π-Accepting-Pincer Rhodium Complexes: An Unusual Coordination Mode of PCP-Type Systems

Elizaveta Kossoy,[a] Mark A. Iron,[a] Boris Rybtchinski,[a] Yehoshoa Ben-David,[a] Linda J. W. Shimon,[b] Leonid Konstantinovski,[b] Jan M. L. Martin,*[a] and David Milstein*[a]

Abstract: The novel π-accepting, pincer-type ligand, *dipy*rrolyl*p*hosphino*x*ylene (DPyPX), is introduced. This ligand has the strongest π-accepting phosphines used so far in the PCP family of ligands and this results in some unusual coordination chemistry. The rhodium(I) complex, [(DPyPX)Rh(CO)(PR_3)] (**4**, R = Ph, Et, pyrrolyl) is prepared by treating the relevant [(DPyPX)Rh(PR_3)] (**3**) complex with CO and is remarkably resistant to loss of either ligand. X-ray crystallographic analysis of complex **4b** (R = Et) reveals an unusual *cisoid* coordination of the PCP phosphine ligands. These observations are supported by density functional theory (DFT) calculations.

Keywords: coordination modes · P ligands · pincer ligands · rhodium · tridentate ligands

Introduction

The rigid chelation in pincer ECE ligands (ECE = tridentate monoanionic species, E is a neutral donor moiety) gives rise to exceptionally stable metal complexes. In addition, excellent electronic and steric tuning of the metal center can be achieved.[1,2] Pincer-type complexes are active in a variety of important catalytic processes, invaluable for mechanistic studies and for the stabilization of unusual structures, and useful as functional materials, as described in recent reviews.[1–7] A variety of donors (E = N, P, As, O, S) have been used in ECE systems. Nonetheless, no moieties with strong π-accepting abilities have been introduced. In such a system, back donation from the metal to the ECE ligand will lower the electron density on the metal center while retaining the rigid coordination, which can lead to new properties and applications.

Here we report on the synthesis of the first π-accepting PCP ligand bearing pyrrolyl substituents, *dipy*rrolyl*p*hosphino*x*ylene (**1**, DPyPX-H), and the synthesis of rhodium complexes based on this ligand. The coordination chemistry of Rh-DPyPX complexes differs from that of typical pincer complexes. Thus, due to the strong π-accepting ability of DPyPX, formation of the first stable d^8ML_5 PCP-based complexes was observed. Moreover, the PCP phosphorus atoms in these complexes adopt a *cisoid* rather than *trans* configuration, in contrast to the structures of all the PCP type complexes reported so far.[2]

Results and Discussion

Ligand **1** was prepared by the reaction of $ClPPyr_2$ (Pyr = *N*-pyrrolyl) with the Grignard reagent derived from α,α′-dichloro-*m*-xylene. To the best of our knowledge, this ligand has the strongest π-accepting phosphine ligands in the PCP ligand family. The π-accepting ability of tris(*N*-pyrrolyl)-phosphine ($PPyr_3$) was found to fit the following trend: fluoroalkyl phosphines > $PPyr_3$ ≈ $P(C_6F_5)_3$ > $P(OPh)_3$.[8]

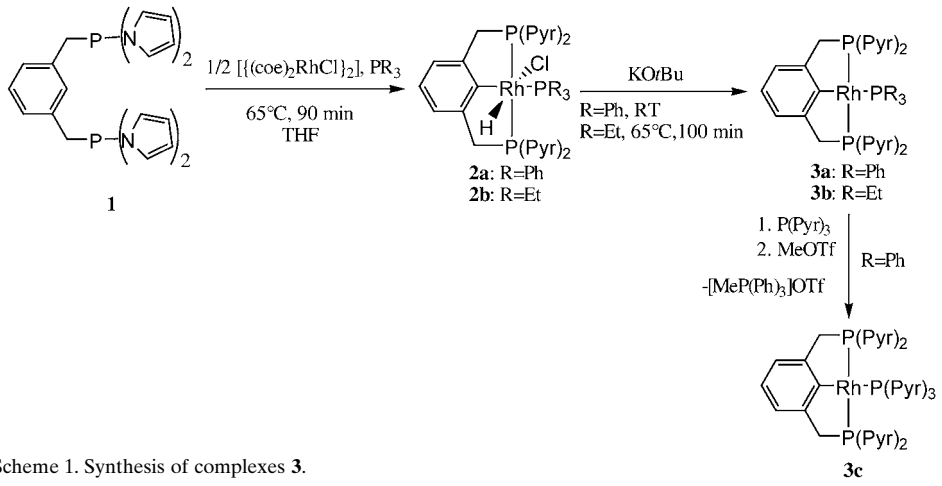
The reaction of stoichiometric amounts of [{Rh(coe)$_2$μ-Cl}$_2$] (coe = cyclooctene) with L (**a**: L = PPh_3; **b**: L = PEt_3) and the DPyPX ligand **1** at 65 °C in THF resulted in metalation to yield the rhodium(III) hydride complexes **2a,b** (Scheme 1). Both complexes were characterized by NMR

[a] E. Kossoy, M. A. Iron, Dr. B. Rybtchinski, Y. Ben-David, Prof. J. M. L. Martin, Prof. D. Milstein
Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot, 76100 (Israel)
Fax: (+972) 8-934-4142
E-mail: comartin@wicc.weizmann.ac.il
david.milstein@weizmann.ac.il

[b] Dr. L. J. W. Shimon, Dr. L. Konstantinovski
Chemical Research Support
The Weizmann Institute of Science
Rehovot, 76100 (Israel)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

 DOI: 10.1002/chem.200401116

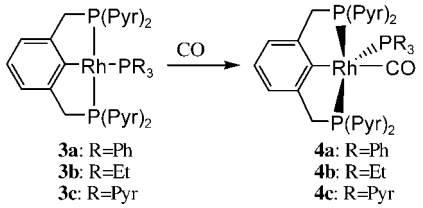


Scheme 1. Synthesis of complexes **3**.

spectroscopy. Subsequent addition of KO*t*Bu to solutions of crude **2a** and **2b** resulted in deprotonation to form the rhodium(I) complexes **3a** and **3b**, respectively (Scheme 1). Both complexes were characterized by NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum of complex **3a** exhibits a dd[9] at $\delta = 124.6$ ppm ($^1J_{Rh,P} = 208.3$ Hz, $^2J_{P,P} = 38.2$ Hz, 2P) and a dt at $\delta = 36.9$ ppm ($^1J_{Rh,P} = 119.0$ Hz, 1P). The methylene groups of the "arms" give rise to an unresolved virtual triplet (vt) in the ^1H NMR spectrum at $\delta = 3.8$ ppm, indicating that the complex has two symmetry planes passing through the PCP-metal chelate core (i.e., a C_{2v} symmetry on the NMR time scale). The signal of the *ipso* carbon atom in the $^{13}C\{^1H\}$ NMR spectrum appears as a ddt centered at 172.8 ppm with $^2J_{P,C,trans} = 69.9$ Hz, confirming the *trans* Ar-Rh-L arrangement. Complex **3b** has similar NMR spectral features. An X-ray diffraction study on a crystal of **3a**[10] confirmed its square-planar geometry (Figure 1).

Complex **3c** was obtained by adding one equivalent of $PPyr_3$ to **3a** followed by one equivalent of MeOTf to precipitate the displaced PPh_3 as its phosphonium salt (Scheme 1). Complex **3c** was characterized by NMR spectroscopy and elemental analysis, and was found to have similar NMR spectral features as complexes **3a,b** indicating a similar structure. Complex **3c** is an example of a complex in which all neutral donor ligands are π-accepting pyrrolyl phosphines.

Interestingly, complexes **3a–c** react with one equivalent of CO to form pentacoordinate rhodium(I) PCP-based complexes **4a–c** (Scheme 2). These thermally stable complexes



Scheme 2. Formation of pentacoordinate, *cisoid* complexes **4**.

were characterized by NMR and IR spectroscopy, and elemental analysis. Remarkably, none of these compounds loses CO or PR_3, either under vacuum or by bubbling with inert gas.

An X-ray diffraction study reveals that complex **4b**[11] has a trigonal-bipyramidal (tbp) geometry.[12,13] The carbonyl group is coordinated *trans* to the *ipso*-carbon atom (Figure 2), *while all three phosphine groups occupy equatorial positions.* The DPyPX phosphine ligands coor-

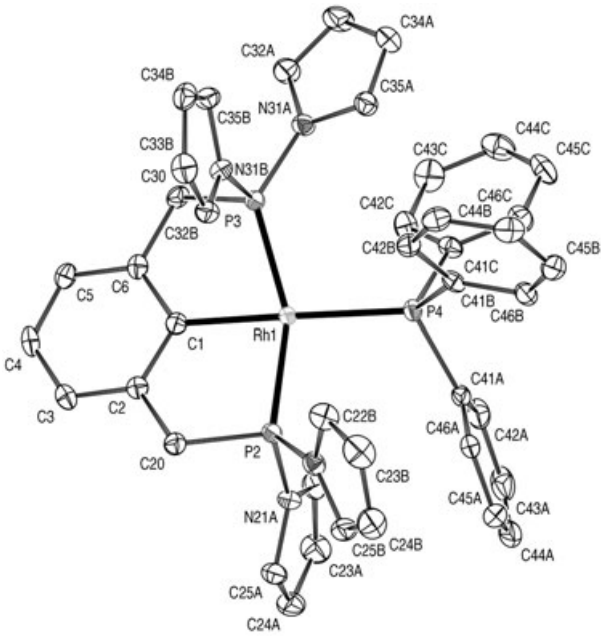


Figure 1. Molecular structure of **3a** (ORTEP drawing; hydrogen atoms omitted for clarity).

dinated to the rhodium center form an unprecedented narrow angle for a PCP system of 128.31°.

The $^{31}P\{^1H\}$ NMR spectrum of **4b** exhibits a dd at $\delta = 124.06$ ppm ($^1J_{Rh,P} = 190.8$ Hz, $^2J_{P,P} = 164$ Hz, 2P) and a td at $\delta = 4.63$ ppm ($^1J_{Rh,P} = 132.4$ Hz, 1P). The methylene groups of DPyPX give rise to two signals in ^1H NMR spectrum: a dvt at $\delta = 3.92$ ppm ($^2J_{H,H} = 15.9$ Hz, $^2J_{P,H} = 5.3$ Hz) and a d at $\delta = 3.71$ ppm ($^2J_{H,H} = 15.9$ Hz), indicating that the compound has only one symmetry plane passing perpendicular to the PCP–Rh plane. The $^{13}C\{^1H\}$ NMR signal of the *ipso*-carbon atom appears as a ddt centered at 166.3 ppm ($^1J_{Rh,C} = 22$ Hz, $^2J_{P,C,DPyPX} = {}^2J_{PC,PEt_3} = 11$ Hz); and the $^{13}C\{^1H\}$ NMR signal of the CO appears as a ddt centered at 204.2 ppm ($^1J_{Rh,C} = 48$ Hz, $^2J_{P,C,DPyPX} = {}^2J_{PC,PEt_3} = 11$ Hz). Similarity between $^2J_{P,C,DPyPX}$ and $^2J_{PC,PEt_3}$ coupling constants suggests that all

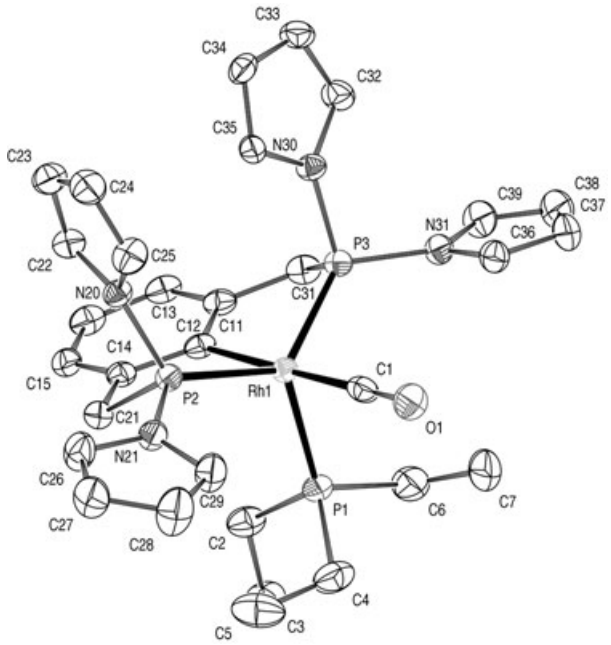


Figure 2. Molecular structure of **4b** (ORTEP drawing; hydrogen atoms omitted for clarity).

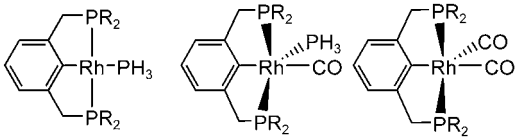
three phosphine ligands of **4b** occupy similar positions relative to the carbonyl ligand and the *ipso*-carbon atoms. Unlike the NMR spectrum of complex **4b**, the signals in the NMR spectra of **4a,c** at 293 K are broad, as a result of an equilibrium involving free PR_3, indicated by the fact that the coordinatively saturated complex **4c** reacts with PPh_3 to form complex **4a**, which in turn reacts with PEt_3 to form **4b**. Low-temperature (243 K) NMR spectra of **4a–c** are very similar, suggesting that the ligands in **4a**,**c** are arranged in a similar fashion as in **4b**. As expected, the π-backbonding to CO increases with increasing electron donation ability of the ancillary phosphine ligand (ν: 2008 (**4c**), 1987 (**4a**), 1975 (**4b**) cm^{-1} (C≡O)).

Although pentacoordinate rhodium(I) complexes are known,[14–16] to the best of our knowledge **4a–c** are the *first stable PCP d^8 ML_5 complexes.* CO usually replaces an ancillary ligand when it reacts with PCP rhodium(I) complexes.[17,18] For example, [(DiPPX)RhPEt$_3$] (DiPPX = *di*iso*p*ropyl*p*hosphino*x*ylene) reacts with one equivalent of CO in benzene to give [(DiPPX)RhCO] (see Experimental Section for details). *Reversible* formation of NCN d^8ML_5 (M = Pt, Ni) was previously reported.[19,20] Interestingly, X-ray diffraction studies revealed square-pyramidal geometries with *trans*-disposed amine donors, rather than trigonal-bipyramidal geometries, for these complexes.[21]

Ligand substitutions at rhodium(I) centers have been observed to follow both associative[22–25] and dissociative[26,27] mechanisms. Complexes **4a–c** can be viewed as arrested intermediates in an associative substitution process involving PCP type complexes.

In general, the addition of a fifth ligand to square-planar d^8ML_4 is unfavorable due to occupied–occupied orbital repulsive interactions between the d_{z^2} (HOMO) orbital of the complex and the HOMO orbital of the incoming ligand.[28] Such interactions are especially pronounced in rigid pincer systems. Previous theoretical studies showed that the addition of a fifth ligand can proceed via a bent ML_4 geometry.[29] The key consequence of bending a planar $[Ru(CO)_2(PH_3)_2]$ complex is a dramatic stabilization of the d_{z^2} orbital and its replacement by d_{yz} as the HOMO.[30] The π-accepting pyrrolyl ligands will enhance this effect, further facilitating the coordination of the fifth ligand.[31]

To evaluate the effect of the pyrrolyl substituents on the coordination of the fifth ligand, calculations were carried out at the COSMO(C_6H_6)-B97–1/SDB-cc-pVDZ//B97–1/SDD level of theory[32] on two model compounds, **4d** and **4d′** (as **4d**, but with the PCP Pyr substituents replaced by H atoms) (Scheme 3). In all cases, the computed geometries



3d: R=Pyr **3d'**: R=H **4d**: R=Pyr **4d'**: R=H **4e**: R=Pyr **4e'**: R=H

Scheme 3. Model compounds for computations.

were very similar to the experimentally determined structures. The loss of either CO or PH_3 from these complexes was examined. In both cases, the loss of CO is unfavorable ($\Delta G_{298} = 11.1$ (**4d′**) and 12.3 (**4d**) kcal mol^{-1}). The loss of PH_3 from **4d′**, as expected, occurs ($\Delta G_{298} = -5.1$ kcal mol^{-1}). From **4d**, however, the loss is only $\Delta G_{298} = -1.2$ kcal mol^{-1}, a value that is isoergonic to within the expected error of the computational method. Nonetheless, one can clearly see that both ligands are more strongly bound in **4d**.

The result that the Rh–CO bond is stronger in **4d** than in **4d′** seems counter-intuitive. Because of the electron withdrawing PCP ligand in **4d**, one would expect that coordination of strong π-accepting ligands, such as CO, would be unfavorable. The rhodium(I) center in **4d**, however, is now so electron-poor that it would benefit from any σ-donating ligand, even if they are π-accepting. In fact, loss of an equatorial CO from [(PCP)Rh(CO)$_2$] (**4e**, **4e′**) (Scheme 3) was calculated to be disfavored by 3.3 and 2.4 kcal mol^{-1}, respectively. The retention of the second CO can be explained by π-backdonation from Rh being dominant in the electron-rich **4e′**, whereas the electron-poor Rh center in **4e** makes σ-donation from CO the major factor.

The stability of the pentacoordinate **4a–c** may in part be explained by the effects the electron-withdrawing pyrrolyl groups have on the molecular orbitals of **3**. Figure 3 depicts the metal d orbital energy diagram of complexes **3d** and **3d′** (as **3d**, but with the PCP pyrrolyl substituents replaced by H atoms) (Scheme 3) and compares them to those in which the PCP phosphine arms have been bent into a "see-saw" configuration to allow CO coordination. There are two most dramatic observations. The first is that all of the orbitals are lower in energy in complex **3d**. The second is that the ef-

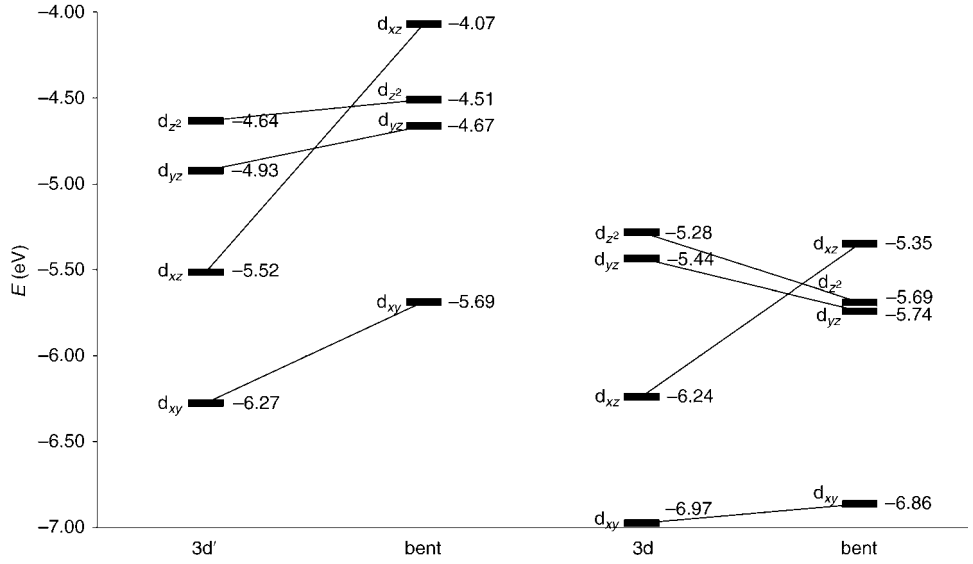


Figure 3. Partial molecular orbital diagram showing the metal *d*-orbitals of complexes **3d** (right) and **3d′** (left), and their bent configurations (see text).

fects of bending the PCP arms are attenuated. While in both cases bending causes a large rise in the energy of the d_{xz} orbital, so much so that it rises above d_{z^2} to become the HOMO, in **3d** this stabilizes the d_{z^2} orbital. Furthermore, because the rise in energy of d_{xz} is reduced, the energy of the HOMO in complex **3d** barely changes ($\Delta E = -0.07$ eV) as a result of the bending. Thus, the Pyr ligands clearly makes **3d** much more amenable to ligand coordination than its electron donating counterparts.

Overall, the geometries of the d^8ML_5-type complexes are determined by the preference of the σ-donating aryl ligand to occupy an axial, rather than equatorial, position[33,34] and by the steric demand of the large phosphines which dictates that they occupy the equatorial plane of the tbp complex.[33]

Summary

A novel π-accepting PCP ligand and its rhodium complexes were synthesized. The coordination chemistry of this system differs significantly from that of other pincer-type ligands. Thus, the first stable d^8ML_5 PCP complexes were synthesized. Moreover, the pincer framework of these complexes bears the phosphine donor atoms in *cisoid* (rather than in the normally observed *trans*) positions. Their unusual stability is due to the π-accepting nature of the PCP ligand, which disfavors formation of the coordinately unsaturated ML_4 complexes. The implications of these features for catalysis are currently under study.

Experimental Section

General procedures: All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40–2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glove box over 4 Å molecular sieves. Commercially available reagents were used as received. $[\{Rh(coe)_2\mu\text{-}Cl\}_2]$ was prepared according to a literature procedure.[35]

^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 400 MHz, 100 MHz, and 162 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 295 K, unless otherwise noted. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. The $^1H\{^{103}Rh\}$ NMR spectrum (**2a**) was measured at 9.4T on a Bruker AMX-400 spectrometer and standard four-pulse HMQC sequence with continuous proton decoupling was applied. The $^{31}P\{^{103}Rh\}$ NMR spectra (**3a–c**) were measured at 11.7 T on a Bruker "Avance"-500 spectrometer, equipped with triple-resonance inverse probe with ^1H, ^{31}P and broadband channels. Typical conditions for HMBC experiment: ^{31}P and ^{103}Rh pulse lengths were 11.2 μs and 70 μs correspondingly, a spectral width in f_2 (^{31}P) was 40–140 ppm, in f_1 (^{103}Rh) was 80–1000 ppm (resolution in f1 5 Hz per point). ^{103}Rh chemical shifts were referenced to 3.16 MHz at a temperature 295 K.

Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Muelheim, Germany.

Synthesis of DPyPX (1): Mg was activated with 1,2-dibromoethane before use. To prepare the Grignard reagent, bis-α-chloro-*m*-xylene (11.080 g) in dry THF (780 mL) was added dropwise to Mg (6.2 g) in dry THF (90 mL). The resulting solution was stirred for 24 h at room temperature and then cannulated under argon pressure into a 1 L dropping funnel. $ClP(pyrrolyl)_2$ (26.362 g, 133 mmol) in dry THF (350 mL) was placed in a 1 L Schlenk flask equipped with a magnetic stirring bar and the above dropping funnel, and then cooled to −30 °C. Then the Grignard reagent was added dropwise over a few hours. The resulting solution was allowed to warm up to room temperature and then stirred for 48 h at ambient temperature. Solvents were removed under high vacuum. The residue was introduced into the glovebox, treated with toluene (450 mL), filtered by using a sinter funnel, and dried under high vacuum, resulting in white crystals. The compound was mixed with pentane (300 mL) and filtered again, then dissolved in hot toluene, treated with carbon black, filtered, and crystallized by the addition of pentane to give white crystals (18.105 g; 80%).

$^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 68.75$ (s); ^1H NMR (C_6D_6): $\delta = 6.79$ (m, 8H; Pyr, *H*C-N), 6.48 (m, 3H; Ar), 6.3 (m, 1H; Ar), 6.25 (m, 8H; Pyr, *H*C-CH-N), 3.08 ppm (d, $^2J_{P,H} = 3.47$ Hz, 4H; Ar-CH_2-P); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 133.93$ (m, 2C; Ar, C_1, C_3), 130.27 (m, 1C; Ar, C_2), 128.93 (m, 2C; Ar, C_4, C_6), 127.57 (br s, 1C; Ar, C_5), 123.50 (d, $^2J_{P,C} = 14.03$ Hz, 8C; Pyr, *C*H-N), 112.35 (d, $^3J_{P,C} = 4.11$ Hz, 8C; *C*H-CH-N), 38.2 ppm (d, $^1J_{P,C} = 13.71$ Hz, 2C; Ar-*C*H_2-P).

[Rh(DPyPX)H(PPh_3)Cl] (2a): A solution of PPh_3 (219 mg, 0.835 mmol) in THF (2 mL) was slowly added to a solution of $[\{Rh(coe)_2\mu\text{-}Cl\}_2]$ (300 mg, 0.418 mmol) in THF (3 mL). The resulting solution was stirred for 5 min at room temperature during which time it became clear orange. Then a solution of ligand **1** (359.9 mg, 0.836 mmol) in THF (2 mL) was

added dropwise while stirring. The resulting mixture was heated under stirring at 65 °C for 1.5 h to give a deep red solution of **2a**. The $^{31}P\{^1H\}$ NMR showed that no starting material remained.

$^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 121.5$ (dd, $^1J_{Rh,P} = 138.52$, $^2J_{P,P} = 31.38$ Hz, 2P), 19.3 ppm (dt, $^1J_{Rh,P} = 83.33$, $^2J_{P,P} = 31.38$ Hz, 1P); ^1H NMR (C_6D_6): $\delta = 7.6$ (m, 6H; Ph, *ortho* to P), 7.25–6.7 (m, 20H; Ph *meta* and *para* to P; Ar, *meta* and *para* to Rh; Pyr, *H*C-N), 6.3 (br s, 4H; Pyr, *H*C-CH-N), 6.0 (br s, 4H; Pyr, *H*C-CH-N), 4.6 (dvt, ABX_2 pattern, $^2J_{H,H} = 16$ Hz, unresolved t, 2H; Ar-C*H*(H)-P), 3.6 (dvt, ABX_2 pattern, $^2J_{H,H} = 16$, $^2J_{P,H} = 4.8$ Hz, 2H; Ar-C*H*(H)-P), −15.5 ppm (ddt, $^1J_{Rh,H} = 22.3$, $^2J_{P,H} = 13.3$ Hz, 1H; *H*-Rh); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 162.10$ (ddt, $^2J_{P,C,\ trans} = 93.72$ Hz, $^1J_{Rh,C} = 24.49$ Hz, unresolved t, 1C; C_{ipso}-Rh), 140.12 (vtd, $^2J_{P,C} = 9.89$, $J = 3.06$ Hz, 2C; Ar, *C*-C-Rh), 135–126 (m, 19C; Ph Ar, *C*H-CH-C-C-Rh), 124.26 (t, unresolved, 4C; Pyr, *C*H-N-P), 124.17 (vt, $^2J_{P,C} = 3$ Hz, 4C; Pyr, *C*H-N-P), 123.25 (vtd, $^3J_{P,C} = 10.83$, $J = 4.74$ Hz, 2C; Ar, *C*H-C-C-Rh), 112.60 (vt, $^3J_{P,C} = 2.83$ Hz, 4C; Pyr, *C*H-CH-N-P), 112.46 (t, $J = 2.59$ Hz, 4C; Pyr, *C*H-CH-N-P), 51.97 ppm (vtdd, $^1J_{P,C} = 19.78$ Hz, unresolved dd, 2C; Ar-CH_2-P); ^{103}Rh NMR ([D$_8$]toluene): $\delta = -89.5$ ppm.

[Rh(DPyPX)H(PEt$_3$)Cl] (2b): Neat PEt_3 (7.6 μL, 5.6×10^{-5} mol) was slowly added to [{Rh(coe)$_2$μ-Cl}$_2$] (20 mg, 2.8×10^{-5} mol) in THF (1 mL). The resulting solution was left to stir for 5 min at room temperature during which time it became clear red. Then ligand **1** (24 mg, 5.6×10^{-5} mol) in THF (1 mL) was added dropwise while stirring. The resulting mixture was heated under stirring at 65 °C for 1.5 h to give a deep yellow solution of **2b**. The $^{31}P\{^1H\}$ NMR spectra showed that no starting material remained.

$^{31}P\{^1H\}$ NMR ([D$_8$]THF): $\delta = 123$ (dd, $^1J_{Rh,P} = 138$, $^2J_{P,P} = 30.3$ Hz, 2P), 8.8 ppm (dt, $^1J_{Rh,P} = 83.8$, $^2J_{P,P} = 30.3$ Hz, 1P); ^1H NMR ([D$_8$]THF): $\delta = 7.38$ (m, 4H; Pyr, *H*C-N-P), 6.99 (m, 4H; Pyr, *H*C-N-P), 6.83 (t, $^3J_{H,H} = 7.4$ Hz, 1H; Ar, *para* to Rh), 6.27 (t, $J = 2.0$ Hz, 4H; Pyr, *H*C-HC-N-P), 6.25 (t, $J = 2.0$ Hz, 4H; Pyr, *H*C-HC-N-P), 4.9 (dvt, ABX_2 pattern, $^2J_{H,H} = 15.9$, $^2J_{P,H} = 4.8$ Hz, 2H; Ar-*H*(H)C-P), 4.2 (dvt, ABX_2 pattern, $^2J_{H,H} = 15.9$, $^2J_{P,H} = 3.8$ Hz, 2H; Ar-*H*(H)C-P), 1.16 (m, 6H; Et, H_2C-P), 0.87 (m, 9H; Et, H_3C), −16.1 ppm (ddt, $^1J_{Rh,H} = 23.8$, $^2J_{P,H} = 13.4$ Hz, 1H; *H*-Rh); $^{13}C\{^1H\}$ NMR ([D$_8$]THF): $\delta = 164.5$ (ddt, $^2J_{P,C,\ trans} = 92.4$, $^1J_{Rh,C} = 23.2$, $^2J_{P,C} = 5.5$ Hz, 1C; C_{ipso}-Rh), 141.5 (vtd $^2J_{P,C} = 9.8$, $J = 3.07$ Hz, 2C; Ar, *C*-C-Rh), 130.75 (s, 1C; Ar, *C*H-CH-C-C-Rh), 125.86 (t, $J = 2.46$ Hz, 4C; Pyr, *C*H-N-P), 124.91 (vt, $^2J_{P,C} = 3.3$ Hz, 4C; Pyr, *C*H-N-P), 123.2 (vtd, $^3J_{P,C} = 11$, $J = 4.8$ Hz, 2C; Ar, *C*H-C-C-Rh), 113.06 (vt, $^3J_{P,C} = 2.7$ Hz, 4C; Pyr, *C*H-CH-N-P), 112.67 (t, $J = 2.65$ Hz, 4C; Pyr, *C*H-CH-N-P), 52.2 (vtdd, $^1J_{P,C} = 20.5$, $^2J_{Rh,C} = {}^3J_{P,C} = 4.3$ Hz, 2C; Ar-CH_2-P), 17.5 (d, $^1J_{P,C} = 21.7$ Hz, 3C; Et, CH_2-P), 8.4 ppm (d, $^2J_{P,C} = 3.13$ Hz, 3C; CH_3); elemental analysis (%): calcd: C 52.45, H 5.72; found: C 52.54, H 5.81.

[Rh(DPyPX)PPh$_3$] (3a): A solution of KO*t*Bu (94 mg, 0.836 mmol) in THF (1 mL) was added dropwise to a solution of crude **2a** (0.835 mmol, see synthesis of **2a**) in THF, and the reaction mixture was stirred for 0.5 h inside the glove box. The solution became much darker immediately after the addition of KO*t*Bu. The solvent was evaporated under vacuum and the resulting solid was extracted with MeOH. Evaporation of MeOH under vacuum resulted in a yellow solid that was redissolved in benzene and filtered through a cotton pad. The solvent was evaporated under vacuum to yield compound **3a** as a deep yellow solid (320 mg; 48%).

$^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 124.6$ (dd, $^1J_{Rh,P} = 208.3$, $^2J_{P,P} = 38.2$ Hz, 2P), 36.9 ppm (dt, $^1J_{Rh,P} = 119.0$, $^2J_{P,P} = 38.2$ Hz, 1P); ^1H NMR (C_6D_6): $\delta = 7.5$ (m, 6H; Ph, *ortho* to P), 7.0–6.8 (m, 12H; Ph, *meta* and *para* to P, Ar, *meta* and *para* to Rh), 6.72 (m, 8H; Pyr, *H*C-N), 6.01 (t, $J = 2.0$ Hz, 8H; Pyr, *H*C-HC-N), 3.8 ppm (vt, unresolved t, 4H; Ar-CH_2-P); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 172.8$ (ddt, $^2J_{P,C,trans} = 69.9$, $^1J_{Rh,C} = 30.4$, $^2J_{P,C,\ cis} = 9.6$ Hz, 1C; C_{ipso}-Rh), 143.8 (vt, $^2J_{P,C} = 12.5$ Hz, 2C; Ar, *C*-C-Rh), 137.6 (dvt, $^1J_{P,C} = 34.6$, $^3J_{P,C} = 2$ Hz, 3C; Ph, *C*-P), 134.3 (d, $J = 13.5$ Hz, 6C; Ph), 129.5 (d, $^4J_{P,C} = 1.6$ Hz, 3C; Ph, *C*H-CH-CH-C-P), 125.9 (s, 1C; Ar, *C*H-CH-C-C-Rh), 123.9 (vt, $^2J_{P,C} = 3.7$ Hz, 8C; Pyr, *C*H-N), 122.4 (vtd, $^3J_{P,C} = 10.9$, $J = 3.1$ Hz, 2C; Ar, *C*H-C-C-Rh), 111.8 (vt, $^3J_{P,C} = 2.4$ Hz, 8C; Pyr, *C*H-CH-N), 52.7 ppm (vtdd, $^1J_{P,C} = 16.1$, $^2J_{Rh,C} = {}^3J_{P,C} = 5.2$ Hz, 2C; Ar-CH_2-P); ^{103}Rh NMR ([D$_8$]THF): $\delta = -734$ ppm; elemental analysis (%): calcd: C 63.48, H 4.82; found: C 63.70, H 4.76.

X-ray analysis of the structure of [Rh(DPyPX)PPh$_3$] (3a): Orange monoclinic crystals of **3a** were obtained by slow diffusion of pentane into a concentrated solution of **3a** in toluene, in a 5 mm NMR tube, left at room temperature for three days.

Crystal data: $C_{42}H_{38}N_4P_3Rh$, orange, plate, $0.2\times0.2\times0.2$ mm^3, monoclinic, $P2(1)/n$ (no.14), $a = 14.390(3)$, $b = 12.275(3)$, $c = 21.659(3)$ Å, $\beta = 108.75(3)°$, from 15 degrees of data, $T = 120(2)$ K, $V = 3622.7(13)$ Å^3, $Z = 4$, Fw = 794.58, $\rho_{calcd} = 1.457$ Mg m^{-3}, $\mu = 0.641$ mm^{-1}.

Data collection and processing: Nonius KappaCCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), graphite monochromator, $0 \le h \le 17$, $0 \le k \le 14$, $-25 \le l \le 24$, frame scan width = 1.5°, scan speed 1.0° per 60 s, typical peak mosaicity 0.42°, 6944 independent reflections ($R_{int} = 0.040$). The data were processed with Denzo-Scalepack.

Solution and refinement: structure was solved by direct methods with SHELXS-97. Full-matrix least-squares refinement based on F^2 with SHELXS-97. A total of 451 parameters with 0 restraints, final $R_1 = 0.0359$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0525$ on 6609 reflections, goodness-of-fit on $F^2 = 1.036$, largest electron density peak = 0.847 e Å^{-3}.[10]

[Rh(DPyPX)PEt$_3$] (3b): A solution of KO*t*Bu (6.2 mg, 5.6×10^{-5} mol) in THF (0.5 mL) was added dropwise under stirring to a solution of **2b** (5.6×10^{-5} mol, see synthesis of **2b**) in THF. The reaction mixture became darker immediately and it was heated to 65 °C for 1 h 40 min while stirring. Then the solvent was evaporated under vacuum and the resulting solid was redissolved in toluene, filtered through a cotton pad, and the solvent was removed under vacuum to yield **3b** (32.6 mg; 89.9%). (Note: in one preparation, trace impurities were present and these were removed by extraction of **3b** with MeOH.)

$^{31}P\{^1H\}$ NMR ([D$_8$]toluene): $\delta = 128.0$ (dd, $^1J_{Rh,P} = 207.3$ Hz, $^2J_{P,P} = 39.5$ Hz, 2P), 20.8 ppm (td, $^1J_{Rh,P} = 114.7$, $^2J_{P,P} = 39.5$ Hz, 1P); ^1H NMR ([D$_8$]toluene): $\delta = 6.92$ (m, 8H; Pyr, *H*C-N-P), 6.88 (br s, 3H; Ar, *meta* and *para* to Rh), 6.24 (t, $J = 2.0$ Hz, 8H; Pyr, *H*C-HC-N-P), 3.77 (vt, $^2J_{P,H} = 3$ Hz, 4H; Ar-H_2C-P), 0.96 (m, 6H; Et, H_2C-P), 0.83 ppm (m, 9H; Et, H_3C); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene): $\delta = 174.43$ (ddt, $^2J_{P,C,\ trans} = 69.8$, $^1J_{Rh,C} = 29.4$, $^2J_{P,C,cis} = 9.6$ Hz, 1C; C_{ipso}-Rh), 143.63 (vtdd, unresolved dd, $^2J_{P,C} = 12.5$ Hz, 2C; Ar, *C*-C-Rh), 125.53 (s, 1C; Ar, *C*H-CH-C-C-Rh), 124.04 (vt, $^2J_{P,C} = 4.0$ Hz, 8C; Pyr, *C*H-N-P), 122.08 (vtd, $^3J_{P,C} = 10.9$ Hz, J = 3.3 Hz, 2C; Ar, *C*H-C-C-Rh), 112.23 (vt, $^3J_{P,C} = 2.5$ Hz, 8C; Pyr, *C*H-CH-N-P), 52.73 (vtdd, $^1J_{P,C} = 15.6$, $^2J_{Rh,C} = {}^3J_{P,C} = 5.3$ Hz, 2C; Ar-*C*H_2-P), 18.79 (dt, $^1J_{P,C} = 20.8$, $^3J_{P,C} = 3$ Hz, 3C; Et, CH_2-P), 9.24 ppm (s, 3C; Et, CH_3); ^{103}Rh NMR (C_6D_6): $\delta = -781$ ppm; elemental analysis (%): calcd: C 55.39, H 5.89; found: C 55.46, H 5.79.

[Rh(DPyPX)PPyr$_3$] (3c): A solution of $PPyr_3$ (30.5 mg, 1.3×10^{-4} mol) in toluene (0.5 mL) was added to a solution of **3a** (105.6 mg, 1.3×10^{-4} mol) in toluene (0.5 mL). Neat MeOTf (14.95 μL, 1.3×10^{-4} mol) was added and the suspension formed was left for 2 h at room temperature until a clear solution was obtained. A white precipitate ($MePPh_3OTf$) appeared. The solution was left at −37 °C overnight, the precipitate was filtered off using a cotton pad, and the solvent was removed from the resulting solution by evaporation under vacuum to yield **3c** as a yellow solid (97.8 mg; 96.6%). (Note: in one case the product contained trace impurities and was recrystallized from pentane.)

$^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 123$ (dd, $^1J_{Rh,P} = 198.5$, $^2J_{P,P} = 45.18$ Hz, 2P), 108.8 ppm (dt, $^1J_{Rh,P} = 177.8$, $^2J_{P,P} = 45.38$ Hz, 1P); ^1H NMR (C_6D_6): $\delta = 6.97$ (t, $^3J_{H,H} = 7.3$ Hz, 1H; Ar, *para* to Rh), 6.88 (d, $^3J_{H,H} = 7.3$ Hz, 2H; *meta* to Rh), 6.69 (m, 14H; Pyr, *H*C-N-P) 6.09 (m, 8H; Pyr, *H*C-HC-N-P), 6.05 (m, 6H; Pyr, *H*C-HC-N-$P_{ancillary}$), 3.72 ppm (vt, $^2J_{P,H} = 3.4$ Hz, 4H; Ar-H_2C-P); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene): $\delta = 171.5$ (ddt, $^2J_{P,C,\ trans} = 104.6$, $^1J_{Rh,C} = 29.4$, $^2J_{P,C,\ cis} = 9.4$ Hz, 1C; C_{ipso}-Rh), 144.2 (vt, $^2J_{P,C} = 12.8$ Hz, 2C; Ar, *C*-C-Rh), 123.7 (m, 14C; Pyr, *C*H-N-P), 122.7 (vtd, $^3J_{P,C} = 11.4$, $J = 4.9$ Hz, 2C; Ar, *C*H-C-C-Rh), 112.8 (m, 14C; Pyr, *C*H-CH-N-P), 51.9 (vtdd, $^1J_{P,C} = 16.7$, $^2J_{RhC} = {}^3J_{P,C} = 5.7$ Hz, 2C; Ar-*C*H_2-P); ^{103}Rh NMR ([D$_8$]toluene): $\delta = -853.7$ ppm; elemental analysis (%): calcd: C 56.78, H 4.63; found: C 56.67, H 4.70.

[Rh(DPyPX)PPh$_3$CO] (4a): CO (0.55 mL, 2.4×10^{-5} mol) was injected with a syringe into a solution of **3a** (19.3 mg, 2.4×10^{-5} mol) in toluene (0.7 mL) in a reaction tube fitted with a septum. The reaction tube was

vigorously shaken until the solution became light yellow. The solvent was removed under vacuum and the product was recrystallized from a saturated MeOH solution, to yield **4a** as a yellow solid (12 mg; 61%).

$^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 295 K): $\delta = 125.0$ (br dd, $^1J_{Rh,P} = 195.5$, $^2J_{P,P} = 143$), 21.2 ppm (br dt, $^1J_{Rh,P} = 130$, $^2J_{P,P} = 145$ Hz); ^{1}H NMR ([D$_8$]toluene, 295 K): $\delta = 6.98$ (s, 4H; Pyr, *H*C-N-P), 6.96 (m, 3H; Ph, *para* to P), 6.86 (br s, 12H; *meta* and *ortho* to P), 6.79 (t, $^3J_{H,H} = 7.4$ Hz, 1H; Ar, *para* to Rh), 6.67 (d, $^3J_{H,H} = 7.4$ Hz, 2H; Ar, *meta* to Rh; 2H), 6.55 (br s, 4H; Pyr, *H*C-N-P), 6.32 (br s, 4H; Pyr, *H*C-HC-N-P), 6.08 (br s, 4H; Pyr, *H*C-HC-N-P), 3.52 (br s, 2H; Ar-*H*(H)C-P), 3.08 ppm (br s, 2H; Ar-*H*(H)C-P); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 295 K): $\delta = 202.5$ (dt, $^1J_{Rh,C} = 48.8$, $^2J_{P,P} = 14.5$ Hz, 1C; CO), 166.14 (m, 1C; C_{ipso}-Rh), 143.09 (vt, $^2J_{P,C} = 16.3$ Hz, 2C; Ar, *C*-C-Rh), 136.6 (d, $^1J_{P,C} = 25.6$ Hz, 3C; Ph, *C*-P), 133.1 (d, $^2J_{P,C} = 13.8$ Hz, 6C; Ph, *C*H-C-P), 130–127 (overlapped with [D$_8$]toluene, 9C; Ph), 124.5 (s, 1C; Ar, *C*H-CH-C-C-Rh), 123.6, (br s, 4C; Pyr, *C*H-N-P), 123.3 (vt, $^3J_{P,C} = 11.3$ Hz, 2C; Ar, *C*H-C-C-Rh), 123.0 (br s, 4C; Pyr, *C*H-N-P), 112.5 (br s, 8C; Pyr, *C*H-CH-N-P), 50.75 ppm (vtd, unresolved d, $^1J_{P,C} = 16.0$ Hz, 2C; Ar-*C*H$_2$-P); $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 243 K); $\delta = 125.9$ (dd, $^1J_{Rh,P} = 197.7$ Hz, $^2J_{P,P} = 154.8$ Hz, 2P), 21.5 ppm (td, $^1J_{Rh,P} = 126.1$, $^2J_{P,P} = 154.8$ Hz, 1P); ^{1}H NMR ([D$_8$]toluene, 243 K): $\delta = 6.96$ (s, 4H; Pyr, *H*C-N-P), 6.92 (m, 3H; Ph, *para* to P), 6.82 (m, 13H; Ph, *meta* and *ortho* to P, and Ar, *para* to Rh), 6.65 (d, $^3J_{H,H} = 7.5$ Hz, 2H; Ar, *meta* to Rh), 6.59 (br s, 4H; Pyr, *H*C-N-P), 6.36 (t, $J = 2$ Hz, 4H; Pyr, *H*C-HC-N-P), 6.11 (t, $J = 2$ Hz, 4H; Pyr, *H*C-HC-N-P), 3.42 (dvt, ABX$_2$ pattern, $^2J_{H,H} = 15.6$, $^2J_{P,H} = 5.6$ Hz, 2H; Ar-*H*(H)C-P), 2.95 ppm (d, AB pattern, $^2J_{H,H} = 15.6$ Hz, 2H; Ar-*H*(H)C-P); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 243 K): $\delta =$ 202.6 (dtd, $^1J_{RhC} = 49$, $^2J_{PC,DPyPX} = 15$, $^2J_{PC,PPh_3} = 9.6$ Hz, 1 C; CO), 166.1 (ddt, $^1J_{Rh,C} = 22$ Hz, $^2J_{PC,DPyPX} = {}^2J_{PC,PPh_3} = 11$ Hz, 1C; C_{ipso}-Rh), 142.9 (vtd, $^2J_{P,C} = 16.2$ Hz, $J = 3.2$ Hz, 2C; Ar, *C*-C-Rh), 136.2 (d, $^1J_{P,C} = 26.6$ Hz, 3C; Ph, *C*-P), 133.0 (d, $^2J_{P,C} = 13.7$ Hz, 6C; Ph, *C*H-C-P), 130–127 (overlapped with [D$_8$]toluene, 9C; Ph), 124.4 (s, 1C, Ar, *C*H-CH-C-C-Rh), 123.7 (s, 4C; Pyr, *C*H-N-P), 123.4 (vt, $^3J_{P,C} = 10.2$ Hz, 2C; Ar, *C*H-C-C-Rh), 123.0 (s, 4C; Pyr, *C*H-N-P), 112.8 (s, 4C; Pyr, *C*H-CH-N-P), 112.4 (s, 4C; Pyr, *C*H-CH-N-P), 50.4 ppm (vt, $^1J_{P,C} = 16$ Hz, 2C; Ar-*C*H$_2$-P); IR (film): $\tilde{\nu} = 1987$ cm^{-1} (C≡O); elemental analysis (%): calcd: C 62.78, H 4.66; found: C 62.63, H 4.71.

[Rh(DPyPX)PEt$_3$CO] (4b): CO (0.6 mL, 2.6×10^{-5} mol) was added to **3b** (17.4 mg, 2.6×10^{-5} mol) in benzene (0.7 mL). The solution was vigorously shaken to dissolve CO, resulting in a lighter yellow color. The solvent was removed by evaporation and the product was recrystallized from a saturated pentane solution, to yielding **4b** as a yellow solid (10 mg; 55%).

$^{31}P\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 124.06$ (dd, $^1J_{Rh,P} = 190.8$ Hz, $^2J_{P,P} = 164$ Hz, 2P), 4.63 ppm (td, $^1J_{Rh,P} = 132.4$ Hz, $^2J_{P,P} = 164$ Hz, 1P); ^{1}H NMR ([D$_8$]toluene, 295 K): $\delta = 7.11$ (m, 4H; Pyr, *H*C-N-P), 6.89 (d, $^3J_{H,H} = 7$ Hz, 2H; Ar, *meta* to Rh), 6.84 (t, $^3J_{H,H} = 7$ Hz, 1H; Ar, *para*-to-Rh), 6.52 (br s, 4H; Pyr, *H*C-N-P), 6.33 (br s, 4H; Pyr, *H*C-CH-N-P), 6.08 (br s, 4H; Pyr, *H*C-CH-N-P), 3.92 (dvt, ABX$_2$ pattern, $^2J_{H,H} = 15.9$, $^2J_{P,H} = 5.3$ Hz, 2H; Ar-C*H*(H)-P), 3.71 (d, AB pattern, $^2J_{H,H} = 15.9$ Hz, 2H; Ar-C*H*(H)-P), 1.03 (m, 6H; Et, H_2C-P), 0.46 ppm (m, 9H; Et, H_3C-H$_2$C-P); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 295 K): $\delta = 204.2$ (ddt, $^1J_{Rh,C} = 48$, $^2J_{PC,DPyPX} = {}^2J_{PC,PEt_3} = 11$ Hz, 1C; CO), 166.3 (ddt, $^1J_{Rh,C} = 22$, $^2J_{PC,DPyPX} = {}^2J_{PC,PEt_3} = 11$ Hz, 1C; C_{ipso}-Rh), 143.0 (vt, $^2J_{P,C} = 16$ Hz, 2C; Ar, *C*-C-Rh), 124.4 (s, 1C; Ar, *C*H-CH-C-C-Rh), 124.0 (br s, 4C; Pyr, *C*H-N-P), 122.9 (vt, $^3J_{P,C} = 10$ Hz, 2C; Ar, CH-C-C-Rh), 122.7 (br s, 4C; Pyr, *C*H-N-P), 112.6 (s, 4C; Pyr, *C*H-CH-N-P), 112.2 (s, 4C; Pyr, *C*H-CH-N-P), 53.0 (vt, $^1J_{P,C} = 16.4$ Hz, 2C; Ar-*C*H$_2$-P), the signal of *C*H$_2$-P$_{Et}$ overlaps with [D$_8$]toluene signal, 7.0 ppm (s, 3C; Et, *C*H$_3$); $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 243 K): $\delta =$ 124.1 (dd, $^1J_{Rh,P} = 190.5$ Hz, $^2J_{P,P} = 165$ Hz, 2P), 4.9 ppm (td, $^1J_{Rh,P} = 133.4$ Hz, $^2J_{P,P} = 165$ Hz, 1P); ^{1}H NMR ([D$_8$]toluene, 243 K): $\delta = 7.11$ (m, 4H; Pyr, *H*C-N-P), 6.92 (m, 3H; Ar, *meta* and *para* to Rh), 6.53 (m, 4H; Pyr, *H*C-N-P), 6.37 (m, 4H; Pyr, *H*C-CH-N-P), 6.13 (m, 4H; Pyr, *H*C-CH-N-P), 3.83 (dvt, ABX$_2$ pattern, $^2J_{H,H} = 15.8$, $^2J_{PH} = 5$ Hz, 2H; Ar-C*H*(H)-P), 3.60 (d, AB pattern, $^2J_{H,H} = 15.9$ Hz, 2H; Ar-C*H*(H)-P), 0.96 (m, 6H; Et, H_2C-P), 0.39 ppm (m, 9H; Et, H_3C); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 243 K): $\delta = 204.4$ (ddt, $^1J_{Rh,C} = 48$, $^2J_{PC,DPyPX} = {}^2J_{PC,PEt_3} = 13$ Hz, 1C; CO), 166.4 (ddt, $^1J_{RhC} = 22$, $^2J_{P,C,DPyPX} = {}^2J_{PC,PEt_3} = 11$ Hz, 1C; C_{ipso}-Rh), 142.9 (vtd, $^2J_{P,C} = 17$, $J = 3.4$ Hz, 2C; Ar, *C*-C-Rh), 124.4 (s, 1C; Ar, CH-C-C-C-Rh), 124.01 (br s, 4C; Pyr, *C*H-N-P), 122.95 (vt, $^3J_{P,C} = 10$ Hz, 2C; Ar, *C*H-C-C-Rh), 122.73 (br s, 4C; Pyr, *C*H-N-P), 112.68 (s, 4C; Pyr, *C*H-CH-N-P), 112.24 (s, 4C; Pyr, *C*H-CH-N-P), 52.78 (vt, $^1J_{P,C} = 17$ Hz, 2C; Ar-*C*H$_2$-P), the signal of *C*H$_2$-P$_{Et}$ overlaps with [D$_8$]toluene signal, 6.92 ppm (s, 3C; Et, CH$_3$); IR (film): $\tilde{\nu} = 1975$ cm^{-1} (C≡O); elemental analysis (%): calcd: C 54.88, H 5.65; found: C 55.04, H 5.58.

X-ray analysis of the structure of [Rh(DPyPX)PEt$_3$CO] (4b): Colorless orthorhombic crystals of **4b** were obtained by recrystallization of **4b** from a pentane solution. For this purpose, a toluene solution of **4b** (20 mg) was dried under vacuum to obtain a solid film of **4b** at the bottom of a 20 mL Wheaton vial. Then the obtained layer was covered by pentane (2 mL) and left at 15–20 °C for three days. Crystals appeared on the bottom of the vial.

Crystal data: $C_{31}H_{38}N_4O_1P_3Rh$, colorless, prism, $0.1\times0.1\times0.1$ mm^3, orthorhombic, *Pbca*, $a = 15.2900(3)$, $b = 19.2050(2)$, $c = 21.4960(2)$ Å, from 15 degrees of data, $T = 120(2$ K, $V = 6312.18(15)$ Å^3, $Z = 8$, $Fw = 678.47$, $\rho_{calcd} = 1.428$ Mg m^{-3}, $\mu = 0.724$ mm^{-1}.

Data collection and processing: Nonius KappaCCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), graphite monochromator, $-19 \le h \le 19$, $-24 \le k \le 24$, $-27 \le l \le 27$, frame scan width = 1.0°, scan speed 1.0° per 30 s, typical peak mosaicity 0.64°, 71911 reflections collected, 14813 independent reflections ($R_{int} = 0.094$). The data were processed with Denzo-Scalepack.

Solution and refinement: structure was solved by direct methods with SHELXS-97. Full-matrix least-squares refinement based on F^2 with SHELXS-97. 428 parameters with 0 restraints, final $R_1 = 0.0404$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0688$ on 7205 reflections, goodness-of-fit on $F^2 = 1.039$, largest electron density peak = 1.214.

[Rh(DPyPX)PPyr$_3$CO] (4c): CO (0.4 mL, 2.0×10^{-5} mol) was added to a solution of **3c** (15 mg, 2.0×10^{-5} mol) in toluene (0.7 mL), resulting in the quantitative formation of [Rh(PCP)PPyr$_3$CO] (**4c**).

$^{31}P\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 119.6$ (br d, $^1J_{Rh,P} = 184.9$ Hz, 2P), 93.1 ppm (br s, 1P); ^{1}H NMR (C_6D_6, 295 K): $\delta = 6.83$ (t, $^3J_{H,H} = 7.45$ Hz, 1H; Ar, *para* to Rh), 6.70 (d, 2H; $^3J_{H,H} = 7.45$ Hz, *meta* to Rh), 7.0–6.55 (br s, 8H; Pyr, *H*C-N-P), 6.20 (br s, 8H; Pyr, *H*C-HC-N-P), 6.15 (br s, 6H; Pyr, *H*C-N-P$_{ancillary}$), 6.06 (t, $J = 2.1$ Hz, 6H; Pyr, *H*C-CH-N-P$_{ancillary}$), 3.54 ppm (br s, 4H; Ar-C*H*$_2$-P); $^{13}C\{^1H\}$ NMR (C_6D_6, 295 K): $\delta = 199.8$ (br d, $^1J_{Rh,C} = 44.2$ Hz, 1C; CO), 160 (br s, 1C; C_{ipso}-Rh), 143.6 (vt, $^2J_{P,C} = 15.4$ Hz, 2C; Ar, *C*-C-Rh), 125.79 (s, 1C; Ar, *C*H-CH-C-C-Rh), 123.81 (vt, $^3J_{P,C} = 10.9$ Hz, 2C; Ar, *C*H-C-C-Rh), 123.41 (s, 8C; Pyr, *C*H-N-P), 123.36 (d, partially overlapped with the s at 123.41, 6C; Pyr, *C*H-N-P$_{ancillary}$), 113.37 (br s, 8C; Pyr, *C*H-CH-N-P), 112.86 (d, $^3J_{P,C} = 4.7$ Hz, 6C; Pyr, *C*H-CH-N-P$_{ancillary}$), 51.10 ppm (vt, $^1J_{P,C} = 16.3$ Hz, 2C; Ar-*C*H$_2$-P); $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 243 K): $\delta = 126.27$ (br dd, $^1J_{Rh,P} = 188$ Hz, $^2J_{P,P} = 229$ Hz, 2P), 99.5 ppm (ddd, $^1J_{Rh,P} = 194$, $^2J_{P,P} = 223.5$, $^2J_{P,P} = 234.5$ Hz, 1P); ^{1}H NMR ([D$_8$]toluene, 243 K): $\delta = 6.86$ (br s, 4H; Pyr, *H*C-N-P), 6.78 (m, 1H; Ar, *para* to Rh), 6.64 (d, $^3J_{H,H} = 7.46$ Hz, 2H; Ar, *meta* to Rh), 6.40 (br s, 4H; Pyr, *H*C-N-P), 6.29 (m, 6H; Pyr, *H*C-N-P$_{ancillary}$), 6.03 (m, 14H; Pyr, *H*C-HC-N-P), 3.43 (dvt, ABX$_2$ pattern, $^2J_{H,H} = 15.8$, $^2J_{P,H} = 5.45$ Hz, 2H; Ar-*H*(H)C-P), 3.34 ppm (d, AB pattern, $^2J_{H,H} = 15.9$ Hz, 2H; Ar-*H*(H)C-P); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 243 K): $\delta = 199.76$ (ddt, $^1J_{RhC} = 49$, $^2J_{PC,DPyPX} = {}^2J_{PC,PPyr_3} = 14$ Hz, 1C; CO), 159.79 (ddt, $^1J_{Rh,C} = 19$, $^2J_{PC,DPyPX} = {}^2J_{PC,PPyr_3} = 10$ Hz, 1C; C_{ipso}-Rh), 143.44 (vtd, $^2J_{P,C} = 15.6$ Hz, unresolved d, 2C; Ar, *C*-C-Rh), 125.62 (s, 1C; Ar, *C*H-CH-C-C-Rh), 123.74 (vt, $^3J_{P,C} = 9$ Hz, 2C; Ar, *C*H-C-C-Rh), 123.5 (s, 4C; Pyr, *C*H-N-P), 123.23 (s, 4C; Pyr, *C*H-N-P), 123.10 (d, $^2J_{P,C} = 19.20$ Hz, 6C; Pyr, *C*H-N-P$_{ancillary}$), 113.68 (s, 4C; Pyr, *C*H-CH-N-P), 112.90 (s, 4C; Pyr, *C*H-CH-N-P), 112.73 (d, partially overlapped with the s at 112.90, 6C; Pyr, *C*H-CH-N-P$_{ancillary}$), 50.71 ppm (vt, $^1J_{P,C} = 16.84$ Hz, 2C; Ar-*C*H$_2$-P); IR (film): $\nu = 2008$ cm^{-1} (C≡O); elemental analysis (%): calcd: C 56.28, H 4.47; found: C 56.41, H 4.51.

Reaction of [Rh(DPyPX)(PPy$_3$)CO] (4c) with PPh$_3$: PPh_3 (6.5 mg, 2.5×10^{-5} mol) in toluene (0.3 mL) was added to a solution of **4c** (19.7 mg, 2.5×10^{-5} mol) in toluene (0.7 mL). The reaction became slightly darker yellow. $^{31}P\{^1H\}$ and ^{1}H NMR ([D$_8$]toluene, **243 K**) spectra indicated formation of **4a**, when **4a**:**4c** = 4:1. The **4a**:**4c** ratio did not change after heating the solution at 70 °C for 40 min.

Reaction of [Rh(DPyPX)(PPh$_3$)CO] (4a) with PEt$_3$: Neat PEt$_3$ (3.2 μL, 2.4×10^{-5} mol) was added to a solution of **4a** (19.5 mg, 2.4×10^{-5} mol) in toluene (0.7 mL). ^{31}P{^{1}H} and ^{1}H NMR ([D$_8$]toluene, **243 K**) spectra indicated immediate quantitative formation of **4b**.

[Rh(DiPPX)H(PEt$_3$)Cl]: PEt$_3$ (7.6 μL, 5.6×10^{-5} mol) was added to a solution of [{Rh(coe)$_2$μ-Cl$_2$}] (20 mg, 2.8×10^{-5} mol) in THF (1.5 mL). To the resulting mixture, a solution of DiPPX-H (1,3-bis[(diisopropylphosphino)methyl]benzene)[36] (21.5 μL, 5.6×10^{-5} mol) in THF (1 mL) was added. The solution was heated under stirring at 65 °C for 2.5 h, to give an orange solution of [Rh(DiPPX)H(PEt$_3$)Cl]. The ^{31}P{^{1}H} NMR spectrum did not show any remaining starting material.

^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta=64.15$ (dd, $^1J_{Rh,P}=106$, $^2J_{P,P}=24.5$ Hz, 2P), 2.37 ppm (dt, $^1J_{Rh,P}=82.5$, $^2J_{P,P}=24.5$ Hz, 1P); ^{1}H NMR (C$_6$D$_6$): $\delta=7.2$–7.1 (Ar, 3H; *meta* and *para* to Rh), 3.79 (dvt, ABX$_2$ pattern, $^2J_{H,H}=14.7$, $^2J_{P,H}=3.4$ Hz, 2H; Ar-C*H*(H)-P), 2.98 (dvt, ABX$_2$ pattern, $^2J_{H,H}=14.7$, $^2J_{P,H}=3.9$ Hz, 2H; Ar-C*H*(H)-P), 2.3–0.7 (m, 43H; *i*Pr, Et), −18.41 ppm (ddt, $^1J_{Rh,H}=23.64$, $^2J_{P,H}=12.83$ Hz, 1H; *H*-Rh); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta=168.6$ (ddt, $^2J_{P,C,\ trans}=103.7$ Hz , $^1J_{Rh,C}=25.4$ $^2J_{P,C,\ cis}=4.2$ Hz, 1C; C_{ipso}-Rh), 145.8 (vtd, $^2J_{P,C}=7.64$ Hz, unresolved d, 2C; Ar, *C*-C-Rh), 124.08 (s, 1C; Ar, *C*H-CH-C-C-Rh), 121.3 (vtd, $^3J_{P,C}=8.15$, $J=4.7$ Hz, 2C; Ar, *C*H-C-C-Rh), 36.84 (vtdd, $^1J_{P,C}=14.04$, $J=8.29$ Hz, $J=2.07$ Hz, 2C; Ar-*C*H$_2$-P), 26.97 (vt, $^1J_{P,C}=10.01$ Hz, 2C; *i*Pr, *C*H-P), 25.36 (vt, $^1J_{P,C}=11.26$ Hz, 2C; *i*Pr, *C*H-P), 20.35 (dvt, $^1J_{P,C}=16.77$ Hz, unresolved t, 3C; Et, *C*H$_2$-P), 19.8 (s, 4C; *i*Pr, CH$_3$), 18.8 (s, 4C; *i*Pr, CH$_3$), 8.84 (d, $^2J_{P,C}=3.04$ Hz, 3C; Et, CH$_3$).

[Rh(DiPPX)PEt$_3$]: A solution of KO*t*Bu (6.3 mg, 5.6×10^{-5} mol) in THF (1 mL) was added dropwise to a solution of crude [Rh(DiPPX)H-(PEt$_3$)Cl] (2.8×10^{-5} mol, see synthesis of [Rh(DiPPX)H(PEt$_3$)Cl]) in THF. The resulting solution was heated to 60 °C for 1 h to give almost quantitative formation of dark brown [Rh(DiPPX)PEt$_3$]. The product was dried under vacuum and fully extracted with pentane, leaving KCl as white solid. The pentane solvent was removed under vacuum, to yield [Rh(DiPPX)PEt$_3$] as a brown solid (30 mg; 96 %).

^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta=62.6$ (dd, $^1J_{Rh,P}=154.3$, $^2J_{P,P}=30.8$ Hz, 2P), 14.9 ppm (dt, $^1J_{Rh,P}=113.7$, $^2J_{P,P}=30.8$ Hz, 1P); ^{1}H NMR (C$_6$D$_6$): $\delta=7.30$ (d, $^3J_{H,H}=7.2$ Hz, 2H; Ar, *meta* to Rh), 7.21 (t, $^3J_{H,H}=7.2$ Hz, 1H; *para* to Rh), 3.16 (vt, $^2J_{P,H}=3.5$ Hz, 4H; Ar-C*H*$_2$-P), 1.88 (m, 4H; *i*Pr, C*H*-P), 1.59 (m, 6H; Et, C*H*$_2$-P) 1.16 (m, 12H; *i*Pr, C*H*$_3$-CH-P), 1.08 (m, 9H; Et, C*H*$_3$-CH$_2$-P), 0.95 ppm (m, 12H; *i*Pr, C*H*$_3$-CH-P); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta=180.1$ (ddt, $^2J_{P,C,\ trans}=85.0$, $^1J_{Rh,C}=32.2$, $^2J_{P,C,\ cis}=7.62$ Hz, 1C; C_{ipso}-Rh), 149.79 (vt, $^2J_{P,C}=11.3$ Hz, 2C; Ar, *C*-C-Rh), 123.19 (s, 1C; Ar, *C*H-CH-C-C-Rh), 120.13 (vtd, $^3J_{P,C}=8.90$, $J=2.9$ Hz, 2C; Ar, *C*H-C-C-Rh), 39.74 (vtdd, $^1J_{P,C}=12.05$, $J=9.3$, $J=2.85$ Hz, 2C; Ar-*C*H$_2$-P), 27.30 (vtd, $^1J_{P,C}=8.98$, $J=1.72$ Hz, 4C; *i*Pr, *C*H-P), 21.40 (dt, $^1J_{P,C}=16.0$ Hz, unresolved t, 3C; Et, *C*H$_2$-P), 20.16 (vt, $^2J_{P,C}=3.35$ Hz, 4C; *i*Pr, CH$_3$), 19.34 (s, 4C; *i*Pr, CH$_3$), 9.39 (s, 3C; Et, CH$_3$); elemental analysis (%): calcd: C 55.91, H 9.02; found: C 55.73, H 8.85.

[Rh(DiPPX)CO]: CO (1.2 mL, 5.4×10^{-5} mol) was added to [Rh(DiPPX)PEt$_3$] (30 mg, 5.4×10^{-5} mol) in benzene (0.7 mL). The solution was vigorously shaken to dissolve CO, resulting in the quantitative formation of [Rh(DiPPX)CO], which is lighter brown in color than the starting material. Volatile compounds were removed by evaporation.

^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta=74.5$ ppm (d, $^1J_{Rh,P}=144.0$ Hz, 2P); ^{1}H NMR (C$_6$D$_6$): $\delta=7.19$ (d, $^3J_{H,H}=7.4$ Hz, 2H; Ar, *meta* to Rh), 7.13 (partially overlapped with the solvent signal, 1H; Ar, *para* to Rh), 3.16 (vt, $^2J_{P,H}=4.1$ Hz, 4H; Ar-C*H*$_2$-P), 1.89 (m, 4H; *i*Pr, *H*C-P), 1.17 (m, 12H; *i*Pr, *H*$_3$C), 0.93 ppm (m, 12H; *i*Pr, *H*$_3$C); ^{13}C {^{1}H} NMR (C$_6$D$_6$): $\delta=200.04$ (dt, $^1J_{Rh,C}=54.95$, $^2J_{P,C}=12.05$ Hz, 1C; CO), 178.83 (dt, $^1J_{Rh,C}=29.8$ Hz, $^2J_{P,C}=6.96$ Hz, C_{ipso}-Rh, 1C), 152.88 (vtd, $^2J_{P,C}=12.35$, $^2J_{Rh,C}=3.12$ Hz, 2C; Ar, *C*-C-Rh), 125.55 (s, 1C; Ar, *C*H-CH-C-C-Rh), 120.99 (vt, $^3J_{P,C}=9.77$ Hz, 2C; *C*H-C-C-Rh), 38.16 (vtd, $^1J_{P,C}=11.97$, $^2J_{Rh,C}=3.03$ Hz, 2C; Ar-*C*H$_2$-P), 26.18 (vt, $^1J_{P,C}=11.26$ Hz, 4C; *i*Pr, *C*H-P), 19.79 (vt, $^2J_{P,C}=3.0$ Hz, 4C; *i*Pr, CH$_3$), 18.85 ppm (s, 4C; *i*Pr, CH$_3$); IR (film): $\tilde{\nu}=1943$ cm^{-1} (C≡O); elemental analysis (%): calcd: C 53.85, H 7.53; found: C 53.72, H 7.52.

Computational details: All calculations were carried out using Gaussian 03 Rev B.02.[37] The density functional theory (DFT) B97–1 hybrid exchange-correlation functional[38] was used throughout. This is Handy et al.'s reparameterization[4] of Becke's B97 functional.[39] Two basis set-RECP (relativistic effective core potential) combinations were used. The first, denoted SDD, is the combination of the Huzinaga-Dunning double-ζ basis set on lighter elements with the Stuttgart–Dresden basis set-RECP combination[40] on transition metals. The second, denoted SDB-cc-pVDZ, combines the Dunning cc-pVDZ basis set[41] on the main group elements and the Stuttgart-Dresden basis set-RECP on the transition metals with an added f-type polarization exponent taken as the geometric average of the two f-exponents given in the Appendix to reference [42]. Geometry optimizations were carried out using the former basis set, while the energetics of the reaction were calculated at these reference geometries with the latter basis set; this level of theory is conventionally denoted as B97–1/SDB-cc-pVDZ//B97–1/SDD. Bulk solvation effects[43] were approximated using a conductor-like screening solvation model (COSMO)[44,45] with benzene as the solvent, just as with the experimental system. The molecular orbitals (MOs) were visualized by using GaussView[46] and the MO energies were taken as the Kohn–Sham (KS) orbital energies, both from the B97–1/SDB-cc-pVDZ energy calculation. The applicability of the KS orbital energies as ionization energies, for valence orbitals in closed shell systems, has been clearly demonstrated.[47–49]

Acknowledgements

This work was supported by the Israel Science Foundation (Jerusalem, Israel), the Helen and Martin Kimmel Center for Molecular Design and the Minerva Foundation (Munich, Germany). J.M.L.M. is the incumbent of the Baroness Thatcher Professorial Chair in Chemistry and a member of the Lise Meitner-Minerva Center for Computational Quantum Chemistry. D.M. is the The Israel Matz Professorial Chair of Organic Chemistry. E.K., M.A.I., and B.R. acknowledge the Feinberg Graduate School of the Weizmann Institute of Science for Ph.D. fellowships.

[1] M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866–3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781.
[2] M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792.
[3] B. Rybtchinski, D. Milstein, *Angew. Chem.* **1999**, *111*, 918–932; *Angew. Chem. Int. Ed.* **1999**, *38*, 870–883.
[4] J. T. Singleton, *Tetrahedron* **2003**, *59*, 1837–1857.
[5] A. Vigalok, D. Milstein, *Acc. Chem. Res.* **2001**, *34*, 798–807.
[6] D. Milstein, *Pure Appl. Chem.* **2003**, *75*, 445–460.
[7] C. M. Jensen, *Chem. Commun.* **1999**, *24*, 2443–2449.
[8] K. G. Moloy, J. L. Petersen, *J. Am. Chem. Soc.* **1995**, *117*, 7696–7710.
[9] d = doublet, t = triplet, vt = virtual triplet, q = quartet, dd = doublet of doublets, and so forth.
[10] CCDC-248612 contains the supplementary crystallographic data for complex **3a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[11] CCDC-248613 contains the supplementary crystallographic data for complex **4b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[12] P. Meakin, J. P. Jesson, *J. Am. Chem. Soc.* **1973**, *95*, 7272–7281.
[13] J. P. Jesson, P. Meakin, *J. Am. Chem. Soc.* **1973**, *95*, 1344–1346.
[14] J. P. Collman, F. D. Vastine, W. R. Roper, *J. Am. Chem. Soc.* **1968**, *90*, 2282–2287.
[15] H.-S. Lee, J.-Y. Bae, J. Ko, Y. S. Kang, H. S. Kim, S.-J. Kim, J.-H. Chung, S. O. Kang, *J. Organomet. Chem.* **2000**, *614–615*, 83–91.
[16] M. C. Nicasio, M. Paneque, P. J. Pérez, A. Pizzano, M. L. Poveda, L. Rey, S. Sirol, S. Taboada, M. Trujillo, A. Monge, C. Ruiz, E. Carmona, *Inorg. Chem.* **2000**, *39*, 180–188.
[17] A. Weisman, M. Gozin, H.-B. Kraatz, D. Milstein, *Inorg. Chem.* **1996**, *35*, 1792–1797.
[18] M. Gozin, Ph. D. Thesis, Weizmann Institute of Science, Rehovot, Israel, January **1995**.

[19] J. Terheijden, G. van Koten, W. P. Mul, D. J. Stufkens, F. Muller, C. H. Stam, *Organometallics* **1986**, *5*, 519–525.
[20] M. Albrecht, M. Lutz, A. M. M. Schreurs, E. T. H. Lutz, A. L. Spek, G. van Koten, *J. Chem. Soc. Dalton Trans.* **2000**, 3797–3804.
[21] Facial η^3 coordination of an NCN-type ligand of a tantalum alkylidene complex was reported: H. C. L. Abbenhuis, N. Feiken, D. M. Grove, J. T. B. H. Jastrzebski, H. Kooijman, P. van der Sluis, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1992**, *114*, 9773–9781.
[22] P. E. Garrou, G. E. Hartwell, *Inorg. Chem.* **1976**, *15*, 646–650.
[23] J. G. Leipoldt, G. J. Lamprecht, E. C. Steynberg, *J. Organomet. Chem.* **1990**, *397*, 239–244.
[24] J. G. Leipoldt, G. J. Lamprecht, E. C. Steynberg, *J. Organomet. Chem.* **1991**, *402*, 259–263.
[25] M. A. Alonso, J. A. Casares, P. Espinet, K. Soulantica, *Angew. Chem.* **1999**, *111*, 554–557; *Angew. Chem. Int. Ed.* **1999**, *38*, 533–535.
[26] B. Crociani, S. Antonaroli, M. L. Di Vona, S. Licoccia, *J. Organomet. Chem.* **2001**, *631*, 117–124.
[27] R. E. Bossio, N. W. Hoffman, T. R. Cundari, A. G. Marshall, *Organometallics* **2004**, *23*, 144–148.
[28] K. Krogh-Jespersen, M. Czerw, K. Zhu, B. Singh, M. Kanzelberger, N. Darji, P. D. Achord, K. B. Renkema, A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 10797–10809.
[29] J.-Y. Saillard, R. Hoffmann, *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.
[30] M. Ogasawara, S. A. Macgregor, W. E. Streib, K. Folting, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1996**, *118*, 10189–10199.
[31] M. J. Burk, M. P. McGrath, R. Wheeler, R. H. Crabtree, *J. Am. Chem. Soc.* **1988**, *110*, 5034–5039.
[32] M. J. Frisch, et al. Gaussian 03 rev. B.02, Gaussian Inc., Pittsburgh, PA, **2003**.
[33] M. Ogasawara, F. Maseras, N. Gallego-Planas, K. Kawamura, K. Ito, K. Toyota, W. E. Streib, S. Komiya, O. Eisenstein, K. G. Caulton, *Organometallics* **1997**, *16*, 1979–1993.
[34] A. R. Rossi, R. Hoffmann, *Inorg. Chem.* **1975**, *14*, 365–374.
[35] P. Hofmann, C. Meier, U. Englert, M. U. Schmidt, *Chem. Ber.* **1992**, *125*, 353–365.
[36] B. Rybtchinski, Y. Ben-David, D. Milstein, *Organometallics* **1997**, *16*, 3786–3793.
[37] Gaussian 03, Revision B.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2003**.
[38] F. A. Hamprecht, A. J. Cohen, D. J. Tozer, N. C. Handy, *J. Chem. Phys.* **1998**, *109*, 6264–6271.
[39] A. D. Becke, *J. Chem. Phys.* **1997**, *107*, 8554–8560.
[40] M. Dolg in *Modern Methods and Algorithms of Quantum Chemistry*, *Vol. 1* (Ed.: J. Grotendorst), John von Neumann Institute for Computing, Jülich, **2000**, pp. 479–508.
[41] T. H. Dunning Jr., *J. Chem. Phys.* **1989**, *90*, 1007–1023.
[42] J. M. L. Martin, A. Sundermann, *J. Chem. Phys.* **2001**, *114*, 3408–3420.
[43] C. J. Cramer in *Essentials of Computational Chemistry: Theories and Models*, Wiley, Chichester, UK, **2002**, pp. 347–383.
[44] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
[45] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.
[46] GaussView 3.0, Gaussian Inc., Pittsburgh, PA, 2003.
[47] D. P. Chong, O. V. Gritsenko, E.-J. Baerends, *J. Chem. Phys.* **2002**, *116*, 1760–1772.
[48] O. V. Gritsenko, B. Braïda, E. J. Baerends, *J. Chem. Phys.* **2003**, *119*, 1937–1950.
[49] C.-G. Zhan, J. A. Nichols, D. A. Dixon, *J. Phys. Chem. A* **2003**, *107*, 4184–4195.

Received: November 5, 2004
Published online: January 10, 2005