

Unsaturated Rh(I) and Rh(III) Naphthyl-Based PCP Complexes. Major Steric Effect on Reactivity

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The addition of an equimolar amount of hydrochloric acid (~4.0 M in dioxane) to THF solutions of the binuclear Rh(I) complex $[(C_{10}H_5(CH_2P^iPr_2)_2Rh(\eta^1-N_2))_2]$ (**1a**) at room temperature led to an inseparable mixture of **1a**, $[(C_{10}H_5(CH_2P^iPr_2)_2Rh(Cl)(H))]$ (**2a**), and $[(C_{10}H_5(CH_2P^iPr_2)_2Rh(Cl)_2(dioxane))_2]$ (**3a**). Exclusive formation of **2a** was achieved by slow addition of an equimolar amount of hydrochloric acid (~0.4 M in dioxane) to a THF solution of **1a** at $-35^\circ C$, whereas exclusive formation of **3a** was obtained when a second equivalent or an excess (~10 equiv) of hydrochloric acid (~4.0 M in dioxane) was added to THF solutions of **2a** (or to reaction mixtures, which consist of **1a**, **2a**, and **3a**). **3a** was structurally characterized. In striking difference to the reactivity pattern of **1a**, treatment of THF solutions of the bulky *t*Bu derivative **1b** with an equimolar amount or even a large excess (~25 equiv) of hydrochloric acid (~4.0 M in dioxane) exclusively yielded the hydrido chloro complex $[(C_{10}H_5(CH_2P^iBu_2)_2Rh(Cl)(H))]$ (**2b**). Chloride abstraction from **2a** and **2b** with $AgBF_4$ exclusively yielded the hydrido rhodium(III) complexes $[(C_{10}H_5(CH_2PR_2)_2Rh(H)(F-BF_3))]$ (**9a** and **9b**) with coordination of the counteranion. On the other hand, when an equimolar amount of $AgBARF_4$ was added to methylene chloride (or diethyl ether) solutions of **2a** and **2b** the cationic, the solvent-stabilized rhodium hydride complexes of type $[(C_{10}H_5(CH_2PR_2)_2Rh(solvent)(H)][BARF_4]]$ (**10a** and **10b**) were formed. If the electron density of the metal centers of **9** (and **10**) is reduced further by substitution of the coordinated anion of **9** (or the solvent molecule of **10**) with a carbonyl ligand, instant migration of the hydride ligand to the aromatic unit to yield the stable carbonyl complexes of type $[(C_{10}H_5(CH_2PR_2)_2(H)Rh(CO)][X]]$ (**X** = $BARF_4$ **11a**, **11b**; **X** = BF_4 **11a'**, **11b'**) with $\eta^2 C_{aryl}-H$ agostic interactions was observed. Treatment of **2b** with CO gas yielded both isomeric forms of $[(C_{10}H_5(CH_2P^iBu_2)_2Rh(H)(Cl)(CO))]$ **14b** (CO trans to the hydride ligand) and **14b'** (CO trans to the aromatic pincer core). In contrast, when an excess of CO gas was added to THF (or methylene chloride), solutions of **2a**, **14a'** was exclusively formed within 20 min at room temperature.

Introduction

Catalytic processes are initiated by the coordination and activation of substrate molecules by coordinatively unsaturated metal centers,¹ which are stabilized in solution by coordination of solvent molecules,² counteranions,³ or agostic interactions with ligands.⁴ The degree of stabilization and hence the reactivity of a transition-metal complex toward substrate molecules depend on the electronic properties and steric bulk of the coordinated ligands, the counteranion, and the solvent. Consequently, these properties can be of high importance in catalysis. Therefore, efforts to prepare and investigate d^6 and

d^8 $14e^-$ complexes, which have frequently been postulated as intermediates in carbon–carbon⁵ and carbon–hydrogen^{6,7} bond activation and functionalization, considerably increased. Thus, formally $14e^-$ d^6 iridium,^{4a} rhodium,⁸ ruthenium,^{2,4b} and d^8 rhodium^{4c,9} complexes as well as examples of unsaturated platinum d^6 complexes were described.¹⁰

We report here different reactivity modes of seemingly very similar rhodium pincer complexes that are controlled by steric effects. In addition, we describe the facile synthesis of highly unsaturated formally $14e^-$ rhodium d^6 complexes, which are,

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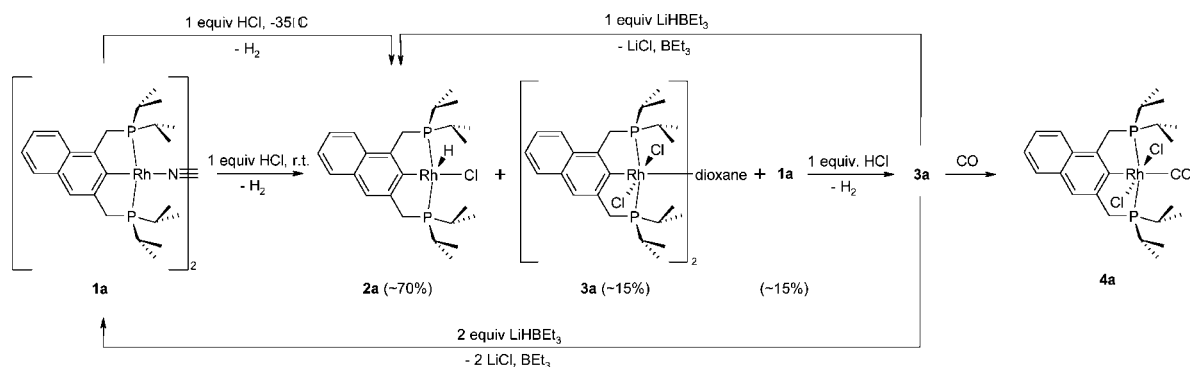
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Scheme 1. Reaction of **1a** with Hydrochloric Acid and Subsequent Reactions

depending on the steric bulk of the counteranion, stabilized either by coordination of a solvent molecule or by the counteranion.

Results and Discussion

The addition of an equimolar amount (relative to the metal) of hydrochloric acid (~4.0 M in dioxane) to THF solutions of the binuclear Rh(I) complex [(C₁₀H₅(CH₂PⁱPr₂)₂Rh(η¹-N₂)]₂¹¹ (**1a**) at room temperature led to an inseparable mixture of **1a**, [(C₁₀H₅(CH₂PⁱPr₂)₂Rh(Cl)(H))] (**2a**), and [(C₁₀H₅(CH₂PⁱPr₂)₂-Rh(Cl)₂(dioxane)]₂ (**3a**) (Scheme 1).

The ³¹P{¹H} NMR spectrum of this reaction mixture displayed three different signals centered at δ = 50.23, 64.23, and 66.34 ppm, of which the latter belongs to **1a**. The signal at δ = 64.23 ppm, attributed to the rhodium hydride complex **2a**, has a dd (AB) pattern with its center at δ = 64.46 and 64.00 ppm with coupling constants of ²J_{PP} = 396.2 and ¹J_{RhP} = 117.5 Hz. **2a** was formed in approximately 70% yield, while both **1a** and **3a** were obtained in a yield of ~15% (by integration). The ¹H NMR spectrum of this mixture displayed, in addition to all the resonances due to the pincer ligands, a sharp and characteristic hydride signal at δ = -24.53 ppm with dt pattern and coupling constants of ¹J_{RhH} = 44.6 and ²J_{PH} = 7.8 Hz, which confirms the formation of a rhodium hydride complex, such as **2a**. The high-field signal is typical for a hydride situated trans to a vacant coordination site and suggests a square pyramidal environment of the metal center with the hydride ligand in the apical position. Exclusive formation of **2a** was achieved by slow addition of an equimolar amount of hydrochloric acid (~0.4 M in dioxane) to a THF solution of **1a** at -35 °C. Interestingly, when a second equivalent or an excess (~10 equiv) of hydrochloric acid (~4.0 M in dioxane) was added to THF solutions of **2a** (or to reaction mixtures, which consist of **1a**, **2a**, and **3a**) the dichloro rhodium(III) complex [(C₁₀H₅(CH₂PⁱPr₂)₂Rh(Cl)₂(dioxane)]₂ (**3a**) was exclusively formed and isolated in high yield. The formation of **3a** is accompanied by dihydrogen evolution. Formation of dihydrogen was confirmed by NMR spectroscopy: A sharp singlet at δ = 4.40 ppm was detectable in the ²H spectrum when THF solutions of **1a** were treated with an excess (~2.5 equiv) of deuterium chloride (~1.0 M in diethyl ether). Dihydrogen generation along the synthesis of **3a** implies a direct attack of the proton on the hydride ligand of **2a**, since attack at

the metal center would lead to a *trans*-dihydride complex in a square pyramidal arrangement.¹² Indeed, no intermediates were detected by ³¹P{¹H} NMR spectroscopy when an equimolar amount of hydrochloric acid (~4.0 M in dioxane) was added to THF solutions of **2a** even at -35 °C. When 2 equiv or an excess (~5 equiv) of the hydride reagent LiHBEt₃ (~1.0 M in THF) was added to THF (or benzene) solutions of **3a**, **1a** was quantitatively formed. Treatment of cold (-35 °C) THF solutions of **3a** with an equimolar amount of LiHBEt₃ exclusively yielded the rhodium hydride complex **2a**. The ³¹P{¹H} NMR spectrum of **3a** exhibits two resonance signals with dd (AB) pattern centered at δ = 50.75 and 49.82 ppm with coupling constants of ²J_{PP} = 360.7 and ¹J_{RhP} = 96.2 Hz, indicating a Rh^{III} center. In addition to all the signals attributed to the pincer ligand in the ¹H and ¹³C{¹H} NMR spectra, resonance signals at δ = 3.72 and 67.7 ppm, respectively, were detected, indicating a coordinated dioxane molecule in **3a**. Dioxane coordination was confirmed by X-ray diffraction crystallographic analysis of single crystals of **3a**. Suitable crystals of complex **3a** were grown from a concentrated benzene solution at room temperature. The crystal structure of **3a** revealed a dinuclear rhodium dichloro complex, bridged by a dioxane molecule. **3a** is the first crystallographically characterized rhodium–dioxane complex reported (Figure 1). The rhodium centers have slightly distorted octahedral geometries with axially arranged chloride ligands. The dioxane molecule is trans coordinated to the C_{ipso} carbon atom and twisted around the C–Rh–dioxane–Rh–C axis. The dihedral angles of C12–Rh1–O1–C25 and C12–Rh1–O1–C26 are 122.0(1) and -75.9(1)°, respectively. The Rh1–O1 and Rh1A–O1A bond distances measure 2.371(3) Å and are some of the longest reported when compared with the few structurally characterized rhodium complexes containing Rh–O_{THF} interactions, whose Rh–O_{THF} bond lengths vary in the range of 2.077–2.450 Å.^{13,14}

(12) Isomerization of an initially formed octahedral *trans* complex to a *cis*-dihydride and/or mechanisms with the involvement of σ -arenum intermediates (see also ref 17) are expected to have higher barriers.

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Partial liberation of the metal-coordinated dioxane molecule of **3a** was observed under reduced pressure, most probably yielding their pentacoordinated solvent-free dichloro complexes. However, when an excess (~50 equiv relative to rhodium) of CO gas was added to methylene chloride solutions of **3a** quantitative substitution of dioxane to give the mononuclear carbonyl derivative $[(C_{10}H_5(CH_2P^iPr_2)_2)Rh(CO)(Cl)_2]$ (**4a**) was observed. The IR spectrum of **4a** exhibits a characteristic carbonyl absorption band at 1949 cm^{-1} . The $^{31}P\{^1H\}$ NMR spectrum of **4a** displays two signals with dd (AB) pattern centered at $\delta = 64.45$ and 62.56 ppm with coupling constants of $^2J_{PP} = 312.6$ and $^1J_{RHP} = 85.5\text{ Hz}$ for both signals. The $^{13}C\{^1H\}$ NMR spectrum gave rise to a signal with dd pattern at $\delta = 187.92\text{ ppm}$ with coupling constants of $^2J_{PC} = 40.2$ and $^1J_{RhC} = 8.1\text{ Hz}$. Attempts to selectively abstract one of the chloride ligands of **3a** with an equimolar amount of silver salts, such as $AgBF_4$ or $AgBAR^F_4$, led to inseparable mixtures, which consist of **3a** and several other unidentified phosphorus-containing compounds. Complete decomposition was obtained when ≥ 2 equiv (relative to rhodium) of a silver salt was added to methylene chloride solutions of **3a** and **4a**, respectively. Similarly, the addition of an equimolar amount (relative to rhodium) of methyl lithium (~1.6 M in diethyl ether) to methylene chloride solutions of **3a** at room temperature yielded an inseparable mixture of phosphorus-containing products. The presence of the methyl chloride complex $[(C_{10}H_5(CH_2P^iPr_2)_2)Rh(CH_3)(Cl)]$ (**5a**) in this reaction mixture (~28%) was established by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. For instance, the $^{31}P\{^1H\}$ NMR spectrum exhibits two signals centered at $\delta = 47.12$ and 47.47 ppm with dd (AB) pattern and coupling constants of $^1J_{RHP} = 116.2$ and $^2J_{PP} = 52.4\text{ Hz}$. The $^{13}C\{^1H\}$ NMR spectrum exhibits a signal with dt pattern at $\delta = -4.72\text{ ppm}$ and coupling constants of $^1J_{RhC} = 31.2$ and $^2J_{PC} = 5.2\text{ Hz}$, which is in the chemical shift range characteristic for metal-coordinated methyl groups of complexes of type **5a**. Indeed, the NMR data compare well with those of its methyl iodide derivative $[(C_{10}H_5(CH_2P^iPr_2)_2)Rh(CH_3)(I)]$ (**6a**). Further evidence for the identity of **5a** was gained by the addition of a slight excess (~1.2 equiv relative to rhodium of **3a**) of $AgBF_4$ to that reaction mixture under rigorous exclusion of light, which yielded the BF_4 -coordinated complex $[(C_{10}H_5(CH_2P^iPr_2)_2)Rh(CH_3)(F-BF_3)]$ (**7a**) in approximately 27% yield (by integration). The identity of **7a** was confirmed by its independent synthesis, achieved by treatment of methylene chloride solutions of **6a** with an equimolar amount of $AgBF_4$. Upon treatment with CO, **7a** underwent methyl migration to the C_{ipso} , exclusively forming the η^2 C–C agostic complex $[(C_{10}H_5(CH_2P^iPr_2)_2)(CH_3)Rh(CO)][BF_4]$ (**8a**), similar to the reactivity pattern of related rhodium pincer complexes.^{13,15–17}

Remarkably, in striking difference to the reactivity pattern of **1a**, treatment of THF solutions of the bulky *t*Bu derivative **1b** with an equimolar amount or even a large excess (~25 equiv) of hydrochloric acid (~4.0 M in dioxane) exclusively yielded the hydrido chloro complex $[(C_{10}H_5(CH_2P^iBu_2)_2)Rh(Cl)(H)]$ (**2b**). The formation of dichloro Rh^{III} complexes was not obtained. The $^{31}P\{^1H\}$ NMR spectrum of **2b** exhibits two signals with dd (AB) pattern centered at $\delta = 74.12$ and 74.04 ppm . Their coupling constants are $^1J_{RHP} = 114.4$ and $^2J_{PP} = 34.2\text{ Hz}$, respectively. The presence of a Rh–H bond was established by 1H NMR spectroscopy, displaying an intense signal with dt

pattern at $\delta = -27.42\text{ ppm}$ ($^1J_{RhH} = 44.2$ and $^2J_{PH} = 8.0\text{ Hz}$), characteristic for hydride ligands situated trans to a vacant coordination site. The exclusive formation of **2b** is unexpected, since the higher electron density on the metal center of **1b** (as compared to **1a**) would favor the electrophilic attack on the hydride ligand.¹⁵ **1b** toward hydrochloric acid is attributed to steric effects, which lead to a weaker Rh–Cl interaction in **2b**. This in turn could result in a stronger Rh–H bond preventing liberation of dihydrogen from **2b** in acidic media. This anticipation was supported by an experiment in which THF solutions of **1a** and **1b** were reacted with equimolar amounts or an excess (~5 equiv) of 57% $HF_4 \cdot Et_2O$, resulting in exclusive formation of the hydrido rhodium(III) complexes $[(C_{10}H_5(CH_2PR_2)_2)Rh(H)(F-BF_3)]$ (**9a** and **9b**) in both systems. The $^{31}P\{^1H\}$ NMR spectrum of **9a** recorded in C_6D_6 displays two signals with a dd (AB) pattern at $\delta = 67.23$ and 65.97 ppm with coupling constants of $^1J_{RHP} = 113.4$ and $^2J_{PP} = 11.8\text{ Hz}$ for both signals. The 1H NMR spectrum exhibits a broad hydride signal with dt pattern at $\delta = -24.32\text{ ppm}$ ($^1J_{RhH} = 46.4$ and $^2J_{PH} = 12.4\text{ Hz}$). Coordination of the counteranion was indicated by $^{19}F\{^1H\}$ NMR spectroscopy, which exhibits a very broad singlet at $\delta = -158.35\text{ ppm}$. Free BF_4 gives rise to a sharp signal at $\delta \approx -152.60\text{ ppm}$.¹⁸ Coordination of BF_4 counteranions was already observed in related rhodium methyl complexes, having an important effect with regard of the stabilization of the Rh–CH₃ bond.^{8,15,17} The $^{31}P\{^1H\}$ NMR spectrum of **9b** exhibits a signal with a dd pattern at $\delta = 74.21\text{ ppm}$ and coupling constants of $^1J_{RHP} = 120.1$ and $^2J_{PP} = 24.5\text{ Hz}$. The 1H NMR spectrum showed a broad doublet of triplet at $\delta = -27.27\text{ ppm}$ ($^1J_{RhH} = 53.8$ and $^2J_{PH} = 12.6\text{ Hz}$). Alternative syntheses of **9a** and **9b** were achieved by the addition of equimolar amounts of $AgBF_4$ to methylene chloride solutions of **2a** and **2b** under rigorous exclusion of light. On the other hand, when an equimolar amount of $AgBAR^F_4$ was added to methylene chloride (or diethyl ether) solutions of **2a** and **2b** the cationic, solvent-stabilized rhodium hydride complexes $[(C_{10}H_5(CH_2PR_2)_2)Rh(solv)(H)][BAR^F_4]$ (**10a** and **10b**) were formed. Their $^{31}P\{^1H\}$ NMR spectra exhibit very broad signals at $\delta = 63.13$ and 76.94 ppm at room temperature, most probably as a consequence of the labile coordination of the solvent molecules. Indeed, when the $^{31}P\{^1H\}$ NMR spectra were recorded at $-70\text{ }^\circ\text{C}$, the signals sharpened and exhibited broad dd-like patterns, as expected. Migration of the hydride ligands to the aromatic ring was not observed, as indicated by 1H and $^{13}C\{^1H\}$ NMR spectroscopy. For instance, in the 1H NMR spectra broad doublets at $\delta = -20.04$ (for **10a**) and -27.18 ppm (for **10b**) with coupling constants of $^1J_{RhH} = 52.6$ and $^1J_{RhH} = 55.4\text{ Hz}$, respectively, were detected. The $^{13}C\{^1H\}$ NMR spectra exhibit broad singlets at $\delta = 160.21$ and 164.42 ppm , respectively, which are attributed to the σ bound Rh– C_{ipso} carbon atoms of the pincer core. Coordination of a solvent molecule to the metal centers of **10a** and **10b** was confirmed by 1H and $^{13}C\{^1H\}$ NMR spectroscopy (as well as elemental analysis in the case of THF). For instance, when the 1H and $^{13}C\{^1H\}$ NMR spectra of dry **10a** and **10b** (prepared in methylene chloride) were recorded in THF-*d*₈, signals due to an equimolar amount (by integration) of “free” methylene chloride were detected, indicating that a coordinated methylene chloride molecule was substituted by a molecule of THF. Similarly, when the NMR spectra of dry **10a** and **10b** (prepared in diethyl ether) were recorded in CD_2Cl_2 , signals due to a corresponding amount of “free” diethyl ether were detected. These findings are interesting, since methylene chloride is

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(16) See the Experimental Section.

(17) Vigalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 895.(18) See, for instance, $^{31}F\{^1H\}$ NMR data of **11a'** in the Experimental Section.

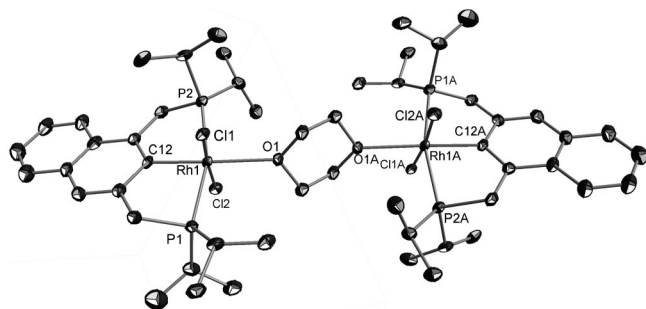


Figure 1. DIAMOND drawing of a molecule of **3a**, showing the atom labeling scheme (50% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh1–C12 = 2.014(4), Rh1–P1 = 2.3611(11), Rh1–P2 = 2.3447(11), Rh1–Cl1 = 2.3600(11), Rh1–Cl2 = 2.3467(11), Rh1–O1 = 2.371(3); P1–Rh1–P2 = 163.46(4), Cl2–Rh1–Cl2 = 174.39(4), C12–Rh1–O1 = 172.39(13).

considered one of the weakest ligands and, hence,^{3a} its coordination to late transition-metals complexes is extremely rare.^{2,8,19} Thus, **10a** and **10b** can be viewed as highly unsaturated solvent-stabilized Rh(III) 14e[−] intermediates.^{2,4,8–10,20} To conclude, the choice of the counteranion (BARF₄ or BF₄) controls the mode of stabilization of the metal center, either by the anion (**9a** and **9b**) or by the solvent (**10a** and **10b**) (Scheme 2). If the electron density of the metal centers of **9** (and **10**) is reduced further by substitution of the coordinated anion of **9** (or the solvent molecule of **10**) with a carbonyl ligand, instant migration of the hydride ligand to the aromatic unit to yield the stable carbonyl complexes of type [(C₁₀H₅(CH₂PR₂)₂(H)Rh(CO))[X] (X = BARF₄ **11a**, **11b**; X = BF₄ **11a'**, **11b'**) with η² C_{aryl}–H agostic interactions was observed. Strongly related literature examples for migration of hydride or methyl groups from the metal center to the aryl ligand are known.^{15,17,21} The ³¹P{¹H} NMR spectra of **11a** and **11a'** as well as those of **11b** and **11b'** are identical and exhibit signals with dd (AX) pattern at δ ≈ 35.5 (²J_{PP} ≈ 248 and ¹J_{RhP} ≈ 105 Hz) and 16.8 ppm (²J_{PP} ≈ 248 and ¹J_{RhP} ≈ 104 Hz) as well as at δ ≈ 47.6 (²J_{PP} ≈ 247 and ¹J_{RhP} ≈ 103 Hz) and 30.9 ppm (²J_{PP} ≈ 247 and ¹J_{RhP} ≈ 100 Hz), respectively. The ¹H NMR spectra display, in addition to all the signals due to the naphthalene-based pincer ligand, doublets at δ ≈ 3.9 ppm with coupling constants of ¹J_{RhH} ≈ 11 (for **11a** and **11a'**) and ¹J_{RhH} ≈ 17 Hz (for **11b** and **11b'**), which are attributed to the η² C_{aryl}–H hydrogen atoms. η² C_{aryl}–H carbon atoms give rise to singlets at δ ≈ 110 ppm in the ¹³C{¹H} NMR spectra. The significant upfield shifts (Δδ ≈ −55 ppm) in the ¹³C{¹H} NMR spectra of **9** (and **10**) as compared with that of **11** (and **11'**) is typical of such structural changes.^{16,19} Alternative syntheses of **11** and **11'** were achieved by the addition of equimolar amounts 57% HBF₄·Et₂O and [H(Et₂O)₂][BARF₄], respectively, to ethereal solutions of [(C₁₀H₅(CH₂PR₂)₂–Rh(CO))] (**12a** and **12b**). As observed with the phenyl-based analogue of **11a'**,²¹ upon treatment with CO exclusive formation

of the hydrido dicarbonyl rhodium complex [(C₁₀H₅(CH₂PⁱPr₂)₂–Rh(H)(CO)₂][BF₄] (**13a**) was observed. **13a** is stable under CO atmosphere (~1.5 atm) but readily loses a carbonyl ligand (to form **11a'**) under N₂ atmosphere or under reduced pressure. C–H activation to form the hydride complex **13a** became evident by ¹H and ¹³C{¹H} NMR spectroscopy. For instance, a broad hydride signal appeared at −7.88 ppm in the ¹H NMR spectrum. In the ¹³C{¹H} NMR spectrum, two signals with dvt pattern at δ = 184.43 (¹J_{RhP} = 40.7 and J_{PC} = 6.8 Hz) and 183.87 ppm (¹J_{RhP} = 42.1 and J_{PC} = 7.1 Hz) were detected, which were assigned to the carbonyl ligands. In addition, a doublet due to the C_{ipso} carbon atom at δ = 146.42 ppm (¹J_{RhC} = 22.5 Hz) was detectable. In analogy to the literature example mentioned above, no spectroscopic evidence for the formation of the hydrido rhodium(III) dicarbonyl complex **13b** was observed in the case of the bulky *t*Bu derivative **11b'**.

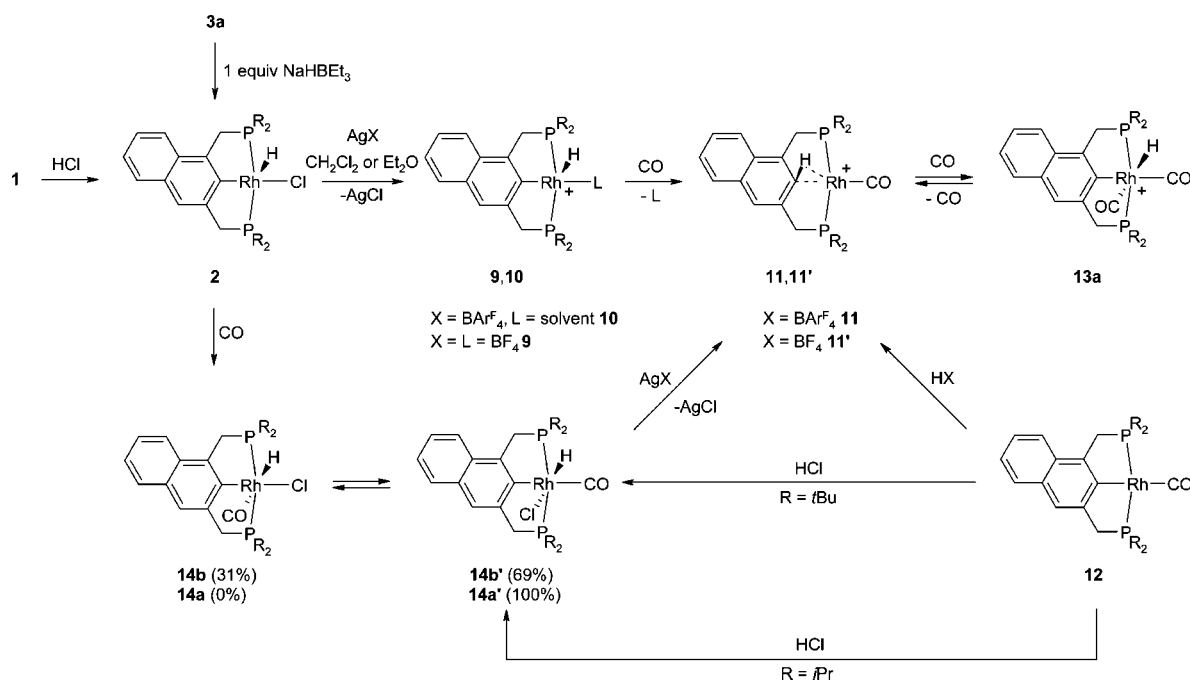
Similar to the reactivity pattern of [(C₁₀H₅(CH₂PⁱPr₂)₂–Rh(CH₃)(I)] (**6a**), where formation of an isomeric mixture of its carbonyl adducts was obtained by treatment with CO gas,¹⁵ both isomeric forms of [(C₁₀H₅(CH₂PⁱBu₂)₂–Rh(H)(Cl)(CO))] **14b** (CO trans to the hydride ligand) and **14b'** (CO trans to the aromatic pincer core) were obtained when CO gas was added to methylene chloride solutions of **2b** (Scheme 2). This is in sharp contrast to the reactivity pattern of its methyl iodide derivative **6b**, where slow, quantitative reductive elimination of methyl iodide to form the carbonyl complex [(C₁₀H₅(CH₂PⁱBu₂)₂–Rh(CO))] (**12b**) took place by treatment with an excess (~100 equiv) of CO gas. The reactivity difference of **2b** with respect to that of **6b** indicates that reductive elimination of methyl iodide from **6b** to form **12b** is induced by steric effects. When the reaction of **2b** with CO gas was performed at −50 °C, **14b** was exclusively formed, indicating that it is the kinetic product. Upon warming to room temperature, an equilibrium mixture of **14b** (31%) and **14b'** (69%) was formed within a few minutes, which did not change upon cooling to −50 °C. Exclusive formation of **14b'** was obtained when **12b** was treated with an equimolar amount of hydrochloric acid (~4.0 M in dioxane) at −50 °C. Warming the reaction mixture to room temperature yielded again the equilibrium mixture of **14b** (31%) and **14b'** (69%). The ³¹P{¹H} NMR spectrum of that mixture exhibits two sets of signals with dd (AB) pattern. The signals assigned to **14b'** are centered at δ = 95.21 and 94.15 ppm and have coupling constants of ²J_{PP} = 315.4 and ¹J_{RhP} = 98.4 Hz, while those belonging to **14b** are centered at δ = 86.74 and 86.44 ppm and have coupling constants of ²J_{PP} = 328.8 and ¹J_{RhP} = 104.5 Hz. The hydride ligands in the ¹H NMR spectrum exhibit two doublets of triplet signals and are positioned at δ = −15.32 and −7.64 ppm. The signal centered at δ = −15.32 ppm belongs to **14b'**, whereas the signal at δ = −7.64 ppm was assigned to **14b**. The coupling constants of these hydride signals are ²J_{PH} = 9.1 and ¹J_{RhH} = 4.2 Hz and ¹J_{RhH} = 8.6 and ²J_{PH} = 8.4 Hz, respectively. The substantial difference in the chemical shifts indicates different ligands trans to the Rh–H bond. The isomeric nature of **14b** and **14b'** was confirmed by treatment of its methylene chloride solutions with AgBARF₄ and AgBF₄, which cleanly yielded **11b** and **11b'**, respectively. In contrast, when an excess of CO gas was added to THF (or methylene chloride), solutions of **2a** and **14a'** were exclusively formed within 20 min at room temperature. The same result was obtained by treatment of THF solutions of **12a** with an equimolar amount of hydrochloric acid (~4.0 M in dioxane). The exclusive formation of **14a'** is attributed to steric effects; the *i*Pr substituents of **14a'** apparently allow Rh–Cl interactions trans to the hydride ligand which are stronger when

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Scheme 2. Reactions of 1b with Hydrochloric Acid and Subsequent Reactions



compared with the more bulky *t*Bu derivative **14b'** (see also the explanation of the reactivity difference of **1a** and **1b** toward hydrochloric acid). However, the $^1\text{P}\{^1\text{H}\}$ NMR spectrum of **14a'** shows a signal with a dd pattern centered at $\delta = 79.03$ and 78.44 ppm with coupling constants of $^2J_{\text{PP}} = 320.4$ and $^1J_{\text{RHP}} = 97.1$ Hz. The ^1H NMR spectrum exhibits a sharp doublet of triplet at -14.89 ppm ($^2J_{\text{PH}} = 27.0$ Hz and $^1J_{\text{RHH}} = 9.4$ Hz). Treatment of its methylene chloride solutions with $\text{AgBAR}^{\text{F}_4}$ and AgBF_4 cleanly yielded **11a** and **11a'**, respectively. Unexpectedly, **14a'** is not stable in solution. Methylene chloride solutions of **14a'** led to the precipitation of a yellow, insoluble microcrystalline solid overnight. Similarly, when **14a'** was dissolved in THF its conversion into new species (signals centered at $\delta = 42.77$ ppm were detected in the $^1\text{P}\{^1\text{H}\}$ NMR spectrum) was observed overnight. Neither a signal attributable to a rhodium-hydride bond nor evidence for migration of the hydride ligand to the aromatic pincer core was obtained by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Furthermore, precipitation of a yellow, insoluble microcrystalline solid was observed within a few days in THF, indicating that probably cluster formation occurred, formation of which might be retarded in a coordinating solvent such as THF when compared with methylene chloride. The identity of the product(s) could not be determined.

In conclusion, seemingly very similar rhodium pincer complexes show significantly different reactivity modes that are controlled by steric effects. Furthermore, the synthesis of highly unsaturated 14-electron Rh d⁶ complexes was described, and the complexes are, depending on the steric bulk of the counteranion, stabilized either by coordination of a solvent molecule or by the counteranion.

Experimental Section

General Procedures. All synthetic operations were carried out in oven-dried glassware under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier. Solvents were reagent grade or better, dried, distilled, and degassed before introduction into the glovebox, where they were stored over activated 4 Å molecular sieves. Deuterated solvents were purchased from Aldrich or Armar and were degassed

and stored over activated 4 Å molecular sieves in the glove-box. All the commercial available chemicals were used as received.

Analysis. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and ^{19}F NMR data were recorded at 500.13, 125.76, 202.46, and 235.40 MHz, respectively, on a Bruker DRX-500 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm), and coupling constants (J) are in hertz. The ^1H and ^{13}C NMR chemical shifts are relative tetramethylsilane; the resonances of the residual protons of the solvents were used as internal standard for ^1H (δ 7.15 (C_6D_6); 7.26 (CDCl_3); 5.32 (CD_2Cl_2); 3.58 and 1.73 ppm (THF)) and *all-d* solvent peaks for ^{13}C (δ 128.0 (C_6D_6); 77.0 (CDCl_3); 53.8 (CD_2Cl_2); 68.00 and 25.77 ppm (THF)). ^{31}P NMR chemical shifts are reported downfield relative to external 85% H_3PO_4 in D_2O at $\delta = 0.0$ ppm. All measurements were carried out at 298 K. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; v, virtual. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Germany, and at the Department of Inorganic Chemistry at the University of Zurich.

Preparation of [(C₁₀H₅(CH₂P⁽ⁱPr)₂)Rh(H)(Cl)] (2a). To a cooled (−35 °C) THF solution (10 mL) of [(C₁₀H₅(CH₂P⁽ⁱPr)₂)₂-Rh(η¹-N₂)]₂ (25 mg, 0.025 mmol), an equimolar amount of hydrochloric acid (~0.4 M in dioxane) was added and stirred for 15 min. The solvent was removed under reduced pressure. The product was extracted (2 × 5 mL) with diethyl ether. The solvent was removed under reduced pressure, yielding 20.4 mg (0.039 mmol, 78%) of pure **2a**. **2a** was also obtained when an equimolar amount of LiHBet₃ (~1 M in THF) was added to a cooled (−35 °C) THF solution (10 mL) of [(C₁₀H₅(CH₂P⁽ⁱPr)₂)Rh(dioxane)]₂ (30 mg, 0.025 mmol) and stirred for 15 min.

$^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 ; δ , ppm): 64.46 (dd (AB), $J_{\text{PP}} = 396.2$ Hz, $J_{\text{RHP}} = 117.5$ Hz), 64.00 (dd (AB), $J_{\text{PP}} = 396.2$ Hz, $J_{\text{RHP}} = 117.5$ Hz). ^1H NMR (δ , ppm): 7.85 (d, $J_{\text{HH}} = 7.1$ Hz, 1H, Ar), 7.71 (d, $J_{\text{HH}} = 7.2$ Hz, 1H, Ar), 7.69 (s, 1H, Ar), 7.34 (m, 2H, Ar), 3.53 (dd, $J_{\text{PH}} = 14.8$ Hz, $J_{\text{RHH}} = 9.8$ Hz, 1H, CH_2P), 3.34 (dd, $J_{\text{PH}} = 14.7$ Hz, $J_{\text{RHH}} = 6.9$ Hz, 1H, CH_2P), 3.27 (dd, $J_{\text{PH}} = 14.9$ Hz, $J_{\text{RHH}} = 6.9$ Hz, 1H, CH_2P), 2.96 (dd, $J_{\text{PH}} = 14.8$ Hz, $J_{\text{RHH}} = 9.8$ Hz, 1H, CH_2P), 2.77 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.64 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.34 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 1.31 (m, 24H, $\text{PCH}(\text{CH}_3)_2$), -24.53 (dt, $J_{\text{RHH}} = 44.6$ Hz, $J_{\text{PH}} = 7.8$ Hz, 1H, RhH). $^{13}\text{C}\{\text{H}\}$ NMR (δ , ppm): 160.54 (d, $J = 30.1$ Hz, C_{iso}), 148.18 (dd, $J_{\text{PC}} =$

12.8 Hz, $J_{\text{RhC}} = 6.4$ Hz, Ar), 144.35 (dd, $J_{\text{PC}} = 12.9$ Hz, $J_{\text{RhC}} = 6.3$ Hz, Ar), 131.91 (s, Ar), 129.23 (s, Ar), 128.15 (s, Ar), 127.00 (s, Ar), 125.59 (s, Ar), 124.43 (s, Ar), 121.40 (d, $J = 11.8$ Hz, Ar), 33.63 (d, $J = 16.9$ Hz, CH_2P), 30.31 (d, $J = 16.9$ Hz, CH_2P), 25.21 (dd, $J = 24.2$ Hz, $J = 2.3$ Hz, $\text{PCH}(\text{CH}_3)_2$), 24.75 (dd, $J = 26.5$ Hz, $J = 3.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 19.05 (m, $\text{PCH}(\text{CH}_3)_2$), 18.78 (m, $\text{PCH}(\text{CH}_3)_2$). Elemental analysis calcd for $\text{C}_{24}\text{H}_{38}\text{ClP}_2\text{Rh}$: C, 54.71; H, 7.27. Found: C, 55.00; H, 7.47.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2))_2\text{Rh}(\text{H})(\text{Cl}))(\text{2b})]$. To a THF solution (5 mL) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2))_2\text{Rh}(\eta^1\text{-N}_2))]$ (20 mg, 0.034 mmol) a slight excess (~1.5 equiv) of hydrogen chloride (~4 M in dioxane) was added, which was accompanied by a color change from brown to bright yellow. The solvent was removed under reduced pressure. The residue was washed with pentane (2 \times 5 mL). Extraction of **2b** with methylene chloride yielded 20.5 mg (0.033 mmol, >98%) of **2b** as a bright yellow solid.

$^1\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 74.12 (dd (AB), $^1J_{\text{RHP}} = 114.4$ Hz, $^2J_{\text{PP}} = 34.2$ Hz), 74.04 (dd (AB), $^1J_{\text{RHP}} = 114.4$ Hz, $^2J_{\text{PP}} = 34.2$ Hz). ^1H NMR (δ , ppm): 7.91 (d, $J = 8.0$ Hz, 1H, Ar), 7.69 (d, $J = 8.0$ Hz, 1H, Ar), 7.54 (s, 1H, Ar), 7.39 (m, 2H, Ar), 3.66 (m, ~6H, CH_2P overlapped with the signal of some dioxane), 3.45 (ddd, $J = 44.5$ Hz, $J = 15.7$ Hz, $J = 3.6$ Hz, 2H, CH_2P), 1.42 (m, 36H, $\text{PC}(\text{CH}_3)_3$), -27.42 (dt, $J = 44.2$ Hz, $J = 8.0$ Hz, 3H, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 161.02 (ddd, $J = 32.2$ Hz, $J = 5.2$ Hz, $J = 2.5$ Hz, C_{ipso}), 149.88 (ddd, $J = 11.8$ Hz, $J = 7.2$ Hz, $J = 0.8$ Hz, Ar), 146.54 (ddd, $J = 12.0$ Hz, $J = 8.1$ Hz, $J = 0.8$ Hz, Ar), 131.49 (s, Ar), 127.75 (s, Ar), 126.63 (s, Ar), 125.11 (s, Ar), 124.13 (s, Ar), 123.96 (s, Ar), 120.51 (dd, $J = 10.1$ Hz, $J = 5.0$ Hz, Ar), 36.47 (ddd, $J = 28.4$ Hz, $J = 9.4$ Hz, $J = 6.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.76 (ddd, $J = 16.2$ Hz, $J = 6.3$ Hz, $J = 1.9$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.35 (ddd, $J = 18.6$ Hz, $J = 6.2$ Hz, $J = 2.0$ Hz, CH_2P), 30.75 (ddd, $J = 18.9$ Hz, $J = 5.3$ Hz, $J = 3.1$ Hz, CH_2P), 29.89 (vt, $J = 2.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.54 (vt, $J = 3.0$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.45 (vt, $J = 2.0$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.18 (vt, $J = 3.0$ Hz, $\text{PC}(\text{CH}_3)_3$). Elemental analysis calcd for $\text{C}_{28}\text{H}_{46}\text{ClP}_2\text{Rh}$: C, 57.69; H, 7.95. Found: C, 57.56; H, 8.06.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2))_2\text{Rh}(\text{Cl})_2(\text{dioxane}))_2(\text{3a})]$. To a benzene solution (5 mL) of 45 mg (0.045 mmol) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2))_2\text{Rh}(\eta^1\text{-N}_2))]$, an excess (~5 equiv) of HCl (~4 M in dioxane) was added, accompanied by a color change from brown to yellow-brown. The reaction mixture was filtered over a cotton pad, and the solvent was removed under reduced pressure. The residue was washed with pentane (3 \times 5 mL) and dried again. The product was obtained in 44.7 mg (0.036 mmol, 82%) as a yellow-brown solid.

$^1\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 50.75 (dd (AB), $^2J_{\text{PP}} = 360.7$, $^1J_{\text{RHP}} = 96.2$ Hz), 49.82 (dd (AB), $^2J_{\text{PP}} = 360.7$, $^1J_{\text{RHP}} = 96.2$ Hz). ^1H NMR (δ , ppm): 7.41 (d, $J = 7.5$ Hz, 1H, Ar), 7.32 (d, $J = 7.5$ Hz, 1H, Ar), 7.00 (m, 2H, Ar), 6.87 (s, 1H, Ar), 3.72 (m, ~4H, CH_2 of dioxane), 3.23 (d, $J = 9.8$ Hz, 2H, CH_2P), 3.03 (d, $J = 9.7$ Hz, 2H, CH_2P), 2.49 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 2.41 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 0.96 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 0.84 (m, 12H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 141.84 (dd, $J = 11.5$ Hz, $J = 3.4$ Hz, Ar), 138.99 (dd, $J = 12.6$ Hz, $J = 3.4$ Hz, Ar), 137.50 (dt, $J = 32.9$ Hz, $J = 4.6$ Hz, C_{ipso}), 130.69 (s, Ar), 128.10 (t, $J = 6.3$ Hz, Ar), 124.72 (s, Ar), 123.08 (s, Ar), 122.33 (s, Ar), 121.21 (s, Ar), 120.27 (d, $J = 15.0$ Hz, Ar), 67.7 (s, CH_2 of dioxane), 31.25 (d, $J = 25.0$ Hz, CH_2P), 26.95 (d, $J = 27.3$ Hz, CH_2P), 22.21 (dd, $J = 16.7$ Hz, $J = 3.8$ Hz, $\text{PCH}(\text{CH}_3)_2$), 21.67 (dd, $J = 16.7$ Hz, $J = 3.9$ Hz, $\text{PCH}(\text{CH}_3)_2$), 17.54 (s, $\text{PCH}(\text{CH}_3)_2$), 17.48 (s, $\text{PCH}(\text{CH}_3)_2$), 16.61 (s, $\text{PCH}(\text{CH}_3)_2$), 16.44 (s, $\text{PCH}(\text{CH}_3)_2$). Elemental analysis calcd for $\text{C}_{52}\text{H}_{82}\text{Cl}_4\text{O}_2\text{P}_4\text{Rh}_2$: C, 51.59; H, 6.83. Found: C, 51.31; H, 6.57.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2))_2\text{Rh}(\text{CO})(\text{Cl})_2(\text{4a}))]$. To a methylene chloride solution (5 mL) of **3a** (30 mg, 0.024 mmol), CO was bubbled through the reaction solution for one minute. The color of the reaction mixture turned from yellow-brown to bright

yellow. After filtration over a cotton pad, the solvent was removed under reduced pressure, and the residue was washed with pentane (2 \times 5 mL) and dried again. **5a** was obtained in 28.0 mg (0.048 mmol, >98%) as a yellow solid.

$^1\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; δ , ppm): 64.45 (dd (AB), $^2J_{\text{PP}} = 312.6$ Hz, $^1J_{\text{RHP}} = 85.5$ Hz), 62.56 (dd (AB), $^2J_{\text{PP}} = 312.6$ Hz, $^1J_{\text{RHP}} = 85.5$ Hz). ^1H NMR (δ , ppm): 7.86 (broad s, 1H, Ar), 7.73 (broad s, 1H, Ar), 7.62 (broad s, 1H, Ar), 7.43 (m, 2H, Ar), 4.02 (d, $J = 8.0$ Hz, 2H, CH_2P), 3.84 (d, $J = 8.1$ Hz, 2H, CH_2P), 3.78 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 3.66 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.93 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.82 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 1.45 (m, 24H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 187.92 (dt, $J = 40.2$ Hz, $J = 8.1$ Hz, CO), 163.31 (broad d, $J = 21.1$ Hz, C_{ipso}), 143.86 (dd, $J = 13.4$ Hz, $J = 3.3$ Hz, Ar), 140.96 (dd, $J = 13.8$ Hz, $J = 3.4$ Hz, Ar), 132.72 (s, Ar), 128.88 (s, Ar), 128.05 (s, Ar), 125.33 (s, Ar), 124.59 (s, Ar), 124.37 (s, Ar), 122.35 (d, $J = 16.2$ Hz, Ar), 36.59 (d, $J = 29.6$ Hz, CH_2P), 33.20 (d, $J = 31.8$ Hz, CH_2P), 24.83 (dd, $J = 19.2$ Hz, $J = 4.2$ Hz, $\text{PCH}(\text{CH}_3)_2$), 24.23 (dd, $J = 15.7$ Hz, $J = 4.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.12 (s, $\text{PCH}(\text{CH}_3)_2$), 20.08 (s, $\text{PCH}(\text{CH}_3)_2$), 19.36 (s, $\text{PCH}(\text{CH}_3)_2$), 19.07 (s, $\text{PCH}(\text{CH}_3)_2$). IR (film; cm^{-1}) ν 1949 cm^{-1} (s, CO). Elemental analysis calcd for $\text{C}_{25}\text{H}_{37}\text{Cl}_2\text{OP}_2\text{Rh}$: C, 50.95; H, 6.33. Found: C, 51.08; H, 6.42.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2))_2\text{Rh}(\text{CH}_3)(\text{F}-\text{BF}_3))(\text{7a})]$. To a solution of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2))_2\text{Rh}(\text{CH}_3)(\text{I}))]$ (25 mg, 0.050 mmol) in 5 mL of methylene chloride, 1 equiv of AgBF_4 (9.6 mg, 0.0540 mmol) was added. After 15 min, the reaction mixture was filtered through celite, and the solvent was removed under reduced pressure. The residue was washed with pentane (2 \times 5 mL) and dried again. The product was obtained as a red-brown solid in almost quantitative yield (0.048 mmol, >95%).

$^1\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; δ , ppm): 74.12 (dd, $^1J_{\text{RHP}} = 120.2$ Hz, $^2J_{\text{PP}} = 47.1$ Hz), ^1H NMR (δ , ppm): 7.82 (d, $J = 7.3$ Hz, 1H, Ar), 7.75 (d, $J = 7.3$ Hz, 1H, Ar), 7.46 (m, 2H, Ar), 7.36 (s, 1H, Ar), 3.38 (dd, $J = 7.3$ Hz, $J = 3.1$ Hz, 1H, CH_2P), 2.91 (m, 2H, CH_2P), 2.83 (dd, $J = 7.3$ Hz, $J = 3.0$ Hz, 1H, CH_2P), 2.79 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.66 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.17 (dist sixt, $J = 2.1$ Hz, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.08 (dist sixt, $J = 2.1$ Hz, 1H, $\text{P}-\text{CH}(\text{CH}_3)_2$), 1.56 (broad s, 3H, Rh- CH_3), 1.26 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 1.17 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 0.92 (m, 6H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 152.18 (dt, $J = 39.2$ Hz, $J = 6.7$ Hz, C_{ipso}), 147.67 (broad s, Ar), 146.18 (broad s, Ar), 132.08 (s, Ar), 129.06 (s, Ar), 126.68 (s, Ar), 125.42 (s, Ar), 124.67 (s, Ar), 123.92 (s, Ar), 122.09 (d, $J = 11.5$ Hz, Ar), 29.96 (broad s, CH_2P), 26.83 (broad s, CH_2P), 24.73 (dt, $J = 28.8$ Hz, $J = 8.7$ Hz, $\text{PCH}(\text{CH}_3)_2$), 23.95 (dt, $J = 28.9$ Hz, $J = 8.8$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.00 (s, $\text{PCH}(\text{CH}_3)_2$), 19.70 (s, $\text{PCH}(\text{CH}_3)_2$), 18.64 (s, $\text{PCH}(\text{CH}_3)_2$), 18.35 (s, $\text{PCH}(\text{CH}_3)_2$), 18.03 (broad s, $\text{PCH}(\text{CH}_3)_2$), 17.68 (s, $\text{PCH}(\text{CH}_3)_2$), 17.47 (s, $\text{PCH}(\text{CH}_3)_2$), -3.43 (broad d, $J = 28.7$ Hz, Rh CH_3). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -167.7 (broad s, Rh $\text{F}(\text{BF}_3)$). Elemental analysis calcd for $\text{C}_{25}\text{H}_{40}\text{BF}_4\text{P}_2\text{Rh}$: C, 50.70; H, 6.81. Found: C, 50.75; H, 6.43.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2))_2\text{Rh}(\text{CO}))(\text{BF}_4)(\text{8a})]$. To a methylene chloride solution (5 mL) of **7a** (30 mg, 0.050 mmol), an excess (~50 equiv) of CO gas was added. While the reaction was being stirred for a few minutes, formation of **8a** occurred. The reaction mixture was filtrated through celite, and the solvent was removed under reduced pressure. The crude product was washed with pentane (2 \times 5 mL) and dried again. The yield of **8a** was 28.6 mg (94%).

$^1\text{P}\{^1\text{H}\}$ NMR (C_6D_6 ; δ , ppm): 23.72 (dd (AB), $J = 261.7$ Hz, $J = 101.2$ Hz), -4.97 (dd (AB), $J = 261.7$ Hz, $J = 101.2$ Hz). ^1H NMR (δ , ppm): 8.14 (d, $J_{\text{HH}} = 8.1$ Hz, 1H, Ar), 7.83 (d, $J_{\text{HH}} = 6.8$ Hz, 1H, Ar), 7.66 (t, $J_{\text{HH}} = 6.7$ Hz, 1H, Ar), 7.62 (t, $J_{\text{HH}} = 6.8$ Hz, 1H, Ar), 7.53 (s, 1H, Ar), 4.25 (dt, $J = 13.5$ Hz, $J = 4.2$ Hz, 1H, CH_2P), 3.69 (dd, $J = 14.8$ Hz, $J = 9.5$ Hz, 1H, CH_2P), 3.60 (dd, $J = 14.8$ Hz, $J = 9.5$ Hz, 1H, CH_2P), 3.36 (dt, $J = 14.8$ Hz, $J = 4.2$ Hz, 1H, CH_2P), 2.40 (s, 3H, Ar CH_3), 2.28 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 2.16 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 1.39 (m, 6H, $\text{PCH}(\text{CH}_3)_2$), 1.30 (m, 6H,

$\text{PCH}(\text{CH}_3)_2$, 1.04 (m, 12H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 187.08 (dvt, $J = 97.7$ Hz, $J = 12.5$ Hz, CO), 140.3 (s, Ar), 137.28 (s, Ar), 134.83 (s, Ar), 129.50 (d, $J = 6.7$ Hz, Ar), 128.89 (s, Ar), 128.31 (s, Ar), 127.24 (d, $J = 9.4$ Hz, Ar), 126.47 (s, Ar), 124.90 (s, Ar), 103.48 (s, ArCH₃), 26.12 (d, $J_{\text{PC}} = 18.7$ Hz, CH_2P), 25.84 (d, $J_{\text{PC}} = 22.7$ Hz, $\text{PCH}(\text{CH}_3)_2$), 25.59 (d, $J = 24.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 24.51 (d, $J = 18.7$ Hz, $\text{PCH}(\text{CH}_3)_2$), 23.90 (d, $J = 18.7$ Hz, $\text{PCH}(\text{CH}_3)_2$), 20.29 (d, $J_{\text{PC}} = 20.1$ Hz, CH_2P), 19.28 (s, $\text{PCH}(\text{CH}_3)_2$), 19.02 (s, $\text{PCH}(\text{CH}_3)_2$), 18.74 (s, $\text{PCH}(\text{CH}_3)_2$), 18.63 (s, $\text{PCH}(\text{CH}_3)_2$), 18.60 (s, $\text{PCH}(\text{CH}_3)_2$), 18.58 (s, $\text{PCH}(\text{CH}_3)_2$), 18.52 (s, $\text{PCH}(\text{CH}_3)_2$), 18.13 (s, $\text{PCH}(\text{CH}_3)_2$), 5.98 (s, ArCH₃). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -152.60 (s, BF_4). IR (film; cm^{-1}) ν 1974 (cm^{-1} (s, CO). Elemental analysis calcd for $\text{C}_{26}\text{H}_{40}\text{BF}_4\text{OP}_2\text{Rh}$: C, 50.35; H, 6.50. Found: C, 50.14; H, 6.33.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{H})(\text{F}-\text{BF}_3)]$ (9a**).** To a THF solution (5 mL) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\eta^1\text{-N}_2)]$ (30 mg, 0.030 mmol), an equimolar amount of 57% $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was slowly added. After a few minutes, the solvent was removed. The residue was washed with diethyl ether (3×10 mL), extracted with methylene chloride, and dried under vacuum to afford 28.7 mg (0.049 mmol, 82%) of **9a** as a yellow-brown solid. An alternative synthesis is possible: The addition of an equimolar amount of AgBF_4 to methylene chloride solutions of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{H})(\text{Cl})]$ (**2a**) also exclusively yielded complex **9a**.

$^3\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; δ , ppm): 67.23 (dd (AB), $^1J_{\text{RHP}} = 113.4$, $^2J_{\text{PP}} = 11.8$ Hz), 65.97 (dd (AB), $^1J_{\text{RHP}} = 113.4$, $^2J_{\text{PP}} = 11.8$ Hz). ^1H NMR (δ , ppm): 7.78 (d, $J = 5.2$ Hz, 1H, Ar), 7.64 (d, $J = 5.2$ Hz, 1H, Ar), 7.41 (m, 2H, Ar), 7.37 (t, $J = 5.2$ Hz, 1H, Ar), 3.45 (m, 3H, CH_2P), 3.23 (dvt, $J = 31.2$ Hz, $J = 7.6$ Hz, 1H, CH_2P), 2.79 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 2.26 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 1.25 (m, 24H, $\text{PCH}(\text{CH}_3)_2$), -24.32 (dt, $^1J_{\text{RHH}} = 46.4$ Hz, $^2J_{\text{PH}} = 12.4$ Hz, 1H, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 160.22 (dt, $J = 36.3$ Hz, $J = 6.8$ Hz, C_{ipso}), 148.46 (vt, $J = 7.2$ Hz, Ar), 146.31 (dd, $J = 16.3$ Hz, $J = 8.7$ Hz, Ar), 132.03 (s, Ar), 128.57 (s, Ar), 127.31 (s, Ar), 125.24 (s, Ar), 124.53 (s, Ar), 123.12 (s, Ar), 121.13 (dd, $J = 12.2$ Hz, $J = 4.8$ Hz, Ar), 34.17 (dd, $J = 12.6$ Hz, $J = 2.8$ Hz, CH_2P), 33.84 (d, $J = 12.7$ Hz, $J = 2.7$ Hz, CH_2P), 25.69 (dd, $J = 22.2$ Hz, $J = 2.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 24.75 (dd, $J = 22.5$ Hz, $J = 2.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 18.86 (m, $\text{PCH}(\text{CH}_3)_2$), 18.58 (m, $\text{PCH}(\text{CH}_3)_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -158.35 (broad s, BF_4). Elemental analysis calcd for $\text{C}_{24}\text{H}_{38}\text{BF}_4\text{P}_2\text{Rh}$: C, 49.85; H, 6.62. Found: C, 50.07; H, 6.83.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{H})(\text{F}-\text{BF}_3)]$ (9b**).** To a THF solution (5 mL) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\eta^1\text{-N}_2)]$ (40 mg, 0.068 mmol), an equimolar amount of 57% $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was slowly added. After a few minutes, the solvent was removed under reduced pressure. The residue was washed with diethyl ether (3×10 mL), extracted with methylene chloride, and dried under vacuum to afford 34.1 mg (0.054 mmol, 79%) of **9b** as a yellow-brown solid. An alternative synthesis is possible: The addition of an equimolar amount of AgBF_4 to methylene chloride solutions of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{H})(\text{Cl})]$ (**2b**) also exclusively yielded complex **9b**.

$^3\text{P}\{^1\text{H}\}$ NMR (C_6D_6 ; δ , ppm): 74.21 (dd, $J = 120.1$ Hz, $J = 24.5$ Hz). ^1H NMR (δ , ppm): 7.90 (d, $J = 8.1$ Hz, 1H, Ar), 7.74 (d, $J = 8.1$ Hz, 1H, Ar), 7.61 (s, 1H, Ar), 7.45 (t, $J = 8.1$ Hz, 1H, Ar), 7.42 (t, $J = 8.1$ Hz, 1H, Ar), 3.76 (broad s, 2H, CH_2P), 3.39 (broad s, 2H, CH_2P), 1.48 (m, 18H, $\text{PC}(\text{CH}_3)_3$), 1.32 (m, 9H, $\text{PC}(\text{CH}_3)_3$), 1.24 (m, 9H, $\text{PC}(\text{CH}_3)_3$), -27.27 (dt, $J = 53.8$ Hz, $J = 12.6$ Hz, 1H, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 164.83 (s, C_{ipso}), 148.02 (vt, $J = 8.1$ Hz, Ar), 146.93 (dd, $J = 16.6$ Hz, $J = 9.6$ Hz, Ar), 131.90 (s, Ar), 128.60 (s, Ar), 127.77 (s, Ar), 125.64 (s, Ar), 124.85 (s, Ar), 123.47 (s, Ar), 121.31 (dd, $J = 12.4$ Hz, $J = 5.0$ Hz, Ar), 37.45 (dd, $J = 12.1$ Hz, $J = 6.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 36.16 (broad t, $J = 8.3$ Hz, $\text{PC}(\text{CH}_3)_3$), 35.92 (dd, $J = 12.8$ Hz, $J = 7.4$ Hz, CH_2P), 30.58 (s, $\text{PC}(\text{CH}_3)_3$), 30.42 (s, $\text{PC}(\text{CH}_3)_3$), 28.91 (s, $\text{PC}(\text{CH}_3)_3$), 28.84 (s, $\text{PC}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -158.63

(broad s, BF_4). Elemental analysis calcd for $\text{C}_{28}\text{H}_{46}\text{BF}_4\text{P}_2\text{Rh}$: C, 53.02; H, 7.31. Found: C, 52.89; H, 7.16.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{H})(\text{CH}_2\text{Cl}_2)][\text{BAr}^F_4]$ (10a**).** To methylene chloride solution (5 mL) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{H})(\text{Cl})]$ (25 mg, 0.047 mmol), an equimolar amount of AgBAr^F_4 (41.6 mg, 0.047 mmol) was added. While the reaction mixture was being stirred for 15 min, AgCl was precipitated. The reaction mixture was filtrated through celite. Removal of the solvent under reduced pressure yielded 47.4 mg (0.033 mmol, >98%) of **10a** as a yellow oil. The oily residue was washed with 5 mL of pentane. The pentane was then decanted, and the residue was dried under reduced pressure to afford the product as a solid.

$^3\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 63.13 (very broad s). ^1H NMR (δ , ppm): 8.03 (d, $J = 8.0$ Hz, 1H, Ar), 7.81 (d, $J = 8.0$ Hz, 1H, Ar), 7.62 (s overlapped by a BAr^F_4 signal, 1H, Ar), 7.45 (m, 2H, Ar), 3.60 (dd, $J_{\text{PH}} = 14.8$ Hz, $J_{\text{RHH}} = 9.7$ Hz, 2H, CH_2P), 3.41 (dd, $J_{\text{PH}} = 14.9$ Hz, $J_{\text{RHH}} = 8.2$ Hz, 2H, CH_2P), 2.78 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.61 (m, 1H, $\text{PCH}(\text{CH}_3)_2$), 2.22 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 1.31 (m, 24H, $\text{PCH}(\text{CH}_3)_2$), -20.04 (broad d, $^1J_{\text{RHH}} = 52.6$ Hz, 1H, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 160.21 (broad s, C_{ipso}), 148.02 (dd, $J_{\text{PC}} = 13.2$ Hz, $J_{\text{RHC}} = 6.8$ Hz, Ar), 143.89 (dd, $J_{\text{PC}} = 13.0$ Hz, $J_{\text{RHC}} = 6.5$ Hz, Ar), 133.41 (s, Ar), 120.03 (s, Ar), 126.43 (s, Ar), 124.97 (s, Ar), 124.76 (s, Ar), 124.02 (s, Ar), 116.11 (d, $J = 11.4$ Hz, Ar), 38.17 (d, $J = 16.5$ Hz, CH_2P), 33.44 (d, $J = 16.6$ Hz, CH_2P), 25.89 (dd, $J = 23.8$ Hz, $J = 2.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 24.59 (dd, $J = 26.2$ Hz, $J = 2.7$ Hz, $\text{PCH}(\text{CH}_3)_2$), 18.93 (m, $\text{PCH}(\text{CH}_3)_2$), 18.75 (m, $\text{PCH}(\text{CH}_3)_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -63.33 (s, BAr^F_4). Elemental analysis of **10a** obtained from THF solution: calcd for $\text{C}_{60}\text{H}_{58}\text{BF}_{24}\text{OP}_2\text{Rh}$: C, 50.51; H, 4.10. Found: C, 50.73; H, 4.35.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{H})(\text{CH}_2\text{Cl}_2)][\text{BAr}^F_4]$ (10b**).** To methylene chloride solution (5 mL) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{H})(\text{Cl})]$ (20 mg, 0.034 mmol), an equimolar amount of AgBAr^F_4 (33.3 mg, 0.034 mmol) was added and stirred for 20 min. The reaction mixture was filtrated through celite. Removal of the solvent under reduced pressure yielded 47.4 mg (0.033 mmol, >98%) of **10b** as a yellow oil. The oily residue was washed with 5 mL of pentane. The pentane was then decanted, and the residue was dried under reduced pressure to afford the product as a solid.

$^3\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 76.94 (very broad s). ^1H NMR (δ , ppm): 7.95 (d, $J = 7.9$ Hz, 1H, Ar), 7.76 (d, $J = 8.0$ Hz, 1H, Ar), 7.63 (s overlapped by a BAr^F_4 signal, 1H, Ar), 7.49 (m, 2H, Ar), 3.71 (d, $J = 8.0$ Hz, 2H, CH_2P), 3.51 (ddd, $J = 48.8$ Hz, $J = 16.2$ Hz, $J = 8.0$ Hz, 2H, CH_2P), 1.36 (m, 36H, $\text{PC}(\text{CH}_3)_3$), -27.18 (broad d, $J = 55.4$ Hz, 1H, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 164.42 (broad s, C_{ipso}), 147.14 (ddd, $J = 14.3$ Hz, $J = 5.3$ Hz, $J = 0.9$ Hz, Ar), 142.28 (m, Ar), 132.28 (s, Ar), 130.41 (d, $J = 8.3$ Hz, Ar), 128.12 (s, Ar), 126.16 (s, Ar), 125.85 (s, Ar), 124.13 (s, Ar), 115.55 (d, $J = 11.2$ Hz, Ar), 36.82 (ddd, $J = 15.1$ Hz, $J = 13.3$ Hz, $J = 3.6$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.83 (ddd, $J = 18.5$ Hz, $J = 13.1$ Hz, $J = 3.9$ Hz, $\text{PC}(\text{CH}_3)_3$), 32.41 (broad d, $J = 16.5$ Hz, 2 CH_2P), 30.08 (s, $\text{PC}(\text{CH}_3)_3$), 29.72 (s, $\text{PC}(\text{CH}_3)_3$), 29.51 (s, $\text{PC}(\text{CH}_3)_3$), 29.25 (s, $\text{PC}(\text{CH}_3)_3$). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -63.26 (s, BAr^F_4). Elemental analysis of **10b** obtained from THF solution: calcd for $\text{C}_{64}\text{H}_{66}\text{BF}_{24}\text{OP}_2\text{Rh}$: C, 51.85; H, 4.49. Found: C, 52.07; H, 4.71.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{CO}))[\text{X}]]$ (X** = BAr^F_4 **11a**, **X** = BF_4 **11a'**).** To an etheral solution (5 mL) of 35 mg (0.067 mmol) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{CO}))]$, an equimolar amount of $[\text{H}(\text{Et}_2\text{O})][\text{BAr}^F_4]$ was added. A few minutes after its addition, the solvent was evaporated under reduced pressure. The residue was washed with pentane (5×5 mL) and dried, affording 73.4 mg (0.053 mmol, 78%) of **11a**. To an etheral solution (5 mL) of 35 mg (0.067 mmol) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{CO}))]$, an equimolar amount of 57% $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was slowly added. During the addition, a yellow powder precipitated. The solvent was decanted, and the residue was washed with diethyl ether (2×10 mL) and dried under reduced pressure to afford 36.4 mg (0.060 mmol, 89%) of **11a'** as a bright yellow solid.

Data for **11a**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 35.52 (dd left part of an AX system, $J = 248.2$ Hz, $J = 104.5$ Hz), 16.86 (dd right part of an AX system, $J = 248.2$ Hz, $J = 103.8$ Hz). ^1H NMR (δ , ppm): 8.19 (d, $J = 7.8$ Hz, 1H, Ar), 7.84 (d, $J = 7.8$ Hz, 1H, Ar), 7.77 (s, 1H, Ar), 7.66 (m, 2H, Ar), 3.91 (d, 1H, $J = 10.8$ Hz, ArHRh), 3.73 (m, 3H, overlapping signals of CH_2P), 3.37 (vtd, 1H, $J = 12.0$ Hz, $J = 3.9$ Hz, CH_2P), 2.37 (m, 4H, $\text{PCH}(\text{CH}_3)_2$), 1.37 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 1.04 (m, 12H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 183.95 (dt, $J = 90.5$ Hz, $J = 12.1$ Hz, CO), 155.74 (s, Ar), 144.12 (s, Ar), 141.80 (s, Ar), 138.86 (s, Ar), 130.80 (s, Ar), 129.34 (s, Ar), 128.42 (d, $J = 7.8$ Hz, Ar), 127.60 (d, $J = 20.4$ Hz, Ar), 124.42 (s, Ar), 110.13 (s, Ar), 32.07 (d, $J = 16.5$ Hz, CH_2P), 30.98 (d, $J = 16.5$ Hz, CH_2P), 26.42 (dd, $J = 23.5$ Hz, $J = 2.0$ Hz, $\text{PCH}(\text{CH}_3)_2$), 24.72 (dd, $J = 24.0$ Hz, $J = 2.2$ Hz, $\text{PCH}(\text{CH}_3)_2$), 19.07 (m, $\text{PCH}(\text{CH}_3)_2$), 18.42 (m, $\text{PCH}(\text{CH}_3)_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -63.31 (s, BArF_4). IR (film; cm^{-1}) ν 1997 cm^{-1} (s, CO). Elemental analysis calcd for $\text{C}_{57}\text{H}_{50}\text{BF}_{24}\text{OP}_2\text{Rh}$: C, 49.52; H, 6.64. Found: C, 49.23; H, 6.52. Data for **11a'**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 35.52 (dd left part of an AX system, $J = 248.2$ Hz, $J = 104.5$ Hz), 16.86 (dd right part of an AX system, $J = 248.2$ Hz, $J = 103.8$ Hz). ^1H NMR (δ , ppm): 8.14 (d, $J = 7.8$ Hz, 1H, Ar), 7.80 (d, $J = 7.8$ Hz, 1H, Ar), 7.76 (s, 1H, Ar), 7.67 (m, 2H, Ar), 3.90 (d, 1H, $J = 10.8$ Hz, ArHRh), 3.74 (m, 3H, overlapping signals of CH_2P), 3.39 (vtd, 1H, $J = 12.0$ Hz, $J = 3.9$ Hz, CH_2P), 2.42 (m, 4H, $\text{PCH}(\text{CH}_3)_2$), 1.35 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 1.11 (m, 12H, $\text{PCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 183.89 (dt, $J = 90.5$ Hz, $J = 12.1$ Hz, CO), 155.69 (s, Ar), 144.10 (s, Ar), 141.82 (s, Ar), 138.81 (s, Ar), 130.97 (s, Ar), 129.32 (s, Ar), 128.41 (d, $J = 7.8$ Hz, Ar), 127.59 (d, $J = 20.4$ Hz, Ar), 124.42 (s, Ar), 109.94 (s, Ar), 31.99 (d, $J = 16.5$ Hz, CH_2P), 31.02 (d, $J = 16.5$ Hz, CH_2P), 26.39 (dd, $J = 23.8$ Hz, $J = 2.0$ Hz, $\text{PCH}(\text{CH}_3)_2$), 24.72 (dd, $J = 24.1$ Hz, $J = 2.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 19.15 (m, $\text{PCH}(\text{CH}_3)_2$), 18.68 (m, $\text{PCH}(\text{CH}_3)_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -152.64 (s, BF_4). IR (film; cm^{-1}) ν 1997 cm^{-1} (s, CO). Elemental analysis calcd for $\text{C}_{25}\text{H}_{38}\text{BF}_4\text{OP}_2\text{Rh}$: C, 49.53; H, 6.32. Found: C, 49.46; H, 6.28.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{H})(\text{CO}))][\text{X}]$ ($\text{X} = \text{BArF}_4$ **11b, $\text{X} = \text{BF}_4$ **11b'**).** To an ethereal solution (5 mL) of 30 mg (0.052 mmol) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{CO}))]$, an equimolar amount of $[\text{H}(\text{Et}_2\text{O})][\text{BArF}_4]$ was added. A few minutes after the addition, the solvent was evaporated under reduced pressure. The residue was washed with pentane (5×5 mL) and dried, affording 55.6 mg (0.039 mmol, 74%) of **10b**. To an ethereal solution (5 mL) of 30 mg (0.052 mmol) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{CO}))]$, an equimolar amount of 57% $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was slowly added. During the addition, a yellow powder precipitated. The solvent was decanted, and the residue was washed with diethyl ether (2×10 mL) and dried under reduced pressure to afford 33.4 mg (0.050 mmol, 97%) of **11b'** as a bright yellow solid.

Data for **11b**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 47.57 (dd left part of an AX system, $J = 247.2$ Hz, $J = 103.1$ Hz), 30.89 (dd right part of an AX system, $J = 247.2$ Hz, $J = 99.6$ Hz). ^1H NMR (δ , ppm): 8.18 (d, $J = 8.0$ Hz, 1H, Ar), 7.93 (d, $J = 8.0$ Hz, 1H, Ar), 7.77 (m, 2H, Ar), 7.66 (s, 1H, Ar), 4.10 (broad t, $J = 12.2$ Hz, 1H, CH_2P), 3.87 (d, $J = 16.5$ Hz, 1H, ArHRh), 3.64 (ddd, $J = 36.7$ Hz, $J = 20.1$ Hz, $J = 8.0$ Hz, 2H, CH_2P), 3.44 (broad t, $J = 12.1$ Hz, 1H, CH_2P), 1.57 (d, $J = 14.5$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$), 1.53 (d, $J = 14.5$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$), 1.27 (d, $J = 14.5$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 188.62 (dt, $J = 91.3$ Hz, $J = 11.6$ Hz, CO), 156.28 (s, Ar), 144.56 (s, Ar), 138.77 (s, Ar), 131.56 (s, Ar), 129.89 (s, Ar), 129.62 (d, $J = 8.0$ Hz, Ar), 129.26 (s, Ar), 127.03 (d, $J = 19.4$ Hz, Ar), 125.90 (s, Ar), 109.65 (s, Ar), 37.74 (dd, $J = 29.8$ Hz, $J = 14.4$ Hz, $\text{PC}(\text{CH}_3)_3$), 35.57 (dd, $J = 16.2$ Hz, $J = 9.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 31.23 (d, $J = 17.7$ Hz, CH_2P), 29.90 (d, $J = 2.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.62 (d, $J = 3.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.20 (d, $J = 3.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.08 (d, $J = 3.4$ Hz, $\text{PC}(\text{CH}_3)_3$), 26.35 (d, $J = 17.8$ Hz, CH_2P). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -63.12 (s, BArF_4). IR (film; cm^{-1}) ν 1987 cm^{-1} (s, CO). Elemental analysis calcd for

$\text{C}_{61}\text{H}_{58}\text{BF}_{24}\text{OP}_2\text{Rh}$: C, 50.92; H, 4.06. Found: C, 50.94; H, 4.19. Data for **11b'**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 47.61 (dd left part of an AX system, $J = 247.1$ Hz, $J = 102.9$ Hz), 30.86 (dd right part of an AX system, $J = 247.2$ Hz, $J = 99.5$ Hz). ^1H NMR (δ , ppm): 8.18 (d, $J = 8.0$ Hz, 1H, Ar), 7.91 (d, $J = 8.0$ Hz, 1H, Ar), 7.79 (m, 2H, Ar), 7.67 (s, 1H, Ar), 4.11 (broad t, $J = 12.1$ Hz, 1H, CH_2P), 3.87 (d, $J = 16.4$ Hz, 1H, ArHRh), 3.63 (ddd, $J = 36.6$ Hz, $J = 20.2$ Hz, $J = 8.1$ Hz, 2H, CH_2P), 3.46 (broad t, $J = 12.2$ Hz, 1H, CH_2P), 1.54 (d, $J = 14.5$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$), 1.50 (d, $J = 14.5$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$), 1.25 (d, $J = 14.4$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 188.65 (dt, $J = 91.2$ Hz, $J = 11.6$ Hz, CO), 156.298 (s, Ar), 144.60 (s, Ar), 138.81 (s, Ar), 131.52 (s, Ar), 129.87 (s, Ar), 129.62 (d, $J = 8.0$ Hz, Ar), 129.26 (s, Ar), 127.01 (d, $J = 19.3$ Hz, Ar), 125.94 (s, Ar), 109.64 (s, Ar), 37.78 (dd, $J = 29.8$ Hz, $J = 14.4$ Hz, $\text{PC}(\text{CH}_3)_3$), 35.55 (dd, $J = 16.2$ Hz, $J = 9.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 31.22 (d, $J = 17.5$ Hz, CH_2P), 29.93 (d, $J = 2.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.62 (d, $J = 3.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.20 (d, $J = 3.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.11 (d, $J = 3.4$ Hz, $\text{PC}(\text{CH}_3)_3$), 26.38 (d, $J = 17.8$ Hz, CH_2P). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -152.52 (s, BF_4). IR (film; cm^{-1}) ν 1987 cm^{-1} (s, CO). Elemental analysis calcd for $\text{C}_{29}\text{H}_{46}\text{BF}_4\text{OP}_2\text{Rh}$: C, 52.59; H, 7.00. Found: C, 52.74; H, 7.15.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{H})(\text{CO}))][\text{BF}_4]$ (13a**).** A young NMR tube containing 25 mg (0.041 mmol) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Pr}_2)_2)\text{Rh}(\text{CO}))][\text{BF}_4]$ dissolved in 0.7 mL of CDCl_3 was charged with CO gas (1.5 atm). The orange solution turned to bright yellow immediately, exclusively yielding complex **13a**.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 ; δ , ppm, -50°C): 79.54 (dd, $^1J_{\text{RHP}} = 92.8$ Hz, $^2J_{\text{PP}} = 51.9$ Hz). ^1H NMR (δ , ppm, -50°C): 7.83 (d, $J = 5.1$ Hz, 1H, Ar), 7.68 (d, $J = 5.1$ Hz, 1H, Ar), 7.67 (s, 1H, Ar), 7.44 (m, 2H, Ar), 3.93 (vt, $J = 5.3$ Hz, 1H, CH_2P), 3.91 (vt, $J = 5.2$ Hz, 1H, CH_2P), 3.70 (vt, $J = 5.5$ Hz, 2H, CH_2P), 2.63 (m, 4H, $\text{PCH}(\text{CH}_3)_2$), 1.39 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), 1.07 (m, 12H, $\text{PCH}(\text{CH}_3)_2$), -7.88 (broad s, 1H, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm, -50°C): 184.43 (dvt, $^1J_{\text{RHP}} = 40.7$ Hz, $J_{\text{PC}} = 6.8$ Hz, CO), 183.87 (dvt, $^1J_{\text{RHP}} = 42.1$ Hz, $J_{\text{PC}} = 7.1$ Hz, CO), 146.42 (d, $^1J_{\text{RHC}} = 22.5$ Hz, Ar), 142.60 (d, $^2J_{\text{PC}} = 7.5$ Hz, Ar), 141.86 (d, $J = 7.1$ Hz, Ar), 132.74 (s, Ar), 129.77 (s, Ar), 128.25 (s, Ar), 126.84 (s, Ar), 126.04 (s, Ar), 124.61 (s, Ar), 124.05 (vt, $J = 6.8$ Hz, Ar), 36.97 (vt, $J = 15.8$ Hz, CH_2P), 34.68 (vt, $J = 15.4$ Hz, CH_2P), 27.78 (dvt, $^2J_{\text{RHP}} = 40.7$ Hz, $J_{\text{PP}} = 12.2$ Hz, $\text{PCH}(\text{CH}_3)_2$), 26.37 (dvt, $J = 12.5$ Hz, $^2J_{\text{RHP}} = 1.1$ Hz, $\text{PCH}(\text{CH}_3)_2$), 19.29 (m, $\text{PCH}(\text{CH}_3)_2$), 18.44 (m, $\text{PCH}(\text{CH}_3)_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR (δ , ppm): -153.57 (s, BF_4). IR (CHCl_3 ; cm^{-1}) ν 2129 (m), 2120 (w), 2097 (s), 2085 (s). An elemental analysis was not possible because of liberation of CO ligand under reduced pressure.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{Bu}_2)_2)\text{Rh}(\text{H})(\text{Cl})(\text{CO}))]$ (14b** and **14b'**).** Methylene chloride solutions (5 mL) of 30 mg of **2b** (0.045 mmol) were set under a CO atmosphere. After the solvent was removed under reduced pressure, the residue was washed with diethyl ether (3×5 mL) and dried under reduced pressure, affording 20.7 mg (0.034 mmol, 74%) of an isomeric mixture of **14b** and **14b'** as bright yellow powder.

Data for **14b'**: $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 95.21 (dd left part of an AB system, $^2J_{\text{PP}} = 315.4$ Hz, $^1J_{\text{RHP}} = 98.4$ Hz), 94.15 (dd right part of an AB system, $^2J_{\text{PP}} = 315.4$ Hz, $^1J_{\text{RHP}} = 98.4$ Hz). ^1H NMR (δ , ppm): 7.81 (d, $J = 8.1$ Hz, 1H, Ar), 7.61 (d, $J = 8.1$ Hz, 1H, Ar), 7.48 (s, 1H, Ar), 7.37 (m, 2H, Ar), 4.07 (dd, $J = 15.8$ Hz, $J = 8.7$ Hz, 1H, CH_2P), 3.56 (m, 4H, overlapped with CH_2P signals of **14b**), 3.09 (dd, $J = 10.3$ Hz, $J = 5.7$ Hz, 1H, CH_2P), 1.41 (m, 18H, overlapped with $\text{PC}(\text{CH}_3)_3$ signals of **14b**), 1.26 (m, 18H, overlapped with $\text{PC}(\text{CH}_3)_3$ signals of **14b**), -15.32 (dt, 1H, $^2J_{\text{PH}} = 9.2$ Hz, $^1J_{\text{RHH}} = 4.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 193.81 (dt, $J = 43.9$ Hz, $J = 9.5$ Hz, CO), 169.75 (d, $^1J_{\text{RHC}} = 25.9$ Hz, C_{ipso}), 146.44 (dd, $^2J_{\text{PC}} = 12.7$ Hz, $^2J_{\text{RHC}} = 3.2$ Hz, Ar), 141.57 (dd, $^2J_{\text{PC}} = 9.5$ Hz, $^2J_{\text{RHC}} = 5.1$ Hz, Ar), 133.11 (s, Ar), 128.87 (s, Ar), 128.43 (s, Ar), 126.92 (s, Ar), 125.13 (s, Ar), 124.94 (s, Ar), 121.02 (d, $J = 15.7$ Hz, Ar), 38.09 (dvt, $J = 34.1$ Hz, $J = 8.2$ Hz,

overlapping signals with $\text{PC}(\text{CH}_3)_3$ of **14b**), 36.73 (m, overlapping signals with $\text{PC}(\text{CH}_3)_3$ of **14b**), 33.78 (d, $J = 21.3$ Hz, CH_2P), 29.76 (d, $J = 4.0$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.54 (d, $J = 3.9$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.14 (d, $J = 2.8$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.03 (d, $J = 3.8$ Hz, $\text{PC}(\text{CH}_3)_3$), 28.52 (d, $J = 20.8$ Hz, CH_2P). IR (film; cm^{-1}) ν 2033 cm^{-1} (s, CO). Data for **14b**: $^1\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 ; δ , ppm): 86.74 (dd left part of an AB system, $^2J_{\text{PP}} = 328.8$ Hz, $^1J_{\text{RHP}} = 104.5$ Hz), 86.44 (dd right part of an AB system, $^2J_{\text{PP}} = 328.8$ Hz, $^1J_{\text{RHP}} = 104.5$ Hz). ^1H NMR (δ , ppm): 7.78 (d, $J = 8.1$ Hz, 1H, Ar), 7.70 (d, $J = 8.0$ Hz, 1H, Ar), 7.34 (m, 2H, Ar), 7.25 (s, 1H, Ar), 3.97 (dd, $J = 15.6$ Hz, $J = 8.7$ Hz, 1H, CH_2P), 3.56 (m, 4H, overlapped with CH_2P signals of **14b'**), 2.98 (dd, $J = 10.5$ Hz, $J = 7.1$ Hz, 1H, CH_2P), 1.41 (m, 18H, overlapped with $\text{PC}(\text{CH}_3)_3$ signals of **14b'**), 1.26 (m, 18H, overlapped with $\text{PC}(\text{CH}_3)_3$ signals of **14b'**), -7.67 (dt, 1H, $^2J_{\text{PH}} = 8.6$ Hz, $^1J_{\text{RHH}} = 8.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 188.62 (dt, $J = 45.2$ Hz, $J = 5.7$ Hz, CO), 155.97 (d, $^1J_{\text{RHC}} = 29.9$ Hz, C_{ipso}), 145.74 (dd, $^2J_{\text{PC}} = 9.5$ Hz, $^2J_{\text{RHC}} = 5.7$ Hz, Ar), 140.69 (dd, $^2J_{\text{PC}} = 14.6$ Hz, $^2J_{\text{RHC}} = 3.2$ Hz, Ar), 133.38 (s, Ar), 129.03 (s, Ar), 128.65 (s, Ar), 125.64 (s, Ar), 124.77 (s, Ar), 124.10 (s, Ar), 121.48 (d, $J = 12.8$ Hz, Ar), 38.09 (dvt, $J = 34.1$ Hz, $J = 8.2$ Hz, overlapping signals with $\text{PC}(\text{CH}_3)_3$ of **14b**), 36.73 (m, overlapping signals with $\text{PC}(\text{CH}_3)_3$ of **14b**), 32.56 (d, $J = 21.3$ Hz, CH_2P), 29.94 (d, $J = 4.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.62 (d, $J = 3.8$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.20 (d, $J = 3.1$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.08 (d, $J = 3.6$ Hz, $\text{PC}(\text{CH}_3)_3$), 28.76 (d, $J = 21.0$ Hz, CH_2P). IR (film; cm^{-1}) ν 2062 cm^{-1} (s, CO). Elemental analysis calcd for $\text{C}_{29}\text{H}_{46}\text{ClOP}_2\text{Rh}$: C, 57.01; H, 7.59. Found: C, 56.86; H, 7.34.

Preparation of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{iPr})_2)\text{Rh}(\text{H})(\text{Cl})(\text{CO}))]$ (14a'**).** THF solutions (5 mL) of 20.0 mg (0.038 mmol) of $[(\text{C}_{10}\text{H}_5(\text{CH}_2\text{P}(\text{iPr})_2)\text{Rh}(\text{CO}))]$ were treated with an equimolar amount of hydrochloric acid (~4.0 M in dioxane). After the solvent was removed under reduced pressure, the residue was extracted with

diethyl ether (2×5 mL) and dried under reduced pressure, affording 20.2 mg (0.036 mmol, 96%) of **14a'** as bright yellow powder.

$^1\text{P}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$; δ , ppm): 79.03 (dd (AB), $^2J_{\text{PP}} = 320.4$ Hz, $^1J_{\text{RHP}} = 97.1$ Hz), 78.44 (dd (AB), $^2J_{\text{PP}} = 320.4$ Hz, $^1J_{\text{RHP}} = 97.1$ Hz). ^1H NMR (δ , ppm): 7.79 (d, $J = 7.9$ Hz, 1H, Ar), 7.59 (d, $J = 7.9$ Hz, 1H, Ar), 7.47 (s, 1H, Ar), 7.31 (m, 2H, Ar), 3.94 (dvt, 2H, $^2J_{\text{PH}} = 8.0$ Hz, CH_2P), 3.53 (dvt, 2H, $^2J_{\text{PH}} = 8.0$ Hz, CH_2P), 2.92 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 2.35 (m, 2H, $\text{PCH}(\text{CH}_3)_2$), 1.29 (m, 24H, $\text{PCH}(\text{CH}_3)_2$), -14.89 (dt, 1H, $^2J_{\text{PH}} = 27.0$ Hz, $^1J_{\text{RHH}} = 9.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 189.78 (dt, $J = 41.2$ Hz, $J = 9.3$ Hz, CO), 169.13 (d, $^1J_{\text{RHC}} = 26.1$ Hz, C_{ipso}), 145.23 (dd, $^2J_{\text{PC}} = 12.5$ Hz, $^2J_{\text{RHC}} = 3.0$ Hz, Ar), 141.31 (dd, $^2J_{\text{PC}} = 9.2$ Hz, $^2J_{\text{RHC}} = 4.9$ Hz, Ar), 133.41 (s, Ar), 129.02 (s, Ar), 128.29 (s, Ar), 126.43 (s, Ar), 125.01 (s, Ar), 124.87 (s, Ar), 121.31 (d, $J = 15.8$ Hz, Ar), 37.77 (dvt, $J = 34.2$ Hz, $J = 8.1$ Hz), 36.58 (m), 33.63 (d, $J = 21.1$ Hz, CH_2P), 29.49 (d, $J = 3.8$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.32 (d, $J = 3.9$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.04 (d, $J = 2.7$ Hz, $\text{PC}(\text{CH}_3)_3$), 28.94 (d, $J = 3.6$ Hz, $\text{PC}(\text{CH}_3)_3$), 28.47 (d, $J = 20.9$ Hz, CH_2P). IR (film; cm^{-1}) ν 2041 cm^{-1} (s, CO). Elemental analysis calcd for $\text{C}_{25}\text{H}_{38}\text{ClOP}_2\text{Rh}$: C, 54.12; H, 6.90. Found: C, 54.44; H, 7.21.

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Supporting Information Available: CIF file containing X-ray crystallographic data for complex **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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