Exclusive C−C Activation and an Apparent α-H Elimination with a Rhodium Phosphinite Pincer Complex

Hiyam Salem,[†] Yehoshoa Ben-David,[†] Linda J. W. Shimon,[‡] and David Milstein*,[†]

Department of Organic Chemistry and Unit of Chemical Research Support, The Weizmann Institute of Science, Rehovot, 76100, Israel

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Exclusive C−C bond activation involving the new bisphosphinite ligand $\{C_6H_3(CH_3)[OP(^iPr)_2]_2\}$ (**1**) was observed at room temperature, upon reaction with the cationic complex $[Rh(COE)_2(THF)_2]BF_4$ (COE = cyclooctene) in THF, yielding the Rh(III) complex $[(POCOP)Rh(Me)]BF_4$ (**2**) (POCOP = $C_6H_3[OP(^iPr)_2]_2$). No parallel C−H activation was observed. This preference is assumed to be governed by the better directed phosphinite-bound metal center toward the C−C bond. A single-crystal X-ray diffraction analysis of complex **2** revealed a square pyramidal geometry with the BF_4^- ion coordinated to the metal center. Complex **2** reacted with H_2 at room temperature in THF to yield the Rh(III)-hydrido complex **3** and methane. Deprotonation of **3** with KO^{t}Bu yielded the Rh(I) dinitrogen complex $[(POCOP)Rh]_2(\mu\text{-}N_2)$ (**4**), which upon reaction with 1 equiv of CO or ethylene formed (POCOP)Rh(CO) (**5**) or (POCOP)Rh-(C_2H_4) (**6**), respectively. Complex **4** readily underwent oxidative addition of MeI, benzyl chloride, and benzyl bromide, forming complexes **7**, **8**, and **9**, respectively. Halide abstraction from complex **9** with $AgBF_4$ led to the cationic benzyl complex **12**, bearing a coordinated BF_4^- ion as observed by a single-crystal X-ray diffraction analysis. Finally, we report an apparent α-H elimination from Rh(III)−Me, which takes place upon heating of the C−C activation product **2** at 150 °C in the solid state, yielding the hydride complex **3** and ethylene.

Introduction

Insertion of transition metal complexes into C−C single bonds in solution is a topic of considerable current interest.[1−3] C−H activation is normally expected to be thermodynamically and kinetically favored over C−C activation,[1,4] although systems that can provide thermodynamic and kinetic driving forces for C−C bond activation can be designed. We have demonstrated that PCP[3a,5] (i.e., symmetric pincer system with two phosphine arms), and PCN[3b] and PCO[3i] (asymmetric pincer systems with one phosphine arm and one amine or methoxy arm, respectively) undergo very facile activation of strong, nonstrained C−C bonds situated between the two chelating arms of the ligand. We reported the first observation of a single-step metal insertion into a C−C bond in solution (which takes place at a temperature as low as −70 °C) and have provided the activation parameters for such a process.[3f] The balance between the competitive C−C and C−H activation processes, which proceed from the same intermediates, is sensitive to the nature of the ligand "arms", as observed experimentally[3,5] and theoretically.[6] Using a PCN−Rh system, we observed a unique preference for C−C activation, the normally competing C−H activation process not being detected.[3a] In these studies we employed phosphine-type pincer ligands. It was of interest to us to see the effect of employing the weaker *σ*-donor phosphinite (rather than phosphine) ligands on the C−C and C−H activation processes.

Here we report a direct metal insertion into a strong C−C bond with a new *phosphinite* pincer-type ligand and a cationic Rh(I) system, which takes place at *room temperature*. This system gives exclusively the C−C insertion product, which is characterized crystallographically, with no observation of

* Corresponding author. E-mail: david.milstein@weizmann.ac.il. Fax: 972-8-9344142.

† Department of Organic Chemistry.

‡ Unit of Chemical Research Support.

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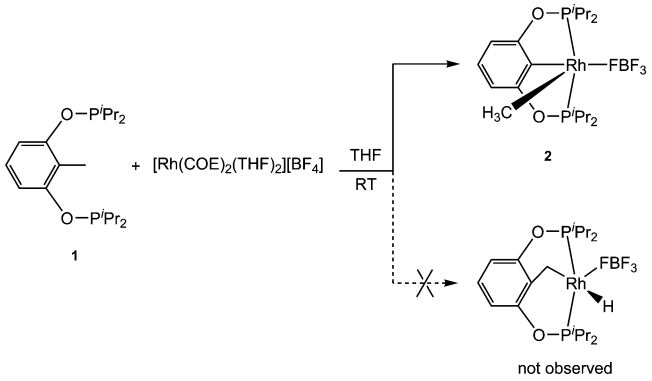
Scheme 1



parallel formation of the C−H activation product. Moreover, we report a rare α-H elimination process that takes place upon heating of the C−C activation product in the solid state. Reactivity of the new phosphinite POCOP-type rhodium complexes is also reported.

Results and Discussion

Formation of [(POCOP)Rh(CH$_3$)]BF$_4$ by C−C Activation. Ligand **1**, 1,3-(di-isopropylphosphino)-2-methylresorcinol, was synthesized in analogy with a reported synthesis of {C$_6$H$_3$-1,3-P(O^{i}Pr$_2$)$_2$},[7] by diphosphination of 2-methyl resorcinol with di-isopropylchlorophosphine using 4-(dimethylamino)pyridine as a base. Reaction of [Rh(COE)$_2$Cl]$_2$[8] (COE = cyclooctene) with ligand **1** in benzene resulted in a mixture of compounds. On the other hand, reaction of the cationic complex [Rh(COE)$_2$(THF)$_2$]BF$_4$[9] with ligand **1** *at room temperature* led to the immediate formation of the C−C activation complex [(POCOP)-Rh(CH$_3$)]BF$_4$ (**2**) (Scheme 1) as the main product (∼70%). No Rh−H complex was formed. Complex **2** was purified by crystallization. Phosphinite pincer complexes of Rh are not known. However, phosphinite pincer complexes of Ir[10] and Pd[11] have been reported recently.

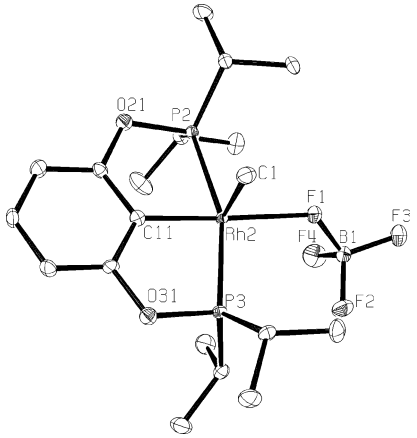


Figure 1. ORTEP plot of complex **2** at the 50% probability level. Hydrogen atoms are omitted for clarity.

The ^{31}P{^{1}H} NMR spectrum of **2** exhibits a doublet at δ 172.78 with a $^1J_{Rh,P}$ of 128.3 Hz, indicative of two chemically equivalent phosphorus nuclei coordinated to a Rh(III) center. The Rh−Me group exhibits a triplet of doublets and a doublet of triplets in ^{1}H and ^{13}C NMR at δ 1.37 and 1.31 ($^2J_{Rh,H}$ = 2.2 Hz, $^3J_{P,H}$ = 5.2 Hz, $^1J_{Rh,C}$ = 28.8 Hz, $^2J_{P,C}$ = 5.2 Hz), respectively. These data are characteristic of a methyl group *trans* to a vacant coordination site.[3a,c] ^{19}F NMR of **2** in benzene exhibits a broad singlet at δ −163.26, indicative of BF$_4^-$ ion coordination to the metal center (free BF$_4^-$ ion exhibits a singlet at δ −151). The broad BF$_4$ signal indicates that it is fluxional. Similar chemical shift and broadening in the ^{19}F NMR signal were observed recently with a Rh PCN system involving coordinated BF$_4^-$.[12]

Crystals of complex **2** suitable for X-ray analysis were grown from a warm benzene solution. The rhodium atom is centered in the base of a slightly distorted square pyramid, with the methyl group at the axial position (Figure 1). The angles C(1)−Rh−P(2)/P(3), C(11)−Rh−C(1), and C(1)−Rh−F(1) are close to 90° (92.40°, 90.77°, 89.11°, and 91.64°, respectively). The Rh−CH$_3$ bond length is 2.05 Å, while the Rh−C$_{ipso}$ bond length is 1.97 Å (Table 1). Analogous PCP and PCO systems having an apical methyl group are the neutral Rh(Me){2,6-(CH$_2$P^{t}Bu$_2$)$_2$-3,5-(CH$_3$)$_2$-C$_6$H}Cl[3a] and the cationic Rh(CH$_3$){2-(CH$_2$P-^{t}Bu$_2$)6-(CH$_2$OMe)C$_6$H$_3$}BF$_4$,[3i] where the Rh−CH$_3$ bonds are 2.16 and 2.02 Å, respectively, and the Rh−C$_{ipso}$ bond lengths are 2.02 and 1.95 Å, respectively. Thus, the Rh−CH$_3$ and Rh−C$_{ipso}$ bond lengths of the cationic complexes are considerably shorter than in the neutral complex.

The position *trans* to the *ipso* carbon is occupied by BF$_4^-$, which is coordinated to the rhodium center through one of its

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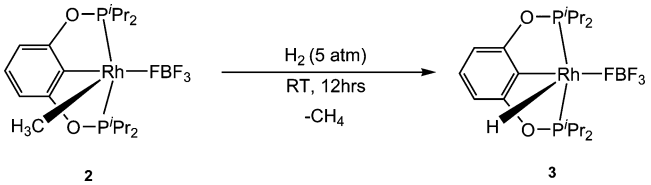
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Rh(2)−C(11)	1.973 (3)	F(1)−B(1)	1.449 (4)
Rh(2)−C(1)	2.050 (3)	F(2)−B(1)	1.384 (4)
Rh(2)−P(2)	2.3130 (10)	F(3)−B(1)	1.374 (4)
Rh(2)−P(3)	2.3164 (11)	F(4)−B(1)	1.383 (5)
Rh(2)−F(1)	2.243 (2)		
C(11)−Rh(2)−C(1)	89.11 (14)	P(2)−Rh(2)−P(3)	160.98 (3)
C(1)−Rh(2)−F(1)	91.64 (11)	C(11)−Rh(2)−P(2)	80.37 (10)
C(1)−Rh(2)-P(2)	92.40 (10)	C(11)−Rh(2)-P(3)	80.94 (10)
C(1)−Rh(2)-P(3)	90.77 (10)	F(1)−Rh(2)-P(2)	96.49 (6)
C(11)−Rh(2)-F(1)	176.80 (10)	F(1)−Rh(2)-P(3)	102.16 (6)

Scheme 2



fluorine atoms, F(1). The length of the Rh−F(1) bond is 2.24 Å. The B−F(1) bond (1.45 Å) is longer than the other B−F bonds (1.37−1.38 Å), as expected from BF_4^- coordination to the metal center. Coordination of BF_4^- is not common. To the best of our knowledge, only one other crystal structure containing a Rh−FBF_3 was reported,[3i] and three Rh−FBF_3 complexes were characterized in solution.[3i,12,13]

Since no hydride complex was observed in the ^{1}H NMR spectrum of the reaction mixture before purification (measured at 25 and −80 °C), formation of a C−H activation product can be excluded.

In prior work from our group, we have observed that for a cationic PCP rhodium system the reaction can be driven toward exclusive C−C or C−H activation at room temperature by solvent choice, C−C activation being observed in THF, while exclusive C−H activation was observed in acetonitrile.[14] However, carrying out the reaction of Scheme 2 in acetonitrile instead of THF resulted in a number of products exhibiting no hydride ligands in the ^{1}H NMR spectrum. This outcome may support the notion that this system is kinetically and thermodynamically selective for C−C activation. Additional support for kinetic preference comes from the observation that no C−H activation was observed when the π-allyl [Rh($^3\eta$-C_3H_5)(P^{i}Pr$_3$)$_2$] or π-benzyl [Rh($^3\eta$-$CH_2C_6H_5$)(P^{i}Pr$_3$)$_2$] complexes were reacted with ligand **1**; C−H activation, had it taken place, would have been expected to be followed by facile alkene elimination. In addition, treatment of complex **2** with the base KO^{t}Bu did not form the expected deprotonation product, had **2** been in equilibrium with the C−H activation product.

On the basis of a theoretical study performed by Martin and co-workers,[6a] electron-withdrawing groups attached to phosphorus in the PCP systems increase the activation barriers for both C−H and C−C activation processes, which proceed via a common intermediate. Thus, the lower donicity of the phosphinite versus the phosphine ligands in the pincer systems is unlikely to be the reason for a kinetically favored C−C activation.

Exclusive C−C activation was observed before with a phosphine-based PCN system and a Rh(I) precursor.[3b] This high selectivity could be a result of kinetically preferred C−C activation or a fast, reversible C−H process, which might not be detected by NMR, ultimately forming the thermodynamically more stable C−C activation product. In the PCN system the shorter amine arm might place the metal center closer to the Ar−Me bond and consequently results in easier cleavage, although on the basis of a theoretical study by Martin and coworkers[6b] of the PCN system, fast reversible C−H activation should be possible in this system, eventually leading to the thermodynamically more stable C−C activation product.

We believe that in the case of the phosphinite POCOP ligand the positioning of the metal plays a major role in the selectivity toward the C−C activation process, while the electronic effect of the phosphinite ligand is not pronounced. This is supported by an X-ray crystal structure of the dinitrogen complex **4b** (vide infra), which exhibits a shorter phosphinite "arm" than that of the analogous phosphine complex.

Reaction of 2 with Dihydrogen. Formation of [(POCOP)-Rh(H)]BF_4 (3). When complex **2** was treated with 5 atm hydrogen at room temperature, the rhodium hydrido complex **3** was formed (Scheme 2). The ^{31}P{^{1}H} NMR spectrum of **3** exhibits a doublet at δ 185.27 with $^1J_{Rh,P}$ = 124.7 Hz. The hydride ligand exhibits a broad doublet at δ −24.41 with a $^1J_{Rh,H}$ = 41.2 Hz in the ^{1}H NMR spectrum at room temperature. Coupling with P is too small to be observed. The IR spectrum shows a weak band at 2182 cm^{-1}, which is assigned to Rh−H. ^{19}F NMR of **3** in benzene exhibits a broad singlet at δ −165.38, indicating that the BF_4^- ion is coordinated to the metal center through one of its fluorine atoms, as in the case of **2**.

Deprotonation of 3. Formation of Dinitrogen Complexes 4a,b. Complex **3** underwent deprotonation upon reaction with KO^{t}Bu, leading to the dinitrogen complexes **4a** and **4b** (Scheme 3). Both the dinuclear (**4b**) and mononuclear (**4a**) forms exist in solution, the dinuclear form being the dominant one, the molar ratio being 9:1. Such dinuclear−mononuclear equilibria of pincer-type dinitrogen complexes were reported.[15] Complexes **4a**,**b** were also prepared by treatment of the C−C activation product **2** with 1 equiv of $NaHBEt_3$ in THF.

When argon was briskly bubbled for 45 min through a C_6D_6 solution containing complexes **4a** and **4b**, the mononuclear **4a** was completely converted to **4b**. The ^{31}P{^{1}H} NMR spectrum of the dinuclear **4b** exhibits a doublet at δ 192.12 ($^1J_{Rh,P}$ = 170.4 Hz), indicating two equivalent phosphorus nuclei coordinated to a Rh(I) center. To identify the "end on" bound dinitrogen complex **4a**, dinitrogen was bubbled through a solution of the two complexes for 1 h, leading to a slight increase in the concentration of **4a**. This solution was used to identify the characteristic stretch in the IR, which showed as a weak band at 2162 cm^{-1}.

Since the phosphinite ligand **1** is more π-acidic than alkyl phosphine-based PCP ligands, less back-bonding to the N_2 is expected and, as a result, a higher frequency band in the IR. However, the observed frequency of the N_2 stretch of complex **4a** is in the range of other Rh−N_2 "end on" bound phosphine pincer-type complexes. Selected IR data of a number of mononuclear PCP-type dinitrogen complexes are summarized in Table 2.

The pentane-soluble dinitrogen complex (**4b**) was crystallized from a pentane solution. The X-ray structure revealed a dinuclear complex with a distorted square planar structure around the metal centers (Figure 2, Table 3). The N_2 bond length is

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Scheme 3

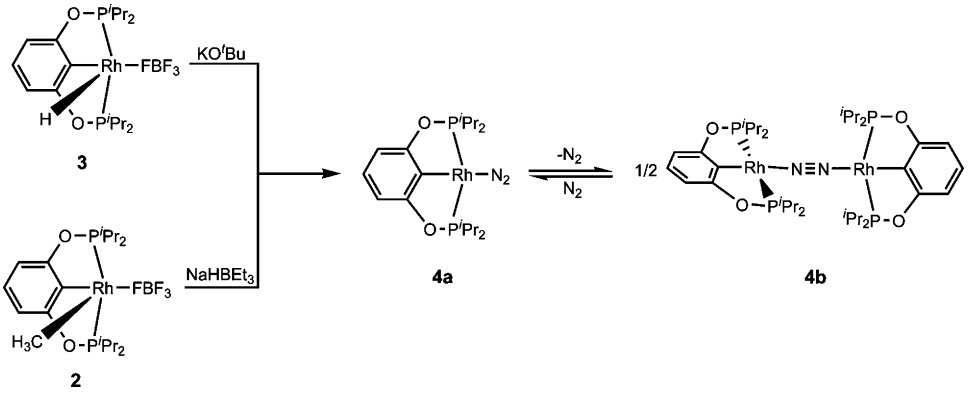
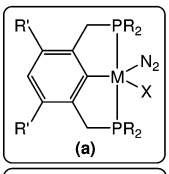
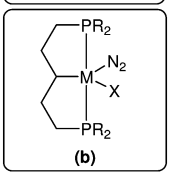


Table 2. Selected IR Data of Mononuclear Dinitrogen PCP Complexes[15a,b,16]

	PCP (a)				ν (N_2) [cm^{-1}]
	R	**R'**	**M**	**X**	
 (a)	^{t}Bu	H	Ru	H	2088
	Cy	H	Ru	H	2134
	^{i}Pr	H	Rh		2165
	^{t}Bu	H	Rh		2133
	^{t}Bu	CH_3	Rh		2120
	PCP (b)				
 (b)	**R**		**M**	**X**	
	^{t}Bu		Ru	H	2061 (or 2075)
	^{t}Bu		Rh		2108

1.122(11) Å, which is normal for a bridging N−N bond, and it is longer than that of a free N_2 (1.098 Å) (Table 3). The two square planar POCOP−Rh units are bridged by the dinitrogen molecule and are twisted around the RhNNRh axis with a dihedral angle of 72.5°. The Rh(1)−C(1) bond length of 2.015(9) Å is slightly shorter relative to the analogous PCP dinitrogen complex, where the bond length is 2.039(2) Å, indicating a stronger Rh−C_{ipso} bond.

Significantly, the O−P bond length of 1.658−1.673 Å is 0.17−0.18 Å shorter than the corresponding C−P bond in the analogous PCP ligand system (1.838−1.842 Å).[15b] Moreover, the C_{Ar}−O (1.395−1.398 Å) is significantly shorter than the C_{Ar}−C (1.510−1.517 Å). Thus, the shorter phosphinite arm in the complexed ligand **1** can better direct the metal toward the C−C bond rather than the C−H bond and make C−C activation more favorable, providing a likely explanation for the exclusive C−C activation observed with **1**.

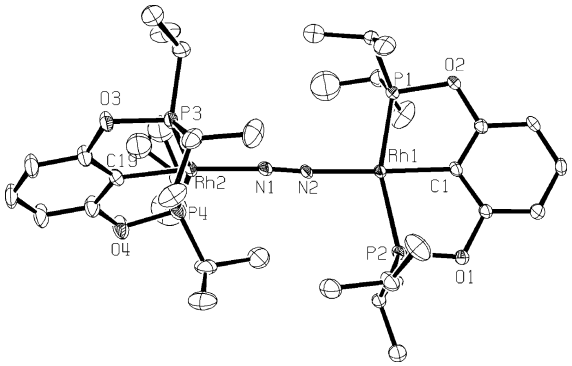


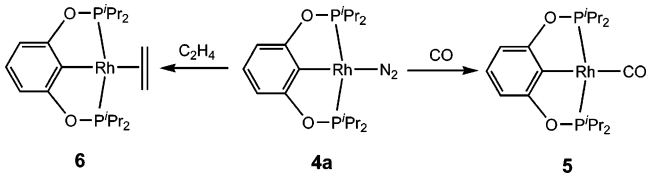
Figure 2. ORTEP plot of complex **4b**. Hydrogen atoms are omitted for clarity. Ellipsoidal probability is 20%.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4b

Rh(1)−N(2)	1.965 (8)	Rh(2)−N(1)	1.991 (9)
Rh(1)−C(1)	2.015 (9)	Rh(2)−C(19)	1.996 (10)
Rh(1)−P(1)	2.250 (3)	Rh(2)−P(3)	2.266 (3)
Rh(1)−P(2)	2.270 (3)	Rh(2)−P(4)	2.240 (3)
N(1)−N(2)	1.122 (11)	P(1)−O(2)	1.673 (6)
		P(2)−O(1)	1.658 (7)
C(1)−Rh(1)−N(2)	177.4 (4)	C(19)−Rh(2)−N(1)	172.4 (4)
N(2)−Rh(1)−P(1)	98.7 (2)	N(1)−Rh(2)−P(3)	100.7 (3)
N(2)−Rh(1)−P(2)	102.7 (2)	N(1)−Rh(2)−P(4)	101.8 (3)
C(1)−Rh(1)−P(1)	79.2 (3)	C(19)−Rh(2)−P(3)	79.5 (3)
C(1)−Rh(1)−P(2)	79.4 (3)	C(19)−Rh(2)−P(4)	78.5 (3)
P(1)−Rh(1)−P(2)	158.56 (9)	P(3)−Rh(2)−P(4)	157.29 (11)

Reaction of Complexes 4a,b with Small Molecules. Reaction with CO. Formation of (POCOP)Rh(CO) (5). When a solution containing the dinitrogen complexes **4a**,**b** was treated with 1 equiv of CO, an immediate and quantitative formation of **5** was observed (Scheme 4). The $^{31}P\{^1H\}$ NMR spectrum of

Scheme 4[a]

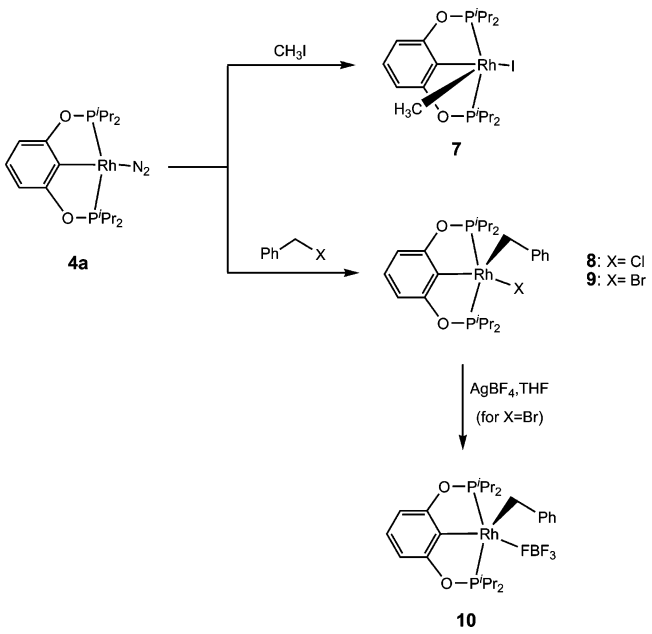


[a] For simplicity we depict complexes **4a/b** as the monomer one (**4a**) in all schemes although the dimeric form is the dominant one.

5 exhibits a doublet at δ 204.9 with $^1J_{Rh,P}$ = 155.6 Hz, indicating two equivalent phosphorus nuclei coordinated to a Rh(I) center. The CO ligand appears in the $^{13}C\{^1H\}$ NMR spectrum as a double triplet at δ 200.75 with $^1J_{Rh,C}$ = 58.5 Hz and $^1J_{P,C}$ = 9.9 Hz, and IR shows a strong band at 1962 cm^{-1}. For direct comparison, the exact phosphine analogue of **5** was prepared. The IR stretch of the (^{i}Pr-PCP)Rh(CO) gives rise to a signal at 1941 cm^{-1}. The observed lower frequency of this complex is in line with phosphine ligands being better σ-donors than phosphinite ligands, resulting in lower back-bonding to the CO ligand with the latter, although the observed difference of 21 cm^{-1} is not large. A similar effect was observed with analogous Ir complexes.[10c] The lower donicity of the phosphinite in POCOP as compared with phosphine in the analogous PCP system may be partially compensated by π donation of the oxygen atoms to the aryl ring, as previously discussed.[10d] On the basis of DFT calculations, the higher CO frequency in (POCOP)Ir−CO as compared with (PCP)Ir−CO complexes is attributable to electrostatic effects.[10d]

Reaction with Ethylene. Formation of (POCOP)Rh(C_2H_4) (6). Upon treatment of the dinitrogen complexes **4a,b** with 1

Scheme 5



equiv of ethylene, immediate and quantitative formation of the ethylene complex **7** took place (Scheme 4). The $^{31}P\{^1H\}$ NMR spectrum of complex **6** exhibits a doublet at δ 206.78 with $^1J_{Rh,P}$ = 155.85 Hz, indicating two equivalent phosphorus nuclei coordinated to a Rh(I) center. In the ^1H NMR spectrum at room temperature, the protons of the bound ethylene give rise to a broad singlet (an unresolved multiplet, probably as a result of hindered rotation), whereas when measured at 60 °C, they exhibit a triplet of doublets at δ 2.78 (about 3 ppm upfield from that of free ethylene), with $^1J_{Rh,H}$ = 1.4 Hz and $^1J_{P,H}$ = 2.6 Hz. In the $^{13}C\{^1H\}$ NMR spectrum at room temperature, the carbons of the bound ethylene appear at δ 47.33 as a broad doublet. The ethylene ligand is bound quite strongly; complex **6** is stable in solution under nitrogen atmosphere, and its conversion back to the dinitrogen complex was not observed. In a ^{t}Bu−PCP system ethylene was reported to bind less strongly than N_2, probably as a result of steric hindrance.[16d]

Reaction of 4 with MeI. Formation of (POCOP)Rh(Me)(I) (7). Treatment of complexes **4a**,**b** with 1 equiv of MeI in C_6D_6 at room temperature led to the immediate and selective formation of **7** (Scheme 5). $^{31}P\{^1H\}$ NMR of **7** shows a doublet at δ 178.41 with $^1J_{Rh,P}$ = 122.6 Hz, indicating two equivalent phosphorus nuclei coordinated to a Rh(III) center. The structure of **7** is fully supported by ^1H and ^{13}C NMR. For instance, the Rh−CH_3 group appears in ^1H NMR at δ 1.59 as a triplet of doublets with $^3J_{P,H}$ = 5.5 Hz and $^2J_{Rh,H}$ = 2.6 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the methyl group appears at δ 1.78 with $^1J_{Rh,C}$ = 26.8 Hz and $^2J_{P,C}$ = 5.7 Hz. This complex differs from the cationic complex **2**, indicating that the iodide is coordinated to the metal center. Treatment of complex **7** with $AgBF_4$ led to formation of complex **2**.

The *ipso* carbon of **7** appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 165.99, a value similar to the ones observed for the *ipso*-carbons of analogous, structurally determined aryl pincer rhodium halide complexes. For instance, the *ipso* carbon of Rh(Me){2,6-($CH_2P^tBu_2$)$_2$-3,5-(CH_3)$_2$-C_6H}Cl gives rise to a signal at 168.80,[3a] and in the case of Rh(Me){2-($CH_2P^tBu_2$)-6-($CH_2N(C_2H_5)_2$-3,5-(CH_3)$_2$-C_6H}Cl it appears at 170.04.[3b] This indicates that the aryl group of complex **7** is bound to the metal center *trans* to the halide ligand. The strongest *trans* director, the methyl group, is positioned *trans* to the vacant coordination site, as observed in crystallographically determined structures of analogous square pyramidal PCP and PCN-type rhodium(III) and iridium(III) complexes.[17]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 10

Rh(1)−C(1)	1.976 (3)	B(1)−F(1)	1.438(3)
Rh(1)−C(10)	2.078 (2)	B(1)−F(2)	1.387(4)
Rh(1)−F(1)	2.2289(17)	B(1)−F(3)	1.379(3)
Rh(1)−P(2)	2.3194 (8)	B(1)−F(4)	1.381(4)
Rh(1)−P(3)	2.3283 (8)		
C(1)−Rh(1)−C(10)	89.07 (10)	P(2)−Rh(1)−C(1)	80.94 (8)
C(1)−Rh(1)−F(1)	177.36 (8)	P(3)−Rh(1)−C(1)	79.28 (8)
P(2)−Rh(1)−P(3)	158.11 (2)	C(10)−Rh(1)−F(1)	89.31 (9)
P(2)−Rh(1)−F(1)	101.06 (5)	C(10)−Rh(1)−P(2)	87.20 (8)
P(3)−Rh(1)−F(1)	99.01 (5)	C(10)−Rh(1)−P(3)	101.75 (7)

Oxidative Addition of Benzyl Chloride and Bromide to 4a,b. Treatment of complexes **4a,b** with 1 equiv of benzyl chloride led to the oxidative addition product **8** quantitatively. $^{31}P\{^1H\}$ NMR of **8** exhibits a doublet at 172.20 with $^1J_{Rh,P}$ = 133.9 Hz. Similarly, benzyl bromide oxidatively added to **4a,b** to yield complex **9**, which exhibits a doublet at 173.6 with $^1J_{Rh,P}$ = 132.5 Hz (Scheme 5). Treatment of complex **9** with 1 equiv of $AgBF_4$ led to bromide abstraction to form the cationic complex **10** (Scheme 5). In contrast, abstraction of the chloride ligand of complex **8** with $AgBF_4$ was not possible, leading to a mixture containing metallic silver.

Crystals of **10** suitable for X-ray analysis were grown by diffusion of pentane into its benzene solution. As in the case of complex **2**, the crystal structure revealed that the BF_4^- anion is coordinated to the metal center via one of its fluorine atoms (Figure 3). The length of the Rh−F(1) bond is 2.23 Å, and the

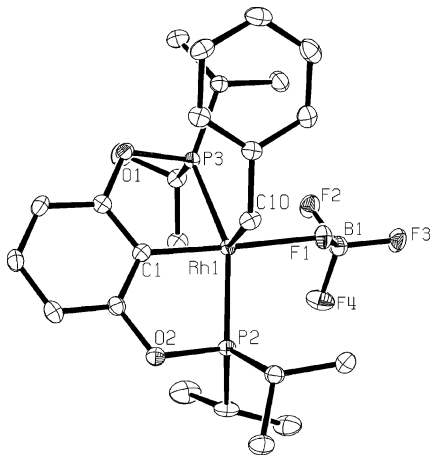


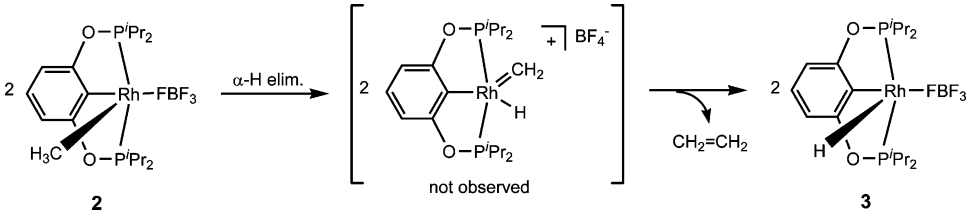
Figure 3. ORTEP plot of complex **10**. Hydrogen atoms are omitted for clarity. Ellipsoids are at the 50% probability level.

B−F(1) bond (1.44 Å) is longer than the other B−F bonds (1.38 Å), as expected for a BF_4^- ion bound to a metal center (Table 4). The rhodium atom is centered in the base of a slightly distorted square pyramid, with the benzyl group at the axial position (Figure 3). The C(1)−Rh−P(2)/P(3), C(10)−Rh−C(1), and C(10)−Rh−F(1) are close to 90° (80.94°, 79.28°, 89.07°,

(16) (a) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839. (b) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 13415. (c) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2061. (d) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 5091. (e) Amoroso, D.; Jabri, A.; Yap, G. P. A.; Gusev, D. G.; dos Santos, E. N.; Fogg, D. E. *Organometallics* **2004**, *23*, 4047−4054

(17) Rybtchinski, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786.

Scheme 6



and 89.31°, respectively). The Rh−C(10) bond length is 2.08 Å. The Rh−C_{ipso} bond (1.98 Å) is similar to the one observed for **2** and shorter than that of the Rh(I) complex **4b**.

Apparent α-H Elimination Reaction of [(POCOP)Rh-(CH_3)]BF_4 (2). Surprisingly, when the C−C activation product **2** was heated in benzene at 60 °C for approximately two weeks, loss of a methylene group took place and the rhodium-hydride complex **3** was obtained as the only product, as shown by NMR. No conversion of **2** to a methylene-bridged C−H activation product was observed; the absence of a methylene group was confirmed by a ^{13}C DEPT NMR experiment.

A possible explanation for the missing methylene group is that the complex reacted with the benzene solvent by a methylene transfer reaction, via equilibrium with the C−H activation product.[5b,18] However, no organic products that can result from such a reaction (e.g., toluene, biphenyl, or diphenylmethane) were detected in solution by GC analysis. Heating of complex **2** under the same conditions in other solvents such as triethylbenzene and pentafluorotoluene resulted in the same conversion.

In an attempt to detect the missing methylene group, the labeled analogue of complex **2** was prepared by oxidatively adding 1 equiv of $^{13}CH_3I$ to complexes **4a,b** followed by abstraction of the iodide with $AgBF_4$. While the labeled methyl group of complex **2** could be followed all along the conversion, labeled products arising from the missing methylene group could not be observed in solution. However, analysis of the gas phase by GC/MS indicated the presence of $^{13}CH_4$. Thus, the solvent might be involved in transferring a proton to the methyl group. One can envision a scenario in which such a reaction would result in a Rh−Ph complex, which could react with the benzene solvent again, to yield the observed hydride complex **3** and biphenyl. However, biphenyl or other possible organic products were not detected. Thus, the nature of the process leading to formation of methane in solution is not clear.

To avoid solvent participation, complex **2** was heated in the solid state under argon at 150 °C for 2 days. The reaction was complete and GC/MS analysis of the gas phase revealed the quantitative formation of ethylene, as compared with a sample containing a known concentration of ethylene in argon. This result suggests the possibility of an α-H elimination followed by a binuclear reaction, leading to the formation of ethylene gas (Scheme 6).

In addition to ethylene, traces of cyclopropane were detected, indicating the possibility of cyclopropanation of the formed ethylene by an intermediate Rh-hydrido carbene complex. Indeed when complex **2** was heated at 150 °C under 1 atm of ethylene, a significant amount of cyclopropane was obtained (about a 1/3 of the equivalent amount).

In contrast to early transition metals, α-H elimination to give hydrido-carbene complexes is not common for late transition metals.[19] To the best of our knowledge, this is the first example reported for rhodium.

Summary

POCOP-based cationic Rh(III) and neutral Rh(I) pincer systems were synthesized from a new phosphinite ligand. The POCOP−Rh system demonstrated remarkable selectivity toward C−C activation. No parallel formation of the C−H activation product was observed. This is probably a result of better orientation of the metal vis-à-vis the C−C bond. The crystal structure of the C−C activation product **2** revealed coordination of the BF_4^- ion to the rhodium center. Complex **2** reacted with dihydrogen to give methane and the Rh−H complex **3**. Heating of complex **2** in the solid state led to the formation of **3** and ethylene, via an apparent α-H elimination process, followed by a binuclear carbene coupling yielding ethylene. Deprotonation of complex **3** led to the formation of mono- and dinuclear Rh(I) dinitrogen complexes **4a**,**b**, the latter structurally characterized complex being the major one. The dinitrogen ligand is readily displaced by 1 equiv of ethylene or CO. Only a minor effect of the phosphinite POCOP pincer ligand (as compared with the corresponding PCP pincer ligand) on the stretching frequencies of the CO and N_2 ligands was observed.

Experimental Section

General Procedures. All experiments with metal complexes and the phosphinite ligand were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier, or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were dried over 4 Å molecular sieves. Commercially available reagents were used as received. ^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded at 400, 100, 162, and 376 MHz, respectively, using a Bruker AMX-400 NMR spectrometer and at 500, 125, and 202 MHz, respectively,

(18) (a) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. *Chem. Commun.* **1996**, 2167. (b) van der Boom, M. E.; Kraatz, H.-B.; Hassner, L.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 3873. (c) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687. (d) Cohen, R.; van der Boom, M. E.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *J. Am. Chem. Soc.* **2000,** *122*, 7723. (e) Cohen, R.; Milstein, D.; Martin, J. M. L. *Organometallics* **2004,** *23*, 2336.

(19) (a) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2158. (b) Coalter, J. N.; Huffman, J. C.; Caulton, K. G. *Chem. Commun.* **2001**, 1158. (c) Kuznetsov, V. F.; Yap, G. P. A.; Alper, H. *Organometallics* **2001**, *20*, 1300−1309. (d) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Chem. Commun.* **2001**, 1158−1159. (e) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Onate, E. *Organometallics* **2001**, *20*, 2635. (f) Kuznetsov, V. F.; Lough, A. J.; Gusev, D. G. *Chem. Commun.* **2002**, 2432. (g) Ferrando-Miguel, G.; Coalter, J. N., III; Gerard, H.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2002**, *26*, 687−700. (h) Kuznetsov, V. F.; Lough, A. J.; Gusev, D. G. *Chem. Commun.* **2002**, 2432−2433. (i) Carmona, E.; Paneque, M.; Poveda, M. L. *Dalton Trans.* **2003**, 4022. (j) Ho, V. M.; A.Watson, L.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, *27*, 1446−1450. (k) Clot, E.; Chen, J.; Lee, D.-H.; Sung, S. Y.; Appelhans, L. N.; Faller, J. W.; Crabtree, R. H.; Eisenstein, O. *J. Am. Chem. Soc.* **2004**, *126*, 8795−8804. (l) Grotjahn, D. B.; Hoerter, J. M.; Hubbard, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 8866. (m) Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3603. (n) Ingleson, M. J.; Yang, X.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2005**, *127*, 10846.

for ^{1}H, ^{13}C, and ^{31}P, using a Bruker Avance-500 NMR spectrometer. All spectra were recorded at 23 °C unless stated otherwise. NMR measurements were performed in $CDCl_3$ and C_6D_6. ^{1}H and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvent (7.15 ppm for benzene, 7.24 ppm for chloroform). In $^{13}C\{^1H\}$ NMR measurements the signal of deuterated benzene (128.0 ppm) was used as a reference. ^{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. 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; dist, distorted.

Synthesis of Ligand 1. To a THF solution (60 mL) of 2-methylresorcinol (0.81 g, 6.66 mmol) and 4-(dimethylamino)-pyridine (1.62 g, 13.20 mmol) was added a THF solution (40 mL) of ClP^iPr_2 (2 g, 13.10 mmol) dropwise, while stirring at 0 °C. The reaction mixture was allowed to reach room temperature and then kept under stirring for an additional 24 h. The solvent was removed under vacuum, and the ligand was extracted from the resulting white solid with toluene (2 × 40 mL). The combined extracts were filtered through a Celite pad, and the toluene was removed under vacuum. The product was further purified by distillation (bp 128−130 °C, 0.05 mmHg), giving a colorless oil. Yield: 65% (1.5 g). $^{31}P\{^1H\}$ NMR (C_6D_6): 144.06 (s). ^{1}H NMR (C_6D_6): 7.22 (dd,, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 3.7 Hz, 2H, Ar), 6.99 (t, $^3J_{H,H}$ = 7.9 Hz, 1H, Ar), 2.41 (s, Ar−C*H*$_3$, 3H) 1.75 (m, $^3J_{P,H}$ = 3.1 Hz, $^3J_{H,H}$ = 7.0 Hz, 4H, P−C*H*$(CH_3)_2$), 1.10 (dd, $^3J_{H,H}$ = 7.0 Hz,$^3J_{P,H}$ = 10.6 Hz, 12H, P−CH(C*H*$_3)_2$), 0.96 (dd, $^3J_{H,H}$ = 7.3 Hz, $^3J_{P,H}$ = 15.5 Hz, 12H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 158.44 (t, $^3J_{P,C}$ = 8.7 Hz, Ar−C_{ipso}), 126.23 (s, Ar), 117.61 (t, $^3J_{P,C}$ = 1.6 Hz, Ar), 110.36 (d, $^2J_{P,C}$ = 22.1 Hz, Ar), 28.49 (d, $^2J_{P,C}$ = 18.7 Hz, P−*C*H$(CH_3)_2$), 17.77 (d, $^1J_{P,C}$ = 20.1 Hz, P−CH(*C*H$_3)_2$), 17.11 (d, $^1J_{P,C}$ = 8.9 Hz, P−CH(*C*H$_3)_2$), 9.58 (s, Ar−*C*H$_3$).

Reaction of $[Rh(COE)_2(THF)_2]BF_4$ with Ligand 1. Formation of $[(POCOP)Rh(CH_3)]BF_4$ (2). Two equivalents of $AgBF_4$ (108.7 mg, 0.56 mmol) in THF (4 mL) were added to a red-orange THF solution (20 mL) of $[Rh(COE)_2Cl]_2$ (200 mg, 0.28 mmol), leading to massive formation of a white precipitate of AgCl and a color change to a light orange. The precipitate was removed by filtration through a cotton pad and Celite. Ligand **1** (198.7 mg, 0.56 mmol) in THF (4 mL) was added immediately to the filtrate, resulting in a color change from orange to brown and the formation of a brown solid. The solution was kept for 15 min at room temperature until the solid settled down. The solid was separated by filtration through a cotton pad, and the solvent was removed from the filtrate under vacuum, resulting in a dark red-orange solid of **2**. Complex **2** was further purified by crystallization from a hot benzene solution, resulting in 37% (114 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 172.78 (d, $^1J_{Rh,P}$ = 128.3 Hz). ^{1}H NMR (C_6D_6): 6.77 (t, $^3J_{H,H}$ = 8.0 Hz, 1H, Ar), 6.59 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, Ar), 2.56 (m, $^3J_{H,H}$ = 7.1 Hz, 2H, P−C*H*$(CH_3)_2$), 2.21 (m, $^3J_{H,H}$ = 8.0 Hz, 2H, P−C*H*$(CH_3)_2$), 1.37 (td, $^2J_{Rh,H}$ = 2.2 Hz, $^3J_{P,H}$ = 5.2 Hz, 3H, Rh−C*H*$_3$), 1.18 (dd, $^3J_{H,H}$ = 7.3 Hz, $^3J_{P,H}$ = 17.3 Hz, 6H, P−CH(C*H*$_3)_2$), 1.11 (2 overlapping dist. dd, $^3J_{H,H}$ = 7.3 Hz, $^3J_{P,H}$ = 15.3 Hz, 12H, P−CH(C*H*$_3)_2$), 0.99 (dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{P,H}$ = 14.2 Hz, 6H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 168.41 (t, $^2J_{P,C}$ = 6.4 Hz, C_{ipso}, Rh−Ar), 129.75 (s, Ar), 127.50 (s, Ar), 108.42 (t, $^2J_{P,C}$ = 5.8 Hz, Ar), 31.90 (t, $^1J_{P,C}$ = 10.2 Hz, P−*C*H$(CH_3)_2$), 28.47 (t, $^1J_{P,C}$ = 11.9 Hz, P−*C*H$(CH_3)_2$), 18.92 (s, P−CH(*C*H$_3)_2$), 18.58 (s, P−CH(*C*H$_3)_2$), 17.59 (s, P−CH(*C*H$_3)_2$), 16.62 (s, P−CH(*C*H$_3)_2$), 1.31 (dt, $^1J_{Rh,C}$ = 28.8 Hz, $^2J_{P,C}$ = 5.2 Hz, Rh−*C*H$_3$). ^{19}F NMR (C_6D_6): −163.26 (br s). Anal. Calcd for $C_{19}H_{34}BF_4O_2P_2Rh$: C, 41.78; H, 6.28. Found: C, 41.75; H, 6.36.

X-ray Structural Analysis of 2. Crystal Data: $C_{19}H_{34}O_2P_2BF_4Rh$, orange prisms, 0.1 × 0.1 × 0.05 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 8.011(2) Å, b = 12.127(2) Å, c = 12.268(3) Å, α = 102.62(3)°, β = 100.65(3)°, γ = 95.03(3)°, from 15 degrees of data, T = 120(2) K, V = 1132.8(4) Å^3, Z = 2, fw = 546.12, D_c = 1.601 Mg/m^3, μ = 0.941 mm^{-1}.

Data Collection and Processing: Nonius KappaCCD diffractometer, Mo Kα (λ = 0.71073 Å), graphite monochromator, 0 ≤ h ≤ 9, −15 ≤ k ≤ 15, −15 ≤ l ≤ 14, frame scan width = 1.0°, scan speed 1.0° per 20 s, typical peak mosaicity 0.91°, 10 829 reflections collected, 4726 independent reflections (R_{int} = 0.048). The data were processed with Denzo-Scalepack.

Solution and Refinement: Structure solved by direct methods with SHELXS-97. Full matrix least-squares refinement based on F^2 with SHELXL-97; 263 parameters with 0 restraints, final R_1 = 0.0404 (based on F^2) for data with $I > 2\sigma(I)$, and R_1 = 0.0433 on 4101 reflections, goodness-of-fit on F^2 = 1.035, largest electron density peak = 1.282 e Å^{-3}.

Formation of $[(POCOP)Rh(H)]BF_4$ (3). A THF solution (2 mL) of complex **2** (40 mg, 0.073 mmol) was treated with an excess of dihydrogen (5 atm) in a glass pressure vessel (90 mL) for 12 h, forming complex **3** in a 97% (38 mg) yield as a brownish-yellow solid. Complex **3** was used without further purification. $^{31}P\{^1H\}$ NMR (C_6D_6): 185.27 (d, $^1J_{Rh,P}$ = 124.7 Hz). ^{1}H NMR (C_6D_6): 6.75 (t, $^3J_{H,H}$ = 7.8 Hz, Ar), 6.53 (d, $^3J_{H,H}$ = 7.7 Hz, Ar), 2.67 (m, $^3J_{H,H}$ = 6.9 Hz, P−C*H*$(CH_3)_2$), 2.00 (m, $^3J_{H,H}$ = 5.3 Hz, P−C*H*$(CH_3)_2$), 1.28 (dist. dd, $^3J_{H,H}$ = 7.8 Hz, $^3J_{P,H}$ = 16.1 Hz, P−CH(C*H*$_3)_2$), 1.25 (dist. dd, $^3J_{H,H}$ = 6.6 Hz, $^3J_{P,H}$ = 13.5 Hz P−CH(C*H*$_3)_2$), 1.97 (dist. dd, $^3J_{H,H}$ = 7.6 Hz, $^3J_{P,H}$ = 15.7 Hz P−CH(C*H*$_3)_2$), −24.41 (br d, $^1J_{Rh,H}$ = 41.2 Hz, Rh−*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): 166.29 (dist. t, C_{ipso}, Rh−Ar), 128.53 (s, Ar), 127.22 (s, Ar), 106.53 (s, Ar), 29.04 (dt, $^1J_{Rh,C}$ = 114.9 Hz, $^1J_{P,C}$ = 14.1 Hz, P−*C*H$(CH_3)_2$), 27.18 (s, P−*C*H$(CH_3)_2$), 25.7 (s, P−*C*H$(CH_3)_2$), 17.7 (s, P−CH(*C*H$_3)_2$), 16.7 (s, P−CH(*C*H$_3)_2$), 16.22 (s, P−CH(*C*H$_3)_2$). ^{19}F NMR (C_6D_6): −165.38 (br s). IR: 2182 cm^{-1}, ν_{Rh-H}. Anal. Calcd for $C_{18}H_{32}BF_4O_2P_2Rh\cdot C_4H_8O$: C, 43.73; H, 6.67. Found: C, 44.76; H, 6.60.

Formation of $[(POCOP)Rh]_2(N_2\text{-}\mu)$ (4). To a THF solution (1 mL) of complex **3** (20 mg, 0.038 mmol) was added 1 equiv of KO^tBu (4.2 mg, 0.038 mmol) in a THF solution (1 mL). The reaction mixture was stirred at room temperature for 5 min, resulting in the formation of the dinitrogen complexes **4a** and **4b** in a ratio **4a**:**4b** = 1:9. The reaction mixture was dried under vacuum, and the residue was extracted with benzene (3 mL). The extracts were combined and filtered through a cotton pad and Celite in order to remove inorganic particles, resulting in a pure product in 94% (16.7 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 192.12 (d, $^1J_{Rh,P}$ = 170.4 Hz). ^{1}H NMR (C_6D_6): 6.91 (t, $^3J_{H,H}$ = 7.7 Hz, 1H, Ar), 6.81 (d, $^3J_{H,H}$ = 7.0 Hz, 2H, Ar), 2.15 (m, $^3J_{H,H}$ = 6.8 Hz, 4H, P−C*H*$(CH_3)_2$), 1.24 (m, 24H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 168.73 (t, $^2J_{P,C}$ = 9.3 Hz, C_{ipso}, Rh−Ar), 139.5 (dt, $^1J_{Rh,C}$ = 33.2 Hz, $^1J_{P,C}$ = 9.71 Hz, Ar), 126.51 (s, Ar), 108.42 (t, $^2J_{P,C}$ = 6.8 Hz, Ar), 30.69 (td, $^1J_{Rh,C}$ = 2.0 Hz, $^1J_{P,C}$ = 10.8 Hz, P−*C*H$(CH_3)_2$), 18.68 (t, $^2J_{P,C}$ = 5.1 Hz, P−CH(*C*H$_3)_2$), 17.78 (s, P−CH(*C*H$_3)_2$). IR: 2162 cm^{-1}, ν_{N2}. Anal. Calcd for $C_{36}H_{62}N_2O_4P_4Rh_2$: C, 47.17; H, 6.82. Found: C, 47.66; H, 6.77.

X-ray Structural Analysis of 4b. Crystal Data: $C_{36}H_{72}N_2O_4P_4Rh_2$, yellow prisms, 0.1 × 0.1 × 0.1 mm^3, monoclinic, $P2(1)/c$, a = 13.925(3) Å, b = 17.773(4) Å, c = 36.020(7) Å, β = 94.03(3)° from 15 degrees of data, T = 120(2) K, V = 8892(3) Å^3, Z = 4, fw = 916.55, D_c = 1.369 Mg/m^3, μ = 0.921 mm^{-1}.

Data Collection and Processing: Nonius KappaCCD diffractometer, Mo Kα (λ = 0.71073 Å), graphite monochromator, −15 ≤ h ≤ 15, 0 ≤ k ≤ 19, 0 ≤ l ≤ 40, frame scan width = 0.8°, scan speed 1.0° per 180 s, typical peak mosaicity 0.43°, 61 792 reflections collected, 21 117 independent reflections (R_{int} = 0.065). The data were processed with Denzo-Scalepack.

Solution and Refinement: Structure solved by direct methods with SHELXS-97. Full matrix least-squares refinement based on F^2 with SHELXL-97; 866 parameters with 449 restraints on

temperature factors and on ring planarity, final $R_1 = 0.0792$ (based on F^2) for data with $I > 2\sigma(I)$ and, $R_1 = 0.0969$ on 12 734 reflections, goodness-of-fit on $F^2 = 1.044$, largest electron density peak = 3.265 e Å^{-3}. Some disorder was seen on one-half of the second dimer, and some atoms have been modeled in two alternate positions.

Reaction of 4a,b with CO. Formation of (POCOP)Rh(CO) (5). To a C_6D_6 solution (0.5 mL) of **4a,b** (10 mg, 0.021 mmol) in a septum-capped NMR tube was added 1 equiv of CO (0.021 mmol, 0.47 mL), leading to a color change to yellow and the immediate formation of **6**. The solvent was removed under vacuum, resulting in a yellow solid in 96% (9.6 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 204.9 (d, $^1J_{Rh,P} = 155.6$ Hz).^{1}H NMR (C_6D_6): 6.95 (t, $^3J_{H,H} = 7.4$ Hz, 1H, Ar), 6.82 (d, $^3J_{H,H} = 7.9$ Hz, 2H, Ar), 2.05 (m, $^3J_{H,H} = 7.0$ Hz, 4H, P−C*H*$(CH_3)_2$), 1.13 (m, 24H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 200.75 (dt, $^1J_{Rh,C} = 58.5$ Hz, $^2J_{P,C} = 9.9$ Hz, Rh−*C*O), 169.83 (t, $^2J_{P,C} = 8.9$ Hz, C_{ipso}, Rh−Ar), 146.42 (dt, $^1J_{Rh,C} =$ 25.2 Hz, $^2J_{P,C} = 9.9$ Hz, Ar), 130.52 (s, Ar), 105.93 (t, $J_{P,C} = 7.0$ Hz, Ar), 31.84 (td, $^2J_{Rh,C} = 2.2$ Hz, $^1J_{P,C} = 12.2$ Hz, P−*C*H$(CH_3)_2$), 19.69 (t,$^2J_{P,C} = 4.6$ Hz, P−CH(*C*H$_3)_2$), 18.83 (s, P−CH(*C*H$_3)_2$). IR: 1962 cm^{-1}, ν_{CO}. Anal. Calcd for $C_{19}H_{31}O_3P_2Rh$: C, 48.32; H, 6.62. Found: C, 48.45; H, 6.56.

Reaction of 4a,b with Ethylene. Formation of (POCOP)Rh-(C_2H_4) (6). To a C_6D_6 solution (0.5 mL) of **4a,b** (10 mg, 0.021 mmol) in a septum-capped NMR tube was added 1 equiv (0.021 mmol, 0.47 mL) of ethylene, resulting in a slight change of color from dark yellow to brownish-yellow. The solvent was removed under vacuum, resulting in a brownish-yellow oil in 98% (9.8 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 206.78 (d, $^1J_{Rh,P} = 155.9$ Hz). ^{1}H NMR (C_6D_6, 60 °C): 6.96 (t, $^3J_{H,H} = 7.1$ Hz, 1H, Ar), 6.9 (d, $^3J_{H,H} = 7.8$ Hz, 2H, Ar), 2.78 (td, $^2J_{Rh,H} = 1.4$ Hz, $^3J_{P,H} = 2.6$ Hz, 4H, bound C_2H_4), 2.20 (m, $^3J_{H,H} = 7.1$ Hz, 4H, P−C*H*$(CH_3)_2$), 1.13 (dd, $^3J_{H,H} = 6.8$ Hz, $^3J_{P,H} = 13.5$ Hz, 12H, P−CH(C*H*$_3)_2$), 1.03 (dd, $^3J_{H,H} = 7.8$ Hz, $^3J_{P,H} = 16.2$ Hz, 12H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 167.73 (t, $^2J_{P,C} = 10.2$ Hz, C_{ipso}, Rh−Ar), 145.58 (d, Ar), 126.50 (s, Ar), 105.65 (t, $^2J_{P,C} = 7.4$ Hz, Ar), 47.33 (br d, $^1J_{Rh,C} = 5.6$ Hz, bound C_2H_4), 31.99 (t, $^1J_{P,C} = 11.9$ Hz, P−*C*H$(CH_3)_2$), 19.64 (t, $^2J_{P,C} = 3.1$ Hz, P−CH(*C*H$_3)_2$), 18.65 (s, P−CH(*C*H$_3)_2$). Anal. Calcd for $C_{20}H_{35}O_2P_2Rh$: C, 50.86; H, 7.47. Found: C, 51.06; H, 7.41.

Reaction of 4a,b with MeI. Formation of (POCOP)Rh(Me)-(I) (7). To a benzene solution (1 mL) of complexes **4a,b** (20 mg, 0.042 mmol) was added 1 equiv of MeI (6 mg, 0.042 mmol), resulting in an immediate color change to deep red. The solvent was removed under vacuum, resulting in a red solid in 70% (14 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 178.41 (d, $^1J_{Rh,P} = 122.6$ Hz). ^{1}H NMR (C_6D_6): 6.93 (t, $^3J_{H,H} = 7.9$ Hz, 1H, Ar), 6.77 (d, $^3J_{H,H} = 7.9$ Hz, 2H, Ar), 2.50 (m, $^2J_{P,H} = 7.0$ Hz, 2H, P−C*H*$(CH_3)_2$), 2.37 (m, 2H, P−C*H*$(CH_3)_2$), 1.59 (td, $^3J_{P,H} = 5.5$ Hz, $^2J_{Rh,H} = 2.6$ Hz, 3H, Rh−C*H*$_3$), 1.36 (dd, $^3J_{H,H} = 7.8$ Hz, $^3J_{P,H} = 16.4$ Hz, 6H, P−CH(C*H*$_3)_2$), 1.27 (dd, $^3J_{H,H} = 7.2$ Hz, $^3J_{P,H} = 14.5$ Hz, 6H, P−CH(C*H*$_3)_2$), 1.18 (dd, $^3J_{H,H} = 7.6$ Hz, $^3J_{P,H} = 16.7$ Hz, 6H, P−CH(C*H*$_3)_2$), 0.95 (dd, $^3J_{H,H} = 7.0$ Hz, $^3J_{P,H} = 14.1$ Hz, 6H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 165.99 (t, $^2J_{P,C} = 6.7$ Hz, C_{ipso}, Rh−Ar), 128.29 (s, Ar), 126.86 (s, Ar), 106.68 (t, $^2J_{P,C} =$ 6.1 Hz, Ar), 30.91 (t, $^2J_{P,C} = 10.8$ Hz, P−*C*H$(CH_3)_2$), 28.37 (td, $^2J_{Rh,C} = 2.1$ Hz, $^1J_{P,C} = 11.9$ Hz, P−*C*H$(CH_3)_2$), 18.33 (dt,$^2J_{P,C} =$ 2.6 Hz, $^2J_{Rh,C} = 29.3$ Hz, P−*C*H$(CH_3)_2$), 17.75 (s, P−CH(*C*H$_3)_2$), 16.76 (s, P−CH(*C*H$_3)_2$), 1.78 (dt, $^1J_{Rh,C} = 26.8$ Hz, $^2J_{P,C} = 5.7$ Hz, Rh−*C*H$_3$). Anal. Calcd for $C_{19}H_{34}IO_2P_2Rh$: C, 38.93; H, 5.85. Found: C, 39.12; H, 5.93.

Reaction of 4a,b with Benzyl Chloride. Formation of (POCOP)Rh(CH_2Ph)(Cl) (8). To a benzene solution (1 mL) of complexes **4a,b** (20 mg, 0.042 mmol) was added 1 equiv of benzyl chloride (5.4 mg, 0.042 mmol), leading to an immediate color change to deep red. The solvent was removed under vacuum, resulting in a deep red solid in 98% (23.7 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 172.20 (d, $^1J_{Rh,P} = 133.9$ Hz). ^{1}H NMR (C_6D_6): 7.35 (d, $^2J_{H,H} = 7.0$ Hz, 2H, Ar), 6.95 (m, 2H, Ar), 6.85 (t, $^3J_{H,H} = 8.4$ Hz, 2H, Ar), 6.81 (d, $^3J_{H,H} = 8.4$ Hz, 2H, Ar), 3.90 (dd, $^3J_{P,H} = 4.2$ Hz, $^3J_{H,Rh} = 7.0$ Hz, C*H*$_2$−Ar) 2.33 (m, $^2J_{P,H} = 7.0$ Hz, 4H, P−C*H*$(CH_3)_2$), 1.32 (dd, $^3J_{H,H} = 8.4$ Hz, $^3J_{P,H} = 16.7$ Hz, 6H, P−CH(C*H*$_3)_2$), 1.18 (dd, $^3J_{H,H} = 8.4$ Hz, $^3J_{P,H} = 16.6$ Hz, 6H, P−CH(C*H*$_3)_2$), 1.14 (dd, $^3J_{H,H} = 7.0$ Hz, $^3J_{P,H} = 12.5$ Hz, 6H, P−CH(C*H*$_3)_2$), 0.94 (dd, $^3J_{H,H} = 7.0$ Hz, $^3J_{P,H} = 13.9$ Hz, 6H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 166.73 (t, $^2J_{C,P} = 6.7$ Hz, C_{ipso}, Rh−Ar), 148.60 (td, $^2J_{Rh,C} = 2.5$ Hz,$^3J_{P,C} = 5.2$ Hz, quaternary C, benzyl ring), 137.62 (dt, $^3J_{Rh,C} = 32.6$ Hz, $^3J_{P,C} = 6.0$ Hz, Ar of benzyl ring), 131.41 (s, Ar of benzyl ring), 129.24 (s, Ar of benzyl ring), 126.92 (s, Ar), 126.53 (s, Ar), 106.63 (t, $^2J_{P,C} = 5.9$ Hz, Ar), 29.25 (t, $^2J_{P,C}$= 8.4 Hz, P−*C*H$(CH_3)_2$), 27.85 (td, $^2J_{Rh,C} = 0.96$ Hz, $^1J_{P,C} = 12.1$ Hz, P−*C*H$(CH_3)_2$), 23.81 (dt,$^2J_{Rh,C} = 25.9$ Hz, $^2J_{P,C} = 3.8$ Hz, *C*H$_2$−Ar, the assignment of this carbon was determined by ^{13}C DEPT NMR), 19.54 (t,$^2J_{P,C} = 5.0$ Hz, P−CH-(*C*H$_3)_2$), 19.38 (s, P−CH(*C*H$_3)_2$), 16.87 (t, $^2J_{P,C} = 4.4$ Hz, P−CH-(*C*H$_3)_2$), 15.52 (s, P−CH(*C*H$_3)_2$). Anal. Calcd for $C_{25}H_{38}BrO_2P_2$-Rh: C, 52.59; H, 6.71. Found: C, 52.33; H, 6.65.

Reaction of 4a,b with Benzyl Bromide. Formation of (POCOP)Rh(CH_2Ph)(Br) (9). To a benzene solution (1 mL) of complexes **4a,b** (20 mg, 0.042 mmol) was added 1 equiv of benzyl bromide (7.2 mg, 0.042 mmol), leading to an immediate color change to deep red. The solvent was removed under vacuum, resulting in a deep red solid in 98% (25.5 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 173.6 (d, $^1J_{Rh,P} = 132.5$ Hz). ^{1}H NMR (C_6D_6): 7.35 (d, $^2J_{H,H} = 7.5$ Hz, 2H, Ar), 6.97 (m, 2H, Ar), 6.84 (t, $^3J_{H,H} = 7.5$ Hz, 2H, Ar), 6.82 (d, $^3J_{H,H} = 8.5$ Hz, 2H, Ar), 3.95 (dd, $^3J_{P,H} = 3.1$ Hz, $^3J_{Rh,H} = 6.1$ Hz, C*H*$_2$−Ar) 2.36 (m, $^2J_{P,H} = 7.0$ Hz, 4H, P−C*H*$(CH_3)_2$), 1.38 (dd, $^3J_{H,H} = 8.5$ Hz, $^3J_{P,H} = 16.7$ Hz, 6H, P−CH(C*H*$_3)_2$), 1.19 (dd, $^3J_{H,H} = 8.5$ Hz, $^3J_{P,H} = 17.4$ Hz, 6H, P−CH(C*H*$_3)_2$), 1.06 (dd, $^3J_{H,H} = 6.5$ Hz, $^3J_{P,H} = 13.0$ Hz, 6H, P−CH(C*H*$_3)_2$), 0.93 (dd, $^3J_{H,H} = 6.8$ Hz, $^3J_{P,H} = 14.0$ Hz, 6H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 166.50 (t, $^2J_{P,C} = 6.6$ Hz, C_{ipso}, Rh−Ar), 148.52 (td, $^2J_{Rh,C} = 2.4$ Hz, $^3J_{P,C} = 5.4$ Hz, quaternary carbon of benzyl ring), 139.14 (dt, $^3J_{Rh,C} = 33.4$ Hz, $^3J_{P,C} = 5.4$ Hz, Ar of benzyl ring), 131.50 (s, Ar of benzyl ring), 129.30 (s, Ar of benzyl ring), 127.01 (s, Ar), 126.51 (s, Ar), 106.70 (t, $^2J_{P,C} = 6.2$ Hz, Ar), 29.61 (t, $^2J_{P,C} = 8.6$ Hz P−*C*H$(CH_3)_2$), 28.30 (td, $^2J_{Rh,C} = 0.96$ Hz, $^1J_{P,C} = 12.4$ Hz, P−*C*H$(CH_3)_2$), 23.93 (dt,$^2J_{Rh,C} = 25.4$ Hz, $^2J_{P,C} = 3.8$ Hz, *C*H$_2$−Ar, the assignment of this carbon was determined by ^{13}C DEPT NMR), 19.70 (t,$^2J_{P,C} =$ 4.8 Hz, P−CH(*C*H$_3)_2$), 19.30 (s, P−CH(*C*H$_3)_2$), 17.53 (t, $^2J_{P,C} =$ 4.2 Hz, P−CH(*C*H$_3)_2$), 15.70 (s, P−CH(*C*H$_3)_2$). Anal. Calcd for $C_{25}H_{38}BrO_2P_2Rh$: C, 48.80; H, 6.22. Found: C, 48.89; H, 6.29.

Reaction of 9 with $AgBF_4$. Formation of [(POCOP)Rh-(CH_2Ph)][BF_4] (10). To a benzene solution (1 mL) of complex **9** (25.5 mg, 0.041 mmol) was added 1 equiv of $AgBF_4$ (8.2 mg, 0.041 mmol) in THF (2 mL), resulting in formation of a white-gray precipitate of AgBr and a color change to red. The precipitate was removed by filtration through a Celite pad, and the solvent was removed from the filtrate under vacuum, resulting in a red solid in 98% (25 mg) yield. $^{31}P\{^1H\}$ NMR (C_6D_6): 173.4 (d, $^1J_{Rh,P} = 138.3$ Hz). ^{1}H NMR (C_6D_6): 7.25 (d, $^2J_{H,H} = 7.7$ Hz, 2H, Ar), 7.05 (m, 2H, Ar), 6.90 (t, $^3J_{H,H} = 7.7$ Hz, 2H, Ar), 6.70 (d, $^3J_{H,H} = 8.1$ Hz, 2H, Ar), 4.0 (dd, $^3J_{P,H}$= 2.9 Hz, $^3J_{Rh,H} = 5.9$ Hz, C*H*$_2$−Ar) 2.50 (m, $^2J_{P,H} = 7.0$ Hz, 4H, P−C*H*$(CH_3)_2$), 1.22 (m, 12H, 2 × P−CH(C*H*$_3)_2$), 1.06 (dd, $^3J_{H,H} = 7.0$ Hz, $^3J_{P,H} = 13.5$ Hz, 6H, P−CH(C*H*$_3)_2$), 0.96 (dd, $^3J_{H,H} = 7.0$ Hz, $^3J_{P,H} = 13.5$ Hz, 6H, P−CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 167.20 (t, $^2J_{P,C} = 6.2$ Hz, C_{ipso}, Rh−Ar), 147.50 (td, $^2J_{Rh,C} = 2.5$ Hz, $^3J_{P,C} = 5.3$ Hz, quaternary of carbon of benzyl ring), 134.03 (s, Ar), 132.12 (s, Ar), 129.70 (s, Ar of benzyl ring), 128.92 (s, Ar of benzyl ring), 127.50 (s, Ar), 107.30 (t, $^2J_{P,C} = 5.8$ Hz, Ar), 30.2 (t, $^2J_{P,C} = 8.7$ Hz P−*C*H$(CH_3)_2$), 27.2 (t, $^1J_{P,C} = 13.1$ Hz, P−*C*H$(CH_3)_2$), 26.32 (dt,$^2J_{Rh,C} = 27.6$ Hz, $^2J_{P,C} = 3.2$ Hz, *C*H$_2$−Ar, the assignment of

this carbon was determined by ^{13}C DEPT NMR), 19.51 (t,$^2J_{P,C}$ = 4.6 Hz, P−CH(CH_3)$_2$), 18.60 (s, P−CH(CH_3)$_2$), 16.20 (t, $^2J_{P,C}$ = 4.6 Hz, P−CH(CH_3)$_2$), 15.30 (s, P−CH(CH_3)$_2$). ^{19}F NMR (C_6D_6): −169.15 (br s).

X-ray Structural Analysis of 10. Crystal Data: $C_{25}H_{38}BF_4O_2P_2Rh$, orange plate, 0.4 × 0.2 × 0.1 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 8.106(2) Å, b = 12.576(3) Å, c = 14.082(3) Å, α = 81.42(3)°, β = 80.96(3)°, γ = 73.63(3)° from 20 degrees of data, T = 120(2) K, V = 1351.9(5) Å^3, Z = 4, fw = 622.21, D_c = 1.529 Mg/m^3, μ = 0.799 mm^{-1}.

Data Collection and Processing: Nonius KappaCCD diffractometer, Mo Kα (λ = 0.71073 Å), graphite monochromator, 0 ≤ h ≤ 10, −15 ≤ k ≤ 16, −17 ≤ l ≤ 18, frame scan width = 2.0°, scan speed 1.0° per 30 s, typical peak mosaicity 0.51°, 30 164 reflections collected, 6202 independent reflections (R_{int} = 0.069). The data were processed with Denzo-Scalepack.

Solution and Refinement: Structure solved by direct methods with SHELXS-97. Full matrix least-squares refinement based on F^2 with SHELXL-97; 324 parameters with 0 restraints, final R_1 = 0.0379 (based on F^2) for data with $I > 2\sigma(I)$ and, R_1 = 0.0428 on 6200 reflections, goodness-of-fit on F^2 = 1.017, largest electron density peak = 0.600 e Å^{-3}.

Preparation of (^{i}Pr-PCP)Rh(CO). To a C_6D_6 solution (0.5 mL) of the reported phosphine complex (^{i}Pr-PCP)RhN_2[13a] (50 mg, 0.107 mmol) in a septum-capped NMR tube was added 1 equiv (0.107 mmol, 2.4 mL) of CO, resulting in a slight color change to yellowish-brown. The solvent was removed under vacuum, resulting in a brown solid in 68% (34 mg) yield. ^{31}P{^{1}H} NMR (C_6D_6): 74.73 (d, $^1J_{Rh,P}$ = 144.3 Hz). ^{1}H NMR (C_6D_6): 7.20 (d,$^3J_{H,H}$ = 7.5 Hz, 2H, Ar), 7.1 (t, $^3J_{H,H}$ = 7.2 Hz, 1H, Ar), 3.2 (vt, 4H, J = 4.1 Hz, Ar−CH_2−P), 1.87 (m, 4H, P−CH(CH_3)$_2$), 1.18 (dist q,$^3J_{H,H}$ = 7.2 Hz,$^3J_{P,H}$ = 16.0 Hz, 12H, P−CH(CH_3)$_2$), 0.94 (dist q,$^3J_{H,H}$ = 7.2 Hz,$^3J_{P,H}$ = 14.0 Hz, 12H, P−CH(CH_3)$_2$).^{13}C{^{1}H} NMR (C_6D_6): 200 (dt, $^1J_{Rh,C}$ = 55.0 Hz, $^2J_{P,C}$ = 12.0 Hz, Rh−CO), 178.9 (dt, $^1J_{Rh,C}$ = 29.8 Hz, $^2J_{P,C}$ = 6.9 Hz, C_{ipso}, Rh−Ar), 152.87 (td, $J_{Rh,C}$ = 12.3 Hz $J_{P,C}$ = 3.0 Hz, Ar), 125.5 (s, Ar), 121.0 (t, $^2J_{P,C}$ = 9.8 Hz, Ar), 38.15 (vtd, $^2J_{Rh,C}$ = 2.8 Hz, $^1J_{C,P}$ = 12.0 Hz, Ar−CH_2−P), 26.2 (t, $^1J_{C,P}$ = 11.3 Hz, P−CH(CH_3)$_2$), 19.78 (vt, $^2J_{P,C}$ = 3.0 Hz, P−CH(CH_3)$_2$), 18.84 (s, P−CH(CH_3)$_2$).

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Supporting Information Available: CIF files containing X-ray crystallographic data for complexes **2**, **4b**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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