which contained according to ^{1}H NMR and elemental analysis 0.5 equiv of C$_5$H$_{12}$. Anal. Calcd for C$_{22}$H$_{19}$NO$_2$PRh·0.5C$_5$H$_{12}$: C, 58.93; H, 5.05; N, 2.81; P, 6.20. Found: C, 58.78; H, 5.00; N, 2.84; P, 6.11. FD mass: found, *m*/*z* = 463 (M$^+$); calcd for C$_{22}$H$_{19}$NO$_2$Rh, M_r = 463.278).

Method 2. CO gas was bubbled through a stirred solution of 30 mg of **3a** (0.06 mmol) in benzene (30 mL) for 0.5 h at room temperature. Evaporation of the solvent in vacuo gave **3c** in quantitative yield.

Attempted Synthesis of [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-NO$_2$-4)(COD)] (3b) and [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-NO$_2$-4)(CO)$_2$] (3d) by Reaction of [RhL$_2$Cl]$_2$ (L = CO, L$_2$ = COD) with Li(CH$_2$PPh$_2$=N-C$_6$H$_4$-NO$_2$-4) (2b). These reactions were performed in a way similar to that described for **3a,c**. During the deprotonation of **1b** with BuLi a color change from yellow to deep red was observed. When [RhL$_2$Cl]$_2$ was added, decomposition took place, indicated by blackening of the reaction mixture. Workup of this mixture by evaporation of the solvent and extraction with Et$_2$O gave a black residue and red extracts. Evaporation of the extracts to dryness gave a red powder. Analysis of this powder by ^{1}H and ^{31}P NMR (C$_6$H$_6$) and IR (KBr pellet) spectroscopy showed that the transmetalation reaction had not occurred (indicated by the presence of free **2b** and [RhL$_2$Cl]$_2$ for ca. 80%). In the ^{31}P NMR spectra signals were found, which can be attributed to the coordination products of **1b** (at 24.6 and 28.9 ppm respectively). The residues contained, according to ^{31}P NMR (C$_6$D$_6$) spectroscopy, besides **1b** and **2b** (total ca. 70%), the same products as found in the extracts (ca. 30%). In both the extracts and the residues no signals were found that could be attributed

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to **3b** or **3d**. Changing the reaction conditions (inverse addition, reaction temperature, reaction time, or solvent) did not give better results with respect to the transmetalation reaction.

Synthesis of [Ir(CH_2PPh_2=N-C_6H_4-CH_3-4)(COD)] (3e). A solution of 252 mg of $[Ir(COD)Cl]_2$ (0.38 mmol) in 40 mL benzene was slowly added at room temperature to a solution of 0.75 mmol of **2a** in 20 mL of benzene. After the mixture was stirred for 3 h, a dark purple solution was obtained. After evaporation of the solvent in vacuo the residue was extracted with hexane (50 mL). Evaporation of the extracts to dryness gave a purple powder (ca. 200 mg). Analysis of this product by ^1H and ^{31}P NMR spectroscopy showed that **3e** was contaminated with free **2a**, due to incomplete reaction. Purification of this mixture by crystallization failed due to slow decomposition reactions into unidentified products. The purple powder is very unstable in moist air and decomposes slowly when stored under N_2, even at 243 K. Attempts to optimize the reactions by changing the reaction conditions (variation of solvent, reaction temperature, or reaction time) were unsuccessful, giving incomplete or decomposition reactions.

Reaction of 3a with HCl. Method 1. To a solution of 17.5 mg of **3a** (0.04 mmol) in 3 mL of benzene was added 169 μL of a 0.224 N HCl solution in Et_2O (=0.04 mmol). After the solution was stirred for 2 h, the solvent was removed in vacuo. After washing with Et_2O (5 mL) and pentane and drying in vacuo, a yellow powder was obtained (ca. 90% yield). Analysis of this product by ^1H and ^{31}P NMR and IR spectroscopy showed that it was a mixture of $[Rh(COD)Cl]_2$ (**1a**) and [Rh($Ph_2P(CH_3)$=N-C_6H_4-CH_3-4)Cl(COD)] (**5a**). These products were present in the same ratio as the reaction products obtained in the reaction of **1a** with $[Rh(COD)Cl]_2$.[21]

Method 2. A 740-μL volume of a 0.167 N HCl solution in Et_2O (=0.12 mmol) was added to a stirred solution of 63.8 mg of **3a** (0.12 mmol) in 20 mL of Et_2O at 213 K. After 1 h at 213 K and 1 h at 298 K, the solvent was evaporated to dryness in vacuo, giving [Rh{$CH_2PPh_2NH(C_6H_4$-CH_3-4)}(COD)]Cl (**6a**) in quantitative yield. IR (KBr pellet): ν(N-H) = 3084, ν(P-N) = 1236 cm^{-1}.

Synthesis of [Rh{$CH_2PPh_2NH(C_6H_4$-CH_3-4)}$(CO)_2$]Cl (6c). A 290-μL volume of a 0.224 N HCl solution in Et_2O was added to 30.6 mg of **3c** (0.066 mmol) in 3 mL of Et_2O. After the solution was stirred for 2 h, the solvent was removed in vacuo, giving yellow **6c** in quantitative yield. IR (KBr pellet): ν(N-H) = 3124, ν(P-N) = 1230 cm^{-1}. FD mass: found, m/z = 499 (M^+); calcd for $C_{22}H_{20}ClNO_2PRh$, M_r = 499.739.

Synthesis of [Rh{$Ph_2P(CH_3)NH(C_6H_4$-CH_3-4)}$Cl(CO)_2$]Cl (7c). Method 1. Dry HCl gas, obtained by adding 98% H_2SO_4 to anhydrous NH_4Cl, was slowly bubbled through a solution of **3c**, **5c**, or **6c** in benzene for 0.5 h. After evaporation of the solvent, washing with Et_2O and pentane, and drying in vacuo, **7c** was obtained in ca. 95% yield.

Method 2. To a solution of 102.5 mg of **1a** (0.34 mmol) in 8 mL of Et_2O was added 1.5 mL of a 0.224 N HCl solution in Et_2O (=0.34 mmol). After 15 min a white solid had precipitated (= [$Ph_2P(CH_3)NH(C_6H_4$-CH_3-4)]Cl). Then a solution of 65.3 mg of $[Rh(CO)_2Cl]_2$ (0.17 mmol) in Et_2O (5 mL) was added slowly to this suspension. After the mixture was stirred for 2 h, a yellow precipitate had formed. After filtration and washing with Et_2O (3 × 5 mL), **7c** was obtained in 90% yield. Anal. Calcd for $C_{22}H_{21}Cl_2NO_2PRh$: C, 49.28; H, 3.95; N, 2.61. Found: C, 48.57; H, 4.10; N, 2.53.

Reaction of 3a,c with RC≡CR′ or RCH=CHR′. Stirring a mixture of **3a** or **3c** and an equimolar quantity of dimethyl acetylenedicarboxylate, methyl acetylenecarboxylate, dimethyl fumarate, or methyl acrylate in CH_2Cl_2 or C_6H_6 for 2 h at 333 K gave no reaction, and **3a** or **3c** was recovered unchanged.

Reaction of 3c with CO. Bubbling CO gas through a solution of **3c** in benzene at room temperature gave no reaction. Raising the temperature to 333 K had no effect, and **3c** could be recovered unchanged.

Reaction of 3a,c with CO_2. Bubbling CO_2 gas, obtained by evaporation of solid CO_2 and dried by passing through sulfuric acid, through a solution of **3a** or **3c** in benzene at 333 K for several hours gave no reaction, and **3a** or **3c** could be obtained unaltered.

Reaction of 3a,c with CH_3X (X = I, OTf). To a solution of **3a** or **3c** in benzene was added an equimolar quantity of CH_3X (X = I, OTf). The reaction was followed by ^{31}P NMR spectroscopy. At room temperature no reaction occurred within 1 day. When the reaction mixture was heated at 353 K for 5 min or stored at room temperature for several days, a reaction occurred. Several new products were formed, which could not be identified.

Table I. Crystal Data and Details of the Structure Determination of [Rh(CH_2PPh_2=N-C_6H_4-CH_3-4)(COD)] (3a)

(a) Crystal Data	
formula	$C_{28}H_{31}NPRh$
mol wt	515.45
space group	$P2_1/n$
cryst syst	monoclinic
a, Å	31.877 (3)
b, Å	12.932 (2)
c, Å	13.579 (2)
β, deg	99.14 (1)
V, Å^3	2405.9 (8)
Z	4
D_x, g·cm^{-3}	1.42
$F(000)$, e	1064
μ(Mo Kα), cm^{-1}	7.78
min and max abs corr	0.84, 1.13
appr cryst size, mm	0.25 × 0.28 × 0.38
(b) Data Collection	
radiation (λ, Å)	Mo Kα (0.710 69)
T, K	295
data set	$-22 \le h \le 22, 0 \le k \le 20, 0 \le l \le 21$
tot. no. of unique reflcns	10 500
no. of obsd data ($I > 2.5\sigma(I)$)	5627
(c) Refinement	
weightg scheme	$w = (5.7 + F_o + 0.013F_o^2)^{-1}$
final R values	$R = 0.041, R_w = 0.043$
min and max res dens, e·Å^{-3}	−0.5, 0.5

Reaction of 6c with CH_3OTf. When 1 equiv of CH_3OTf was added to **6c** in benzene at room temperature, no reaction occurred. Even after being heated at 353 K for 1 h, **6c** could be recovered unchanged.

Crystal Structure Determination of [Rh(CH_2PPh_2=N-C_6H_4-CH_3-4)(COD)] (3a). Crystal data and numerical details of the structure determination are listed in Table I. A crystal with approximate dimensions 0.25 × 0.28 × 0.38 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation and a θ–2θ scan. A total of 10 500 unique reflections were measured within the range $-22 \le h < 22$, $0 \le k \le 20$, $0 \le l \le 21$. The maximum value of $(\sin \theta)/\lambda$ was 0.80 Å^{-1}. Unit cell parameters were refined by a least-squared fitting procedure using 23 reflections with $38 < 2\theta < 40°$. Corrections for Lorentz and polarization effects were applied. The positions of the Rh and P atoms were determined by direct methods with the program SIMPEL.[23] From a ΔF synthesis the rest of the non-hydrogen atoms were derived. After isotropic refinement the H atoms were derived from a subsequent ΔF synthesis. Block-diagonal least-squares refinement on F, anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, converged to $R = 0.041$, $R_w = 0.043$, and $(\Delta/\sigma)_{max} = 1.06$. A weighting scheme $w = (5.7 + F_o + 0.013F_o^2)^{-1}$ was used. The isotropic secondary extinction coefficient refined to 5.3 × 10^{-4}.[24] An empirical absorption correction (DIFABS)[25] was applied, with coefficients in the range of 0.84–1.13. A final difference Fourier map revealed a residual electron density between −0.5 and 0.5 e Å^{-3}. Scattering factors were taken from Cromer and Mann.[26] Anomalous dispersion for Rh and P was corrected for. All calculations were performed with XRAY76.[27]

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Results and Discussion

Synthesis. Formation of transition metal to carbon bonds can be accomplished in several ways. One of the most applicable synthetic methods is the transfer of an organo group from an organolithium or organomagnesium compound to a transition-metal halide. Several complexes containing a Rh–C or Ir–C bond have been obtained in this way.[28-30] The new rhodium(I) and iridium(I) ((*p*-tolylimino)diphenylphosphoranyl)methanide complexes **3a,c,e** were synthesized from $[ML_2Cl]_2$ (M = Rh, L_2 = COD, L = CO; M = Ir; L_2 = COD) and the organolithium compound $[LiCH_2PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4]$ (**2a**) (eq 1). The *N*-*p*-nitrophenyl-substituted compounds **3b,d** could not be obtained by using this method.

$$1/2\,[ML_2Cl]_2 + \underset{\mathbf{2a}}{Li[CH_2PPh_2N\text{-}C_6H_4\text{-}CH_3\text{-}4]} \xrightarrow{C_6H_6} [M(CH_2PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)L_2] \qquad (1)$$

3; **a**: M=Rh, L_2=COD
c: M=Rh, L=CO
e: M=Ir, L_2=COD

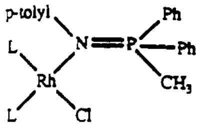
Lithiation of the *P*-CH_3-substituted iminophosphoranes **1a,b** was accomplished by reaction with BuLi in benzene at 283 K. Upon reaction the reaction mixture changed color from beige (**1a**) to yellow (**2a**) or from yellow (**1b**) to deep red (**2b**). This can be explained by delocalization of the negative charge on the methanide group over the entire C–P–N-aryl moiety, which will be particularly favorable when the electron-withdrawing NO_2 group is present on the aryl entity as in the case of **1b** and **2b**.

Reaction of the organolithium compound **2a** with $[ML_2Cl]_2$ in benzene gave the rhodium and iridium (iminophosphoranyl)methanide complexes **3a,c,e** in moderate yield (eq 1). During the reaction slight decomposition was observed, envisaged by a blackening of the reaction mixture. Contrary to expectation, no direct precipitation of LiCl was observed. After evaporation of the solvent and extraction of the residue with pentane or hexane pure **3a** and **3c** were obtained by evaporation of the organic fraction. Compound **3e** could not be obtained in analytically pure state, since during purification (extraction or crystallization) slow decomposition took place, but its structure could unambiguously be assigned by means of ^1H and ^{31}P NMR spectroscopy (vide infra).

The compounds **3a,c,e** are soluble in all common organic aprotic solvents including alkanes. The crude reaction products **3a,c,e** decompose slowly in solution (243 K), whereas the analytically pure compounds **3a,c** are thermally stable up to 353 K in benzene for several hours (vide infra). The complexes **3a,c** are stable in H_2O and CH_3OH at room temperature for at least 2 h but react at elevated temperatures to $Ph_2P(CH_3){=}O$, *p*-toluidine, and some unidientified Rh(0) and Rh(I) compounds (^1H and ^{31}P NMR). Compounds **3a,c** are thermally stable in the solid state in moist air at room temperature and up to 353 K under a nitrogen atmosphere. Compound **3e** decomposes rapidly in moist air at room temperature, and slow decomposition is observed when **3e** is stored under N_2 at 243 K (complete decomposition after 16 h).

The residual products of the transmetalation reaction consisted of LiCl and, according to ^1H and ^{31}P NMR spectroscopy, of several other products of which only free **1a** could be identified. Attempts to optimize the reaction by changing the reaction conditions (inverse addition, reaction temperature, reaction time, solvent) were unsuccessful; the reaction mixture contained either more starting materials or more decomposition products.

Another route for the synthesis of the rhodium (iminophosphoranyl)methanide complexes **3a,c** could be the deprotonation of the methyl group in the coordination complexes of **1a**, i.e. **5a** and **5b**. Unfortunately, no reaction occurred when NEt_3 was used as the base, whereas use of LDA or BuLi led to extensive decomposition and no formation of the complexes **3a,c** was observed.



5a: L_2=COD
5b: L=CO

When the organolithium compound **2b** (R′ = NO_2) was reacted with the Rh complexes $[RhL_2Cl]_2$ (L = CO, L_2 = COD), only decomposition reactions were observed. Analysis of the reaction products by ^1H and ^{31}H NMR spectroscopy revealed that it merely consisted of unreacted **2b** and $[RhL_2Cl]_2$. The difference in reactivity of **2a** and **2b** can be understood in terms of reduced nucleophilicity of the N atom in **2b** with respect to **2a**, due to the electron-withdrawing capacity of the NO_2 substituent on the aryl group in **2b**. So, **2b** is expected to have a lower affinity toward Rh(I) than **2a**. In other work it has been shown that the reactivity of iminophosphoranes ($R_3P{=}NR'$) toward $[RhL_2Cl]_2$ (L = CO, L_2 = COD) is indeed strongly dependent on the nucleophilicity of the N atom.[21] Apparently, also the (((*p*-nitrophenyl)imino)phosphoranyl)methanide species (i.e. the Li compound thereof) is not nucleophilic enough to give the desired reaction.

In analogy to Abel et al.,[4] two mechanisms for the formation of the (iminophosphoranyl)methanide complexes are conceivable (Scheme I). In mechanism I (steps 1, 2, and 3) the first step is the coordination of the imino nitrogen atom to the metal, which is followed by attack of the methanide carbon atom on the metal and elimination of LiCl. In the other mechanism (steps 4 and 5) LiCl is eliminated first upon coordination of the methanide carbon atom, followed by nitrogen coordination. Of these mechanisms, the first is preferred, as it can explain the observed dependence of the product formation on the nucleophilicity of the nitrogen atom as a function of the substituent R′.

The isolated compounds **3a,c** represent rare examples of stable rhodium–diene or –carbonyl complexes containing a Rh(I)–C σ bond.[28-30] The stability of the compounds

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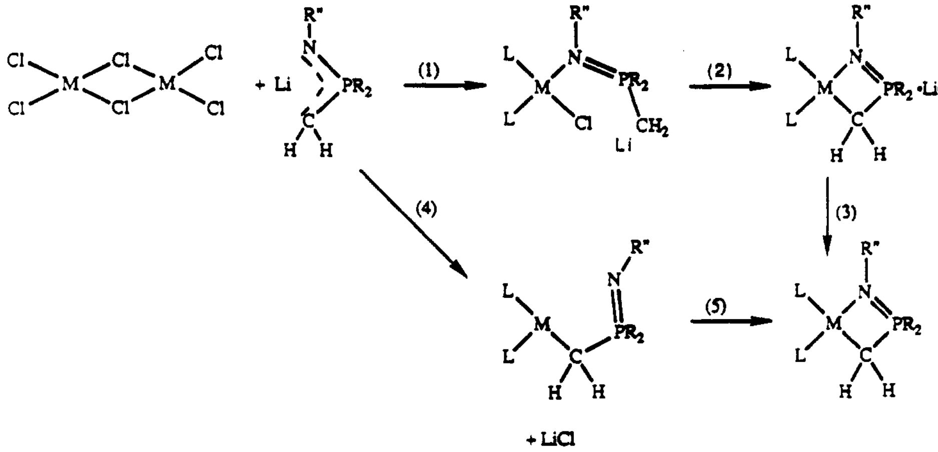
Scheme I. Formation of [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)L$_2$]^a



^{a}R = Ph, R″ = *p*-tolyl.

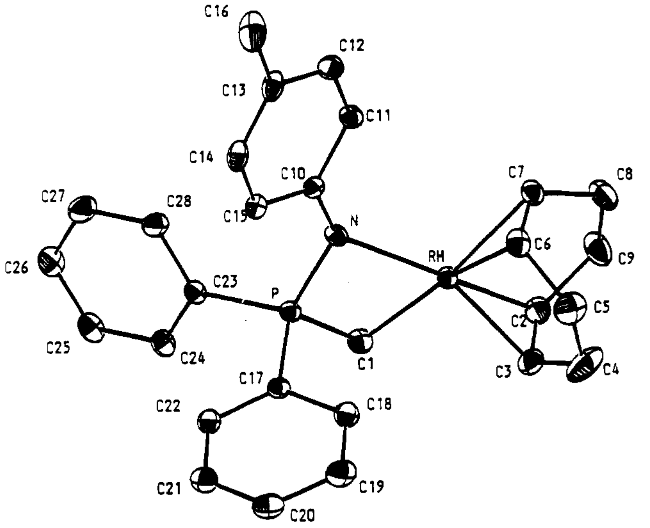


Figure 1. Molecular structure of [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(COD)] (**3a**), with the adopted numbering scheme of the non-H atoms (thermal ellipsoids drawn at 50% probability).

Table II. Selected Interatomic Bond Distances (Å) and Bond and Torsion Angles (deg) for [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(COD)] (3a) with Standard Deviations in Parentheses

	Bonds around Rh		
Rh–C$_1$	2.128 (3)	Rh–C$_7$	2.184 (3)
Rh–C$_2$	2.097 (4)	Rh–M$_1$	1.974 (4)
Rh–C$_3$	2.086 (4)	Rh–M$_2$	2.053 (3)
Rh–C$_6$	2.146 (3)	Rh–P	2.714 (1)
Rh–N	2.132 (3)		
	Bonds in L		
P–C$_1$	1.750 (3)	N–C$_{10}$	1.414 (3)
P–C$_{17}$	1.820 (3)	C$_1$–H$_{111}$	0.93 (3)
P–C$_{23}$	1.814 (3)	C$_1$–H$_{112}$	0.97 (3)
P–N	1.624 (2)		
	Bonds in COD		
C$_2$–C$_3$	1.381 (5)	⟨C$_{sp^2}$–C$_{sp^3}$⟩	1.481 (6)
C$_6$–C$_7$	1.375 (4)	⟨C$_{sp^3}$–C$_{sp^3}$⟩	1.512 (5)
	Angles around Rh		
C$_1$–Rh–N	74.2 (2)	N–Rh–M$_1$	167.8 (1)
C$_1$–Rh–M$_1$	94.7 (1)	N–Rh–M$_2$	103.3 (1)
C$_1$–Rh–M$_2$	176.3 (1)	M$_1$–Rh–M$_2$	87.6 (1)
	Angles around P		
N–P–C$_1$	99.1 (2)	C$_1$–P–C$_{17}$	108.8 (2)
N–P–C$_{17}$	114.3 (2)	C$_1$–P–C$_{23}$	114.4 (2)
N–P–C$_{23}$	113.8 (2)	C$_{17}$–P–C$_{23}$	106.5 (2)
	Angles around C1		
P–C$_1$–Rh	88.3 (2)	Rh–C$_1$–H$_{111}$	117 (3)
P–C$_1$–H$_{111}$	118 (3)	Rh–C$_1$–H$_{112}$	104 (3)
P–C$_1$–H$_{112}$	116 (3)	H$_{111}$–C$_1$–H$_{112}$	112 (4)
	Angles around N		
P–N–Rh	91.5 (2)	Rh–N–C$_{10}$	133.5 (2)
P–N–C$_{10}$	127.6 (2)		
	Angles in COD		
⟨C$_{sp^3}$–C$_{sp^2}$–C$_{sp^2}$⟩	125.1 (4)	⟨C$_{sp^2}$–C$_{sp^3}$–C$_{sp^3}$⟩	114.9 (4)
	Torsion Angles		
C$_1$–P–N–C$_{10}$	185 (1)	Rh–N–C$_{10}$–C$_{11}$	54 (1)
P–N–C$_{10}$–C$_{11}$	165 (1)		

(**3a,c**) is similar to other complexes containing a Rh(I)–C bond in which stabilization of a Rh–R (R = alkyl, aryl) species is attained via intramolecular coordination.[31] In **3a,c** stabilization occurs by internal coordination of an iminophosphorane group. The stability of the thus formed cyclic Rh–N–P–C entity may be enhanced by polarization within this ring induced by coordination of the polar P=N group, giving rise to strong metal to carbon and metal to nitrogen bonds. The stability of the four-membered ring is demonstrated by the thermal stability and the inertness of both **3a** and **3c** toward CO, CO$_2$, RC≡CR′, RCH=CHR′, H$_2$O, and CH$_3$OH (vide infra). Whereas other Rh(I)-alkyl compounds are very prone to C–H bond activation and decomposition reactions,[28,29] **3a,c** are stable in C$_6$H$_6$ at 353 K or in CH$_2$Cl$_2$ at 313 K for several hours.

Solid-State Structure of [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(COD)] (3a). The X-ray crystal structure of **3a** exhibits four discrete monomeric molecules in an unit cell. An ORTEP drawing of the molecular structure of [Rh(CH$_2$PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(COD)] and the adopted numbering scheme are shown in Figure 1. Selected bond distances and angles are given in Table II. The positional and thermal parameters of the non-hydrogen atoms are listed in Table III.

The coordination geometry around Rh is square planar with the coordination positions occupied by the two olefinic bonds of the cyclooctadiene (with M$_1$ and M$_2$ being the

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Table III. Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters for 3a

atom	*x*	*y*	*z*	U_{eq}, Å^2
Rh	0.61474 (2)	0.27058 (2)	0.51327 (2)	0.0331 (1)
P	0.43273 (6)	0.20935 (7)	0.53692 (7)	0.0322 (4)
C_1	0.5024 (3)	0.1686 (3)	0.4474 (3)	0.042 (2)
C_2	0.7132 (3)	0.2272 (4)	0.4185 (3)	0.053 (2)
C_3	0.7269 (3)	0.1657 (4)	0.5027 (4)	0.057 (3)
C_4	0.8108 (4)	0.1764 (5)	0.5887 (5)	0.099 (4)
C_5	0.8005 (4)	0.2578 (5)	0.6620 (4)	0.074 (3)
C_6	0.7220 (3)	0.3368 (4)	0.6271 (3)	0.050 (2)
C_7	0.7181 (3)	0.3983 (3)	0.5440 (3)	0.045 (2)
C_8	0.7935 (4)	0.3965 (4)	0.4752 (4)	0.070 (3)
C_9	0.7775 (4)	0.3153 (4)	0.3963 (5)	0.079 (4)
C_{10}	0.4677 (2)	0.3888 (3)	0.6422 (2)	0.031 (2)
C_{11}	0.5039 (3)	0.4893 (3)	0.6408 (3)	0.038 (2)
C_{12}	0.4884 (3)	0.5607 (3)	0.7129 (3)	0.047 (2)
C_{13}	0.4354 (3)	0.5361 (4)	0.7877 (3)	0.051 (2)
C_{14}	0.3993 (3)	0.4369 (4)	0.7887 (3)	0.048 (2)
C_{15}	0.4139 (3)	0.3636 (3)	0.7175 (3)	0.040 (2)
C_{16}	0.4187 (4)	0.6154 (5)	0.8651 (5)	0.093 (4)
C_{17}	0.4460 (3)	0.1154 (3)	0.6380 (3)	0.034 (2)
C_{18}	0.5395 (3)	0.0926 (3)	0.6864 (3)	0.047 (2)
C_{19}	0.5539 (3)	0.0207 (4)	0.7631 (3)	0.056 (3)
C_{20}	0.4751 (4)	−0.0285 (3)	0.7930 (3)	0.054 (2)
C_{21}	0.3824 (3)	−0.0060 (3)	0.7466 (3)	0.049 (2)
C_{22}	0.3676 (3)	0.0651 (3)	0.6693 (3)	0.041 (2)
C_{23}	0.3030 (2)	0.2198 (3)	0.4912 (2)	0.036 (2)
C_{24}	0.2571 (3)	0.1417 (3)	0.4300 (3)	0.045 (2)
C_{25}	0.1590 (3)	0.1497 (4)	0.3883 (3)	0.050 (2)
C_{26}	0.1064 (3)	0.2354 (4)	0.4060 (3)	0.057 (2)
C_{27}	0.1508 (3)	0.3144 (4)	0.4656 (4)	0.061 (3)
C_{28}	0.2493 (3)	0.3065 (3)	0.5079 (3)	0.049 (2)
N	0.4856 (2)	0.3196 (2)	0.5665 (2)	0.033 (1)

midpoints of C_2–C_3 and C_6–C_7, respectively) and the N and C_1 atoms of the chelating (iminophosphoranyl)methanide. The square-planar coordination mode is slightly distorted, and the metal lies 0.073 Å below the plane defined by M_1, M_2, C_1, and N. The dihedral angle between the planes defined by N–Rh–C_1 and M_1–Rh–M_2 amounts to 5.7°. The Rh–P distance of 2.714 (1) Å is indicative of a nonbonding interaction. So, the (iminophosphoranyl)methanide ligand is coordinated in a *σ*-N,*σ*-C *bidentate chelating mode*, with no further interaction between the ligand and the Rh atom being present.

The Rh–N distance of 2.132 (3) Å is a normal value and can for example be compared to 2.081 (8) Å in [Rh(COD)(*p*-tol-N=PPh$_2$CHPPh$_2$NH-*p*-tol)] (I),[1c] 2.144 (9) and 2.17 (1) Å in [Rh{CH$_2$(PPh$_2$=N-*p*-tol)$_2$}(COD)],[1e] or 2.086 (6)–2.138 (4) Å in [Rh$_2${*μ*-CPh(NPh)$_2$}(tfbb)$_2$].[5]

Only few organorhodium(I) compounds containing a Rh(I) to C(sp^3) bond have been crystallographically authenticated. Therefore, little reference material is available for comparison with the observed Rh–C_1 bonding distance of 2.128 (3) Å in **3a**. However, this value corresponds well to the Rh–C(sp^3) bond values for the bridging alkyl groups in (COD)$_2$Rh(CH$_2$Si(CH$_3$)$_3$)$_2$Li(tmed) (2.134 (5) and 2.114 (5) Å)[28d] or to values of 2.114 (5) and 2.123 (5) Å for complexes containing a Rh(I)–C(sp^2) bond like Rh[C$_6$H$_3$-(CH$_2$N(CH$_3$)$_2$)$_2$-*o*,*o*′](COD)[31g] but is smaller than Rh–C distances found for the bridging methyl groups in [(COD)Rh(CH$_3$)]$_2$ (2.194 (5)–2.225 (5) Å).[28a] The N–Rh–C_1 bite angle of 74.2 (2)° is acute, and its value is close to the 73.1 (1)° for the related bis(iminophosphoranyl)methanide compound [Rh(COD)(*p*-tol-N=PPh$_2$CHPPh$_2$NH-*p*-tol)] (I).[1c] These values are considerably larger than the the values for isoelectronic rhodium amidinate or triazenido complexes,[3,5,32,33] which is a result of the presence of the larger P atom instead of a C or N atom.

The Rh–M_1 bond distance (1.974 (4) Å, trans to N) is shorter than Rh–M_2 (2.053 (3) Å, trans to C_1), a difference that has also been observed in [Rh(COD)(*p*-tol-N=PPh$_2$CHPPh$_2$NH-*p*-tol)] (I)[1c] and that can be ascribed to the higher trans influence of the carbon atom compared to the nitrogen atom of the (iminophosphoranyl)methanide ligand. Both distances are within the range usually found for other molecules containing the Rh–COD fragment, i.e. 1.963 (9) and 1.969 (8) Å for [Rh(COD)Cl$_2$],[34] 1.986 (7) and 2.013 (6) Å for [Rh(COD)Cl(Et$_3$P=N-*p*-tol)],[21], 2.063 and 2.050 Å for (COD)$_2$Rh(CH$_2$Si(CH$_3$)$_3$)$_2$Li(tmed),[28d] or 1.999 (1) and 2.026 (3) Å for I.[1c] Despite the differences between the bond distances from Rh to the midpoints of the olefinic bonds, there is not significant difference in the olefinic bond distances themselves (1.381 (5) Å for C_2–C_3 and 1.374 (4) Å for C_6–C_7). This lack of correlation between C=C distances on the one hand and the Rh–M distances on the other hand has been ascribed to local repulsions within the coordination sphere.[31a,35] The COD ligand has a slightly distorted boat conformation, and the M_1–Rh–M_2 angle of 87.6 (2)° is close to the expected 90° for a square-planar coordination geometry around Rh.

Within the (iminophosphoranyl)methanide ligand the P atom has a distorted tetrahedral coordination geometry with a small C_1–P–N angle of 99.1 (2)° due to the constraints of the chelating ligand, whereas the other bond angles at phosphorus lie between 108.8 (2) and 114.4 (2)°. The ring constraint within the Rh–N–P–C_1 ring is also responsible for the small angles at N (Rh–N–P = 91.5°) and C_1 (Rh–C_1–P = 88.3 (2)°). The P–N bond distance of 1.624 (2) Å is a normal value for coordinated iminophosphoranes[36] and shows that the P–N bond has a bond order that is considerably larger than unity (cf. a formal single bond value of 1.77 Å[37] and a double bond of ca. 1.57 Å[37,38]). The P–C_1 bond distance of 1.750 (3) Å is slightly shorter than a formal single bond[37,38] but considerably longer than a formal double P–C bond (1.57 Å).[37] As this value is also close to that in coordinated phosphonium ylides, i.e. 1.788 (22) and 1.833 (22) Å in [Pt(PPh$_3$)I-(CH$_2$PPh$_3$)$_2$]I[39] or 1.782 (3) Å in [Rh{P(CH$_3$)$_3$}$_2$Cl$_3${CH$_2$P-(CH$_3$)$_3$}],[40] there may be some ylide character, as has been observed in the Ni(II) complex of the isoelectronic [Ph$_2$P(S)CH$_2$] anion (P–C = 1.776 (8) Å).[41] The plane defined by N, P, and C_1 makes an angle of 30.4° with the coordination plane, which is much larger than the corresponding angle of 2.1° in the comparable Ni(CH$_2$PPh$_2$=S) complex.

All crystallographic data point to an interpretation of the molecular structure of **3a** as depicted in the generic structure 3. However small contributions of the mesomeric ylide structure 3′ may explain the slightly shortened P–C_1

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Table IV. IR and ^{31}P NMR Data

	IR, cm^{-1}			^{31}P NMR^a	
	ν(P–N)^b	ν(CO)^b	ν(CO)^c	δ(P)	^2J(P,Rh), Hz
1a	1322			–0.9 (s)	
1b	1304			4.5 (s)	
3a	1294			40.0 (d)	18.4
3c	1292	2051, 1971	2050, 1970	54.2 (d)	18.5
3e				52.9 (s)	
5a	1261			25.4 (d)	8.4
5c	1249	2071, 1996	2076, 1998	30.4 (d)	9.0
6a	1236			45.4 (d)^d	2.7^d
6c	1230	2045, 1981	2040, 1973	43.3 (d)	4.9
7c	902	2067, 1999, 1985	2074, 1999	35.4 (s)	

^{a} Solvent: C_6D_6. Chemical shift values in ppm relative to 85% H_3PO_4, positive values correspond to higher frequencies. Multiplicity: s; singlet; d = doublet. ^{b} KBr pellets. ^{c} Solvent: CH_2Cl_2. ^{d} Solvent: CD_2Cl_2.

bond as compared to a normal single bond and the lengthening of the P–N bond in comparison with a formal double bond as described above. We note that compound **3a** has a structure which is reminiscent of the coordination sphere in one of the crystallographically analyzed members of type I, [Rh(COD)(*p*-tol-N=PPh$_2$NH-*p*-tol)][Rh(COD)Cl$_2$],[1c] with only minor differences in bond distances and angles. Hence, the substitution of a hydrogen atom at the C atom coordinated to Rh in **3a** by the bulky [-PPh$_2$NH-*p*-tol] entity has only little impact on the structure in solid state.

Spectroscopy. Structure in the Solid State. Selected IR data are given in Table IV. In the IR spectra (KBr pellet) of compounds **3a,c** characteristic bands are found at 1294 and 1287 cm^{-1}, respectively, that can be attributed to ν(P=N). In the corresponding free iminophosphorane **1a** ν(P=N) amounts to 1322 cm^{-1}. The coordination shift $\Delta\nu$(P=N) amounts to ca. 30 cm^{-1} and is smaller than usually found upon coordination of an iminophosphorane ($R_3P{=}NR'$) to a transition metal.[2b,21,42] This finding indicates considerable double-bond character in the P–N bond, in agreement with the results obtained by the X-ray structure determination of **3a** (vide supra).

In the IR spectra of **3c** two signals of approximately equal intensity are found in the metal–carbonyl region (ν(CO) (KBr pellet) 2049, 1977 cm^{-1}), typical of *cis*-dicarbonyl species with C_s symmetry.[43]

FD mass spectra of **3a,c** showed only one signal at m/z = 515 and 463, respectively, confirming the monomeric structure of these compounds. No IR and FDMS spectra of **3e** could be obtained due to its instability.

Structure in Solution. In the ^{1}H NMR spectra of compounds **3a,c,e** (Table V) the signals of the CH_2 protons are found at 0.20, 0.45, and 1.03 ppm, respectively. These signals show a small ^2J(P,H) of 1.6, 3.6, and 2.5 Hz respectively, whereas for the rhodium complexes **3a,c** additional coupling with ^{103}Rh of 1.7 and 1.4 Hz, respectively, is observed. All values are close to those found for the related isoelectronic phosphoniobis(methylide) complexes of Rh and Ir. These complexes were shown to be monomeric or dimeric in solution, dependent on the ligands, P substituents, and the temperature.[13-17] Although the chemical shift and coupling constant values of **3a,c,e** are close to the values of the monomeric rhodium phosphoniobis(methylide) complexes and thus indicate monomeric structures for compounds **3a,c,e** in solution as well, a dimeric structure can not be excluded on the basis of these ^{1}H NMR data alone. The monomeric structure of compounds **3a,c** could unambiguously be established by their ^{31}P NMR spectra (Table IV). For complexes **3a,c** resonances were found at 40.0 and 56.2 ppm that showed a ^2J(Rh,P) coupling with only one rhodium atom of 18.4 and 18.5 Hz, respectively. As Lapinsky et al.[16] have demonstrated, these multiplicities and magnitudes of the coupling constants are characteristic of monomeric rhodium phosphoniobis(methylide) compounds. On the basis of the observed spectral analogies among compounds **3a,c,e**, the monomeric structure **3** can be assigned to compound **3e** in solution as well.

The large difference in ^{31}P chemical shift of **3a,c,e** with respect to the free ligand **1a**[38] cannot be understood by invoking only the coordination of the ligand.[21,42] Probably, differences in bond angles at phosphorus, which are known to have a large influence on ^{31}P chemical shifts and coupling constants,[44] play a role as well. This is in agreement with the results from the X-ray study of **3a** (vide supra), in which it has been shown that the N–P–C$_1$ angle is much smaller than usually found for tetrahedral phosphorus atoms.

In the ^{1}H NMR spectra of **3a,e** two signals are found for the COD olefinic hydrogen atoms, indicating at least C_s symmetry of these complexes in solution. By comparison with other Rh–COD complexes[28,31a] the resonances at higher frequencies can be attributed to the olefinic group trans to the nitrogen atom.

The ^{13}C NMR spectra of **3a,c** (Table VI) confirm the structural assignment, with the methanide carbon at δ = –7.4 ppm (dd, ^1J(Rh,C) = 19.2 and ^1J(P,C) = 72.3 Hz) for **3a** and δ = –13.2 ppm (dd, ^1J(Rh,C) = 14.4 and ^1J(P,C) = 67.0 Hz) for **3c**. For the COD ligand in **3a** the olefinic C-atom resonances are found at 69.6 ppm (d, J(Rh,C) = 13.6 Hz) and 85.5 ppm (d, J(Rh,C) = 9.0 Hz). The resonance at lower frequency (69.6 ppm) may be attributed to the olefinic C atoms in positions trans to the methanide C atom on the basis of its higher trans influence with respect to the N atom.

So, all spectral data for **3a,c** are in agreement with a monomeric structure in solution, similar to that found for these compounds in the solid state (IR, X-ray). Although complete data could not be obtained for the Ir complex **3e**, we assume that this complex has the same structure as the Rh complexes as well, because of the existing spectral analogies to **3a,c** and the iridium phosphoniobis(methylide) complexes.[15]

In the ^{103}Rh NMR spectra of **3a,c** the chemical shifts are found at 787 and –88 ppm, respectively, which values fall within the normal range for Rh(I) compounds.[45] A similar large shift toward high frequency (875 ppm) observed in going from L = CO (**3c**) to L$_2$ = COD (**3a**) has previously been found for [Rh(acac)L$_2$], [Rh(salophen)L$_2$], and [CpRhL$_2$],[46] illustrating the large dependence of the ^{103}Rh chemical shift on both structural and electronic factors. Substitution of CO by COD may cause a pronounced effect on several or all of the factors governing the transition-metal chemical shift, i.e. the average excitation energy ΔE^{-1}, the radial factor $\langle r^{-3}\rangle$, and the charge imbalance factor $\sum Q_n$.[22,47] Although the average excita-

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Table V. ^1H NMR Data[a]

	$\delta(P\text{–}CH_3)$	$\delta(P\text{–}CH_2)$	$^2J(P,H)$	$^2J(Rh,H)$	$\delta(R')$	$\delta(\text{aryl})$[b]	$\delta(\text{Ph})$	$\delta(\text{COD})$[c]	$\delta(N\text{–}H)$[d]
1a	1.61 (d)		12.6		2.22	6.89–7.05 (m)	6.89–7.05 (m) 7.56–7.74 (m)		
1b	1.45 (d)		12.8			6.63 (d, 9.1) 8.04 (dd, 9.1)[e]	6.86–7.09 (m) 7.33–7.55 (m)		
3a		0.20 (dd)	1.7	1.7	2.03	6.8 (br)	7.00–7.11 (m) 7.85–8.06 (m)	1.9 (br), 2.4 (br) 4.01 (br), 4.56 (br)	
3c		0.45 (dd)	3.6	1.4	1.98	6.72 (d, 8.4) 6.95 (d, 8.4)	6.88–7.01 (m) 7.48–7.70 (m)		
3e		1.03 (d)	2.5		2.01	6.74 (d, 8.6) 6.87 (d, 8.6)	6.9–7.1 (m) 7.7–8.0 (m)	1.9 (br), 2.4 (br) 3.83 (br), 4.24 (br)	
5a	2.72 (d)		13.0		2.01	6.8 (br)	6.8–7.2 (m) 7.6–7.9 (m)	1.7 (br), 2.2 (br) 3.78 (br), 5.00 (br)	
5c	2.11 (d)		13.0		1.97	6.74 (d, 8.0) 6.95 (d, 8.0)	6.9–7.0 (m) 7.3–7.6 (m)		
6a[f]		0.72 (dd)	11.8	1.9	2.14	6.7–6.9 (br)	7.3–8.0 (m)	1.9 (br), 2.4 (br) 2.81 (br), 4.19 (br)	9.02 (d, 6.3)
6c		1.63 (dd)	11.4	2.3	1.83	6.56 (d, 8.3) 6.73 (d, 8.3)	6.9–7.0 (m) 7.4–7.7 (m)		8.95 (d, 7.9)
7c	2.38 (d)		13.6		1.85	6.63 (d, 8.0) 7.12 (d, 8.0)	7.0 (br) 7.36–7.55 (m)		8.90 (d, 9.1)

[a] Solvent: C_6D_6. Multiplicity: d = doublet, dd = doublet of doublets, m = multiplet, br = broad signal. *J* values in Hz. [b] $^3J(H,H)$ in parentheses. [c] Aliphatic and olefinic signals, respectively. [d] $^2J(P,H)$ in parentheses. [e] $^4J(P,H) = 1.2$ Hz. [f] Solvent: CD_2Cl_2.

Table VI. ^{13}C[a] and ^{103}Rh[b] NMR Data for Compounds 3a,c

	$\delta(^{13}C)$					
	CH_2	$^1J(Rh,C)$	$C_6H_4\text{-}CH_3\text{-}4$	C_6H_5	COD/CO	$\delta(^{103}Rh)$
3a[c]	−7.4 (72.3)	19.3	147.8 (C_i), 123.9 (12.3, C_o), 129 (obs, C_m), 131.8 (C_p), 21.1 (CH_3)	137.0 (66.4, C_i), 131.9 (10.7, C_o), 129 (obs, C_m), 131.6 (2.6, C_p)	30.9, 33.3, 69.9 (13.6),[d] 85.5 (9.0)[d]	787
3c[e]	−13.2 (67.0)	14.4	146.1 (C_i), 121.2 (13.1, C_o), 129.6 (C_m), 130.0 (C_p), 20.7 (CH_3)	132.1 (71.1, C_i), 131.8 (10.5, C_o), 129.4 (11.1, C_m), 132.9 (2.9, C_p)	187.3 (57.9),[d] 191.0 (65.5)[d]	−88

[a] $J(P,C)$ in parentheses. i = ipso, o = ortho, m = meta, p = para, and obs = obscured by solvent signal. J values in Hz. [b] Measured in C_6D_6 at 295 K; chemical shift values in ppm relative to $\Xi(^{103}Rh) = 3.16$ MHz; positive values correspond to higher frequencies. [c] Solvent: toluene-d_8. [d] $^1J(Rh,C)$. [e] Solvent: CD_2Cl_2. $T = 243$ K.

tion energy is much larger for square-planar complexes than for octahedral ones, and hence the influence of changes in ΔE^{-1} will be less pronounced for **3a,c** compared to octahedral Rh(III) species, the chemical shift will be influenced to a certain extent by ΔE effects. So, when Rh(I) complexes containing COD are compared to those with the better π-acceptor set of two CO ligands, i.e. when **3a** is compared to **3c**, the average excitation energy ΔE will increase, which in turn leads to a decrease in paramagnetic shift contributions and hence a lower δ value, as is indeed observed. As stated before, however, in this type of square-planar complex the radial factor and charge imbalance factor may play a relatively important role. The amount and direction of these effects are difficult to assess for these complexes, but they are expected to counteract the ΔE effect. Further research on a broader range of compounds is necessary in order to obtain a better understanding of the extent of the contributions of each of these factors to the ^{103}Rh chemical shift value.[54]

Reactivity of $[Rh(CH_2PPh_2{=}N\text{-}p\text{-tol})L_2]$ (3a,c). General Considerations. The combination of a reactive d^8 transition-metal center with a polar (iminophosphoranyl)methanide ligand was expected to give rise to interesting chemistry, e.g. reactivity. First, insertion reactions may occur as a result of which the ring strain within the four membered Rh–N–P–C ring will be relieved. Insertion of, for example, alkynes, olefins, or CO into the M–N or M–C bonds could give rise to the formation of five- or six-membered rings. Second, the complex may be susceptible to oxidative-addition reactions at the metal atom upon reaction with electrophiles such as HCl, MeI, or I_2 (XY, eq 2), yielding Rh(III) complexes of the type

$$[Rh(I)(CH_2PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)L_2] + XY \longrightarrow [Rh(III)(CH_2PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)XYL_2] \quad (2)$$

$$R_3P{=}N\text{-}R' + XY \longrightarrow R_3P\text{-}NR'Y]X \quad (3)$$

$$R_3P{=}N\text{-}R' + CO_2 \longrightarrow R_3P{=}O + R'\text{-}N{=}C{=}O \quad (4)$$

$[Rh(CH_2PPh_2{=}N\text{-}p\text{-tol})(X)(Y)L_2]$. Third, reactions may occur that are typical for an iminophosphorane entity, i.e. reactions with electrophiles such as HCl, etc. with formation of an aminophosphonium group (eq 3) instead of oxidative addition or an aza-Wittig reaction with for example CO_2 (eq 4), giving a phosphine oxide and an isocyanate.[38,42]

The observed reactivity of the complexes **3a,c** toward alkynes, olefins, CO, CO_2, HCl, and CH_3X (X = I, OTf) is described below.

Reaction of 3a,c with HCl. The reaction of the rhodium (iminophosphoranyl)methanide complexes **3a,c** with hydrochloric acid yielded different types of complexes, depending on the molar ratio of the reactants, the reaction temperature, and the type of ligands on Rh. The reaction sequence is shown in Scheme II.

Reaction with 1 Equiv of HCl. When **3a** (L_2 = COD) was reacted with 1 equiv of HCl in benzene at room temperature, only $[Rh(Ph_2P(CH_3){=}N\text{-}p\text{-tol})Cl(COD)]$ (**5a**) was formed (reaction i); i.e., a net protonation of the methanide carbon atom had occurred. When the reaction was performed at 213 K in Et_2O, $[Rh(CH_2PPh_2NH\text{-}p\text{-tol})(COD)]Cl$ (**6a**) was formed instead (reaction ii). So, at low temperatures, protonation of the N atom rather than the C atom takes place. When **3c** (L = CO) was

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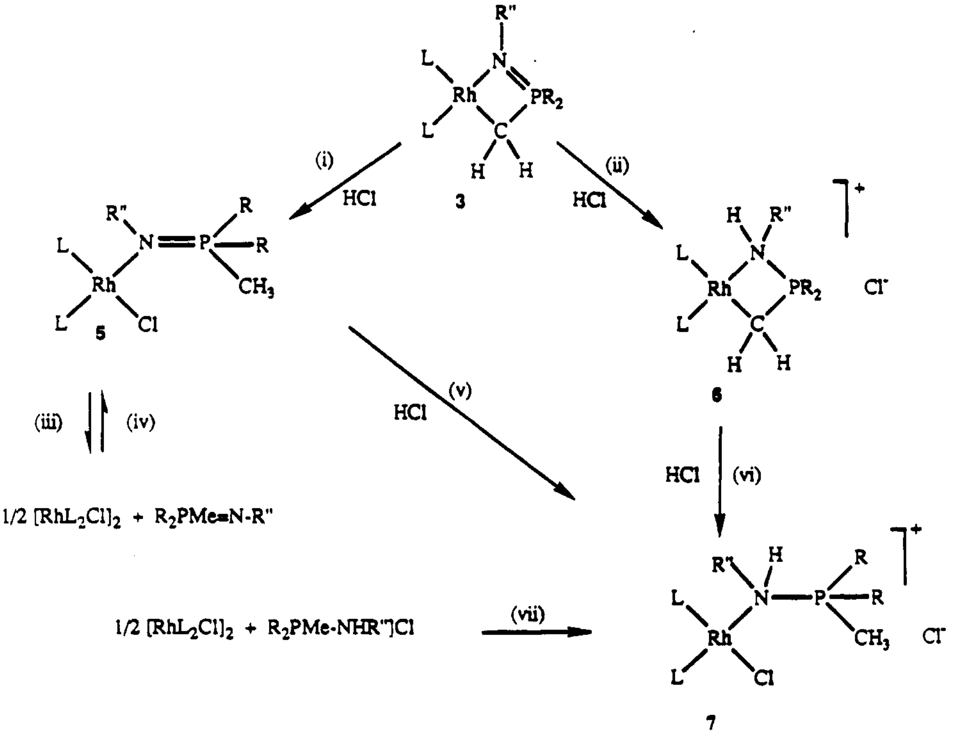
Scheme II. Reaction of [Rh(CH_2PPh_2=N-C_6H_4-CH_3-4)L_2] (3a,c) with HCl[a]



[a] R = Ph, R″ = *p*-tolyl. Conditions are as follows. (i) L_2 = COD, in C_6H_6 at 20 °C. (ii) C_6H_6. (iii) L_2 = COD, in C_6H_6. (iv) 1 equiv of HCl (Et_2O); L_2 = COD, in Et_2O at -60 °C; L = CO in C_6H_6 at 20 °C. (v) 1 equiv of HCl (Et_2O); L = CO, in C_6H_6. (vi) 1 equiv of HCl; L = CO, in C_6H_6. (vii) L = CO, in Et_2O.

reacted with 1 equiv of HCl in benzene, a similar complex (i.e. **6c**) was formed, irrespective of the applied reaction conditions (reaction ii), so for L = CO protonation of the methanide carbon atom did not occur, and hence complex **5c** could not be obtained in this way. Compounds **5a,c** have been synthesized independently (reaction iii)[21] from **1a** and [RhL_2Cl]$_2$ and were used here for comparing spectroscopic data.

The structure of **6a,c** could be established by ^{31}P and ^{1}H NMR and IR spectroscopy and FDMS. In the ^{31}P NMR spectra of **6a,c** one doublet is present at 45.4 and 43.3 ppm with ^2J(Rh,P) of 2.7 and 4.9 Hz, respectively. The coupling with only one Rh nucleus shows that these compounds are monomers in solution. Although a high-frequency shift for **6a,c** with respect to **3a,c** is expected, a low-frequency shift is observed. This phenomenon may be due to structural changes within the four-membered Rh-N-P-C ring upon protonation of nitrogen. Notably changes in bond angles at the P atom[44] as well as relief of the ring strain could explain the observations.

In the ^{1}H NMR spectra of **6a,c** the resonances for the methanide hydrogen atoms are found at 0.72 and 1.63 ppm, respectively. These signals show small ^2J(Rh,H) coupling of 1.9 and 2.3 Hz and additional ^2J(P,H) coupling of 11.8 and 11.4 Hz. The resonances of the hydrogen atom on the N atom are found as doublets at 9.02 and 8.95 ppm for **6a,c**, respectively. The observation of resonances in the IR spectra (KBr pellets) of **6a,c** for ν(P-N) at 1236 and 1230 cm^{-1} and for ν(N-H) at 3084 and 3124 cm^{-1} and the mass found for **6c** (m/z = 499) are in agreement with a structure of **6** as depicted in Scheme II.

When complex **6a** was heated in benzene for 1 h at 353 K, complex **5a** was formed. So, the hydrogen atom at nitrogen has shifted to the methanide carbon.[48] These observations indicate that the reaction of the rhodium (iminophosphoranyl)methanide complexes **3a,c** with HCl proceeds via initial oxidative addition of HCl to Rh with the formation of the rhodium(III) hydride complex [Rh(CH_2PPh_2=N-*p*-tol)(H)(Cl)L_2] (**4a**, L_2 = COD; **4c**, L = CO) as a transient species. This addition is followed by a migration of the hydrogen atom to either the C or the N atom of the ligand. The migration to the N atom appears to be favored for L = CO, whereas with L_2 = COD migration to both the C and the N atom may occur.

Monitoring the reaction of **3c** with 1 equiv of HCl in CH_2Cl_2 by means of IR spectroscopy revealed the presence of a hydridorhodium carbonyl complex. In CH_2Cl_2 this complex showed a characteristic rhodium-hydride absorption at 2197 cm^{-1} and carbonyl bands at 2068 and 1989 cm^{-1}.[49] When the reaction was followed by ^{1}H NMR spectroscopy, the rhodium hydride complex **4c** was not observed, but only signals were found that could be attributed to complex **6c** (even when the reaction was performed at 213 K). The seeming discrepancy in observations in ^{1}H NMR and IR spectroscopy may be ascribed to an equilibrium in solution between **4c** and **6c** (eq 5). According to the ^{1}H NMR spectrum, the equilibrium constant is very high (in favor of **6c**); however, in the IR

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(48) This reaction did not proceed quantitatively, and some unidentified (decomposition) products were formed as envisaged by ^{1}H and ^{31}P NMR spectroscopy.

(49) When **3b** was reacted with 1 equiv of DCl, the carbonyl bands were found at the same frequencies as in the reaction with HCl (2068 and 1989 cm^{-1}). However, the Rh-deuteride absorption, which is expected at ca. 1600 cm^{-1},[50] could not be observed. This signal is most probably obscured by phenyl or tolyl absorptions. In the solid state (KBr pellets), however, only signals of complex **6c** were found, i.e. carbonyl bands at 2053 and 1986 cm^{-1}.

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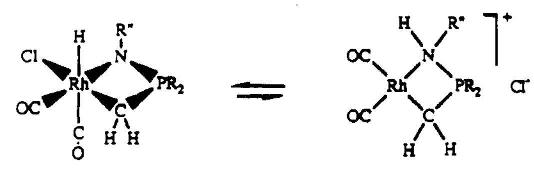


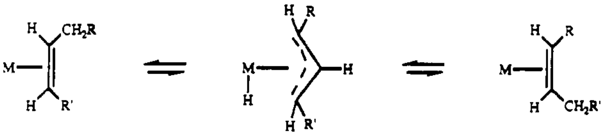
(5)

4c **6c**

spectrum the intensity of the rhodium–hydride absorption of the small amount of **4c** present is strong enough to be observed.

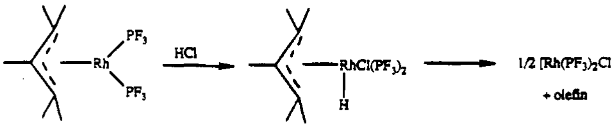
The migration of the hydrogen atom in **4** to the N atom is apparently reversible, as indicated by the observation of the intermediate rhodium hydride complex **4c** (L = CO) by IR spectroscopy and the transformation of **6a** into **5a** (L_2 = COD) at elevated temperature. Hydrogen migration to the C atom and subsequent breaking of the M–C bond is irreversible, as can be inferred from the fact that C–H activation in the *P*-methyl group in complexes **5a,c** does not occur, even in the presence of bases (Et_3N, LDA, or BuLi) or at 353 K in benzene.

Hydrogen migration reactions of the type discussed above are suggested to occur in metal-assisted alkene isomerization reactions via allylmetal hydride complexes (eq 6).[51] However, to our knowledge only in a few cases



(6)

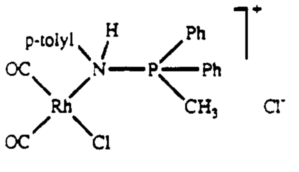
hydrogen migration from the metal atom to the coordinated allyl group have been demonstrated.[52,53] For instance, Nixon et al.[53] showed that the reaction of allylrhodium (I) phosphine complexes with HCl to yield olefins proceeds via an intermediate allylrhodium(III) hydride complex (eq 7). Generally, the product formation, and hence the allyl-carbon site to which the hydrogen atom migrates, is largely determined by steric factors.[51b,53]



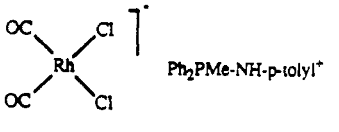
(7)

In the present rhodium (iminophosphoranyl)methanide complexes large differences in reactivity of the different sites within the "heteroallyl" ligand are expected because of the presence of the heteroatoms N and P. As was shown above, hydrogen migration from Rh to the N atom is preferred in **3c** and the formed complex (**6c**) is stabilized by coordination of both the N and the C atom to Rh(I). In the reaction of **3a** with 1 equiv of HCl, formation of **6a** is kinetically preferred but complex **5a** is thermodynamically most stable. The different course of the reaction of **3a,c** with HCl can be understood by invoking the relative stability of the intermediate complexes **5** and **6**. The N-protonated complexes **6** are better stabilized for L = CO, since this ligand has a better π-acceptor capacity than COD and hence is able to stabilize the M–C bond more effectively. So, complex **6c** (L = CO) is kinetically and thermodynamically preferred compared to **5c**. In **6a** this stabilization of the M–C bond is less pronounced and hence H migration to the carbon atom becomes competitive, with subsequent irreversible M–C bond fission.

Reaction with 2 Equiv of HCl. Addition of another 1 equiv of HCl to **6c** or 2 equiv of HCl to **3c** gave protonation of the carbon atom and breaking of the M–C bond with formation of $[Rh(Ph_2P(CH_3)NH\text{-}p\text{-}tol)Cl(CO)_2]Cl$ (**7c**). In order to compare spectroscopic data, this complex has been synthesized independently by reaction of **5c** with 1 equiv of HCl or of $[Rh(CO)_2Cl]_2$ with $[Ph_2P(CH_3)NH\text{-}p\text{-}tol]Cl$, the protonated form of **1a**. In the ^{31}P NMR spectrum of **7c** one signal was found at 35.4 ppm, without coupling to Rh. The presence of resonances in the ^1H NMR spectrum (C_6D_6) at 1.85 (s, 3 H, CH_3), 2.38 (s, 3 H, PCH_3), and 8.90 ppm (d, 1 H, NH) and signals in the aryl region (Table III) indicate a $Ph_2P(CH_3)NH\text{-}p\text{-}tol$ entity in complex **7c**. In the IR spectra signals are found in the carbonyl region at 2067, 1999, and 1985 cm^{-1} (KBr pellet) or 2074 and 1999 cm^{-1} (CH_2Cl_2). On the basis of these data, two different structures can a priori be attributed to this complex, i.e. **7c** in which the aminophosphonium ligand is coordinated to Rh and **7c′** in which the organic aminophosphonium fragment acts as a cation and $[Rh(CO)_2Cl_2]^-$ as the anion. Because of the observed high-frequency shift of ca. 4 ppm in the ^{31}P NMR spectrum of **7c** with respect to uncoordinated $[Ph_2P(CH_3)NH\text{-}p\text{-}tol]^+$ and the fact that exchange of the aminophosphonium entity for Na^+ (using excess of NaBr) was not possible, structure **7c** is the correct one.



7c



7c′

Other Reactions of 3a,c. The rhodium (iminophosphoranyl)methanide complexes **3a,c** were also reacted with CH_3I and $CH_3OSO_2CF_3$ (=CH_3OTf). Whereas the reaction of **3a** or **3c** with HCl proceeds readily even at 213 K, with CH_3I or CH_3OTf no reaction was observed at room temperature. Reaction took place only after heating a mixture of **3a** or **3c** with CH_3I or CH_3OTf at 353 K in benzene. However, these reactions were not selective, as evidenced by the formation of several (unidentified) products (^1H, ^{31}P NMR). Other reagents such as CO, CO_2, $CH_3O_2CC{\equiv}CCO_2CH_3$, $CH_3O_2CC{\equiv}CH$, $CH_3O_2CCH{=}CHCO_2CH_3$, and $CH_3O_2CCH{=}CH_2$ did not react with **3a** or **3c** in benzene or CH_2Cl_2, even at higher temperatures.

One explanation for the difference in reactivity in **3a,c** with CH_3X as compared to HCl may be that the carbon electrophile (especially for CH_3OTf) or radical (from CH_3X) directly attacks the (iminophosphoranyl)methanide ligand. Another possibility could be that, assuming a

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(51) See for example: (a) Keim, W. *Transition Metals in Homogeneous Catalysis*; Marcel Dekker: New York, 1971, and references therein. (b) Trost, B. M.; Verhoeven, T. R. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, England, 1982; Vol. 8, p 799 and references therein.

(52) Bönnemann, B. *Angew. Chem.* **1970**, *82*, 699.

(53) (a) Nixon, J. F.; Wilkins, B. *J. Organomet. Chem.* **1972**, *44*, C25. (b) Nixon, J. F.; Wilkins, B. *J. Organomet. Chem.* **1974**, *80*, 129.

(54) Note added in proof: It has been established that indeed Δ*E* effects determine the chemical shifts of Rh(I) complexes, but these are relatively unimportant compared to the radial and charge imbalance factors within a series of Rh(I) complexes; cf.: Ernsting, J. M.; Elsevier, C. J.; de Lange, W. G. J.; Timmer, K. *Magn. Reson. Chem.*, submitted for publication.

similar reaction mechanism as observed for the reaction of **3a** or **3c** with HCl, the lower nucleophilic character of the Rh atom compared to, for instance, phosphine-substituted Rh(I) complexes plays a role. Due to the coordination of the iminophosphorane entity, electron density is withdrawn from Rh by the (iminophosphoranyl)methanide ligand within the polarized metallacycle. This means that the rhodium(I) center is relatively hard in terms of HSAB. Hence, soft ligands such as CH_3X, alkynes, and CO_2 will, contrary to HCl, add sluggishly or not at all to the Rh center. So, alkynes and CO are not being activated for insertion and CH_3X will undergo direct, less specific reactions with the ligands instead of giving rise to a metal-mediated methylation (which is usually more specific).

The fact that molecules like CO, CO_2, olefins, and alkynes fail to insert into the Rh–C or Rh–N bonds indicates that the Rh–N–P–C ring is a very stable entity and that no insertion reactions take place, although upon insertion a lowering of the ring strain would occur. Insertion reactions are inhibited due to the low propensity of **3** to bind a fifth ligand that needs π back-bonding from the metal and/or the reluctance to undergo dissociation of one of the ligand atoms in the coordination plane of square-planar **3**. Furthermore the inertness of **3a,c** toward CO_2 shows that coordination of the iminophosphorane group brings about a substantial decrease in its typical reactivity, i.e. no aza-Wittig reaction with CO_2 takes place (eq 4). This result emphasizes the stability of the four-membered Rh–N–P–C ring.

Conclusions

Intramolecular coordination of an iminophosphorane group stabilizes a M(I)–C(sp^3) bond (M = Rh, Ir) in complexes of the type [M(CH_2PPh_2=N-*p*-tol)L_2]. In these complexes the (iminophosphoranyl)methanide ligand is coordinated in a σ-N,σ-C chelating mode, giving rise to a stable four-membered M–N–P–C ring. Reaction of the rhodium (iminophosphoranyl)methanide complexes with HCl proceeds via oxidative addition at the hard Rh(I) center and subsequent migration of the hydrogen atom to either the C or the N atom of the N,C-chelated ligand.

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Supplementary Material Available: Tables of hydrogen coordinates and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (5 pages); a table of structure factors (38 pages). Ordering information is given on any current masthead page.

The Carbon–Carbon Bond-Forming Step in Catalytic Cross-Coupling: Migration or Elimination?

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Two alternative pathways for reductive elimination of adjacent sp^3 and sp^2 carbon substituents from palladium have been examined by the extended Hückel method, with *cis*-(PH_3)Pd(CH_3)CH=CH_2 as a model. A brief comparison with the nickel analogue has been made. In the first set of calculations, concomitant lengthening of both Pd–C bonds was permitted to proceed synchronously, leading to an isolated molecule of propene and to $(PH_3)_2$Pd. This conventional pathway for reductive elimination, which demonstrated behavior very similar to that calculated previously by the extended Hückel method for *cis*-(PH_3)Pd$(CH_3)_2$, was compared with an alternative in which cleavage of the Pd–CH_3 bond is more advanced and occurs with synchronous migration to the C_α carbon of the vinyl group. The intermediate produced in this way can form an η^2-propene complex by geometric reorganization. When calculations for the two energy surfaces are compared, the migration pathway is favored. It is particularly advantageous when the P–Pd–P angle is permitted to relax as reaction proceeds. Comparison is made with experimental evidence, and the calculations are in accord with the observed ease of elimination from square-planar 16e aryl or vinyl complexes.

Introduction

Cross-coupling reactions between an organic electrophile and an organometallic nucleophile have played a significant role in synthesis.[1] The catalyst is most frequently a Pd or Ni phosphine complex, with 1,1′-bis(diphenylphosphino)ferrocene the preferred ligand.[2] X-ray analysis of its square-planar complexes[3] reveals a cis chelate with a bite angle of 99°, very similar to the typical angle in *cis*-$(PPh_3)_2$M square-planar complexes [98°].[4] The catalytic reaction has most generality when the electrophilic entity is unsaturated; vinyl, aryl, and allyl halides have all

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