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B−C Bond Cleavage of BAr$_F$ Anion Upon Oxidation of Rhodium(I) with AgBAr$_F$. Phosphinite Rhodium(I), Rhodium(II), and Rhodium(III) Pincer Complexes

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A rare case of BAr$_F$ anion cleavage (BAr_F^- = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) by a metal complex is described. Reaction of the Rh(I) dinitrogen complexes **5a**,**b** and **6a**,**b**, based on the phosphinite pincer ligands $\{C_6H_4[OP(^tBu)_2]_2\}$ (**2**), with 2 equiv of AgBAr$_F$ at room temperature resulted in B−C bond cleavage of one of the BAr$_F$ anions and aryl transfer to afford the Rh(III) aryl complexes **7** and **8**, respectively. The X-ray structure of **8** revealed a square-pyramidal geometry with a coordinated acetone molecule. The aryl transfer occurred as a result of electrophilic attack by unsaturated Rh(III) on one of the aryl rings of the BAr$_F$ anion. Utilizing different solvents yielded the same product, except when CH_3CN was used, in which case one-electron oxidation took place, yielding complex **9**. Treatment of **6a**,**b** with 1 equiv of AgX (X = BAr$_F$, BF_4, PF_6) resulted in a one-electron oxidation to yield the paramagnetic Rh(II) complexes **9**−**11**, respectively. Complex **11** was characterized by X-ray diffraction, revealing a mononuclear square-planar Rh(II) complex.

Introduction

Noncoordinating or weakly coordinating anions play major roles in bond activation and catalysis by cationic transition-metal complexes,[1] including C−H activation and polymerization reactions. The BAr$_F$ anion (BAr_F^- = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) has been widely used in this context.[2] It was synthesized by Kobayashi and co-workers[3] as its sodium salt and was shown to be an excellent stable noncoordinating anion. However, recently two reports revealed that the BAr$_F$ anion can be reactive. Saeed et al. reported[4] a complex in which the BAr$_F$ anion is coordinated to silver and rhodium metal centers through η^3, η^4, and η^6 modes. Kubas reported[5] the only example of B−C bond cleavage of the BAr$_F$ anion; this reaction took place with the cationic complex *trans*-$[(Ph_3P)_2Pt(Me)(OEt_2)][BAr_F]$ at room temperature or upon refluxing in benzene. The analogous, generally weakly coordinating BPh_4 anion can exhibit η^6 coordination to metal centers,[6] and it is susceptible to attack by electrophilic transition-metal complexes, leading to phenyl group transfer.[6]

Here we report the second example of B−C bond cleavage of the BAr$_F$ anion. This reaction takes place upon two-electron oxidation of a phosphinite pincer Rh(I) complex, and it is preceded by a paramagnetic mononuclear Rh(II) complex. While dinuclear Rh(II) complexes are well-known, the normally less stable mononuclear Rh(II) complexes[7] are less common. Mononuclear Rh(II) complexes can be stabilized by bulky ligands or by electronic effects involving delocalization of the unpaired electron.[8] The most common mononuclear Rh(II) complexes are porphyrin complexes.[7i,8b] Stable pincer-type Rh(II) bis(oxazoline) monomeric complexes were reported by Bergman and Tilley.[7f] Recently, monomeric Rh(II) PNP-type complexes,[7a]

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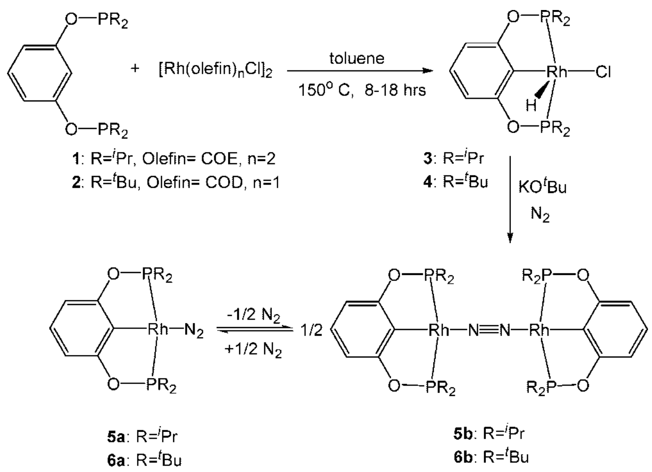
Scheme 1



as well as PC-type Rh(II) complexes,[9] were prepared in our group. To the best of our knowledge, Rh(II) complexes of the common PCP pincer type systems are not known.

Results and Discussion

Synthesis of Hydrido Chloride Rh(III) and Dinitrogen Rh(I) Phosphinite Complexes. We have recently reported the selective C−C bond activation of the phosphinite pincer ligand $C_6H_3(CH_3)[OP(^iPr)_2]_2$ at room temperature, upon reaction with the cationic complex $[Rh(COE)_2(THF)_2]BF_4$ (COE = cyclooctene), yielding the phosphinite Rh(III) complex $[(^i\mathrm{Pr}\text{-}\mathrm{POCOP})Rh(Me)]BF_4$ (^{i}Pr-POCOP = $C_6H_4[OP(^iPr)_2]_2$).[10] This complex underwent an apparent α-H elimination to give the hydrido complex $[(^i\mathrm{Pr}\text{-}\mathrm{POCOP})Rh(H)]BF_4$ and ethylene gas. We have now utilized the previously reported bulky ligands **1**[11] and **2**[12] to prepare the phosphinite complexes **3** and **4** by their reaction with the alkene complexes $[Rh(COE)_2Cl]_2$ and $[Rh(COD)Cl]_2$, respectively, in toluene at 150 °C (Scheme 1). The $^{31}P\{^1H\}$ NMR of **3** exhibits a doublet at δ 188.41 ($^1J_{Rh,P}$ = 122.2 Hz), while the $^{31}P\{^1H\}$ NMR of **4** exhibits two overlapping doublets (in a ratio of 1:1) at δ 190.08 and 201.08 ($^1J_{Rh,P}$ = 120.8 Hz), probably due to the presence of square-pyramidal and trigonal-bipyramidal isomers. In the ^1H NMR, the hydride appears as a broad doublet at δ −25.19 with $^1J_{Rh,H}$ = 39.4 Hz for complex **3** and as a double of triplets at δ −27.13 with $^1J_{Rh,H}$ = 48.9 Hz for complex **4**. Deprotonation of complexes **3** and **4** with 1 equiv or an excess of KO^{t}Bu led to formation of the dinitrogen complexes **5a**,**b** and **6a**,**b**, respectively (Scheme 1). Complexes **5a**,**b** were previously prepared by us by a different route.[10] Complex **6b** exhibits a doublet at δ 202.68 ($^1J_{Rh,P}$ = 172.7 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Complexes analogous to **6a**,**b** with iridium were reported.[13] The ν_{N_2} bands in the IR spectra of complex **6a** and the reported iridium analogue[13] are quite similar (2143 vs 2118 cm^{-1}). The ν_{N_2} band of complex **5a** is slightly higher (2162 cm^{-1}). This trend can be attributed to the higher basicity of the ^{t}Bu groups, which results in more back-bonding to the dinitrogen ligand, with a corresponding weakening of the N−N bond. While several PCP-based dinitrogen complexes are known, only a small number of POCOP-based complexes have been reported.[9,13]

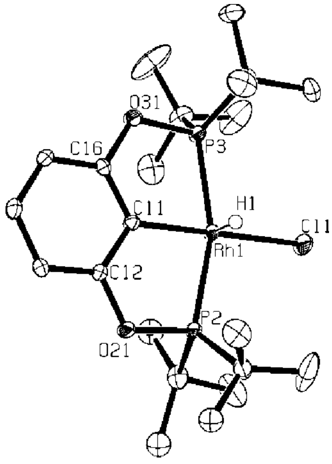


Figure 1. ORTEP drawing of complex **4**. Hydrogen atoms, except for hydride, are omitted for clarity. Ellipsoids are given at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complex 4

Rh(1)−C(11)	1.998(2)	Rh(1)−H(1)	1.57(3)
Rh(1)−P(2)	2.299(1)	P(2)−O(21)	1.659(2)
Rh(1)−P(3)	2.301(1)	P(3)−O(31)	1.657(2)
Rh(1)−Cl(1)	2.405(1)		
C(11)−Rh(1)−Cl(1)	179.52(5)	P(2)−Rh(1)−P(3)	160.34(2)
C(11)−Rh(1)−H(1)	82(1)	P(2)−Rh(1)−Cl(1)	99.44(4)
C(11)−Rh(1)−P(2)	80.35(6)	P(3)−Rh(1)−Cl(1)	100.18(4)
C(11)−Rh(1)−P(3)	80.03(6)		

An X-ray diffraction study of crystals of **4** grown from toluene reveals the expected square-pyramidal geometry (Figure 1, Table 1). The hydride ligand is located at the apical position, in line with its high-field chemical shift value in the ^1H NMR spectrum (−27.13, $^1J_{Rh,H}$ = 48.9 Hz). The chloride atom is *trans* to the *ipso* carbon. The Rh−Cl and Rh−C_{ipso} bond lengths are 2.405(1) and 1.998(2) Å, respectively, the latter being in the range of Rh−C_{ipso} bond lengths in the POCOP rhodium systems reported by us.[10] X-ray structures of two PCP-type hydrido chloride rhodium complexes[14] and two such iridium complexes were reported.[8,15]

Reaction of the Dinitrogen Complexes 5a,b and 6a,b with AgBAr$_F$. Formation of BAr$_F$ Cleavage Products. Reaction of the dinitrogen Rh(I) complexes **5a**,**b** and **6a**,**b** with 2 equiv of AgBAr$_F$ at *room temperature* led to formation of complexes **7** and **8**, respectively, accompanied by metallic silver (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum exhibits new doublets at δ 171.66 for **7** ($^1J_{Rh,P}$ = 119.3 Hz) and at δ 179.56 for **8** ($^1J_{Rh,P}$ = 112.0 Hz). No frequency suitable for a terminal N_2 molecule was detected in the IR spectrum, the absence of which was confirmed by elemental analysis. However, the ^1H and $^{13}C\{^1H\}$ NMR spectra were not sufficiently informative for conclusive structure elucidation. Crystals suitable for X-ray diffraction analysis were grown by vapor diffusion of diethyl ether into an acetone solution of complex **8** at −35 °C. Surprisingly, the crystal structure revealed that B−C bond

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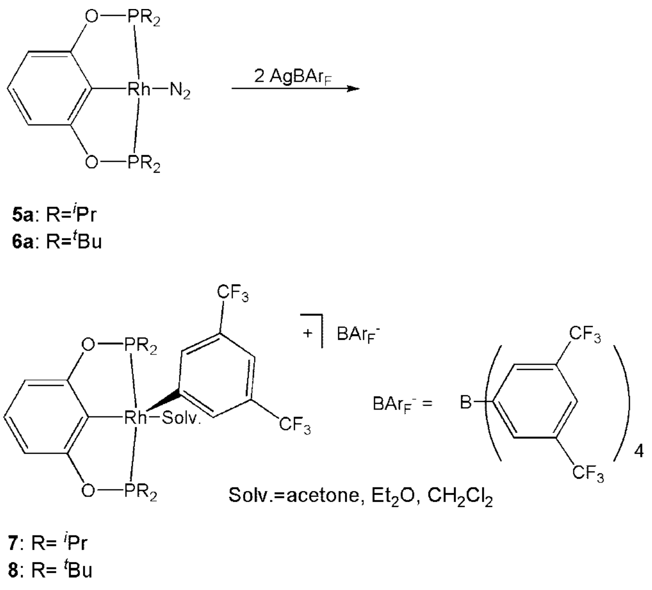
Scheme 2[a]



5a: R=^{i}Pr
6a: R=^{t}Bu

7: R= ^{i}Pr
8: R= ^{t}Bu

[a] For simplicity we depict complexes **5a**,**b** and **6a**,**b** as monomeric (**5a** and **6a**) in all schemes.

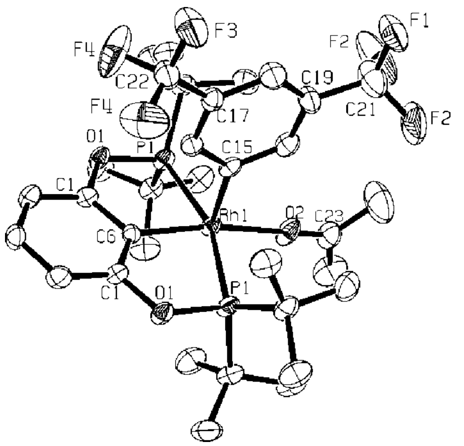


Figure 2. ORTEP drawing of complex **8**. The hydrogen atoms and BAr$_F$ anion are omitted for clarity. Ellipsoids are given at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 8

Rh(1)−C(6)	1.975(5)	Rh(1)−P(1)	2.355(1)
Rh(1)−C(15)	2.000(5)	P(1)−O(1)	1.647(3)
Rh(1)−O(2)	2.186(4)		
C(6)−Rh(1)−C(15)	88.8(2)	C(6)−Rh(1)−P(1)	80.64(3)
C(6)−Rh(1)−O(2)	167.2(2)	C(15)−Rh(1)−P(1)	92.16(4)
C(15)−Rh(1)−O(2)	104.0(2)	O(2)−Rh(1)−P(1)	98.60(3)

cleavage of one of the two BAr$_F$ anions took place, resulting in an aryl transfer to afford a cationic Rh(III) metal center (Figure 2, Table 2).[16]

The rhodium atom in complex **8** is in the center of a distorted square pyramid. The σ-coordinated C_6H_3-(3,5-CF_3) ring is at the axial position and is *trans* to the vacant site, as expected (Figure 2), whereas the position *trans* to the *ipso* carbon of the ^{t}Bu-POCOP ligand is occupied by an acetone molecule.

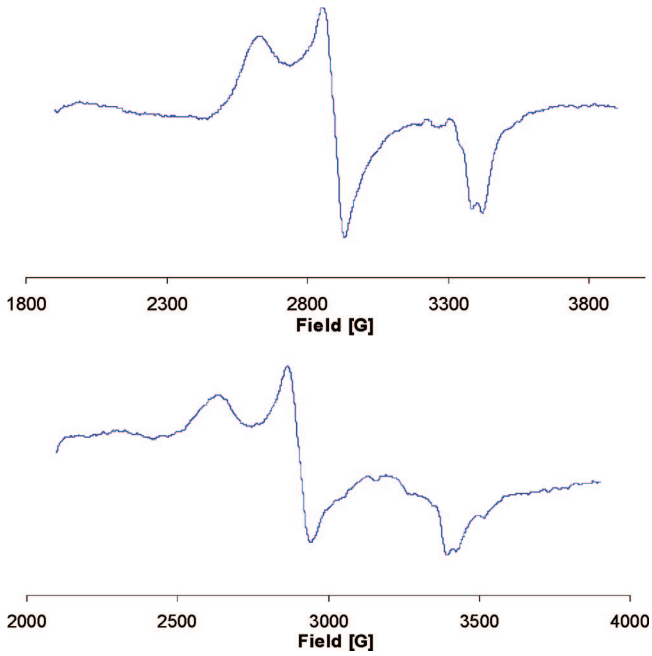


Figure 3. EPR spectra of complexes **9** (upper spectrum) and **11** (lower spectrum) obtained at 125 K in frozen acetone. Experimental conditions: microwave power 31 mW, modulation amplitude 0.8 G, time constant 0.65 s.

The cleaved Ar$_F$ protons exhibit in the ^{1}H NMR spectrum a downfield shift and a change in the relative ratios of the peaks, as observed in the previously reported example.[2b] The *ortho* protons of the coordinated Ar$_F$ ring are shifted upfield relative to its *para* proton, whereas the order is opposite for the BAr$_F$ anion protons. The *ipso* carbons of the cleaved Ar$_F$ groups could not be located in the ^{13}C{^{1}H} NMR spectra of complexes **7** and **8**. We assume that their chemical shifts overlap with those of the *ipso* carbons of the POCOP ligands.

Mechanistic Aspects of the B−C Cleavage of the BAr$_F$ Anion. Characterization of Rh(II) Species. We believe that the unexpected, room-temperature cleavage of the BAr$_F$ anion occurs as a result of an electrophilic attack of an unsaturated Rh(III) cationic center (obtained by two-electron oxidation of the Rh(I) precursor) on the *ipso* carbon of one of the aryl rings of the BAr$_F$ anion.

As the reaction was observed in several solvents, none of which is acidic (see Influence of Solvents on the B−C Bond Cleavage), a mechanism in which the B−C cleavage is promoted by protonation of the *ipso* carbon of the phenyl ring is unlikely.

Treatment of the Rh(I) complexes **5a**,**b** and **6a**,**b** with 2 equiv of NaBAr$_F$ did not lead to any reaction, indicating that Rh(I) species are probably not involved in the B−C bond cleavage reaction. In order to check if the reaction proceeds through an electrophilic attack of a Rh(II) center (i.e., one-electron oxidation of the metal and the BAr$_F$ cleavage take place initially, followed by a second oxidation to afford the Rh(III) center) only 1 equiv of AgBAr$_F$ was utilized. Under these conditions, reaction of **5a**,**b** resulted in a mixture of complexes. Reaction of complexes **6a**,**b** led to a solution that exhibited two doublets in the ^{31}P{^{1}H} NMR spectrum, which turned out to be minor products after their extraction with pentane. The major product was a paramagnetic complex, according to an EPR measurement (Figure 3).

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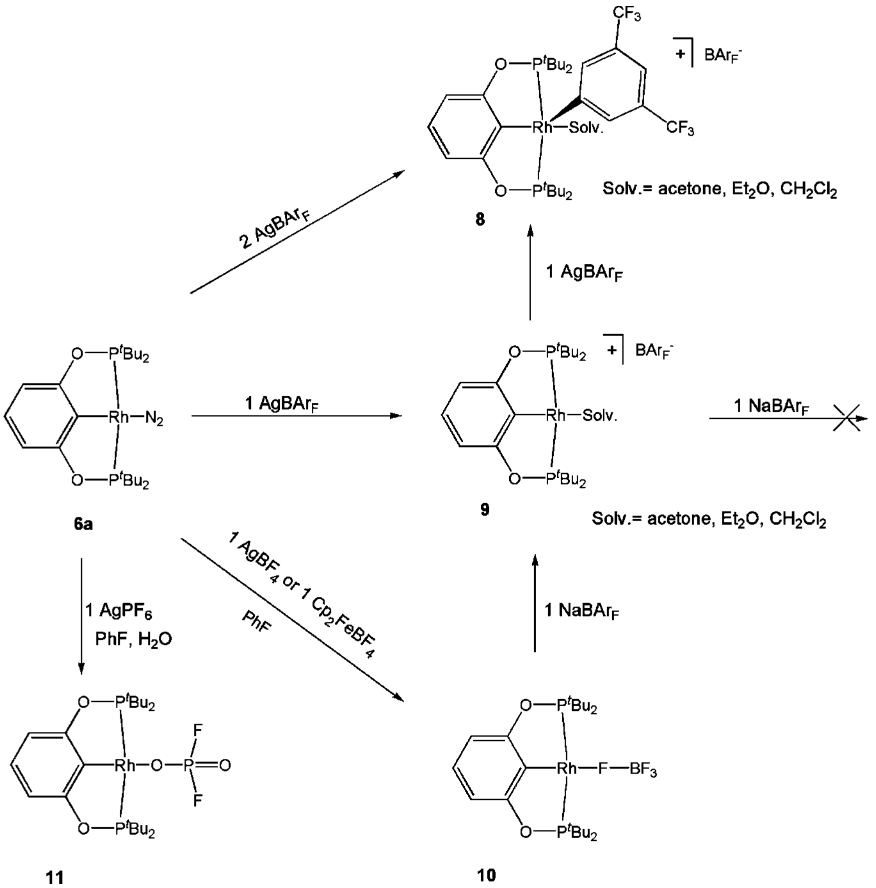
[16] The presumed cleaved product B(C_6H_3(3,5-CF_3))$_3$ could not be detected by ^{19}F NMR of the reaction mixture, perhaps as a result of reaction with adventitious water forming an insoluble compound (a precipitate was observed).

Scheme 3



Since attempts to crystallize the paramagnetic product (which was eventually characterized as complex **9**)[17] were not successful, other oxidants with anions potentially better suited for crystallization were applied. The dinitrogen complexes **6a**,**b** were treated with 1 equiv of AgBF_4 or $[\text{Cp}_2\text{Fe}][\text{BF}_4]$, resulting in an oxidation product similar to that for AgBAr_F according to EPR measurements. Treatment of those products with 1 equiv of NaBAr_F resulted in a color change from reddish brown to violet, but the product remained paramagnetic and only anion exchange took place, as confirmed by an EPR measurement, which exhibited the same spectrum as for **9** (Scheme 3). Moreover, treatment of complex **9** with 1 equiv of NaBAr_F did not lead to any reaction. On the other hand, treatment of those products with 1 equiv of AgBAr_F resulted in the formation of the BAr_F cleavage product **8** (with BF_4^- as a counterion). These results support a mechanism of electrophilic attack at the aryl ring by a Rh(III) center and not by Rh(II).

The product of the oxidation of **6a**,**b** with AgBF_4 described above was the analogue of **9** with a BF_4 anion, the paramagnetic complex $[(^t\text{Bu-POCOP})\text{Rh}^{\text{II}}][\text{BF}_4]$ (**10**) (Scheme 3). Crystals of this complex were grown by diffusion of pentane into its fluorobenzene solution, but the structure obtained by X-ray diffraction was disordered, although it did indicate the connectivity of this structure.

Reaction of AgPF_6 as with **6a**,**b** resulted in the paramagnetic product **11** (Scheme 3), and crystals of it were grown by pentane diffusion into its fluorobenzene solution. X-ray diffraction of these crystals showed a Rh(II) product with $[\text{PF}_2\text{O}_2]^-$ as a coordinated counteranion (Figure 4), which was probably formed by Rh(II)- or Ag^+-catalyzed[18] hydrolysis of PF_6^- with traces of water. Transition-metal complexes containing $[\text{PO}_2\text{F}_2]^-$ as a ligand or counteranion, resulting from PF_6^- hydrolysis, probably promoted by the Lewis-acidic metal center, were reported.[19]

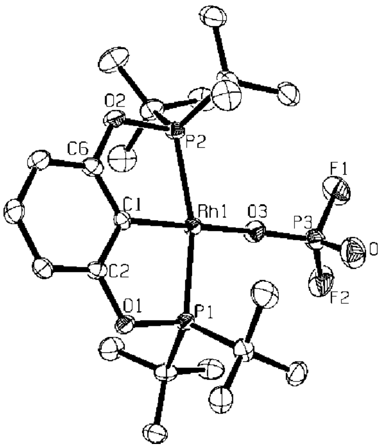


Figure 4. ORTEP drawing of complex **11**. Hydrogen atoms are omitted for clarity. Ellipsoids are given at the 50% probability level.

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[17] Crystals of complex **9** (Scheme 3) were grown by vapor diffusion of pentane into its dichloromethane solution. However, the structure was disordered, although it revealed a Rh(II) product with a coordinated acetone molecule and the BAr_F counteranion.

[18] Catalysed hydrolysis of PF_6^- by Ag^+ was reported: Fernandez-Galan, R.; Manzano, B. R.; Otero, A.; Lanfranchi, M.; Pellinghelli, M. A. *Inorg. Chem.* **1994**, *33*, 2309. The adventitious water in the reaction leading to complex **11** might be derived from the solvent.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) of Complex 11

C(1)−Rh(1)	1.980(3)	P(3)−F(2)	1.549(3)
Rh(1)−O(3)	2.148(2)	P(3)−F(1)	1.550(2)
Rh(1)−P(2)	2.304(1)	P(3)−O(4)	1.449(3)
Rh(1)−P(1)	2.3176(1)	P(3)−O(3)	1.469(3)
C(1)−Rh(1)−O(3)	170.78(11)	P(3)−O(3)−Rh(1)	137.19(15)
P(1)−Rh(1)−P(2)	160.16(3)		

Table 4. EPR Parameters of Complexes 9−11[a]

complex	g_x	g_y	g_z	A_1 (G)
9[b]	2.536	2.331	1.954	17.5
9[c]	2.531	2.328	1.956	17
10[d]	2.532	2.233	1.953	17
10[e]	2.540	2.332	1.955	17.5
11	2.525	2.324	1.956	17

[a] Repetition is due to different synthesis pathways. [b] Obtained from **6a**,**b**. [c] Obtained from **10**. [d] Obtained from $AgBF_4$. [e] Obtained from $[Cp_2Fe][BF_4]$.

The rhodium atom in complex **11** is in the center of a slightly distorted square plane. The Rh−C(1) bond length (1.980(3) Å) is similar to that of the Rh(III) complex **8** (1.975(5) Å) (Table 3).

Formation of the Rh(II) complex **9** upon one-electron oxidation of **6a**,**b**, without B−C cleavage taking place, indicates that Rh(II) is not active in the cleavage of the BAr_F anion. Thus, the likely mechanism of B−C cleavage involves elecrophilic attack of an unsaturated Rh(III) center on the *ipso* carbon of the anion.[20]

The paramagnetic d^7 Rh(II) complexes **9**−**11** were studied by X-band EPR spectroscopy in frozen acetone solutions. For all complexes an EPR rhombic pattern was observed and no hyperfine structure was resolved for the central- and low-field components g_x and g_y (Figure 3). For the g_z component the observed doublet hyperfine splitting can be explained by coupling with the nuclear spin of ^{103}Rh ($I = 1/2$). The EPR data obtained can reflect asymmetric coordination of ligands around the metal center which correspond to the slight distortion of the square-planar geometry exhibited in the X-ray structure of complex **11**. For Rh(II) complexes with bis(phosphinoalkyl)arene[21] and bis(oxazoline)[7e] ligands, spectra in frozen solutions with EPR parameters close to those obtained by us were observed. The EPR parameters of complexes **9**−**11** are outlined in Table 4.

Influence of Solvents on the B−C Bond Cleavage. The oxidation of complexes **5a**,**b** and **6a**,**b** with 2 equiv of $AgBAr_F$, when carried out in coordinating (acetone, diethyl ether) or noncoordinating (PhF, CH_2Cl_2)[22] solvents, afforded the same red products, complexes **7** and **8**, respectively. However, when the reaction of complexes **6a**,**b** was carried out in the strongly coordinating solvent CH_3CN, a green product was obtained, which showed no signals in the $^{31}P\{^1H\}$ NMR spectrum. When the solvent was removed, the color of the residue became violet. The violet product was identified as the Rh(II) complex **9** (Scheme 3), as evidenced by its EPR analysis and confirmed by the reaction of 1 equiv of $AgBAr_F$ with **6a**,**b** in CH_3CN. Thus, only one -electron oxidation takes place in CH_3CN, even when 2 equiv of $AgBAr_F$ is used. The effect of different solvents on the redox potential of Ag^+/Ag has been described in the literature.[23] It was shown that the lowest redox potential among the tested solvents was in CH_3CN, which is probably why the second oxidation did not take place.

On the other hand, when the less bulky complexes **5a**,**b** were oxidized in CH_3CN, a mixture containing two major complexes (in a ratio of 1:1.4) was obtained. The minor complex exhibits in $^{31}P\{^1H\}$ NMR a doublet and a coupling constant similar to the BAr_F cleaved product (**7**). It seems that the combination of the bulkier ^{t}Bu substituents in **6a**,**b** and the use of CH_3CN as a solvent prevents a second oxidation from taking place and therefore the B−C cleavage of BAr_F does not occur.

Complexes **7** and **8** are probably solvent-stabilized, even in the case of the weakly coordinating CH_2Cl_2.[24] In the case of the noncoordinating solvent PhF, agostic interactions with the C−H bonds of the ^{t}Bu substituents might be involved, although we have no evidence for such interactions with the metal center. Repeated attempts to crystallize complexes **7** and **8** in CH_2Cl_2 or PhF were not successful.

Summary

Treatment of the phosphinite dinitrogen Rh(I) complexes (**5a**,**b** and **6a**,**b**) with 2 equiv of $AgBAr_F$ leads unexpectedly to the cleavage of one of the B−C bonds of the BAr_F anion and the transfer of the cleaved aryl group to the rhodium center. The reaction takes place at room temperature via an electrophilic attack of the Rh(III) center on the B−C bond. The reaction of only 1 equiv of $AgBAr_F$ with the dinitrogen complexes **6a**,**b** leads to 1-electron oxidation, affording a 15-electron, square-planar Rh(II) complex (the fourth coordination site being occupied by a solvent molecule or a coordinating anion), with no aryl ring transfer being observed. The reaction of the Rh(II) intermediate **9** with 1 equiv of $NaBAr_F$ does not lead to any reaction, proving that a second oxidation to afford the Rh(III) complex is necessary for the cleavage process to take place. Moreover, the reaction of 2 equiv of $NaBAr_F$ with Rh(I) complexes **6a**,**b** does not lead to any reaction, confirming that metal oxidation to Rh(III) is necessary for the cleavage process to take place. The B−C cleavage product **8** and the Rh(II) intermediate **11** were characterized by X-ray diffraction analysis. Utilization of different solvents resulted in the formation of the same product (**7** and **8**), except in the case of CH_3CN, in which case only one-electron oxidation was possible due to the lower redox potential of silver salts in it.

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 an argon atmosphere. Deuterated solvents were dried over 4 Å molecular sieves. Commercially available reagents were used as received. $[Rh(COE)Cl]_2$,[25] $[Rh(COD)Cl]_2$,[26] $NaBAr_F$,[27] and Ag-

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(20) Attempts to explore the reactivity of unsaturated Rh(III) complexes toward electrophilic attack on the B−C bond were hampered by the lack of such suitable complexes; the oxidation of the Rh(II) complexes **10** and **11** to Rh(III) by treating them with another 1 equiv of $AgBF_4$ or $AgPF_6$, respectively, did not occur.

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(22) Excluding complexes **5a**,**b** in the case of CH_2Cl_2, in which they are not stable. However, complex **7**, obtained in the other solvents, is stable in CH_2Cl_2.

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$\mathrm{BAr_F}$[28] were prepared according to literature procedures. ^{1}H, ^{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, 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 $CDCl_3$, CD_2Cl_2, and C_6D_6. ^{1}H and ^{13}C{^{1}H} 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, 5.32 ppm for dichloromethane, and 7.24 ppm for chloroform). In ^{13}C{^{1}H} NMR measurements the signals of deuterated benzene (128.0 ppm), deuterated dichloromethane (53.8 ppm), and deuterated chloroform (77.0 ppm) were 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. X-band electron spin resonance (ESR) spectra were recorded on a ELEXSYS 500 spectrometer (Bruker, Karlsruhe, Germany). *g* values of the complexes in glassy solutions were determined using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) resonance signal ($g = 2.0037$) as a standard. The variable-temperature ESR experiments were carried out using a temperature unit (Euroterm, ER 4113VT, Bruker) with an accuracy of ±1 K.

Reaction of [Rh(COE)$_2$Cl]$_2$ with ^{i}Pr-POCOP-H (1). Formation of (^{i}Pr-POCOP)Rh(H)(Cl) (3). To a toluene solution (2 mL) of $[Rh(COE)_2Cl]_2$ (50 mg, 0.07 mmol) was added ligand **1** (47.7 mg, 0.14 mmol). The reaction mixture was transferred to a pressure vessel and heated at 150 °C for 8 h. The color changed from orange to brown, and a black fine solid was also formed. The product was filtered in order to remove the black solid through a cotton pad, and the solvent was removed from the filtrate under vacuum, resulting in a 90% pure oily complex in 97.2% (65.0 mg) yield.

^{31}P{^{1}H} NMR (C_6D_6): 188.41 (d, $^{1}J_{\mathrm{Rh,P}} = 122.2$ Hz). ^{1}H NMR (C_6D_6): 6.84 (t, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, 1H, Ar), 6.68 (d, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, 2H, Ar), 2.49 (m, 2H, $PC\mathit{H}(CH_3)_2$), 2.12 (m, 2H, $PC\mathit{H}(CH_3)_2$), 1.13 (overlapping double of doublets, 24H, $PCH(C\mathit{H}_3)_2$), −25.19 (br d, $^{1}J_{\mathrm{Rh,H}} = 39.4$ Hz, 1H, Rh−H). ^{13}C{^{1}H} NMR (C_6D_6): 166.91 (t, $^{2}J_{\mathrm{P,C}} = 6.9$ Hz, C$_{ipso}$, Rh−Ar), 128.53 (s, Ar), 126.78 (s, Ar), 106.38 (t, $^{2}J_{\mathrm{P,C}} = 5.7$ Hz, Ar), 29.91 (t, $^{1}J_{\mathrm{P,C}} = 11.0$ Hz, $P\mathit{C}H(CH_3)_2$), 28.44 (t, $^{1}J_{\mathrm{P,C}} = 13.5$ Hz, $P\mathit{C}H(CH_3)_2$), 17.45 (s, 6H, $PCH(\mathit{C}H_3)_2$), 17.34 (s, 6H, $PCH(\mathit{C}H_3)_2$), 16.94 (s, 6H, $PCH(\mathit{C}H_3)_2$), 16.45 (s, 6H, $PCH(\mathit{C}H_3)_2$). IR: $\nu_{\mathrm{Rh-H}}$ 2150 cm^{-1}. MS: *m/z* 479 (M^{+}, calcd *m/z* 480).

Reaction of [Rh(COD)Cl]$_2$ with ^{t}Bu-POCOP-H (2). Formation of (^{t}Bu-POCOP)Rh(H)(Cl) (4). To a toluene solution (10 mL) of $[Rh(COD)Cl]_2$ (600 mg, 1.2 mmol) was added ligand **2** (970 mg, 2.4 mmol) in toluene (5 mL). The reaction mixture was transferred to a pressure vessel and heated at 150 °C for 18 h. Complex **4** was obtained as an orange precipitate. The vessel was cooled, and the solvent was removed under vacuum, resulting in an orange solid in 83.9% (1096 mg) yield.

^{31}P{^{1}H} NMR ($CDCl_3$): 190.08 (dd (two isomers), $^{1}J_{\mathrm{Rh,P}} = 120.8$ Hz). ^{1}H NMR ($CDCl_3$): 6.89 (t, $^{3}J_{\mathrm{H,H}} = 7.8$ Hz, 1H, Ar), 6.54 (d, $^{3}J_{\mathrm{H,H}} = 7.8$ Hz, 2H, Ar), 1.37 (dd, $^{3}J_{\mathrm{P,H}} = 7.8$ Hz, 36H, $PC(C\mathit{H}_3)_3$), −27.13 (dt, $^{1}J_{\mathrm{Rh,H}} = 48.9$ Hz, $^{2}J_{\mathrm{P,H}} = 10.8$ Hz, 1H, Rh−H). ^{13}C{^{1}H} NMR ($CDCl_3$): 167.51 (t, $^{2}J_{\mathrm{P,C}} = 6.2$ Hz, C$_{ipso}$, Rh−Ar), 129.36 (dq, $^{2}J_{\mathrm{P,C}} = 5.0$ Hz, $^{2}J_{\mathrm{Rh,C}} = 31.3$ Hz), 126.22 (s, Ar), 105.66 (t, $^{2}J_{\mathrm{P,C}} = 5.5$ Hz, Ar), 40.88 (t, $^{1}J_{\mathrm{P,C}} = 8.3$ Hz, $P\mathit{C}(CH_3)_3$), 38.60 (t, $^{1}J_{\mathrm{P,C}} = 9.4$ Hz, $^{2}J_{\mathrm{Rh,C}} = 2.3$ Hz, $P\mathit{C}(CH_3)_3$), 27,65 (dist dd, $^{2}J_{\mathrm{P,C}} = 6.4$ Hz, $^{3}J_{\mathrm{Rh,C}} = 2.8$ Hz, $PC(\mathit{C}H_3)_3$). Anal. Calcd for $C_{22}H_{40}ClO_2P_2Rh$: C, 49.22; H, 7.51. Found: C, 49.37; H, 7.31.

X-ray Structural Analysis of 4. *Crystal data*: $C_{22}H_{40}ClO_2P_2Rh$, orange prisms, 0.7 × 0.5 × 0.3 mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 8.176(2)$ Å, $b = 12.184(2)$ Å, $c = 13.351(3)$ Å, $\alpha = 100.49(3)°$, $\beta = 95.71(3)°$, $\gamma = 103.91(3)°$, from 20° of data, $T = 120(2)$ K, $V = 1255.1(5)$ Å^3, $Z = 2$, fw 536.84, $D_c = 1.421$ Mg/m^3, $\mu = 0.929$ mm^{-1}. *Data collection and processing*: Nonius KappaCCD diffractometer, Mo Kα ($\lambda = 0.71073$ Å), graphite monochromator, $-10 \le h \le 10$, $-15 \le k \le 15$, $0 \le l \le 17$, frame scan width 1.0°, scan speed 1.0° per 30 s, typical peak mosaicity 0.47°, 26 574 reflections collected, 5733 independent reflections ($R_{\mathrm{int}} = 0.027$). 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, 301 parameters with 213 restraints, final R1 = 0.0261 (based on F^2) for data with $I > 2\sigma(I)$ and R1 = 0.0286 on 5361 reflections, goodness of fit on F^2 1.073, largest electron density peak 0.696 e Å^{-3}.

Reaction of (^{t}Bu-POCOP)Rh(H)(Cl) (4) with KO^{t}Bu. Formation of (^{t}Bu-POCOP)Rh(N$_2$) (6a) and [(^{t}Bu-POCOP)Rh]$_2$-(μ-N$_2$) (6b). To a THF solution (5 mL) of **4** (200 mg, 0.37 mmol) was added a slight excess (1.2 equiv, 50.2 mg, 0.44 mmol) of KO^{t}Bu as a solid, leading to a color change to brownish yellow and the immediate formation of the dinitrogen complexes **6a**,**b**. The solvent was removed under vacuum, the residue was extracted with benzene, and the extract was filtered through a cotton pad. The solvent was removed from the filtrate under vacuum, resulting in a yellow powder in 96.9% (190.7 mg) yield. Upon bubbling argon through a C_6D_6 solution of **6a**,**b** in a septum-capped NMR tube for 30 min, complex **6a** was quantitatively converted to complex **6b**.

^{31}P{^{1}H} NMR (C_6D_6): 202.68 (d, $^{1}J_{\mathrm{Rh,P}} = 172.7$ Hz). ^{1}H NMR (C_6D_6): 6.92 (t, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, 1H, Ar), 6.80 (d, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, 2H, Ar), 1.38 (vt, $^{3}J_{\mathrm{P,H}} = 7.6$ Hz, 36H, $PC(C\mathit{H}_3)_3$). ^{13}C{^{1}H} NMR (C_6D_6): 169.30 (t, $^{2}J_{\mathrm{P,C}} = 8.7$ Hz, C$_{ipso}$, Rh−Ar), 138.95 (dt, $^{2}J_{\mathrm{P,C}} = 9.7$ Hz, $^{2}J_{\mathrm{Rh,C}} = 34.5$ Hz), 126.18 (s, Ar), 104.44 (t, $^{2}J_{\mathrm{P,C}} = 6.7$ Hz, Ar), 39.36 (td, $^{1}J_{\mathrm{P,C}} = 2.2$ Hz, $^{2}J_{\mathrm{Rh,C}} = 7.2$ Hz, $P\mathit{C}(CH_3)_3$), 38.60 (t, $^{1}J_{\mathrm{P,C}} = 9.4$ Hz, $^{2}J_{\mathrm{Rh,C}} = 2.3$ Hz, $P\mathit{C}(CH_3)_3$), 27.65 (t, $^{2}J_{\mathrm{P,C}} = 6.4$ Hz, $PC(\mathit{C}H_3)_3$). IR (**6a**): $\nu_{\mathrm{N_2}}$ 2143 cm^{-1}. Anal. Calcd for $C_{22}H_{39}N_2O_2P_2Rh$: C, 50.01; H, 7.44. Found: C, 49.82; H, 7.22.

Reaction of 5a,b with 2 Equiv of AgBAr$_F$. Formation of [(^{i}Pr-POCOP)Rh(C$_6$H$_3$(CF$_3$)$_2$)][BAr$_F$] (7). To a fluorobenzene solution (1 mL) of **5a**,**b** (20.0 mg, 0.04 mmol) was slowly added 2 equiv of $\mathrm{AgBAr_F}$ (82.2 mg, 0.08 mmol) in fluorobenzene (1 mL), resulting in a color change from yellow to orange-red, and metallic silver was immediately massively formed. The reaction mixture was kept at room temperature overnight with protection from light until the reaction was complete. The metallic silver was removed by filtration through a cotton and Celite pad, and the solvent was removed from the filtrate under vacuum, resulting in a red oil. The residue was washed with pentane (3 × 2 mL) and dried again, resulting in a red solid in 96.9% (61.9 mg) yield.

^{31}P{^{1}H} NMR (CD_2Cl_2): 171.66 (d, $^{1}J_{\mathrm{Rh,P}} = 119.3$ Hz). ^{1}H NMR (CD_2Cl_2): 7.58 (br s, 1H, *p*-H of Ar$_F$), 7.50 (br s, 2H, *o*-H of Ar$_F$), 7.38 (br s, 8H, *o*-H of BAr$_F$), 7.22 (br s, 4H, *p*-H of BAr$_F$), 6.92 (t, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, 1H, Ar), 6.49 (d, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, 2H, Ar), 2.28 (m, 2H, $PC\mathit{H}(CH_3)_2$), 1.8 (br m, 2H, $PC\mathit{H}(CH_3)_2$), 0.88 (dd, $^{3}J_{\mathrm{H,H}} = 7.6$ Hz, $^{3}J_{\mathrm{H,P}} = 13.9$ Hz, 6H, $PCH(C\mathit{H}_3)_2$), 0.7–0.8 (overlapping double of doublets, 12H, $PCH(C\mathit{H}_3)_2$), 0.35 (dd, $^{3}J_{\mathrm{H,H}} = 8.9$ Hz, $^{3}J_{\mathrm{H,P}} = 16.5$ Hz, 6H, $PCH(C\mathit{H}_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): 164.92 (t, $^{2}J_{\mathrm{P,C}} = 5.5$ Hz, C$_{ipso}$, Rh−Ar), 162.11 (q, $^{1}J_{\mathrm{B,C}} = 49.73$ Hz, C$_{ipso}$ of BAr$_F$), 135.17 (br s, *o*-C of BAr$_F$), 134.58 (br s, *p*-C of Ar$_F$), 131.02 (s, Ar of POCOP), 129.24 (qq, −C of BAr$_F$), 129.03 (s, Ar of POCOP), 126.33 (s, −C of BAr$_F$), 123.62 (s, *p*-C of Ar$_F$), 121.53 (s, CF$_3$ of Ar$_F$), 119.44 (dd or m, *p*-C of Ar$_F$), 117.84 (br s, *p*-C of BAr$_F$), 109.55 (t, $^{3}J_{\mathrm{P,C}} = 5.8$ Hz, Ar of POCOP), 31.26

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(t, $^1J_{P,C}$ = 10.7 Hz, $\mathrm{P}\mathit{C}\mathrm{H(CH_3)_2}$), 28.39 (t, $^1J_{P,C}$ = 13.7 Hz, $\mathrm{P}\mathit{C}\mathrm{H(CH_3)_2}$), 19.17 (s, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 17.72 (s, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 15.65 (s, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 15.45 (s, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$). ^{19}F NMR ($CD_2Cl_2$): −62.93 (s, 24F, $\mathrm{C}\mathit{F}_3$ of BAr_F anion), −63.32 (s, 3F, $\mathrm{C}\mathit{F}_3$ of Ar_F), −63.80 (s, 3F, $\mathrm{C}\mathit{F}_3$ of Ar_F). Anal. Calcd for $C_{58}H_{46}BF_{30}O_2P_2Rh$: C, 45.81; H, 3.05. Found: C, 45.96; H, 3.15.

Reaction of 6a,b with 2 Equiv of $AgBAr_F$. Formation of $[(^t\mathrm{Bu\text{-}POCOP})Rh(C_6H_3(CF_3)_2)][BAr_F]$ (8). To a fluorobenzene solution (1 mL) of **6a**,**b** (15 mg, 0.03 mmol) was added 2 equiv of $AgBAr_F$ (55.1 mg, 0.06 mmol) in a fluorobenzene solution (1 mL), leading to an immediate color change to violet and formation of metallic silver. The reaction mixture was stirred at room temperature for a few hours, resulting in a color change to red. The solution was filtered through a cotton and Celite pad to remove the metallic silver, and the solvent was removed from the filtrate under vacuum. The residue was washed with pentane (3 × 2 mL) and dried again, resulting in a red solid in 95.8% (42.9 mg) yield.

^{31}P{^{1}H} NMR (CD_2Cl_2): 179.56 (d, $^1J_{Rh,P}$ = 112.0 Hz). ^{1}H NMR (CD_2Cl_2): 7.58 (br s, 1H, *p*-H of Ar_F), 7.50 (br s, 2H, *o*-H of Ar_F), 7.38 (br s, 8H, *o*-H of BAr_F), 7.22 (br s, 4H, *p*-H of BAr_F), 6.92 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, Ar), 6.49 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, Ar), 2.28 (m, 2H, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 1.8 (br m, 2H, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 0.88 (dd, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,P}$ = 13.9 Hz, 6H, $\mathrm{PCH(C}\mathit{H_3}\mathrm{)_2}$), 0.7–0.8 (overlapping double of doublets, 12H, $\mathrm{PCH(C}\mathit{H_3}\mathrm{)_2}$), 0.35 (dd, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,P}$ = 16.5 Hz, 6H, $\mathrm{PCH(C}\mathit{H_3}\mathrm{)_2}$). ^{13}C{^{1}H} NMR ($CD_2Cl_2$): 165.92 (t, $^2J_{P,C}$ = 5.5 Hz, C_{ipso}, Rh−Ar), 162.0 (q, $^1J_{B,C}$ = 49.73 Hz, C_{ipso} of BAr_F), 135.0 (br s, *o*-C of BAr_F), 134.17 (br s, *p*-C of Ar_F), 131.20 (s, Ar of POCOP), 129.10 (qq, −C of BAr_F), 128.84 (s, Ar of POCOP), 126.13 (s, −C of BAr_F), 123.42 (s, *p*-C of Ar_F), 120.71 (s, CF_3 of Ar_F), 119.22 (dd or m, *p*-C of Ar_F), 117.72 (br s, *p*-C of BAr_F), 109.36 (t, $^3J_{P,C}$ = 5.8 Hz, Ar of POCOP), 43.63 (t, $^1J_{P,C}$ = 7.6 Hz, $\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$), 41.47 (td, $^1J_{P,C}$ = 7.6 Hz, $\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$), 29.21 (m, $\mathrm{PC(}\mathit{C}\mathrm{H_3)_3}$), 27.35 (br s, $\mathrm{PC(}\mathit{C}\mathrm{H_3)_3}$). ^{19}F NMR ($CD_2Cl_2$): −63.01 (s, 24F, $\mathrm{C}\mathit{F}_3$ of BAr_F anion), −63.65 (s, 3F, $\mathrm{C}\mathit{F}_3$ of Ar_F), −64.29 (s, 3F, $\mathrm{C}\mathit{F}_3$ of Ar_F). Anal. Calcd for $C_{63}H_{58}BF_{30}O_2P_2Rh$: C, 47.51; H, 3.67. Found: C, 47.45; H, 3.86.

X-ray Structural Analysis of 8. *Crystal data*: $C_{33}H_{48}F_6O_3P_2Rh + C_{32}H_{12}BF_{24}$, red, 0.4 × 0.3 × 0.3 mm^3, monoclinic, $P2_1/m$ (No. 11), a = 13.190(3) Å, b = 19.765(4) Å, c = 13.373(3) Å, β = 97.16(3)°, from 20° of data, T = 120(2) K, V = 3459(1) Å^3, Z = 2, fw 1634.79, D_c = 1.570 Mg/m^3, μ = 0.419 mm^{-1}. *Data collection and processing*: Nonius KappaCCD diffractometer, Mo Kα (λ = 0.710 73 Å), graphite monochromator, $-14 \le h \le 14$, $0 \le k \le 21$, $-14 \le l \le 0$, frame scan width 1.0°, scan speed 1.0° per 400 s, typical peak mosaicity 0.97°, 16 307 reflections collected, 5074 independent reflections (R_{int} = 0.066). 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, 524 parameters with 0 restraints, final R1 = 0.0497 (based on F^2) for data with $I > 2\sigma(I)$ and R1 = 0.0610 on 5018 reflections, goodness of fit on F^2 = 1.125, largest electron density peak 0.419 e Å^{-3}.

Reaction of 6a,b with 1 Equiv of $AgBAr_F$. Formation of $[(^t\mathrm{Bu\text{-}POCOP})Rh^{II}][BAr_F]$ (9). To a fluorobenzene solution (1 mL) of **6a**,**b** (20 mg, 0.04 mmol) was added 1 equiv of $AgBAr_F$ (36.7 mg, 0.04 mmol) as a solid, leading to an immediate formation of metallic silver and a color change to violet. The reaction mixture was kept for additional 2 h at room temperature for reaction completion and then filtered through a cotton and Celite pad for metallic silver removal. The solvent was removed from the filtrate under vacuum, giving a violet solid in 85.3% (44 mg) yield. Anal. Calcd for $C_{54}H_{51}BF_{24}O_2P_2Rh$: C, 47.56; H, 3.77. Found: C, 48.29; H, 3.87.

Reaction of 6a,b with 1 Equiv of $[(C_P)_2Fe][BF_4]$. Formation of $[(^t\mathrm{Bu\text{-}POCOP})Rh^{II}][BF_4]$ (10). To a fluorobenzene solution (1 mL) of **6a**,**b** (15 mg, 0.03 mmol) was added $[(C_P)_2Fe][BF_4]$ (7.7 mg, 0.03 mmol) as a solid, leading to a color change to reddish brown. ^{31}P{^{1}H} NMR showed no signals; the reaction mixture was kept for overnight at room temperature for reaction completion. The solvent was removed under vacuum, and the residue was washed with pentane to remove the formed ferrocene and then extracted with fluorobenzene and filtered through a cotton pad. The solvent was removed from the filtrate under vacuum, resulting in an 89.2% (14.9 mg) yield of complex **10**. Anal. Calcd for $C_{22}H_{39}BF_4O_2P_2Rh$: C, 45.0; H, 6.69. Found: C, 45.12; H, 6.76.

Reaction of 6a,b with 1 Equiv of $AgBF_4$. Formation of $[(^t\mathrm{Bu\text{-}POCOP})Rh^{II}][BF_4]$ (10). To a fluorobenzene solution (1 mL) of **6a**,**b** (20 mg, 0.04 mmol) was added 1 equiv of $AgBF_4$ (7.4 mg, 0.04 mmol) in fluorobenzene, leading to an immediate formation of metallic silver and a color change to violet. The reaction mixture was kept for additional 2 h at room temperature for reaction completion and then filtered through a cotton and Celite pad for metallic silver removal, and the solvent was removed from the filtrate under vacuum, giving a brown solid in 92.8% (20.6 mg) yield. Anal. Calcd for $C_{22}H_{39}BF_4O_2P_2Rh$: C, 45.0; H, 6.69. Found: C, 45.65; H, 6.75.

Reaction of Complex 10 with $NaBAr_F$. Formation of $[(^t\mathrm{Bu\text{-}POCOP})Rh^{II}][BAr_F]$ (9). Upon addition of 1 equiv of $NaBAr^F$ (30.2 mg, 0.034 mmol) to complex **10** (20 mg, 0.034 mmol) in acetone, the color changed immediately to violet. The solvent was removed after 1 h, the residue was extracted with acetone, and the extract was filtered in order to remove the formed $NaBF_4$. The solvent was removed from the filtrate under vacuum, giving a violet solid in 98% (45.4 mg) yield. Anal. Calcd for $C_{54}H_{51}BF_{24}O_2P_2Rh$: C, 47.56; H, 3.77. Found: C, 47.69; H, 3.85.

Reaction of 6a,b with 1 Equiv of $AgPF_6$. Formation of $[(^t\mathrm{Bu\text{-}POCOP})Rh^{II}][PO_2F_2]$ (11). To a fluorobenzene solution (1 mL) of **6a**,**b** (20 mg, 0.04 mmol) was added 1 equiv of $AgPF_6$ (10.7 mg, 0.04 mmol) in fluorobenzene, leading to an immediate formation of metallic silver and a color change to violet. The reaction mixture was kept for an additional 2 h at room temperature for reaction completion and then filtered through a cotton and Celite pad for metallic silver removal. The solvent was removed from the filtrate under vacuum, giving a brown solid in 30.7% (7.5 mg) yield. Anal. Calcd for $C_{22}H_{39}F_2O_4P_3Rh$: C, 43.94; H, 6.54. Found: C, 42.85; H, 6.14.

X-ray Structural Analysis of 11. *Crystal data*: $C_{22}H_{39}F_2O_4P_3Rh$, red, 0.3 × 0.2 × 0.1 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 8.404(2) Å, b = 16.600(3) Å, c = 20.931(4) Å, α = 102.71(3)°, β = 95.99(3)°, γ = 104.26(3)° from 20° of data, T = 120(2) K, V = 2721.6(11) Å^3, Z = 4, fw 601.35, D_c = 1.468 Mg/m^3, μ = 0.842 mm^{-1}. *Data collection and processing*: Nonius KappaCCD diffractometer, Mo Kα (λ = 0.71073 Å), graphite monochromator, $-10 \le h \le 10$, $-21 \le k \le 21$, $0 \le l \le 27$, frame scan width 1.0°, scan speed 1.0° per 30 s, typical peak mosaicity 0.419°, 49 652 reflections collected, 13 354 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, 601 parameters with 0 restraints, final R1 = 0.0461 (based on F^2) for data with $I > 2\sigma(I)$ and R1 = 0.0791 on 12 436 reflections, goodness of fit on F^2 = 1.213, largest electron density peak 1.423 e Å^{-3}.

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Supporting Information Available: CIF files containing X-ray crystallographic data for complexes **4**, **8**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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