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Synthesis, Characterization, and Reactions of Rhodium(I)- and Iridium(I)–Bis(iminophosphoranyl)methanide Complexes in Which the Ligand Acts as a σ-N,σ-C Chelate. X-ray Crystal Structure of [Ir{CH(PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)$_2$}(COD)]

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Reaction of the lithium–bis(iminophosphoranyl)methanide compounds Li[CH(PPh$_2$=N-C$_6$H$_4$-R'-4)$_2$] (**2a**, R' = CH$_3$; **2b**, R' = CH$_3$ and NO$_2$; **2c**, R' = NO$_2$) with [ML$_2$Cl]$_2$ (M = Rh, L$_2$ = COD, L = CO; M = Ir, L$_2$ = COD) yields the novel bis(iminophosphoranyl)methanide complexes [M{CH(PPh$_2$=N-C$_6$H$_4$-R'-4)$_2$}L$_2$] (**3a–d**, **4a–c**), in which the ligand is coordinated as a σ-N,σ-C chelate. Complex **3a** (M = Rh, R' = CH$_3$, L$_2$ = COD) has also been synthesized in the reaction of CH$_2$(PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)$_2$ (**1a**) with [Rh(COD)(OMe)]$_2$. The COD ligand in the Ir–COD compounds **4a–c** can be substituted by reaction with CO to give [Ir{CH(PPh$_2$=N-C$_6$H$_4$-R')$_2$}(CO)$_2$] (**4d–f**). The solid-state structure of **4a** (M = Ir, R' = CH$_3$, L$_2$ = COD) has been determined by an X-ray diffraction study. Compound **4a** crystallizes in the triclinic space group $P\bar{1}$ with a = 10.633 (2) Å, b = 11.766 (2) Å, c = 17.366 (2) Å, α = 99.73 (1)°, β = 90.59 (3)°, γ = 95.42 (2)°, and Z = 2. The structure was refined to R = 0.055 (R_w = 0.060) using 4065 independent observed reflections. The bis(iminophosphoranyl)methanide ligand is coordinated in a σ-N,σ-C chelate mode toward the square planar Ir, giving rise to a four-membered M–N–P–C metallacycle and one pendant iminophosphorane moiety. Important bond distances and angles are P$_1$–N$_1$ = 1.55 (1) Å, P$_2$–N$_2$ = 1.62 (1) Å, P$_1$–C$_1$ = 1.82 (1) Å, P$_2$–C$_1$ = 1.77 (1) Å, Ir–C$_1$ = 2.16 (1) Å, and Ir–N$_2$ = 2.07 (1) Å, and N$_2$–Ir–C$_1$ = 73.4 (4)°, C$_1$–P$_1$–N$_1$ = 119.3 (6)°, and C$_1$–P$_2$–N$_2$ = 96.4 (5)°. In solution the bis(iminophosphoranyl)methanide complexes undergo a dynamic process, in which both halves of the ligand and both coligands become equivalent. The exchange processes for **3a**, **3b**, **4a**, and **4d** have been studied by using variable-temperature ^{1}H and ^{31}P NMR; they occur via a Berry pseudorotation, involving an intermediate five-coordinate complex that is formed via intramolecular attack of the pendant iminophosphorane entity. Additional structural information has been acquired from IR and ^{13}C, ^{103}Rh, and solid state ^{31}P{^{1}H} CP/MAS NMR spectroscopy. Complexes **3a**, **3b**, **4a**, and **4d** react with CO$_2$ in an aza-Wittig reaction to give the (iminophosphoranyl)(oxophosphoranyl)methyl complexes [M{CH(PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(PPh$_2$=O)}L$_2$] (**5a–d**), *p*-tolyl isocyanate, and di-*p*-tolylcarbodiimide. The inertness of the four membered M–N–P–C ring toward CO$_2$ stresses the nonreactivity of this polarized metallacycle. Treatment with CF$_3$COOH results in direct protonation of the nitrogen atom of the free iminophosphorane moiety, affording the complexes [M{CH(PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)(PPh$_2$-NH-C$_6$H$_4$-CH$_3$-4)}L$_2$]$^+$X$^-$ (**II**). Reaction with HCl leads to a net protonation of either the methanide or the nitrogen atoms with formation of the known coordination complexes of bis(iminophosphoranyl)methane, in which the ligand is either coordinated as a σ-N,σ-C chelate (in **II**) or as a σ-N,σ-N' chelate in [M{(4-CH$_3$-C$_6$H$_4$-N=PPh$_2$)$_2$CH$_2$}L$_2$]$^+$X$^-$ (**III**), respectively. This reaction proceeds via initial oxidative addition of HCl to Rh or Ir and a subsequent hydrogen-migration reaction from the metal to either the methanide C atom or the N atom of the coordinated iminophosphorane entity. This has been evidenced by the observation of Ir–hydride complexes (^{1}H NMR) in the reaction of **4a** with 1 equiv of HCl at 193 K. These complexes react further to give **II** and **III** upon raising the temperature to 233 K. Addition of excess HX (X = CF$_3$COO, Cl) to the bis(iminophosphoranyl)methanide complexes **3a**, **3b**, **4a**, and **4d** gives [ML$_2$X]$_2$ and the amino[(aminophosphonio)methyl]phosphonium compounds [CH$_2$(PPh$_2$-NH-C$_6$H$_4$-CH$_3$-4)$_2$]$^{2+}$·2X$^-$ (**IV**).

Introduction

Mono anions that are structurally related to acetyl acetonate are well-known and their coordination chemistry with transition metals has been the subject of several studies. Metal complexes of the bis(phosphoniomethyl)nitride [N(PR$_2$CH$_2$)$_2$]$^-$,[1] bis(thioxophosphoranyl)amide [N(PR$_2$S)$_2$]$^-$,[2] bis(thioxophosphoranyl)methanide [CR'(PR$_2$S)$_2$]$^-$,[3] and bis(methylenephosphoranyl)methanide

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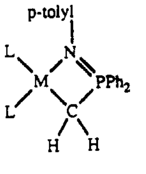
$[CH(PR_2CH_2)_2]^-$ [4] anions, in which the ligand is coordinated in a bidentate mode forming a six-membered metallacycle, have been characterized. However, a coordination mode in which a four-membered metallacycle is formed is uncommon for this type of resonance-stabilized monoanion. Of the few known examples we mention the Pt–bis(thiooxophosphoranyl)methanide complexes, synthesized by Browning et al.,[3b,c] in which the ligand is σ-S,σ-C coordinated to the metal, forming a four-membered Pt–S–P–C ring.

In the course of our research on the coordination and organometallic chemistry of iminophosphoranes in complexes of late transition metals, we have shown that compounds containing an (iminophosphoranyl)methanide entity ($RN{=}PPh_2CHR'$) coordinate as a σ-N,σ-C chelate toward Rh(I) (**I**, **II**),[5] forming a stable four-membered ring that is closely related to the aforementioned Pt–S–P–C metallacycle. In the thus formed M–N–P–C ring the M–C(sp^3) bond is stabilized through intramolecular coordination of the polar iminophosphorane group. On the basis of these results, a similar σ-N,σ-C chelate was expected to occur for the recently synthesized mono anion $[CH(PPh_2{=}N\text{-}p\text{-tolyl})_2]^-$,[6] although a σ-N,σ-N′ coordination mode could not be excluded a priori.



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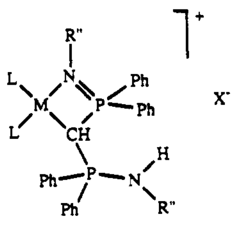

II

In a preliminary communication we reported that the bis(iminophosphoranyl)methanide ligand $[CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3)_2]^-$ (**2a**) is coordinated to Rh(I) in a similar σ-N,σ-C chelating mode as has been found for other complexes containing an (iminophosphoranyl)methanide entity.[5a] In this paper we report on the syntheses and characterization of several new rhodium(I)– and iridium(I)–bis(iminophosphoranyl)methanide complexes. Furthermore, the reactivity of the complexes and the stability of the four-membered metallacycle toward reagents like CO_2, CF_3COOH, and HCl will be discussed.

Experimental Section

General. ^1H 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, using indirect 2D ^{31}P,$^{103}Rh\{^1H\}$ NMR.[7] Solid-state ^{31}P CP/MAS NMR spectra were obtained at the national HF-NMR facility (University of Nijmegen, The Netherlands) on a Bruker AM500 spectrometer (^{31}P frequency, 202.5 MHz) equipped with a Bruker solid-state accessory, employing a probehead with a 7-mm double air bearing MAS assembly. Typically a Hartmann–Hahn mixing time of 2 ms and a 20 s recycle delay was used. Spectra were recorded with spinning speeds varying from 4 to 6 kHz. Some spectra were obtained on a Bruker CXP 300 spectrometer (^{31}P frequency, 121.4 MHz) under similar conditions. Spinning sideband analyses were performed by minimizing the sum of the least-squares of the errors with respect to the Herzfeld and Berger tables.[8] Chemical shift values are in ppm relative to Me_4Si for ^1H and ^{13}C spectra, to 85% H_3PO_4 for ^{31}P spectra, and to $\Xi(^{103}Rh) = 3.16$ 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 section Elemental Analysis of the Institute for Applied Chemistry, ITC/TNO, Zeist, The Netherlands. Solvents were carefully dried and distilled prior to use. Gaseous reactants were purified prior to use. All reactions were performed in an atmosphere of purified nitrogen using standard Schlenk techniques. $[Rh(COD)Cl]_2$,[9] $[Rh(COD)(OMe)]_2$,[10] $[Rh(NBD)Cl]_2$,[11] $[Rh(CO)_2Cl]_2$,[12] $[Ir(COD)Cl]_2$,[13] and the bis(iminophosphoranyl)methanes **1a–c**[6,14] were synthesized by literature procedures.

Lithium–bis(iminophosphoranyl)methanides $[Li\{CH(PPh_2N\text{-}C_6H_4\text{-}R'\text{-}4)_2\}]$ (**2a–c**) were synthesized from **1a–c** and lithium diisopropylamide (LDA) in a similar way as described in ref 6.

Synthesis of the Bis(iminophosphoranyl)methanide Complexes. $[M\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}R'\text{-}4)_2\}L_2]$ (3,4). Method 1. In a typical experiment ca. 0.7 mmol $[ML_2Cl]_2$ (M = Rh, L = CO, L_2 = COD; M = Ir, L_2 = COD) in 8 mL of benzene was added at room temperature to a solution containing exactly 2 equiv of $[Li\{CH(PPh_2N\text{-}C_6H_4\text{-}R'\text{-}4)_2\}]$ (**2a–c**) in 7 mL of benzene. After stirring for 2 h the reaction mixture was filtered. Workup of the product was dependent on the reagents used and is described separately for each compound.

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)_2\}(COD)]$ (3a). The filtrate was evaporated to dryness and extracted with benzene. The combined extracts were evaporated to dryness, giving a yellow powder in 90% yield. Anal. Calcd for $C_{47}H_{47}N_2P_2Rh$: C, 70.15;

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H, 5.89; N, 3.48. Found C, 69.26; H, 6.12; N, 3.29. FD mass found: m/z = 804 (M$^+$; calcd for $C_{47}H_{47}N_2P_2Rh$: M = 804.760).

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)_2\}(CO)_2]$ (3b). The filtrate was evaporated to dryness and subsequently extracted with Et_2O. After removal of the solvent of the combined extracts in vacuo, red **3b** was obtained in 90% yield. Anal. Calcd for $C_{41}H_{35}N_2O_2P_2Rh$: C, 65.43; H, 4.69; N, 3.72; P, 8.23. Found C, 64.38; H, 5.04; N, 3.77; P, 7.50. FD mass found: m/z = 752 (M$^+$; calcd for $C_{41}H_{35}N_2O_2P_2Rh$: M = 752.596).

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)_2\}(NBD)]$ (3c). The orange filtrate was evaporated to dryness and washed with pentane. Drying the residue in vacuo gave yellow **3c** in 95% yield. FD mass found: m/z = 788 (M$^+$; calcd for $C_{46}H_{43}N_2P_2Rh$: M = 788.717).

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2{=}N\text{-}C_6H_4\text{-}NO_2\text{-}4)\}(COD)]$ (3d). The filtrate was evaporated to dryness giving red **3d** in 40% yield. FD mass found: m/z = 835 (M$^+$; calcd for $C_{46}H_{44}N_3O_2P_2Rh$: M = 835.730).

$[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)_2\}(COD)]$ (4a). The filtrate was evaporated to dryness giving **4a** in 80% yield. Anal. Calcd for $C_{47}H_{47}IrN_2P_2$: C, 63.14; H, 5.30; N, 3.13; P, 6.93. Found C, 63.66; H, 6.01; N, 3.13; P, 6.93. FD mass found: m/z = 894 (M$^+$; calcd for $C_{47}H_{47}IrN_2P_2$: M = 894.055). Crystals suitable for X-ray diffraction study were obtained by diffusion of hexane into a solution of **4a** in Et_2O at room temperature for 1 week.

$[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2{=}N\text{-}C_6H_4\text{-}NO_2\text{-}4)\}(COD)]$ (4b). The residue was extracted with benzene (3 × 20 mL). The combined benzene layers were evaporated to dryness. After washing with Et_2O the residue was dried in vacuo, giving **4b** in ca. 80% yield. FD mass found: m/z = 925 (M$^+$; calcd for $C_{46}H_{44}IrN_3O_2P_2$: M = 925.025).

$[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}NO_2\text{-}4)_2\}(COD)]$ (4c). The residue was extracted with benzene (5 × 20 mL). The combined benzene layers were evaporated to dryness and yellow **4c** was obtained in 90% yield. FD mass found: m/z = 955 (M$^+$; calcd for $C_{45}H_{41}IrN_4O_4P_2$: M = 954.987).

Method 2: $[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)_2\}(COD)]$ (3a). Compound **3a** has also been synthesized by addition of 87.6 mg $[Rh(COD)(OMe)]_2$ (0.18 mmol) in 12.5 mL of CH_2Cl_2 to 215.1 mg of **1a** (0.36 mmol) in CH_2Cl_2 (2.5 mL). After stirring for 4 h, the yellow solution was evaporated to dryness in vacuo. After washing the residue with pentane (3 × 5 mL), yellow **3a** was obtained in 80% yield.

Method 3: $[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}R'\text{-}4)_2\}(CO)_2]$ (4d–f). The complexes **4d–f** were prepared by bubbling CO gas through a solution of ca. 0.4 mmol **4a–c** in 10 mL of benzene for 30 min at room temperature. After evaporation of the solvent in vacuo the residue was washed twice with pentane and dried in vacuo, giving **4d–f** in ca. 90% yield. Data for **4d** (R' = CH_3) follow. Anal. Calcd for $C_{41}H_{35}IrN_2O_2P_2$: C, 58.49; H, 4.19; N, 3.33; P, 7.36. Found: C, 58.52; H, 4.24; N, 3.41; P, 7.22. FD mass found: m/z = 842 (M$^+$; calcd for $C_{41}H_{35}IrN_2O_2P_2$: M = 841.891). Data for **4e** (R' = CH_3 and NO_2) follow. FD mass found: m/z = 873 (M$^+$; calcd for $C_{40}H_{32}IrN_3O_4P_2$: M = 872.861). Data for **4f** (R' = NO_2) follow. FD mass found: m/z = 904 (M$^+$; calcd for $C_{39}H_{29}IrN_4O_6P_2$: M = 903.831).

Reaction of 3a, 3b, 4a, and 4d with CO_2. Dry CO_2 gas, which was obtained by evaporation of solid CO_2, was bubbled through a solution of ca. 0.2 mmol **3a**, **3b**, **4a**, or **4d** in 10 mL of benzene or CH_2Cl_2 at room temperature. After 4 h the solvent was evaporated in vacuo. The residue was washed with Et_2O and pentane and dried in vacuo, giving the complexes **5a–d** in ca. 80% yield. The washings contained, according to IR and ^{1}H NMR, *p*-tolyl isocyanate and di-*p*-tolylcarbodiimide.[15]

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2{=}O)\}(COD)]$ (5a). ^{31}P NMR (C_6D_6)/ppm: 28.3 (d, ^2J(P,P) = 7.3 Hz, ^2J(Rh,P) < 1 Hz), 33.4 (dd, ^2J(P,P) = 7.3 Hz, ^2J(Rh,P) = 17.1 Hz). IR (KBr pellet)/cm^{-1}: 1192 (ν(P=O)); 1290 (ν(P=N)). FD mass found: m/z = 715 (M$^+$; calcd for $C_{40}H_{40}NOP_2Rh$: M = 715.619).

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2{=}O)\}(CO)_2]$ (5b). ^{1}H NMR (C_6D_6)/ppm: 1.94 (CH_3), 2.26 (dt, ^2J(P,H) = 9.5 Hz, ^2J(Rh,H) < 1 Hz, PCHP), 6.7–7.1 (m, Tol, *m,p*-Ph), 7.5–8.5 (m, *o*-Ph). ^{31}P NMR (C_6D_6)/ppm: 29.8 (^2J(P,P) < 1 Hz, ^2J(Rh,P) < 1 Hz), 48.7 (d, ^2J(P,P) < 1 Hz, ^2J(Rh,P) = 16.8 Hz). IR (KBr pellet)/cm^{-1}: 1200 (ν(P=O)), 1292 (ν(P=N)), 2065, 1988 (ν(CO)).

$[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2{=}O)\}(COD)]$ (5c). ^{1}H NMR (C_6D_6)/ppm: 1.98 (CH_3), 1.5–2.1 (CH_2), 2.93 (vt, ^2J(P,H) = 12.5 Hz, PCHP), 3.54 (=CH), 4.03 (=CH), 6.4–7.4 (Tol, *m,p*-Ph), 7.5–8.2 (m, *o*-Ph). ^{31}P NMR (C_6D_6)/ppm: 29.2 (d, ^2J(P,P) = 6.2 Hz), 50.5 (d, ^2J(P,P) = 6.2 Hz). IR (KBr pellet)/cm^{-1}: 1196 (ν(P=O)), 1284 (ν(P=N)). FD mass found: m/z = 805 (M$^+$; calcd for $C_{40}H_{40}IrNOP_2$: M = 804.914).

$[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2{=}O)\}(CO)_2]$ (5d). ^{1}H NMR (C_6D_6)/ppm: 1.94 (CH_3), 2.96 (dd, ^2J(P,H) = 11.4, 14.2 Hz, PCHP), 6.43–7.16 (Tol, *m,p*-Ph), 7.57–8.20 (m, *o*-Ph). ^{31}P NMR (C_6D_6)/ppm: 31.7 (d, ^2J(P,P) = 2.3 Hz), 58.2 (d, ^2J(P,P) = 2.3 Hz). IR (KBr pellet)/cm^{-1}: 1205 (ν(P=O)), 1290 (ν(P=N)), 2043, 1965 (ν(CO)). FD mass found: m/z = 753 (M$^+$; calcd for $C_{34}H_{28}IrNO_3P_2$: M = 752.750).

Reaction of 3a, 3b, 4a, and 4d with CF_3COOH. To a solution of 0.2 mmol of **3a**, **3b**, **4a**, or **4d** in 10 mL of benzene was added an equimolar quantity of CF_3COOH at room temperature. After stirring for 1 h, 15 mL of pentane was added. The precipitate was filtered off, washed with pentane, and dried in vacuo, giving **II**[5a] in 80–90% yield.

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2\text{-}NH\text{-}C_6H_4\text{-}CH_3\text{-}4)\}(COD)]CF_3OO$. ^{1}H NMR ($CDCl_3$)/ppm: 1.1–1.4 ($CH_2$), 1.82 ($CH_3$), 1.94 ($CH_3$), 2.0–2.5 ($CH_2$), 3.51 (=CH), 3.85 (ddd, J(P,H) = 18.8 and 3.5 Hz, J(Rh,H) = 1.8 Hz, PCHP), 4.15 (=CH), 6.19 (d, Tol), 6.51 (d, Tol), 6.60 (d, Tol), 6.9–7.4 (m, *m,p*-Ph), 8.0–8.5 (m, *o*-Ph), 10.70 (d, J(P,H) = 6.2 Hz, NH). ^{31}P NMR (CD_2Cl_2)/ppm: 27.9 (dd, J(Rh,P) = 16.2 Hz, J(P,P) = 4.4 Hz), 34.1 (brd, J(Rh,P) < 4 Hz, J(P,P) = 4.4 Hz).

$[Rh\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2\text{-}NH\text{-}C_6H_4\text{-}CH_3\text{-}4)\}(CO)_2]CF_3OO$. ^{1}H NMR ($CD_2Cl_2$)/ppm: 2.05 ($CH_3$), 2.18 ($CH_3$), 3.20 (dbr, J(P,H) = 4.9 Hz, PCHP), 6.50 (d, Tol), 6.67 (d, Tol), 6.75 (d, Tol), 6.79 (d, Tol), 7.36–7.73 (m, Ph), 7.79 (m, *o*-Ph), 8.39 (m, *o*-Ph), 10.4 (br, NH). ^{31}P NMR (C_6D_6)/ppm: 38.7 (dd, J(Rh,P) = 3.9 Hz; J(P,P) = 6.8 Hz), 42.5 (dd, J(Rh,P) = 16.6 Hz, J(P,P) = 6.8 Hz).

$[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2\text{-}NH\text{-}C_6H_4\text{-}CH_3\text{-}4)\}(COD)]CF_3OO$. ^{1}H NMR (Tol-$d_8$)/ppm: 1.5–1.9 ($CH_2$), 1.80 ($CH_3$), 1.96 ($CH_3$), 2.1–2.5 ($CH_2$), 3.25 (=CH), 4.18 (=CH), 5.36 (dd; J(P,H) = 20.6 and 3.9 Hz; PCHP), 6.37 (d, Tol), 6.49 (d, Tol), 6.63 (d, Tol), 6.75–7.40 (m, Tol, Ph), 7.74–7.95 (m, *o*-Ph), 8.24–8.55 (m, *o*-Ph), 11.90 (d, J(P,H) = 6.3 Hz, NH). ^{31}P NMR (Tol-d_8)/ppm: 36.2 (d, J(P,P) = 4.9 Hz), 41.0 (d, J(P,P) = 4.9 Hz).

$[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)(PPh_2\text{-}NH\text{-}C_6H_4\text{-}CH_3\text{-}4)\}(CO)_2]CF_3OO$. ^{1}H NMR (Tol-$d_8$)/ppm: 1.82 ($CH_3$), 1.90 ($CH_3$), 5.63 (dd, J(P,H) = 20.5 and 7.0 Hz; PCHP), 6.46–7.19 (m, Tol, Ph), 7.60–7.84 (m, *o*-Ph), 8.04–8.48 (m, *o*-Ph), 12.59 (d, J(P,H) = 7.0 Hz, NH). ^{31}P NMR (Tol-d_8)/ppm: 40.5 (d, J(P,P) = 8.9 Hz), 54.4 (d, J(P,P) = 8.9 Hz).

Reaction of II with CF_3COOH. To a solution of ca. 0.1 mmol **II** (M = Rh, Ir, L_2 = COD) in 8 mL of chloroform or benzene a 5-fold excess of CF_3COOH was added. After stirring for 1 h the solvent was evaporated in vacuo. The residue was washed with Et_2O and dried in vacuo. Analysis by ^{1}H and ^{31}P NMR and comparison with authentic samples showed that the residue was a mixture of $[M(COD)(CF_3COO)]_2$ and $[CH_2(PPh_2\text{-}NH\text{-}C_6H_4\text{-}CH_3\text{-}4)_2]^{2+}\cdot 2CF_3COO^-$ (**IV**).[6]

$[Rh(COD)(CF_3COO)]_2$. ^{1}H NMR ($CDCl_3$)/ppm: 1.3–1.4 (CH_2), 2.1–2.3 (CH_2), 4.13 (=CH).

$[Ir(COD)(CF_3COO)]_2$. ^{1}H NMR ($CDCl_3$)/ppm: 1.4–1.5 (CH_2), 2.1–2.3 (CH_2), 4.22 (=CH).

$[CH_2(PPh_2\text{-}NH\text{-}C_6H_4\text{-}CH_3\text{-}4)_2]^{2+}\cdot 2CF_3COO^-$. ^{1}H NMR ($CDCl_3$)/ppm: 2.13 ($CH_3$), 6.49 (t, J(P,H) = 15.6 Hz, PCH_2P), 6.65 (d, Tol), 6.79 (d, Tol), 7.41–7.72 (m, *m,p*-Ph), 8.07–8.28 (m, *o*-Ph), 10.87 (d, J(P,H) = 5.6 Hz, NH). ^{31}P NMR ($CDCl_3$)/ppm: 28.7 ppm.

Reaction of 3a, 3b, 4a, and 4d with HCl. (1) Employing 1 equiv of HCl. In a typical experiment 1 equiv of HCl in Et_2O (0.224 N) was added to ca. 0.2 mmol **3a**, **3b**, **4a**, or **4d** in 6 mL of benzene at room temperature. After stirring for 10 min the solvent was evaporated in vacuo. The residue was washed twice with Et_2O and dried in vacuo, yielding quantitatively a mixture of **II** and **III**.

(2) NMR Experiments. After cooling of a solution of ca. 20 mg **3a**, **3b**, **4a**, or **4d** in 0.4 mL CD_2Cl_2 or Tol-d_8 in a 5-mm NMR tube to 195 K, the mixture was put under an atmosphere of dry HCl gas, which was obtained from anhydrous NH_4Cl and 98% H_2SO_4. Subsequently both ^1H and $^{31}P\{^1H\}$ NMR spectras were taken at 193 K. Then the temperature was raised each half-hour in steps of 10 K and at each step both ^1H and ^{31}P NMR spectra were obtained until complete conversion into **II** and/or **III** was observed.

(3) Employing Excess HCl. Gaseous HCl, obtained by adding 98% H_2SO_4 to anhydrous NH_4Cl, was bubbled through a solution of ca. 0.2 mmol **3a**, **3b**, **4a**, or **4d** in 10 mL of chloroform or benzene at room temperature for 10 min. After evaporation of the solvent in vacuo the residue was extracted with benzene. Both the white residue and the filtrate were dried in vacuo. In all cases the residue consisted of $[CH_2(PPh_2\text{-}NH\text{-}C_6H_4\text{-}CH_3\text{-}4)_2]^{2+}\cdot 2Cl^-$ (**IV**) and the filtrate of $[ML_2Cl]_2$ and **IV**. All the products were identified by ^1H and ^{31}P NMR and by comparison with authentic samples.[5,6]

$[Rh\{(4\text{-}CH_3\text{-}C_6H_4\text{-}N{=}PPh_2)_2CH_2\}(COD)]^+$. ^1H NMR (CD_2Cl_2)/ppm: 1.5–1.7 (CH_2), 2.13 (CH_3), 2.3–2.4 (CH_2), 3.37 (=CH), 4.22 (t, 11.6 Hz, PCH_2P), 6.27 (d, Tol), 6.72 (d, Tol), 7.27–7.84 (m, Ph). ^{31}P NMR (CD_2Cl_2)/ppm: 25.7 (d, J(Rh,P) = 0.8 Hz).

$[Rh\{(4\text{-}CH_3\text{-}C_6H_4\text{-}N{=}PPh_2)_2CH_2\}(CO)_2]^+$. ^1H NMR (CD_2Cl_2)/ppm: 2.23 (CH_3), 4.27 (t, 12.4 Hz, PCH_2P), 6.90 (d, Tol), 7.01 (d, Tol), 7.3–8.1 (m, Ph). ^{31}P NMR (CD_2Cl_2)/ppm: 25.9.

$[Ir\{(4\text{-}CH_3\text{-}C_6H_4\text{-}N{=}PPh_2)_2CH_2\}(COD)]^+$. ^1H NMR (CD_2Cl_2)/ppm: 1.1–1.4 (CH_2), 1.7–2.1 (CH_2), 2.16 (CH_3), 3.77 (=CH, CH_2), 6.08 (d, Tol), 6.69 (d, Tol), 7.2–8.4 (m, Ph), PCH_2P signal obscured. ^{31}P NMR (CD_2Cl_2)/ppm: 25.8.

$[Ir\{(4\text{-}CH_3\text{-}C_6H_4\text{-}N{=}PPh_2)_2CH_2\}(CO)_2]^+$. ^{31}P NMR (CD_2Cl_2)/ppm: 36.5.

X-ray Crystal Structure Determination and Refinement of 4a. A yellow needle-shaped crystal was glued on top of a glass-fiber and transferred to an Enraf-Nonius CAD4F diffractometer for data collection. Unit-cell parameters were checked for the presence of higher lattice symmetry.[16] Data were corrected for Lp and for a linear decay (2.7%) of the intensity control reflections during the 130 h of X-ray exposure time but not for absorption; redundant data were merged into an unique dataset. Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.022I)^2$.[17] The structure was solved with standard Patterson methods (SHELXS86)[18] and a series of subsequent difference Fourier analyses. Refinement on F was carried out by full-matrix least-squares techniques. H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, H atoms were refined with one common isotropic thermal parameter (U = 0.083 (7) Å^2). A hexane solvate molecule (on an inversion symmetry site), which could not be located from difference Fourier maps unambiguously, was taken into account in the structure factor and refinement calculations by Fourier transformation of the electron density in the cavity, following the BYPASS method.[19] Weights were introduced in the final refinement cycles; convergence was reached at R = 0.055.

Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table III. Crystal data and numerical details of the structure determination are given in Table I. Neutral atom scattering factors were taken from ref 20 and corrected for anomalous dispersion.[21] All calculations were performed with SHELX76[22] and the EUCLID package[23] (geometrical calculations and illustrations) on a MicroVAX cluster.

Table I. Crystal Data and Details of the Structure Determination of $[Ir\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)_2\}(COD)]$ (4a)

(a) Crystal Data	
formula	$C_{47}H_{47}N_2P_2Ir\cdot{}^1/_2C_6H_{14}$
mol wt	937.15
space group	$P\bar{1}$ (No. 2)
cryst syst	triclinic
a, Å	10.633 (2)
b, Å	11.766 (2)
c, Å	17.366 (2)
α, deg	99.73 (1)
β, deg	90.59 (3)
γ, deg	95.42 (2)
V, Å^3	2131.0 (6)
Z	2
D_{calc}, g·cm^{-3}	1.460
F(000)	950
μ, cm^{-1}	34.3
cryst size, mm	0.53 × 0.05 × 0.03
(b) Data Collection	
radiation	Mo Kα (Zr filtered), 0.71073 Å
θ_{min}, θ_{max}, deg	1.19, 23.00
T, K	295
scan type	$\omega/2\theta$
$\Delta\omega$, deg	0.40 + 0.35tan θ
hor. and vert. aperture (mm)	3.0, 4.0
dist cryst to detector (mm)	173
reference rflns	−2 −1 −3, −2 −1 0
data set	$-11 \le h \le 0, -12 \le k \le 12, -19 \le l \le 19$
total data	11067
total unique data	5915 (R_{int} = 2.81%)
observed data	4065 ($I > 2.5\sigma(I)$)
(c) Refinement	
no. of refined params	471
weighting scheme	$w = 1.0/(\sigma^2(F) + 0.001047F^2)$
final R, R_w, S values	0.055, 0.060, 3.46
$(\Delta/\sigma)_{av}$ in final cycle	0.018
min and max res dens, e/Å^3	−1.51, 1.74

Chart I

Compound	3a	3b	3c	3d
M	Rh	Rh	Rh	Rh
L_2	COD	$(CO)_2$	NBD	COD
R'	CH_3	CH_3	CH_3	CH_3/NO_2

4a	4b	4c	4d	4e	4f
Ir	Ir	Ir	Ir	Ir	Ir
COD	COD	COD	$(CO)_2$	$(CO)_2$	$(CO)_2$
CH_3	CH_3/NO_2	NO_2	CH_3	CH_3/NO_2	NO_2

Results and Discussion

Synthesis of Rh- and Ir-Bis(iminophosphoranyl)methanide Complexes. The new bis(iminophosphoranyl)methanide complexes $[M\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}R'\text{-}4)_2\}L_2]$ (**3**, **4**) have been obtained using three different synthetic routes. The adopted numbering of compounds **3** and **4** is given in Chart I.

Method 1. Reaction of the dimeric complexes $[ML_2Cl]_2$ (M = Rh, L = CO, L_2 = COD, NBD; M = Ir, L_2 =

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COD) with the lithium–Bis(iminophosphoranyl)methanides Li[CH(PPh_2N-C_6H_4-R′-4$)_2$] (**2a–c**: R′ = Me or NO_2), which were freshly prepared from the corresponding bis(iminophosphoranyl)methanes CH_2(PPh_2=N-C_6H_4-R′-4$)_2$ (**1a–c**) and lithium-diisopropylamide,[6] gave the complexes **3a–c** and **4a–c** in excellent (90–95%) yield, whereas **3d** was obtained in modest (40%) yield (eq 1). In this reaction

$$\frac{1}{2}\,[ML_2Cl]_2 + \underset{\substack{\textbf{2a}:\ R'=Me;\ \textbf{2b}:R'=Me/NO_2\\ \textbf{2c}:\ R'=NO_2}}{Li[CH(PPh_2N\text{-}C_6H_4\text{-}R')_2]} \longrightarrow \underset{\textbf{3,4}}{[M\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}R'\text{-}4)_2L_2]} + LiCl \quad (1)$$

M–Cl bridge splitting in $[ML_2Cl]_2$ is achieved by nucleophilic attack of a nitrogen lone pair of **2**, followed by M–C bond formation (vide infra) and LiCl elimination, as has been found for the related mono(iminophosphoranyl)methanide complexes (**I**).[5c]

Complex **3e** (M = Rh, L_2 = COD, R′ = NO_2) could not be obtained in this way, since the nucleophilicity of both N atoms in **2c** is reduced with respect to **2a** (R′ = Me) due to the electron-withdrawing capacity of the NO_2 substituent. Hence Rh–Cl bridge splitting by nucleophilic attack of the nitrogen atom will not occur and formation of complex **3e** is not observed. These observations are in agreement with the results obtained for **I** and other Rh–iminophosphorane complexes, by which it was demonstrated that the *N*-(*p*-nitrophenyl)-substituted iminophosphoranes show a much lower affinity toward Rh than other, more nucleophilic iminophosphoranes.[5c,24]

Method 2. Alternatively complex **3a** (M = Rh, L_2 = COD, R′ = Me) could be obtained via direct reaction between bis(iminophosphoranyl)methane **1a** and [Rh(COD)(OMe)$]_2$ (eq 2), in which the base is present within the precursor Rh complex.

$$\frac{1}{2}\,[Rh(COD)(OMe)]_2 + \underset{\textbf{1a}}{CH_2(PPh_2{=}N\text{-}p\text{-}tolyl)_2} \longrightarrow \underset{\textbf{3a}}{[Rh\{CH(PPh_2{=}N\text{-}p\text{-}tolyl)_2\}(COD)]} + MeOH \quad (2)$$

Method 3. The Ir–carbonyl complexes **4d–f** could be obtained in high yield from the corresponding Ir–COD complexes **4a–c** via substitution of the diene by two molecules of CO.

General Features. Most of the neutral Rh(I) and Ir(I) complexes (**3**, **4**) are soluble in common organic solvents, such as C_6H_6, THF, CH_2Cl_2, $CHCl_3$, and MeCN, and slightly soluble in apolar solvents (i.e., Et_2O, hexane). Generally the solubility of the compounds decreases with an increasing number of NO_2 substituents within the ligand (e.g. **4c** < **4b** < **4a**), whereas the solubility of the carbonyl-containing complexes is higher than that of the corresponding COD or NBD complexes in C_6H_6 or CH_2Cl_2.

The complexes are quite stable in moist air (after 1 week at room temperature only little decomposition was observed, except for **4c**, which decomposed within 5 min) and can be held for several months at room temperature without decomposition when stored under a nitrogen atmosphere. The striking thermal stability of the bis(iminophosphoranyl)methanide complexes **3** and **4** contrasts with the normally observed instability of Rh(I)– and Ir(I)–diene complexes containing a σ-bonded alkyl group, which generally decompose as a result of CH activation or elimination reactions.[25-28] Only Rh(I) and Ir(I) complexes of the general formula $[M(PR'_3)_x(CO)_yR]$ (R = alkyl) are rather stable.[25] Stabilization of Rh(I)– and Ir(I)–C(sp^2) bonds has been accomplished by intramolecular coordination of amine,[29] phosphine,[30] or azo groups.[31] However, to our knowledge, complexs **3** and **4** represent rare examples of stable Rh(I) and Ir(I) compounds containing a M–C(sp^3) bond.[5,32]

The relative thermal stability of **3** and **4** may be explained by invoking both the polar nature of the M–C bond due to the inductively withdrawing P=N function and the chelate effect due to the intramolecular coordination of the nitrogen atom (albeit in a four-membered ring).

X-ray Crystal Structure of [Ir{CH(PPh_2=N-C_6H_4-CH_3-4$)_2$}(COD)] (4a). The molecular structure of **4a** with the adopted atomic labeling scheme is shown in Figure 1. Selected bond distances and bond angles are given in Table II and fractional coordinates in Table III.

The structure of **4a** shows a mononuclear organo-Ir(I) compound in which the Ir atom has a square planar coordination geometry. The coordination positions are occupied by the olefinic bonds of the COD ligand (with M_1 being the midpoint of C_{43}–C_{44} and M_2 the midpoint of C_{40}–C_{47}) and C_1 and N_2 of the bis(iminophosphoranyl)methanide ligand. The square planar coordination mode is considerably distorted, with the Ir atom lying 0.11 (4) Å out of the plane defined by M_1, M_2, C_1, and N_2 and with a dihedral angle of 8.3 (7)° between the planes defined by Ir–M_1–M_2 and Ir–C_1–N_2. The bond distances of Ir to the olefinic bonds of the COD ligand (Ir–M_1 = 2.00 (1) Å, trans to C_1; Ir–M_2 = 1.99 (2) Å, trans to N_2) do not differ significantly. Also, there is no significant difference in the olefinic bond distances (1.36 (2) and 1.37 (2) Å for

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Table II. Selected Interatomic Bond Distances (Å) and Angles (deg) of [Ir{CH(PPh$_2$=N-C$_6$H$_4$-CH$_3$-4)$_2$}(COD)] (4a)[a]

			Distances				
			Around Ir				
$Ir-M_1$	1.99 (2)	$Ir-C_1$	2.16 (1)	$Ir-C_{40}$	2.13 (1)	$Ir-C_{44}$	2.13 (1)
$Ir-M_2$	2.00 (1)	$Ir-N_2$	2.07 (1)	$Ir-C_{43}$	2.10 (2)	$Ir-C_{47}$	2.08 (2)
			Within Ligand				
N_1-P_1	1.55 (1)	N_2-P_2	1.62 (1)	P_1-C_{31}	1.83 (1)	P_1-C_{34}	1.82 (1)
N_1-C_{20}	1.39 (2)	N_2-C_{14}	1.43 (2)	P_2-C_2	1.83 (1)	P_2-C_8	1.79 (1)
P_1-C_1	1.82 (1)	P_2-C_1	1.77 (1)	$C_{17}-C_{32}$	1.53 (2)	$C_{23}-C_{33}$	1.49 (3)
			Within COD				
$C_{40}-C_{47}$	1.36 (2)	$\langle C_{sp2}-C_{sp3}\rangle$	1.52 (2)	$C_{43}-C_{44}$	1.37 (2)	$\langle C_{sp3}-C_{sp3}\rangle$	1.49 (2)

		Angles			
		Around Ir			
M_1-Ir-M_2	87.0 (6)	M_1-Ir-N_2	98.7 (5)	M_1-Ir-C_1	171.1 (5)
M_2-Ir-N_2	170.3 (5)	M_2-Ir-C_1	100.3 (5)	N_2-Ir-C_1	73.4 (4)
		Within Ligand			
$Ir-N_2-P_2$	94.1 (5)	$Ir-N_2-C_{14}$	131.2 (8)	$Ir-C_1-P_1$	114.6 (6)
$Ir-C_1-P_2$	86.9 (5)	$P_1-C_1-P_2$	114.6 (6)	$C_1-P_1-N_1$	119.3 (6)
$C_1-P_1-C_{31}$	102.8 (5)	$C_1-P_1-C_{34}$	107.3 (6)	$C_{31}-P_1-N_1$	177.0 (6)
$C_{34}-P_1-N_1$	104.8 (6)	$C_{31}-P_1-_{34}$	104.4 (6)	$P_1-N_1-C_{20}$	137 (1)
$C_1-P_2-N_2$	96.4 (5)	$C_1-P_2-C_2$	108.7 (6)	$C_1-P_2-C_8$	118.3 (6)
$C_2-P_2-N_2$	116.0 (5)	$C_8-P_2-N_2$	113.1 (6)	$C_2-P_2-C_8$	104.7 (6)
$P_2-N_2-C_{14}$	127.2 (8)				
		Within COD			
$\langle C_{sp2}-C_{sp2}-C_{sp3}\rangle$		124 (1)	$\langle C_{sp3}-C_{sp3}-C_{sp2}\rangle$		114 (1)

[a] Esd are in parentheses.

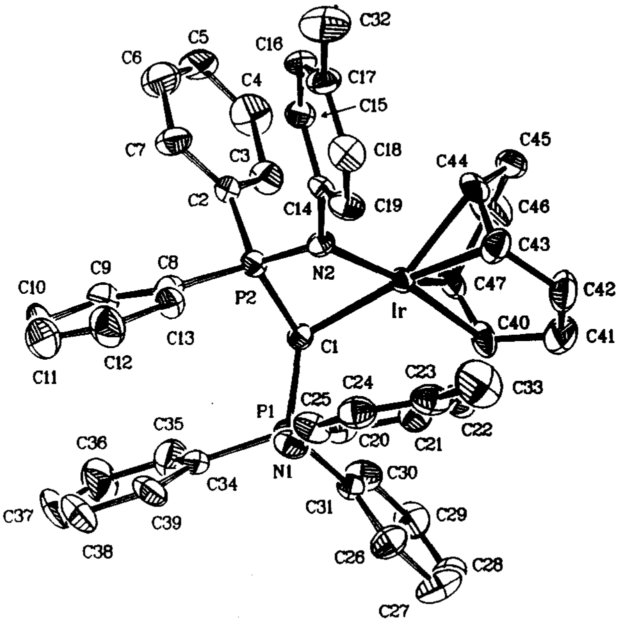

Figure 1. Thermal ellipsoid plot (40% probability) of **4a**. Hydrogen atoms were omitted for clarity.

$C_{40}-C_{47}$ and $C_{43}-C_{44}$, respectively). The COD ligand has a distorted boat conformation, whereas the angles between the olefinic COD bonds and the coordination plane are smaller than the ideal 90°, with angles between $C_{40}-C_{47}$ and $C_{43}-C_{44}$ and the coordination plane of 78.8 (9)° and 88.8 (9)°, respectively. This may be caused by steric repulsions within the molecule due to the presence of the bulky, uncoordinated iminophosphorane entity.

As shown in Figure 1 the bis(iminophosphoranyl)methanide ligand is bonded in a σ-N,σ-C chelating mode toward Ir. This coordination mode gives rise to an acute C_1-Ir-N_2 angle of 73.4 (4)°, a normal value for σ-N,σ-C chelating (iminophosphoranyl)methanides, i.e. 74.2 (2)° in [Rh(CH$_2$PPh$_2$=N-*p*-tolyl)(COD)] (**I**)[5c] or 73.1 (1)° in [Rh(*p*-tolyl-N=PPh$_2$-CH-PPh$_2$-NH-*p*-tolyl)(COD)]$^+$ (**II**).[5a] The $Ir-C_1$ bond length of 2.16 (1) Å is within the range found for other compounds containing an Ir(I)–C bond (from 2.052 (5) to 2.202 (22) Å).[29b,33–35] The $Ir-N_2$ bond distance is short (2.07 (1) Å) but close to 2.087 (7)–2.140 (6) Å for [Ir$_2${μ-CH(N-*p*-tolyl)$_2$}(μ-NH-*p*-tolyl)(COD)$_2$][36] and within the range 2.003 (11)–2.160 (12) Å for [Ir$_2$(μ-NC$_5$H$_4$)$_2$(μ-form)(py)$_2$(MeCN)$_2$].[37] The $N_2-P_2-C_1$ (96.4 (5)°), $Ir-C_1-P_2$ (86.9 (5)°), and $Ir-N_2-P_2$ (94.1 (5)°) angles are smaller than expected due to the constraints within the $Ir-N_2-P_2-C_1$ four-membered ring. Within this ring the bond lengths are similar to the comparable distances within the related Rh–(iminophosphoranyl)methanide complexes **I** and **II**, in which such a four-membered ring is present;[5a,c] i.e. $d(P_2-N_2)$ amounts to 1.62 (1) Å for **4a** whereas distances of 1.624 (2) and 1.613 (8) Å are found for **I** and **II**, respectively, and $d(P_2-C_1)$ is 1.77 (1) Å, comparable to distances of 1.750 (3) and 1.771 (10) Å found for **I** and **II**, respectively. The bond distances and angles within the uncoordinated iminophosphorane entity are similar to values normally observed for free iminophosphoranes. The P_1-N_1 bond distance of 1.55 (1) Å is indicative of a double P–N bond in this type of compounds[38] and is even shorter than in free **1a**, which amounts to 1.568 (2) and 1.566 (2) Å.[6] The P_1-C_1 bond length of 1.82 (1) Å is a normal value for single P–C bonds.[6,39] So, the bis(iminophosphoranyl)methanide ligand in **4a** can be considered to consist of two separate entities, i.e. the

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Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters for 4a[a]

atom	*x*	*y*	*z*	*U*(eq),[b] Å^2
Ir	0.19437 (5)	0.16799 (5)	0.37520 (3)	0.0380 (2)
P_1	0.4235 (3)	0.1828 (3)	0.2448 (2)	0.041 (1)
P_2	0.1400 (3)	0.1693 (3)	0.2220 (2)	0.040 (1)
N_1	0.429 (1)	0.0504 (9)	0.2220 (6)	0.052 (4)
N_2	0.1070 (9)	0.0704 (8)	0.2752 (6)	0.040 (4)
C_1	0.275 (1)	0.238 (1)	0.2774 (6)	0.037 (4)
C_2	0.025 (1)	0.275 (1)	0.2214 (7)	0.040 (4)
C_3	0.024 (1)	0.368 (1)	0.2808 (8)	0.059 (5)
C_4	–0.075 (2)	0.438 (1)	0.284 (1)	0.087 (8)
C_5	–0.172 (2)	0.415 (2)	0.228 (1)	0.087 (8)
C_6	–0.166 (2)	0.323 (2)	0.170 (1)	0.086 (8)
C_7	–0.070 (1)	0.254 (1)	0.1657 (9)	0.062 (6)
C_8	0.158 (1)	0.111 (1)	0.1211 (8)	0.047 (5)
C_9	0.171 (1)	0.182 (1)	0.0643 (8)	0.062 (6)
C_{10}	0.193 (2)	0.135 (2)	–0.0127 (9)	0.078 (7)
C_{11}	0.204 (2)	0.019 (2)	–0.033 (1)	0.089 (8)
C_{12}	0.187 (2)	–0.052 (2)	0.022 (1)	0.082 (7)
C_{13}	0.166 (1)	–0.005 (1)	0.0991 (8)	0.056 (5)
C_{14}	0.002 (1)	–0.016 (1)	0.2651 (7)	0.037 (4)
C_{15}	–0.122 (1)	0.008 (1)	0.2545 (7)	0.047 (5)
C_{16}	–0.219 (1)	–0.079 (1)	0.2432 (8)	0.054 (5)
C_{17}	–0.199 (1)	–0.190 (1)	0.2451 (8)	0.058 (6)
C_{18}	–0.077 (1)	–0.215 (1)	0.2580 (8)	0.061 (6)
C_{19}	0.022 (1)	–0.129 (1)	0.2685 (8)	0.056 (5)
C_{20}	0.403 (1)	–0.046 (1)	0.2569 (9)	0.050 (5)
C_{21}	0.393 (1)	–0.047 (1)	0.3360 (8)	0.057 (5)
C_{22}	0.362 (1)	–0.149 (1)	0.3639 (9)	0.066 (6)
C_{23}	0.341 (1)	–0.255 (1)	0.315 (1)	0.067 (6)
C_{24}	0.348 (1)	–0.254 (1)	0.237 (1)	0.066 (6)
C_{25}	0.379 (1)	–0.154 (1)	0.2076 (9)	0.055 (5)
C_{26}	0.629 (1)	0.200 (1)	0.3425 (9)	0.060 (6)
C_{27}	0.718 (1)	0.250 (2)	0.400 (1)	0.084 (7)
C_{28}	0.715 (2)	0.365 (2)	0.4323 (9)	0.068 (6)
C_{29}	0.626 (2)	0.425 (1)	0.4108 (9)	0.068 (6)
C_{30}	0.536 (1)	0.375 (1)	0.3550 (8)	0.060 (5)
C_{31}	0.538 (1)	0.261 (1)	0.3195 (7)	0.041 (4)
C_{32}	–0.305 (2)	–0.289 (1)	0.233 (1)	0.097 (8)
C_{33}	0.310 (2)	–0.365 (2)	0.346 (1)	0.12 (1)
C_{34}	0.466 (1)	0.241 (1)	0.1569 (7)	0.048 (5)
C_{35}	0.470 (2)	0.356 (2)	0.153 (1)	0.076 (7)
C_{36}	0.498 (2)	0.394 (2)	0.083 (1)	0.097 (9)
C_{37}	0.528 (2)	0.316 (2)	0.020 (1)	0.094 (9)
C_{38}	0.526 (2)	0.205 (2)	0.023 (1)	0.082 (7)
C_{39}	0.496 (1)	0.166 (1)	0.0920 (9)	0.067 (6)
C_{40}	0.315 (2)	0.250 (1)	0.4710 (7)	0.059 (6)
C_{41}	0.314 (2)	0.182 (2)	0.5390 (9)	0.091 (8)
C_{42}	0.230 (2)	0.071 (1)	0.5250 (8)	0.074 (6)
C_{43}	0.142 (1)	0.060 (1)	0.4563 (8)	0.059 (6)
C_{44}	0.049 (1)	0.132 (1)	0.4536 (7)	0.050 (5)
C_{45}	0.029 (1)	0.238 (1)	0.5146 (8)	0.066 (6)
C_{46}	0.113 (2)	0.343 (2)	0.508 (1)	0.093 (8)
C_{47}	0.227 (1)	0.320 (1)	0.4561 (8)	0.060 (6)

[a] Esd are within parentheses. [b] *U*(eq) = $^1/_3$ of the trace of the orthogonalized U matrix.

Table IV. IR and ^{31}P NMR Data of the Complexes $[M\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}R'\text{-}4)_2\}L_2]$ (3, 4)

	IR			^{31}P NMR[a]		
compound	ν(P–N)[b]	ν(CO)[b]	ν(CO)[c]	*T*, K	δ(P)	^2J(Rh,P), Hz
3a	1290			298	11.8 (d)	9.8
	1366			193[d]	11.0 (br)	
3b	1304	1980	1985	298	23.9 (d)	8.5
	1333	2055	2058	178[d]	–0.8 (br)	
					35.0 (br)	
3c	1303			298	15.4 (d)	4.9
	1319					
3d	*e*			298	6.0 (br)	*f*,*g*
					22.3 (d,br)	17.1[g]
4a	1285			298	17.9 (s)	
	1363			193[h]	–3.9 (br)	
					27.2 (br)	
4b	*e*			298	7.5 (br)[g]	
					34.9 (br)[g]	
4c	*e*			298	20.4 (s)	
4d	1279	1963	1965	298	31.7 (s)	
	1340	2045	2042	193[h]	19.1 (br)	
					60.2 (br)	
4e	*e*	1965	1970	298[d]	15.0 (d)[i]	
		2040	2045		55.7 (d)[i]	
4f	*e*	1974	1979	298	35.1 (s)	
		2047	2058			

[a] For ^{103}Rh NMR, see the text. ^{31}P NMR measured in C_6D_6, chemical shifts in ppm relative to external 85% H_3PO_4 with downfield shift positive, coupling constants in Hz; s = singlet, d = doublet, br = broad signal. [b] KBr pellet. [c] Solvent, CH_2Cl_2. [d] Solvent, CD_2Cl_2. [e] Obscured by $\nu(NO_2)$. [f] Not observed. [g] ^2J(P,P) = 3.9 Hz. [h] Solvent, toluene-d_8. [i] ^2J(P,P) = 4.9 Hz.

RN=PPh$_2$CH (iminophosphoranyl)methanide moiety that is coordinated as a σ-N,σ-C chelate and the uncoordinated Ph$_2$P=NR iminophosphorane group as a substituent on the methanide C atom. This substituent has the normal structural features of free iminophosphoranes.

The fact that all known (iminophosphoranyl)methanide complexes (i.e. **4a**, **I**, and **II**)[6a,c] are coordinated in a σ-N,σ-C chelating mode toward the metal indicates that this configuration constitutes the preferred coordination mode of this type of pseudoallylic anions to Rh(I) and Ir(I). The main factors that favor this geometry are probably the remarkable stabilization of the metal to carbon bond by the chelating effect, due to internal coordination of the N atom, and the polarization within the four-membered metallacycle giving rise to strong Ir–C and Ir–N bonds. Interestingly, in the related Rh– and Ir–bis(diphenylthioxophosphoranyl)methanide complexes [M(COD)-{CH(PPh$_2$=S)$_2$}][3b] the ligand does not adopt a similar σ-S,σ-C chelating mode, but instead σ-S,σ-S′ coordination by intramolecular coordination of both thioxophosphorane groups has been observed. However, σ-S,σ-C coordination has been found for the corresponding platinum(II) complexes.[3c]

The striking similarities in structural factors within the M–N–P–C ring of **4a**, **I**, and **II** indicate that substitution of the methanide hydrogen atom in **I** by different groups, i.e. PPh$_2$=N-*p*-tolyl in **4a** and PPh$_2$-NH-*p*-tolyl in **II**, has only little influence on the overall coordination behavior of the (iminophosphoranyl)methanide ligand, but small differences for example in the polarization within the M–N–P–C cycle may occur.

It is noteworthy that in **4a**, although there is no bonding interaction between N_1 and Ir ($d(N_1\text{–}Ir)$ = 3.84 (1) Å), the nitrogen atom N_1 of the pendant iminophosphorane unit is directed toward the Ir atom (torsion angles P_2–C_1–P_1–N_1 = –42.9 (9)° and Ir–C_1–P_1–N_1 = 55.4 (8)°. In the aforementioned compound [Rh(*p*-tolyl-N=PPh$_2$-CH-PPh$_2$-NH-*p*-tolyl)(COD)]$^+$ (**II**) the N atom of the uncoordinated aminophosphonium entity is pointing away from the metal atom (corresponding torsion angles P–C–P–N = 83.5° and Rh–C–P–N = 173.2°).

IR Spectroscopy (Solid State). In all complexes containing the bis[(*p*-tolylimino)diphenylphosphoranyl]-methanide ligand (**3a–c**, **4a**, and **4d**) two bands are found in the IR spectrum (KBr pellet) that can be attributed to ν(P–N) (Table IV). The bands at lower wave numbers (between 1279 and 1304 cm^{-1}) appear at the expected positions for iminophosphorane vibrations in a M–N–P–C four-membered ring[5c] and are somewhat lower than usually found for the free ligand **1a**.[6] The difference in ν(P–N) between uncoordinated and coordinated iminophosphoranes is smaller than is usually observed upon coordination of an iminophosphorane to a transition metal.[40] Hence in these complexes the P–N bond of the coordinated iminophosphorane has considerable double-bond character, in agreement with the X-ray structure determination of **4a**, in which it was shown that the P–N distance is short. The other ν(P–N) bands (between 1313 and 1366 cm^{-1}) can be attributed to the uncoordinated iminophosphorane moiety. It is striking that ν(P–N) for the uncoordinated P–N moiety has in most cases increased with respect to free **1a** (1328 cm^{-1}), implying a somewhat higher bond order for the P=N bond. The increased bond order between N and P may be accomplished by withdrawal of electron density from the M–C bond and hence from the metal. This would imply that polarization within the four-membered metallacycle is increased with respect to, for instance, **I** or **II**. Such reasoning is in accordance with the results from the X-ray structure determination of **4a**, where it was shown that both P–N bonds and the Ir–N_2 bond are short.

In the other compounds, containing at least one C_6H_4-NO_2-4 substituent on the N atoms, ν(P–N) bands are obscured by the intense ν(NO_2) bands at ca. 1300 cm^{-1} and hence no conclusions about the structure of these complexes can be drawn on the basis of their IR spectra. The complexes containing carbonyl ligands (**3b**, **4d–f**) all show two strong bands in the carbonyl region, consistent with local C_s symmetry.[41]

^{31}P NMR in the Solid State. Solid-state ^{31}P CP/MAS NMR spectra of free **1a** and of the complexes **3a**, **3c**, and **4a** have been recorded. In the spectrum of **1a** only one signal with a number of spinning sidebands was observed at –9.5 ppm, which is a much lower value than was found in solution. Note, however, that in solution chemical shifts vary with solvent (0.1 ppm in $CDCl_3$, –2.5 ppm in C_6D_6).[6] Such large differences between solution and solid-state spectra are not uncommon in ^{31}P NMR spectra and are generally attributed to intermolecular packing effects and/or to geometrical changes in the solid state,[42] whereas in solution coordination of the solvent to the molecule may play a role.

For the bis(iminophosphoranyl)methanide complex **3a**, two signals were found at –9.9 and 24.4 ppm (Figure 2), for **3c** at 9.4 and 21.0 ppm, whereas for **4a** two pairs of signals were found at –9.0 and 28.8, and –11.4 and 32.3 ppm, respectively (Figure 3), in all cases with their spinning sidebands. All chemical shifts found in the solid-state ^{31}P NMR experiments are observed at lower frequencies than would be expected from solution ^{31}P NMR (except for **3c**), in agreement with observations for free **1a**.

The observation of two different signals for the complexes is in concert with the results obtained from the IR experiments and the X-ray structure determination of **4a**, in which it was shown that the bis(iminophosphoranyl)methanide complexes contain two different iminophosphorane groups in the solid state, i.e. a structure as depicted in Figure 1. The differences in chemical shift values between the coordinated and uncoordinated iminophosphorane groups in the complexes **3a** (34.3 ppm) and **4a** (37.8 and 43.7 ppm) are close to the expected values, based on the ^{31}P chemical shift values of related compounds in solution, i.e. 40.0 and 52.9 ppm, respectively, for the Rh(I)– and Ir(I)–(iminophosphoranyl)methanide complexes **I**[5c] and of ca. 0 ppm for the free bis(iminophosphoranyl)methane **1a**.[6] For **3c**, a smaller difference in chemical shift values is observed. This is due to a high frequency shift of the pendant iminophosphorane group as compared to **3a** and **4a**, which may be caused by inter- or intramolecular coordination of the N atom to a rhodium center for this specific compound.

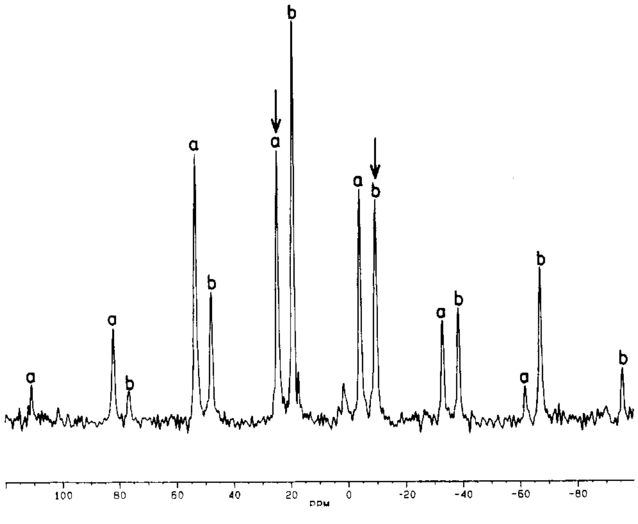

Figure 2. ^{31}P CP/MAS NMR spectrum of **3a**. The arrows indicate the chemical shift positions; the letters indicate the accompanying spinning sidebands.

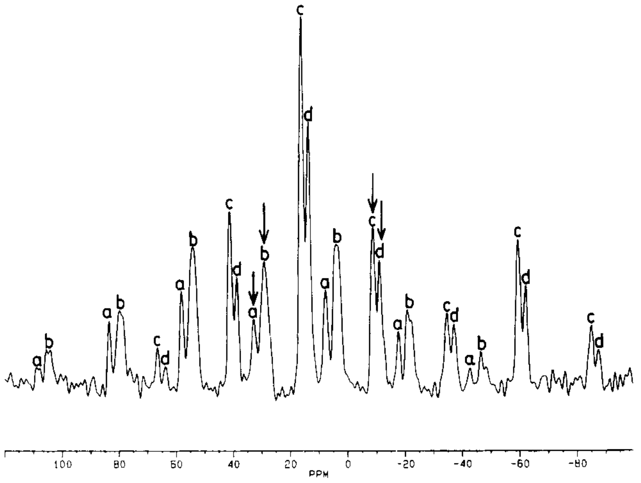

Figure 3. ^{31}P CP/MAS NMR spectrum of **4a**. The arrows indicate the chemical shift positions for the two different compounds; the letters indicate the accompanying spinning sidebands.

The observation of different pairs of signals for **4a** again demonstrates the high sensitivity of ^{31}P solid-state NMR spectra to effects of the environment.[43] In order to rule out the possibility that the observed doublings of the signals are due to *J* couplings or due to residual dipolar coupling to nitrogen, which is not averaged by MAS,[44] spectra were taken at lower field as well. As no change of the spectrum was observed (on the ppm scale), the

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Table V. Chemical Shift Tensor Values Obtained from Spinning Sideband Analyses of the ^{31}P CP/MAS Data of Compounds 1a, 3a, and 3c

		3a		3c	
	1a	$P_{uncoord}$	P_{coord}	$P_{uncoord}$	P_{coord}
isotropic shift σ_i	−9.5	−9.9	24.4	9.4	21.0
σ_{11}	−122	−110	−53	−74	−50
σ_{22}	39	27	27	13	12
σ_{33}	54	53	99	89	100

additional signals may be explained by assuming the presence of two closely related species, which have slightly different conformations. Although such differences have not been observed in the X-ray structure study of **4a**, they appear in the powder. Apparently, there is a difference in packing between the powder used for the NMR experiments and the crystals used for the X-ray study, e.g. due to the presence of hexane in the crystals (vide supra), which was absent in the powder. Spinning sideband analyses of the spectra of free **1a** and complexes **3a** and **3c** allowed a determination of the principal values of the shielding tensor of the observed phosphorus species (Table V). It can be seen that the tensor values of the uncoordinated iminophosphorane group of complex **3a** are similar to those of the free ligand **1a**. Here the local symmetry is close to axial symmetry. Upon inspection of the structure of this compound, it is not obvious that the local symmetry at the phosphorus site should be axial. This symmetry would arise when there is a rapid (on the NMR time scale) rotation about the P–C binding axis. It must be noted, however, that a sideband analysis is not very reliable for determining the asymmetry parameter when it approaches zero, i.e. axial symmetry.[45] As was discussed above, the isotropic shift and of course also the principal tensor values for the uncoordinated group in **3c** deviates substantially from those of the free ligand. Note also that the shielding tensor for this compound is now far from axially symmetric.

A comparison of the principal tensor values of the coordinated iminophosphorane group in complexes **3a** and **3c** reveals that they are identical except for the σ_{22} value. This suggests that the corresponding principal axis is directed toward the Rh atom and that the shift of σ_{22} to lower frequency, when the COD ligand is replaced by NBD, reflects a higher electron affinity of the former group, in contrast with earlier observations[46] that NBD has a higher π-back-bonding capacity than COD. These observations indicate that the sum of σ-donating and π-back-bonding capacity of COD is somewhat lower than that for NBD.

^{1}H, ^{13}C, and ^{31}P NMR Studies in Solution and Exchange Processes. The structure of the bis(iminophosphoranyl)methanide complexes in solution was studied by ^{31}P, ^{1}H, and ^{13}C NMR. The data are collected in Tables IV, VI, and VII, respectively.

At room temperature the ^{1}H NMR spectra of the complexes derived from the symmetric compounds **2a** and **2c** show one signal for the methanide hydrogen atom. This signal is split into a triplet due to coupling with two (equivalent) phosphorus atoms. For the rhodium-containing complexes **3a** and **3b**, an additional coupling to the ^{103}Rh nucleus of 1.5 and 1.2 Hz, respectively, is observed, indicating that, in accordance with the solid-state structure, a Rh–C bond is present in these complexes in solution.[5c,32a,b] For the *N*-aryl substituents, only one AB coupling pattern is found for both groups, whereas for the complexes derived from **2a** (R′ = Me) only one signal is found for both methyl groups. So, at room temperature the bis(iminophosphoranyl)methanide ligands have a magnetically symmetric structure in solution on the ^{1}H NMR time scale. Upon cooling of solutions of **3a**, **3b**, **4a**, or **4d** (in CD_2Cl_2 or Tol-d_8) to 193 K, broadening of all signals was observed. However, contrary to what would be expected if these complexes have a structure as found in the solid state (Figure 1), no splitting of the resonances was observed in the ^{1}H NMR spectra. The ^{13}C NMR spectra of **3a**, **4a**, and **4d** confirm the results obtained from ^{1}H NMR, i.e. a magnetically symmetric structure of the ligand on the NMR time scale at room temperature (**3a**) or 253 K (**4a**, **4d**), as demonstrated by the observation of a triplet for the methanide carbon atom, due to coupling with two equivalent P atoms. For **3a**, an additional ^1J(Rh,C) of 14.2 Hz is present. Furthermore only one methyl resonance and four aromatic resonances are found for both *N*-tolyl groups and four resonances for the *P*-phenyl groups.

Also in the ^{31}P NMR spectra (Table IV) at room temperature only one signal is found. In the complexes **3a–c** a doublet due to coupling with one Rh nucleus is found. The coupling constant (4.9–9.8 Hz) is smaller than observed for the mono(iminophosphoranyl)methanide–rhodium complexes **I** (ca. 18 Hz),[5c] but higher than in coordination complexes of iminophosphoranes with Rh(I) (≤3 Hz).[24] The chemical shift values lie between those found for **I** (40.0 ppm, M = Rh, L_2 = COD)[5c] and the free ligands **1a** (0.1 ppm) or **1c** (1.8 ppm).[6] Upon cooling of solutions of **3a**, **3b**, **4a**, or **4d**, the signals broaden and at 193 K a very broad signal is found for **3a**, whereas for **3b**, **4a**, and **4d** two signals are observed that are separated by ca. 35.8, 31.1, and 41.1 ppm, respectively. Since these signals are still a little broadened at 193 K ^2J(P,P) and ^2J(Rh,P) remain unresolved. The chemical shift values are in agreement with a structure that has been found in the solid state (Figure 1).

Obviously an exchange process occurs that is fast on the ^{31}P NMR time scale at room temperature but which can be brought into the slow or intermediate exchange by cooling down to 193 K. The coalescence temperatures are found at 203 K for **3b** and **4a** and at 243 K for **4d** and are independent of the concentration of the complexes, indicating an intramolecular exchange process in all cases. The $\Delta G^{\#}$ values can be estimated to be 8.8, 8.8, and 10.5 kcal/mol for **3b**, **4a**, and **4d**, respectively, assuming the normal expressions for an intramolecular process.

At this point it is important to emphasize that in the ^{1}H NMR spectra of the complexes containing the diene ligand (**3a**, **3c**, **4a**, and **4c**) only one olefinic signal is observed for the diene at 298 K and that this signal broadens upon cooling to 193 K. In the ^{13}C NMR spectra (Table VII) also one signal is found for the olefinic carbon atoms in **3a** and **4a** and for both carbonyl atoms in **4d**. This proves that the two halves of the bis(iminophosphoranyl)methanide ligand as well as both ligands trans to the N and C atoms become equivalent on the NMR

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Table VI. ^{1}H NMR Data[a] of the Complexes [M{CH(PPh$_2$=N-C$_6$H.R'-4)$_2$}L$_2$] (3, 4)

compd	δ(CH)	^2J(P,H)[b]	δ(R')	δ(aryl)[c]	δ(Ph)	δ(=CH)(diene)[d]	δ(CH$_2$)(diene)[d]
3a	2.01 (dt)	2.6 (1.5)	2.22	7.04 (d, 3.0) 7.12 (d, 3.0)	6.86–7.19 (m) 7.74–7.98 (m)	3.86	1.4–1.7 2.2–2.4
3b	2.29 (dt)	6.3 (1.2)	2.00	6.92 (d, 8.4) 7.05 (d, 8.4)	6.77–7.07 (m) 7.72–7.99 (m)		
3c	1.77 (br)	<0.4	2.19	6.9 (br)	6.7–7.1 (m) 7.7–7.9 (m)	3.46	1.01[e]
3d	*f*		1.87	6.19 (d, 8.0)[f,g] 6.61 (d, 8.2)[h] 8.54 (d, 8.2)[h]	6.7–7.1 (m) 7.3–8.0 (m)	3.6–3.9 (br)	1.2–1.6 1.9–2.3
4a	2.81 (t)	5.2	2.20	6.9 (br)	6.9–7.0 (m) 7.74–7.95	3.57	1.4–1.5 2.2 (br)
4b[g]	2.86 (dd)	3.8 9.9	2.11	5.92 (d, 7.8)[h] 6.6 (d, 7.8)[h] 7.0 (d, 8.8)[i] 8.0 (d, 8.8)[i]	7.3–8.3 (m)	3.04 3.63	1.1–1.4 1.9–2.2
4c[j]	2.75 (t)	5.5		6.52 (d, 8.8) 7.91 (d, 8.8)	7.1–7.9 (m)	3.36	1.1–1.4 1.9–2.2
4d	2.98 (t)	12.2	2.07	6.82 (d, 8.6) *f*	6.8–7.1 (m) 7.63–7.81 (m)		
4e[g]	3.07 (dd)	9.0 12.9	2.16	6.45 (d, 8.0)[h] 6.53 (d, 8.1)[i] 6.79 (d, 8.0)[h] 7.83 (d, 8.1)[i]	7.2–8.0 (m)		
4f	3.00 (t)	13.0		6.51 (d, 8.9) 7.86 (d, 8.9)	7.2–7.8 (m)		

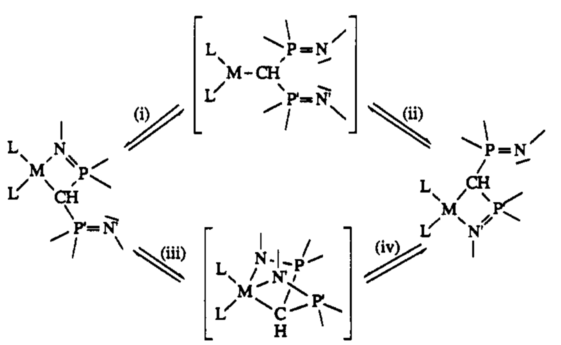
[a] Measured at 100 MHz at room temperature; chemical shift values in ppm relative to TMS, coupling constants in Hz; solvent C$_6$D$_6$; d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad signal. [b] ^2J(Rh,H) in parentheses. [c] For AB doublet ^3J(H,H) in parentheses. [d] Very broad resonance. [e] CH(NBD): 3.53 ppm. [f] Signal obscured. [g] Solvent, CD$_2$Cl$_2$. [h] C$_6$*H*$_4$-CH$_3$-4. [i] C$_6$*H*$_4$-NO$_2$-4. [j] Solvent, CDCl$_3$.

Table VII. ^{13}C NMR Data of Complexes 3a, 4a, and 4d[a]

compd (solvent)	*p*-tolyl	Ph	*C*H	COD/CO
3a (C$_6$D$_6$)	20.9 (CH$_3$), 124.5 (d, 15.2, C$_o$), 128.5 (C$_p$), 129.5 (C$_m$), 148.5 (C$_i$)	127.8 (C$_m$)[b] 127.0 (C$_i$)[b] 130.4 (C$_p$) 132.2 (d, 9.2, C$_o$)	8.5 (dt, 76.2,[c] 14.2[d])	31.1 (C$_{al}$) 77.2 (d, 12.1 Hz,[e] C$_{ol}$)
4a (Tol-*d*$_8$) (253 K)	20.8 (CH$_3$), 123.9 (d, 9.1, C$_o$), 128.7 (C$_p$), 129.2 (C$_m$), 147.3 (C$_i$)	128.3 (d, 10.6, C$_m$) 128.0 (C$_i$)[b] 131.4 (C$_p$) 132.3 (d, 8.2, C$_o$)	*f*	31.8 (C$_{al}$) 60.6 (C$_{ol}$)
4d (CD$_2$Cl$_2$) (253 K)	20.8 (CH$_3$), 122.4 (d, 14.9, C$_o$), 128.7 (C$_p$), 129.3 (C$_m$), 147.8 (C$_i$)	128.6 (d, 11.6, C$_m$) 129.6 (d, 61.6, C$_i$) 132.1 (C$_p$) 132.7 (d, 9.3, C$_o$)	10.9 (t, 68[c])	176.9

[a] Measured at 25.18 MHz; chemical shifts in ppm relative to external TMS; coupling constants in Hz; d = doublet, dt = doublet of triplets, i = ipso, o = ortho, m = meta, p = para, al = aliphatic, ol = olefinic. [b] Obscured by solvent signal. [c] ^1J(P,C). [d] *J*(Rh,C). [e] *J*(Rh,C). [f] Not observed.

Scheme I. Possible Mechanisms for the Intramolecular Exchange Processes of [M{CH(PPh$_2$=N-C$_6$H$_4$-R'-4)$_2$}L$_2$] (3, 4)



time scale. Hence, the exchange process involves a net migration of the bis(iminophosphoranyl)methanide ligand along the metal atom indicated by the extremes in Scheme I.

Based on these data, two mechanisms for the exchange process can be proposed. The first one is a dissociative mechanism in which the M–N bond is broken and isomerization should occur via a T-shaped intermediate (i, ii, Scheme I). The second one involves an associative mechanism in which the exchange process occurs via a five coordinate intermediate (iii, iv, Scheme I). In the latter mechanism the intermediate is formed by coordination of the N atom of the pendant iminophosphorane entity to the metal atom. Isomerization may then occur via a Berry pseudorotation and subsequent M–N bond breaking.

The second mechanism is more likely to occur than the first since (i) the exchange process is a low-energy process, which is characteristic for a Berry pseudorotation as proposed in the second mechanism, isomerization of a T-shaped intermediate being a high-energy process,[47] (ii) it has recently been shown that a terdentate coordination mode for the bis(iminophosphoranyl)methanide ligand, such as proposed in the intermediate five-coordinate complex, occurs for this type of ligand,[48] and (iii) in the unsymmetrically substituted bis(iminophosphoranyl)methanide complexes **3b**, **4b**, and **4e**, no exchange is observed (vide infra). When a dissociative mechanism

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would apply, as indicated in reactions i and ii, isomerization should take place for these complexes as well. Although the tendency for five coordination of Rh(I) is low (especially when hard donor atoms like N are involved), we believe that the molecular and electronic structure within the molecule is in keeping with coordination of the free nitrogen atom to give a five-coordinate complex as a transient species. This is deemed possible due to a lower nucleophilic character of M than in other Rh(I) and Ir(I) complexes by virtue of stabilization of the d_z2 orbital of square planar 3 and 4 via electron withdrawal by the ligand.

Similar mechanisms have been proposed to explain fluxional processes for Rh- and Ir-phosphine complexes: in, for example, $[M(COD)(tripod)]BF_4$ (M = Rh, Ir; tripod = $HC(PPh_2)_3$), attack of the pendant phosphorus atom on the d^8-metal center takes place, followed by isomerization and consecutive M-P bond breaking,[49] whereas exchange of [M(diene)ClL] (M = Rh, Ir; diene = COD, NBD; L = PPh_3, $AsPh_3$) or of $[M(CO)_2(pyridine)Cl]$ occurs with free L via intermolecular association of a phosphine or arsine[46] or pyridine ligand.[50]

The mechanism presented here is quite different from that proposed for the related $[Pt(II)\{CH(PPh_2{=}S)_2\}(PEt_3)Cl]$ (V)[3c] or $[Pt(II)\{C(PPh_2{=}S)_3\}(PEt_3)Cl]$ (VI) compounds.[3a] In these complexes exchange occurs via rotation around a Pt-C (V) or a Pt-S (VI) axis in a three-coordinate species. This pivotal exchange process cannot hold for the complexes in this study, since by exchange via this mechanism the ligands trans to the bis(iminophosphoranyl)methanide ligand would remain anisochronous which, as shown by variable-temperature ^{1}H and ^{13}C NMR, is not the case.

The complexes **3d**, **4b**, and **4e** (R′ = Me and NO_2, respectively) show a solution behavior different from the other bis(iminophosphoranyl)methanide complexes. Up till at least 323 K these complexes are rigid[51] and have a structure as depicted in Figure 1 (vide supra). In the ^{1}H NMR spectra of **4b** and **4e** the methanide hydrogen resonance is found at 2.86 and 3.07 ppm, respectively, and is split into a doublet of doublets due to coupling with the two phosphorus nuclei, i.e. a large coupling (9.9 and 12.9 Hz, respectively) with the P atom of the uncoordinated iminophosphorane and a smaller coupling (3.8 and 9.0 Hz, respectively) with the P atom of the coordinated group.

The olefinic signals of the COD ligand are either very broad (**3d**, 3.6–3.9 ppm) or found as two resonances (**4b**, 3.04 and 3.63 ppm), the latter due to the different trans influence of the substituents trans to the COD ligand. In the ^{31}P NMR spectra of **3d**, **4b**, and **4e**, two resonances are found that can be assigned to the coordinated (22.3, 34.9, and 55.7 ppm, respectively) and to the free (6.0, 7.5, and 15.0 ppm, respectively) iminophosphorane entities. All signals show a small $^2J(P,P)$, whereas in **3d** for the signal at 22.3 ppm additional coupling of 17.1 Hz with the Rh nucleus is found. On the basis of these data and the known[24,34] higher σ-bonding capacity of p-CH_3-C_6H_4-substituted compared to p-NO_2-C_6H_4-substituted iminophosphorane groups, we propose a structure of **3d**, **4b**, and **4e** in which the *N*-*p*-tolyl-substituted part is coordinated to the metal atom. The difference in σ-bonding capacity is also responsible for the rigidity[51] of these complexes. An exchange process as depicted in Scheme I does not occur since this process would involve unfavorable intramolecular attack of the less nucleophilic free *p*-nitrophenyl-substituted nitrogen atom on the metal.

^{103}Rh NMR in Solution. The ^{103}Rh NMR chemical shifts of **3a** and **3b** are found at 917 and 11 ppm, respectively (relative to $\Xi(^{103}Rh)$ = 3.16 MHz). Both values lie within the range of chemical shifts known for Rh(I) compounds.[5c,52] The large difference between the shifts for **3a** and **3b**, i.e. a high frequency shift of ca. 900 ppm in going from L = CO to L_2 = COD, demonstrates the high sensitivity of $\delta(^{103}Rh)$ on both electronic and structural factors.[52] Particularly the paramagnetic shift contribution, which largely determines the chemical shift of transition metal nuclei, is very sensitive to changes within the coordination sphere, and is related to the inverse of the excitation energy ΔE^{-1}, the radial factor $\langle r^{-3}\rangle$, and the charge imbalance factor $\sum Q_n$ (eq 3).

$$\sigma_N^{para} \sim \Sigma Q_N \cdot \langle r^{-3}\rangle \cdot \Delta E^{-1} \qquad (3)$$

In the complexes presented here ΔE will be lower for **3a** than for **3b** because COD is a poorer π-acceptor than two CO ligands. On the basis of this finding one would indeed expect a higher $\delta(^{103}Rh)$ value for **3a** than for **3b**. Possibly, the radial and charge imbalance factors play a role as well, as has been found for other Rh(I) complexes.[7b,52,53] A similar difference in chemical shift values has been found for the mono(iminophosphoranyl)methanide complexes **Ia** (L_2 = COD, 787 ppm) and **Ib** (L = CO, −88 ppm).[5c] However, the differences in chemical shifts in going from **3a** to **Ia** or from **3b** to **Ib**, i.e. replacement of the substituent $PPh_2{=}N$-C_6H_4-CH_3-4 on the methanide carbon atom by a hydrogen atom, are relatively small. It demonstrates that the Rh-(iminophosphoranyl)methanide entities are closely related and that, in agreement with the X-ray and IR data, only small differences exist in electronic and structural properties of this moiety.

Reactions with CO_2. It is well-known that several iminophosphoranes react with compounds containing organic carbonyl groups in an aza-Wittig reaction to give an imine and a phosphine oxide.[40] It has for instance been shown that, upon reaction with CO_2, the bis(iminophosphoranyl)methane **1a** is converted into methylenebis(diphenylphosphine oxide), *p*-tolylisocyanate, and di-*p*-tolylcarbodiimide (eq 4).[6]

$$\underset{\textbf{1a}}{CH_2(PPh_2{=}N\text{-}p\text{-tolyl})_2} + CO_2 \longrightarrow CH_2(PPh_2{=}O)_2 + p\text{-tolyl-}N{=}C{=}O + p\text{-tolyl-}N{=}C{=}N\text{-}p\text{-tolyl} \qquad (4)$$

In order to investigate the kinetic stability of the M-N-P-C metallacycle in the bis(iminophosphoranyl)methanide complexes **3a**, **3b**, **4a**, and **4d**, these compounds were

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(50) Pribula, A. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 2784.

(51) For complexes **3b**, **4b**, and **4e**, no fluxional behavior similar to that observed for the other bis(iminophosphoranyl)methanide complexes has been observed. However, other fluxional processes in which no net structural change occurs, such as for example fast M-N bond breaking/formation, cannot be excluded in these cases.

(52) (a) Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861 and references therein. (b) von Philipsborn, W. *Pure Appl. Chem.* **1986**, *58*, 513 and references therein. (c) Mason, J. *Chem. Rev.* **1987**, *87*, 1299 and references therein.

(53) (a) Maurer, E.; Rieker, S.; Schollbach, M.; Schwenk, A.; Egolf, T.; von Philipsborn, W. *Helv. Chim. Acta* **1982**, *65*, 26. (b) Bonnaire, R.; Davoust, D.; Platzer, N. *Org. Magn. Reson.* **1984**, *22*, 80.

reacted with CO_2. It was found that, under rigorous exclusion of water, the complexes reacted with only 1 equiv of CO_2 under the formation of the new (iminophosphoranyl)(oxophosphoranyl)methyl complexes **5a–d**, *p*-tolyl isocyanate, and di-*p*-tolylcarbodiimide (eq 5). Indeed,

$$\underset{\mathbf{3,4}}{[M\{CH(PPh_2{=}N\text{-}p\text{-tolyl})_2L_2\}]} + CO_2 \longrightarrow [M\{CH(PPh_2{=}N\text{-}p\text{-tolyl})(PPh_2{=}O)\}L_2] + p\text{-tolyl-}N{=}C{=}O + p\text{-tolyl-}N{=}C{=}N\text{-}p\text{-tolyl} \quad (5)$$

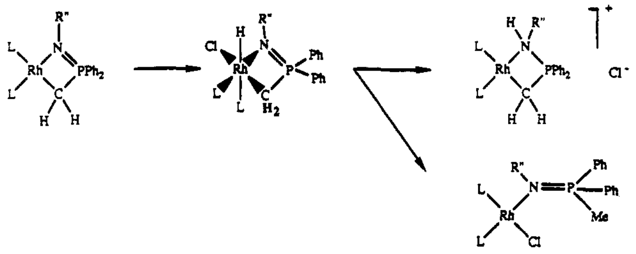
CO_2 reacts only with the pendant iminophosphorane moiety, i.e. one iminophosphorane unit is kinetically stabilized within the metallacycle by coordination to the metal.

The new complexes were fully characterized by ^1H and ^{31}P NMR, IR, and FDMS. In the ^1H NMR spectra the methanide resonances are split into a doublet of doublets due to coupling with both phosphorus atoms. For the olefinic signals a very broad signal is found for **5a** (4.0 ppm) and two signals are found for compound **5c** (4.03 and 3.54 ppm). In the ^{31}P NMR spectra one resonance at ca. 30 ppm and one in the range from 33 to 59 ppm are found for the complexes **5a–d**. Both signals show small $^2J(P,P)$ coupling and for the Rh complexes **5a** and **5b** a coupling of the (iminophosphoranyl)methanide P with the ^{103}Rh nucleus is observed. The chemical shift values indicate a ground-state structure in which the iminophosphoranyl moiety is coordinated to the metal atom and the phosphine oxide group is not coordinated. The ^{31}P chemical shift of ca. 30 ppm is close to the value normally found for free phosphine oxides,[54] whereas the other chemical shift and coupling constant values are close to those found for mono(iminophosphoranyl)methanide complexes.[5a,c] The IR data confirm the structural assignment, i.e. $\nu(P{=}N)$ values indicative of an (iminophosphoranyl)methanide–metal moiety (at ca. 1290 cm^{-1})[5c] and another band at ca. 1200 cm^{-1}, a normal value for $\nu(P{=}O)$ in free phosphine oxides.[55] The rigid structure of the complexes **5a–d** is in agreement with the structure of **3d**, **4b**, and **4e**, i.e. complexes in which two groups are present that have a large difference in affinity toward the metal (vide supra).

The observation that only one of the iminophosphorane entities reacts with CO_2 is in agreement with the results obtained with the Rh–(iminophosphoranyl)methanide complexes **I**. It was shown that, due to the coordination of the (iminophosphoranyl)methanide entity to the metal core, these complexes do not react with CO_2. Accordingly, for complexes **3a**, **3b**, **4a**, and **4d**, the free iminophosphorane entity reacts with CO_2 to give **5a–d**, whereas the iminophosphorane group in the cyclic M–N–P–C entity remains intact. However, the reactivity of the free iminophosphorane moiety in **3a**, **3b**, **4a**, and **4d** toward CO_2 is lower than that found for free **1a**, as demonstrated by the reaction time needed for complete conversion (ca. 4 h for **3a**, **3b**, **4a**, and **4d** and ca. 10 min for **1a** under the same reaction conditions).

Reaction with HX (X = CF_3COO, Cl). The combination of a polar (iminophosphoranyl)methanide moiety and a reactive d^8 transition metal has been shown to give an interesting chemistry.[5c] Compound **I**, for instance, reacts with HCl to give a Rh(III) oxidative addition complex first, that reacts further via hydrogen migration to give either a C- or a N-protonated product (Scheme II). Similar oxidative addition–reductive elimination reactions may be expected for compounds **3a**, **3b**, **4a**, and **4d**. However, other reactions cannot a priori be excluded because a free iminophosphorane entity is present, which is known to react with HX to give aminophosphonium compounds.[40]

Scheme II. Reaction of [Rh($CH_2PPh_2{=}N\text{-}R''$)L_2] (I) with HCl

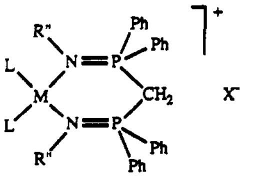


It has been established that reaction of **3a**, **3b**, **4a**, or **4d** with 1 equiv of CF_3COOH leads to the exclusive formation of the known (aminophosphonio)(iminophosphoranyl)methanide complexes **II** (X = CF_3COO).[5a] This reaction occurs readily (even at 193 K, there is complete reaction within 5 min) and **II** can be isolated in quantitative yield.

Addition of excess CF_3COOH to **II** or **3a**, **3b**, **4a**, or **4d** gives amino[(aminophosphonio)methyl]phosphonium bis(trifluoroacetate) (**IV**, eq 6, X = CF_3COO), i.e. the doubly protonated form of **1a**.[6] During the reaction also [ML_2-CF_3COO]$_2$ is formed. The products could unambiguously by identified by ^1H and ^{31}P NMR, IR, and FDMS and by comparison with authentic samples.

$$\underset{\mathbf{3,4}}{[M\{CH(PPh_2{=}N\text{-}p\text{-tolyl})_2L_2\}]} \xrightarrow{HX} [ML_2X]_2 + \underset{\mathbf{IV}}{CH_2(PPh_2\text{-}NH\text{-}p\text{-tolyl})_2]^{2+}.2X^-} \quad (6)$$

In the reaction of **3a**, **3b**, **4a**, or **4d** with 1 equiv of HCl not only **II** (X = Cl) was formed but also a complex in which the bis(iminophosphoranyl)methane is coordinated in a σ-N,σ-N′ coordination mode (**III**). Both products are known: they are also formed when [ML_2Cl]$_2$ is reacted with **1a**.[5a]



III

The product ratio **II**/**III** is dependent on the starting bis(iminophosphoranyl)methanide complex, i.e. **II**/**III** = 4/1 (**3a**), 6/1 (**3b**), 1/1 (**4a**), or 2/1 (**4d**). The reaction with HCl at 193 K occurs within 5 min for **3a**, **3b**, and **4d**, but slowly for **4a**. Hence, the reaction of **4a** with HCl could be monitored using NMR spectroscopy. A solution of **4a** in toluene-d_8 in a NMR tube was placed under an atmosphere of HCl gas at 193 K and the reaction was followed by ^1H and ^{31}P NMR. It was shown that, at 193

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[54] van Wazer, J. R. *Determination of Organic Structures by Physical Methods*; Academic Press: New York, London, 1971; Vol. 4, p 323.

[55] Bellamy, L. J. *Advances in Infrared Group Frequencies*; Methuen & Co Ltd: London, 1969; p 201.

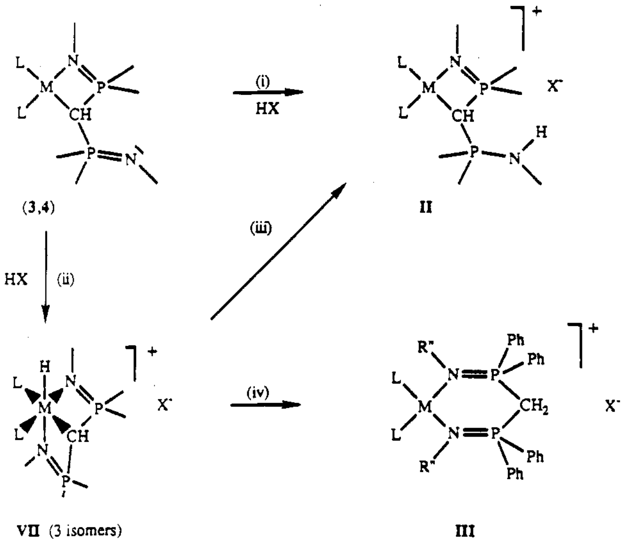
K, three metal hydride complexes were formed (^{1}H NMR) with hydride resonances at −11.2, −12.0, and −13.9 ppm. The ^{31}P NMR spectrum exhibits three large, broad resonances at 29, 35, and 40 ppm, which must be attributed to the final products **II** and **III**. Furthermore, three smaller signals were observed, a sharp one at 60 ppm and two broader ones at 47 and 40 ppm (partly obscured by the resonances due to **II**) in an approximate ratio of 1/1/1, which were attributed to the intermediate iridium hydride complexes. Upon raising the temperature to 233 K, the resonances due to the hydride intermediates disappeared and signals attributed to **II**, **III**, and **IV** appeared (^{1}H and ^{31}P NMR). Besides these, a small peak at −11.75 ppm was observed in the ^{1}H NMR spectrum and at 36.0 ppm in the ^{31}P NMR spectrum which was attributed to an unknown product, probably formed in the reaction of either **II** or **III** with HCl present in the NMR tube.

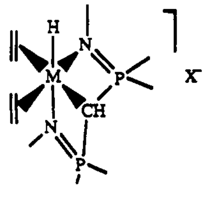
Bubbling HCl through a solution of **II** or **III** in benzene gave exclusively amino[(aminophosphonio)methyl]phosphonium dichloride **IV** (X = Cl) and $[ML_2Cl]_2$ (eq 6). Addition of 1 equiv of HCl to **II** and **III** gave a mixture of products, of which **II**–**IV** and $[ML_2Cl]_2$ could be identified by ^{1}H and ^{31}P NMR. This product formation may be explained by a second protonation of the ligand in **II** or **III** giving $[M(COD)Cl]_2$ and the hydrochloric acid adduct of **1a**, $[CH_2(PPh_2{=}N\text{-}p\text{-tolyl})(PPh_2\text{-}NH\text{-}p\text{-tolyl})]Cl$. The latter is in equilibrium with **1a** and **IV** (X = Cl).[6] Subsequently, $[M(COD)Cl]_2$ and **1a** can react to give **II** and **III** back again. Upon addition of excess HCl the reaction leads to the exclusive formation of **IV** and $[M(COD)Cl]_2$.

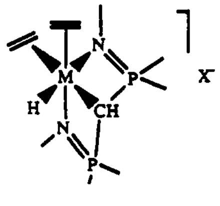
The aforementioned results indicate that the iridium–bis(iminophosphoranyl)methanide complex **4a** reacts with HCl to give initially Ir(III)–hydride complexes via oxidative addition. From the ^{1}H NMR hydride resonance positions it can be deduced that three isomeric Ir–hydrides are involved, in which the hydride is in a trans position to either a C or a N atom.[56] The values of the ^{31}P NMR resonances of these complexes (ca. 40, 47, and 60 ppm) indicate that both iminophosphorane moieties are coordinated to the metal.

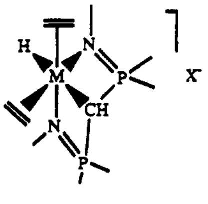
For the reaction of the bis(iminophosphoranyl)methanide complexes with HX (X = Cl, CF_3COO) several mechanisms may be proposed. Based on the data yet available, two mechanisms are most likely to occur. These are depicted in Scheme III. The first mechanism involves a direct attack on the free iminophosphorane entity (route i), analogous to the reaction with CO_2. In the second mechanism initial oxidative addition of HX to the metal occurs (route ii), giving rise to the formation of the M(III)–hydride complexes, followed by migration of the hydrogen atom to either the coordinated N atom (route iii) or C atom (route iv), leading to **II** or **III**, respectively.

Scheme III. Reaction of $[M\{CH(PPh_2{=}N\text{-}C_6H_4\text{-}CH_3\text{-}4)_2\}L_2]$ (3a, 3b, 4a, 4d) with HCl and CF_3COOH




VIIa


VIIb


VIIc

As isomerization of **II** into **III** does not occur,[57] reaction according to the first mechanism should yield the N-protonated species **II** exclusively. In view of the products formed, such a direct attack on nitrogen may play a role in the reaction of **3** or **4** with CF_3COOH (there the N-protonated species **II** are formed exclusively), but not in the reaction of **3** or **4** with HCl because of the concomitant formation of **III**. The observation by ^{1}H NMR of intermediate metal–hydride complexes indicates the occurrence of the second mechanism for the reaction with HCl. As can be inferred from ^{1}H and ^{31}P NMR, initial oxidative addition of HCl gives the M(III) complexes **VII**. ^{1}H NMR clearly reveals the presence of three Ir-hydride complexes (see above) and from ^{31}P NMR spectra it appears that both iminophosphorane moieties are coordinated to the metal ($\Delta\delta$ ca. 30–50 ppm). Together with the fact that protonation at C as well as N occurs in this reaction, this leaves only three possible isomers for the intermediate Ir–hydride cations (**VIIa**–**c**), in which the bis(iminophosphoranyl)methanide ligand acts as a terdentate ligand to the metal. The observation of only three signals in the ^{31}P NMR spectrum, instead of the five expected on the basis of the proposed structures of **VIIa**–**c**, can be explained by assuming the coincidence of the two pairs of signals of **VIIa** and **VIIb** at 40 and 47 ppm. This assumption is reasonable, as these complexes are closely related. The position and shape of the signal at 60 ppm indicate that this resonance must be attributed to two isochronous iminophosphorane groups in **VIIc**. The terdentate coordination mode as proposed for the bis(iminophosphoranyl)methanide ligand in intermediates

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[56] (a) Olgemöller, B.; Beck, W. *Inorg. Chem.* **1983**, *22*, 997. (b) Fernandez, M. J.; Esteruelas, M. A.; Oro, L. A. *Organometallics* **1987**, *6*, 1751. (c) Ball, R. G.; Ghosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341. (d) van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Grove, D. M. *Organometallics* **1988**, *7*, 1556.

[57] Imhoff, P.; van Asselt, R.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chim. Acta* **1991**, *184*, 73.

VIIa–c is corroborated by the isolation of a similar oxidative addition product from the reaction of **4a** with I_2,[48] in which the ligand is terdentate coordinated and one of the iodide atoms is found in a trans position relative to the methanide carbon atom.

In the isomers **VIIa–c** the hydride is present in a cis position to at least one coordinated N atom and hence reductive elimination of N–H with formation of **II** may occur easily. In two isomers (**VIIa** and **VIIb**) the hydride is in a cis position to the C atom of the bis(iminophosphoranyl)methanide ligand as well. From these complexes reductive elimination of a C–H bond (iv) leads to complex **III**.

The bis(iminophosphoranyl)methanide complexes react in a similar way as has been found for the mono(iminophosphoranyl)methanide complexes **I**, i.e. a combination of oxidative addition and reductive elimination reactions resulting in a net protonation of either the N or C atom. Several other reactions are known for related ligand systems in which consecutive oxidative addition–reductive elimination reactions occur. For instance, [Rh(Ph_2P-CH-P(S)Ph_2)(COD)] reacts with MeI to give the oxidative addition product [Rh(III)(Ph_2P-CH-P(S)Ph_2)I(Me)(COD)].[3b] With excess MeI a net methylation of the methanide carbon atom occurs and Rh(III)(Ph_2P-CH(Me)-P(S)Ph_2)I(Me)(COD)]$^+$ is formed, but it was not shown whether or not migration of a methyl group has occurred. The bis(diphenylthioxophosphoranyl)methanide complex [Ir{CH(PPh_2=S)$_2$}(COD)] reacted with MeI to give the complex [Ir{CH(Me)(PPh_2=S)$_2$}(COD)]$^+$, which is methylated at the former methanide carbon atom. The isostructural Pt(II) complex [Pt{CH(PPh_2=S)$_2$(PEt_3)Cl] reacted with HCl to form the Pt(II) complex in which the ligand is S,S coordinated, i.e. a net protonation of the methanide carbon has occurred.[3c] Although in neither of these reactions has an intermediate oxidative addition product been observed, occurrence of a reaction sequence similar to the one outlined in Scheme III (route ii–iv) seems likely.

The reactivity of the bis(iminophosphoranyl)methanide complexes toward reagents such as CO, MeI, and alkynes is low. Either sluggish or no reaction took place at all, which is most probably a result of the low electron density present on the metal center. Hence, the metal(I) center is relatively hard in terms of HSAB and will show less affinity toward soft reagents, e.g. MeI and reagents like alkynes which require π-back-bonding for activation, than toward the hard species HCl.

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Supplementary Material Available: Tables of anisotropic thermal parameters of the non-hydrogen atoms, fractional coordinates and isotropic thermal parameters of the hydrogen atoms, and all bond distances and angles for **4a** (8 pages). Ordering information is given on any current masthead page.

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