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Comparisons of Photoinduced Oxidative Addition of B−H, B−B, and Si−H Bonds at Rhodium(η^5-cyclopentadienyl)phosphine Centers

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Ultraviolet irradiation of [Rh(η^5-C_5H_5)(PMe_3)(C_2H_4)] (**1a**), [Rh(η^5-C_5H_5)(PPh_3)(C_2H_4)] (**1b**), and [Rh(η^5-$C_5H_4CF_3$)(PMe_3)(C_2H_4)] (**1c**) (collectively abbreviated as [Rh(Cp′)(PR_3)(C_2H_4)]) in the presence of HBpin (pinacolate = pin = 1,2-$O_2C_2Me_4$) results in elimination of C_2H_4 and B−H oxidative addition, leading to the formation of boryl hydride complexes [Rh(Cp′)(Bpin)(H)(PR_3)]. Complete conversion is achieved in liquid HBpin or by photolysis in hexane at −10 °C. Similarly, photolysis of **1a**−**c** in the presence of B_2pin_2 in hexane at −10 °C leads to B−B oxidative addition products, [Rh(Cp′)$(Bpin)_2$(PR_3)]. Irradiation at room temperature leads to formation of [Rh(Cp′)$(PR_3)_2$] in addition to the desired products. The rhodium boryl products were characterized by multinuclear NMR spectroscopy and, in the case of [Rh(η^5-C_5H_5)(Bpin)(H)(PPh_3)], by X-ray crystallography. The structure reveals a Rh−B distance of 2.0196(15) Å. The H···B separation of 2.09(2) Å together with the bond angles at the metal suggest some residual H···B interaction. Photolysis of **1a**−**c** in the presence of tertiary and secondary silanes ($HSiEt_3$, HSi^iPr_3, $HSi(OMe)_3$, $HSiMe_2Et$, $HSiMeEt_2$, and H_2SiEt_2) results in rhodium silyl hydride complexes [Rh(Cp′)(SiR'_2R'')(H)(PR_3)]. The structure of [Rh(η^5-C_5H_5)(Si^iPr_3)(H)(PMe_3)] was determined by single-crystal X-ray diffraction, yielding a Rh−Si bond length of 2.3617(3) Å and a Rh−H bond length of 1.508(17) Å. The H···Si distance of 2.278(17) Å and the very unequal H−Rh−P and H−Rh−Si angles suggest some residual H···Si interaction. Competition reactions were performed with **1b** dissolved in hexane in the presence of HBpin and B_2pin_2 simultaneously. ^{31}P NMR measurements, made after brief irradiation, showed a slight preference for B−B oxidative addition over B−H oxidative addition. Similar experiments with three-way competition among HBpin, $HSiMe_2Et$, and HC_6F_5, analyzed by ^1H NMR spectroscopy, showed negligible selectivity among H−B, H−C, and H−Si oxidative addition. Molecular structures were also determined by single-crystal X-ray diffraction for **1b**, **1c**, [Rh(η^5-C_5H_5)$(PPh_3)_2$], and [Rh(η^5-C_5H_5)Cl_2(PPh_3)].

Introduction

In the last few years, major advances have been made in transition-metal-catalyzed borylation of C−H bonds in arenes, alkanes, and heterocyclic compounds.[1−10] These reactions can be considered as a combination of C−H bond activation with either B−H or B−B activation. One of the most effective catalysts is recognized to be $[Ir(cod)(OMe)]_2$ + dtbpy (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), proceeding via the reaction intermediate [Ir$(Bpin)_3$(dtbpy)].[6,11] The borylation of heteroaromatics and polycyclic aromatics with this catalyst has proved very effective.[6,12] The reactions of late transition metal complexes with boranes, $HB(OR)_2$ [$(OR)_2$ is usually pinacolate = pin = 1,2-$O_2C_2Me_4$ or catecholate = cat = 1,2-$O_2C_6H_4$] can involve either B−H oxidative addition to yield boryl hydride complexes[5,13] or formation of σ-B−H com-

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plexes.[14,15] B−H oxidative addition is also implicated in catalytic hydroboration and dehydrogenative borylation of alkenes.[2,16,17] Equivalent principles apply to borylation with diboranes $(RO)_2BB(OR)_2$ where B−B oxidative addition dominates.[5,18] The formation and properties of metal boryl complexes, key intermediates in all of these reactions have been reviewed.[19] Borylation reactions have also been studied in detail by theoretical methods.[20]

Photochemical B−H oxidative addition was first mentioned by Hartwig as a very low yield process for $[W(\eta^5\text{-}C_5H_5)_2H_2]$.[21] In 2004, we reported photoinduced B−H oxidative addition of HBpin at $[Ru(depe)_2H_2]$ and $[Rh(triphos)H_3]$.[22] We used laser flash photolysis to measure the second-order rate constants for oxidative addition of boranes and found that the rate constants for reaction of $\{Ru(depe)_2\}$ and the related intermediates followed the order $k(H_2) > k(HBpin) > k(Et_3SiH)$. Photochemical B−B oxidative addition occurs cleanly on irradiation of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ with $B_2(\text{cat-3,5-}^t\text{Bu})_2$, yielding $[W(\eta^5\text{-}C_5H_5)_2(\text{Bcat-3,5-}^t\text{Bu}_2)_2]$; notably, B−B activation occurs in preference to C−H activation of the benzene solvent or the C−H bonds of the substrate.[21] Similarly, irradiation of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ with B_2pin_2 yields *cis* and *trans* isomers of $[Re(\eta^5\text{-}C_5Me_5)(Bpin)_2(CO)_2]$.[1c]

Hartwig et al. have shown that the photochemical reaction of HBpin in cyclohexane with $[Rh(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_6Me_6)]$ yields boryl hydride complex $[Rh(\eta^5\text{-}C_5Me_5)(H)_2(Bpin)_2]$, which reacts in neat HBpin to form $[Rh(\eta^5\text{-}C_5Me_5)(H)(Bpin)_3]$ and release H_2; both complexes are formally in the Rh(V) oxidation state. Structural and computational investigations suggest that these complexes each involve one partial B···H bond.[23] These two complexes and $[Rh(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_6Me_6)]$ are active catalysts for the borylation of hydrocarbons.[8,23] Thermal reaction of $[Rh(\eta^5\text{-}C_5Me_5)(H)_2(Bpin)_2]$ with $P(p\text{-tol})_3$ yields the Rh(III) complex $[Rh(\eta^5\text{-}C_5Me_5)(H)(Bpin)\{P(p\text{-tol})_3\}]$, while reaction of $[Rh(\eta^5\text{-}C_5Me_5)(H)(Bpin)_3]$ with PEt_3 yields $[Rh(\eta^5\text{-}C_5Me_5)(Bpin)_2(PEt_3)]$. Thermal or photochemical reaction of $[Rh(\eta^5\text{-}C_5Me_5)(H)_2(SiEt_3)_2]$ with HBpin yields $[Rh(\eta^5\text{-}C_5Me_5)(H)_2(SiEt_3)(Bpin)]$, another complex with partial B···H bonding. This species reacts with $P(p\text{-tol})_3$ to give a mixture of boryl hydride and silyl hydride complexes of $[Rh(\eta^5\text{-}C_5Me_5)\{P(p\text{-tol})_3\}]$.[24] The very closely related complex $[Ir(\eta^5\text{-}C_5Me_5)(H)(Bpin)(PMe_3)]$ was synthesized by Iverson and Smith by displacement of cyclohexane from the cyclohexyl hydride complex with HBpin and was the first complex demonstrated to be a catalyst precursor for the borylation of benzene.[7]

Photoinduced Si−H bond oxidative addition is long established,[25] and we have used it as a benchmark in laser studies of the reaction of coordinatively unsaturated complexes derived by photolysis of metal dihydride complexes.[26] We have also studied the oxidative addition of trialkylsilanes at rhodium by photolysis of $[Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2]$ and its derivatives.[27] Related reactions have been reported at C_5Me_5 complexes[28] and at dinuclear rhodium complexes with linked cyclopentadienyl groups.[29] Silyl hydride species are key intermediates in catalytic hydrosilation,[30] a process that is practiced on an industrial scale.[31]

The complex $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(C_2H_4)]$ (**1a**) was first observed in 1975 by Cramer and Seiwell[32] and investigated as a metal base by Werner and Feser.[33] Upon photolysis, loss of ethene from $[Rh(\eta^5\text{-}C_5H_5)(PR_3)(C_2H_4)]$ (R = Me, Ph) complexes leads to the formation of an unsaturated 16e$^-$ species capable

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Table 1. Selected NMR Spectroscopic Data in C_6D_6 [δ (J/Hz)] for Precursors and Products of Photoreaction with Boranes

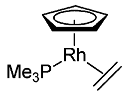
	1a	**1b**	**1c**
^{1}H Cp	5.09 s, 5H	5.06 s, 5H	5.18 br m, 2H 4.99 br m, 2H
^{1}H PR_3	0.77 dd, J_{PH} 9.2, J_{RhH} 1.1, 9H	6.75−7.65 m, 15H	0.71 dd, J_{PH} 9.6 J_{RhH} 1.1, 9H
^{1}H C_2H_4	2.74 m, 2H 1.46 m, 2H	2.83 m, 2H 1.31 m, 2H	2.80 br m, 2H, 1.49 br m, 2H
^{31}P{^{1}H}	4.4 d, J_{RhP} 200	59.5 d, J_{RhP} 210	6.9 dq, J_{RhP} 198, J_{PF} 2
^{19}F			−54.4 m
	2a	**2b**	**2c**
^{1}H hydride	−14.04 dd, J_{PH} 33.7, J_{RhH} 35.1	−13.04 dd, J_{PH} 29.6, J_{RhH} 32.8	−14.58 dd, J_{PH} 34.6, J_{RhH} 36.8
^{1}H Cp	5.36 s	5.33 s	5.19 br s, 5.31 br s, 5.52 br s, 5.75 br s
^{31}P{^{1}H}	12.4 d, J_{RhP} 170	62.5 d, J_{RhP} 180	13.7 d, J_{RhP} 169
^{11}B	45.4	44.8	43.9
	3a	**3b**	**3c**
^{1}H Cp	5.29 s	5.10 s	4.64 br s, 5.01 br s, 5.30 br s, 5.52 vs
^{31}P{^{1}H}	−2.2 d, J_{RhP} 217	58.3 d, J_{RhP} 223	−0.8 d, J_{RhP} 215
	4a	**4b**	**4c**
^{1}H Cp	5.46 s	5.41 s	5.43 br s, 5.76 br s
^{31}P{^{1}H}	14.8 d, J_{RhP}177	55.5 d, J_{RhP} 182	19.0 d, J_{RhP} 176
^{11}B	45.1	43.7	43.8

of activating aromatic C−H bonds and Si−H bonds. The photochemistry of [Rh(η^5-C_5H_5)(PMe_3)(C_2H_4)] (**1a**) was intensively studied by Perutz et al. in C−H bond activation reactions of arenes[34] and partially fluorinated aromatic hydrocarbons.[35] The activation of a C−H bond of benzene was shown by laser flash photolysis to occur via an η^2-C_6H_6 intermediate. Further investigations revealed stable η^2-arene complexes, equilibria between aryl hydride and η^2-arene complexes, and C−F bond activation reactions.[36,37] Complementary studies of η^5-C_5Me_5 analogues, usually formed by thermal reaction of [Rh(η^5-C_5Me_5)(PMe_3)(C_6H_5)(H)] or by photochemical reaction of [Rh(η^5-C_5Me_5)(PMe_3)$(H)_2$], have been studied extensively by Jones et al.[35,36,38,39]

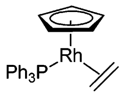
The complex [Rh(η^5-C_5H_5)(PPh_3)(C_2H_4)] (**1b**) was first reported by Oliver and Graham;[40] it was also observed as a photolytic[27] or thermal[41] reaction product of [Rh(η^5-C_5H_5)$(C_2H_4)_2$] in the presence of PPh_3. The photochemistry of **1b** resembles that of **1a**, but has not been investigated as extensively. Partially fluorinated benzenes form C−H bond activation products that are stable at room temperature. Irradiation of **1b** in neat tertiary alkyl silanes R_3SiH (R = Et, ^{i}Pr) generates single products assigned to the Si−H activation complexes; [Rh(η^5-C_5H_5)(PPh_3)(Si^iPr_3)(H)] has been characterized crystallographically.[42] The related complexes [Rh(η^5:η^1-$C_5H_4SiMe_2CH_2PPh_2$)(C_2H_4)] and [Rh(η^5:η^1-$C_5H_4SiMe_2CH_2PPh_2$)$(H)_2$] have been studied by Jones et al.[43]

The effect of an electron-withdrawing CF_3 group on the properties of metallocenes and methylated metallocenes was investigated by Gassman et al.[44,45] Notably, the redox potential of [Fe(η^5-$C_5H_4CF_3$)(η^5-C_5H_5)] is shifted by 0.64 V with respect to ferrocene. The $C_5H_4CF_3$ group also has a marked effect on the kinetics of substitution reactions of cyclopentadienyl rhodium dicarbonyls,[46] but little effect on charge-transfer complexes with sulfur dioxide.[47]

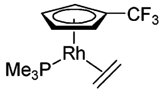
In this paper, we describe the photochemical reactivity of complexes **1a**, **1b**, and [Rh(η^5-$C_5H_4CF_3$)(PMe_3)(C_2H_4)] (**1c**) in the presence of B−H-, B−B-, and Si−H-containing reagents. We show that **1a**−**c** undergo B−H oxidative addition with HBpin, B−B oxidative addition with B_2pin_2, and Si−H oxidative addition with a variety of silanes. All of the products were characterized by NMR spectroscopy, and a few representative examples were chosen for more detailed spectroscopy and crystallography. We also report the relative yields of oxidative addition of B−H, B−B, Si−H, and C−H bonds investigated by competition reactions, the first such comparison.



1a



1b



1c

Results

Starting Materials. Complexes **1a** and **1b** were synthesized by standard procedures, but **1c** has not been reported previously. The sample of **1c** was synthesized by a procedure similar to that for **1b**, but using Tl(η^5-$C_5H_4CF_3$) instead of Li(C_5H_5).[44] NMR data for **1a**, **1b**, and **1c** are summarized in Table 1.

Crystals of **1b**, suitable for X-ray diffraction, were obtained from hexane at −18 °C; the molecular structure of **1b** is shown

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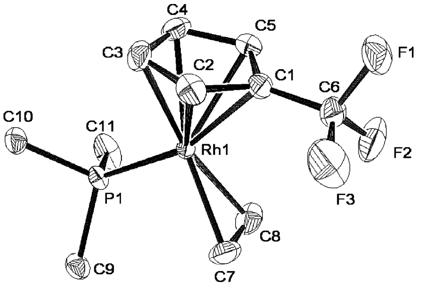

Figure 1. Molecular structure of **1c** (thermal ellipsoids shown at 50% probability, hydrogen atoms omitted).

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

Rh−P(1)	2.2149(5)	C(6)−Rh(1)−C(7)	39.02(14)
Rh(1)−C(7)	2.106(3)	C(7)−Rh(1)−P(1)	94.84(8)
Rh(1)−C(8)	2.106(2)	C(8)−Rh(1)−P(1)	91.46(8)
C(7)−C(8)	1.407(5)	P(1)−Rh(1)−C(1)	162.38(6)
C(1)−C(6)	1.473(3)		
C(6)−F	1.313(3)−1.353(3)		
Rh(1)−C(Cp)	2.232(2)−2.295(2)		

in Figure S1 (Supporting Information). The ethene hydrogen atoms were located and refined. The structure is similar to those of [Rh(η^5-C_5Me_5)(PPh_3)(C_2H_4)][48] and [Rh(η^5-C_5H_5)(PPh_3)(CO)].[49]

Crystals of **1c** suitable for X-ray crystallography were obtained by very slow sublimation under vacuum. The Rh−C bond lengths of the coordinated ethene ligand (Table 2, Figure 1) are equal (2.106 Å) and insignificantly different from those of **1b**; changes in other bond lengths are also minimal. As for **1b**, we can define an approximate mirror plane passing through the rhodium and phosphorus atoms and the center of the ethene C═C bond.

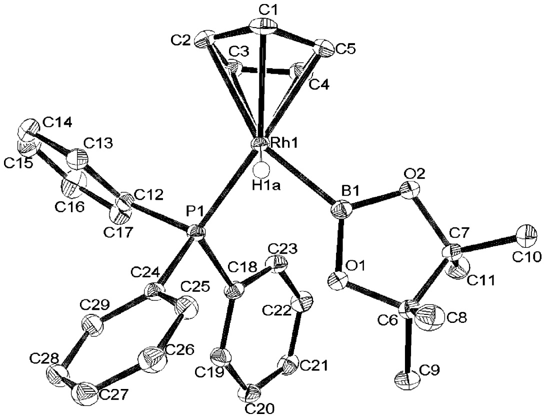

Figure 2. Molecular structure (50% thermal ellipsoids) of **2b**, with hydrogen atoms omitted except for H1A.

Reactions with HBpin. Photochemical reaction of a solution of **1a** and HBpin in hexane, contained in a Pyrex NMR tube (λ > 290 nm), at room temperature, leads to formation of the hydride boryl complex [Rh(η^5-C_5H_5)(H)(Bpin)(PMe_3)] (**2a**) and the bis(phosphine) complex [Rh(η^5-C_5H_5)(PMe_3)$_2$] (**3a**). When the photolysis temperature is reduced to about −10 °C, **2a** is still formed, but there is a drastic decrease in formation of byproduct **3a**. Irradiation of **1a** in neat HBpin at −10 °C leads to formation of the desired product **2a** only; after 15 h, conversion is complete (Scheme 1). Complex **2a** can be purified by sublimation at 35 °C, yielding a white solid. The boryl complex **2a** exhibits a doublet in the $^{31}P\{^1H\}$ NMR spectrum at δ 12.4 with a coupling constant J_{RhP} = 170 Hz characteristic of a half-sandwich Rh(III) complex. In this complex, and its analogues, the ^{31}P resonance is shifted downfield of the precursor, here **1a**. With partial ^1H decoupling, the ^{31}P resonance becomes a doublet of doublets, consistent with the presence of a single hydride in the molecule. In keeping with a Rh(III) complex, the ^1H NMR spectrum reveals a hydride resonance at δ −14.04 as a doublet of doublets (J_{PH} = 33.7, J_{RhH} = 35.1 Hz). The Bpin methyl groups are all coincident at δ 1.16 in the ^1H NMR spectrum. The ^{11}B NMR spectrum of the boryl product **2a** reveals a broad resonance at δ 45.4 in the region characteristic of metal−boryl complexes[19] and to low field of HBpin (δ 27.2). Broad-band proton decoupling did not affect the ^{11}B resonance of **2a** or of the other boryl complexes reported here. In the $^{13}C\{^1H\}$ spectrum, the Bpin resonances of **2a** are found at 81.2 (s, $BO_2C_2(CH_3)_4$), 25.4 (s, $BO_2C_2(CH_3)_4$), and 25.3 (s, $BO_2C_2(CH_3)_4$) compared to free HBpin, which resonates at δ 83.1 and 24.9. As has been observed previously,[22] the quaternary carbon shows an upfield shift on borylation. The chirality of the rhodium center could be expected to lead to four inequivalent methyl resonances in the ^{13}C and in the ^1H NMR spectra. The presence of only two Bpin methyl resonances in the ^{13}C spectrum is consistent with rapid rotation about the Rh−B bond; the corresponding ^1H resonances are not resolved.

Traces of the bis(phosphine) byproduct **3a** were also observed by NMR spectroscopy in reactions of the fragment {Rh(η^5-C_5H_5)(PMe_3)} in the presence of partially fluorinated arenes.[50] Complex **3a** exhibits a doublet in the $^{31}P\{^1H\}$ NMR spectrum at δ −2.2 with a J_{RhP} value of 217 Hz characteristic of a half-sandwich Rh(I) complex.[51]

The photolysis of **1b** at room temperature in the presence of HBpin follows the same path as that for **1a**. The product, [Rh(η^5-C_5H_5)(H)(Bpin)(PPh_3)] (**2b**), shows spectra similar to **2a**, but the coupling constants, J_{PH} = 29.6 and J_{RhH} = 32.8 Hz, of the products are smaller than for the PMe_3 analogue, while J_{RhP} is characteristically larger. Similar changes are observed in the spectra of other complexes on replacing PMe_3 by PPh_3 (see below). Both the ^1H and the ^{13}C NMR spectra show two closely spaced resonances for the Bpin methyl groups. The full widths at half-height of the hydride peaks for **2b** are essentially identical to those for analogues in which the boryl group is replaced by a silyl or a fluoroaryl group (see Competition Reactions below). It follows that any residual BH spin−spin coupling is negligible. Initial reactions carried out on a small scale yielded mixtures of **2b** and **3b**. A larger scale reaction, with careful control of the photolysis time, yielded **2b** only, with complete conversion to product; chromatographic purification yielded an analytically pure sample.

It was already known that **3b** is formed photochemically from [Rh(η^5-C_5H_5)(C_2H_4)$_2$] in the presence of 2 equiv of PPh_3[41] and also thermally from reaction of [Rh(η^5-C_5H_5)(PPh_3)(C_2H_4)] with PPh_3.[27] To establish the source of **3b**, we investigated the thermal reaction of each of **1b** and **2b** with triphenylphosphine by heating to 75 °C overnight. [Rh(η^5-C_5H_5)(PPh_3)$_2$] (**3b**) was formed both from the Rh(I) and from the Rh(III) species.

We succeeded in avoiding the formation of complexes **3a** and **3b** and in obtaining only the boryl complexes, by lowering the photolysis temperature to −10 °C and/or by using HBpin as a solvent as well as a substrate. This strategy also resulted in the desired product [Rh(η^5-$C_5H_4CF_3$)(Bpin)(H)(PMe_3)] (**2c**) on photolysis of [Rh(η^5-$C_5H_4CF_3$)(PMe_3)(C_2H_4)] (**1c**). Relevant

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Scheme 1. Photochemical Reactions of 1a−1c

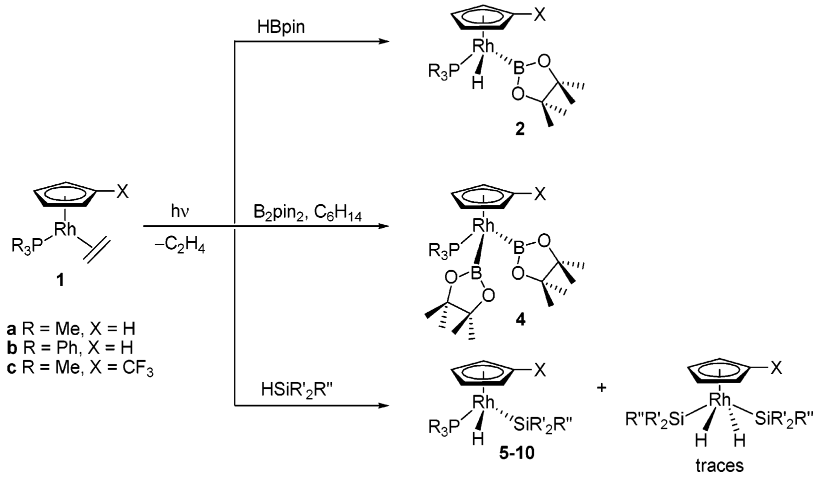

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2b

Rh(1)−P(1)	2.2157(4)	B(1)−Rh(1)−P(1)	88.82(4)
Rh(1)−B(1)	2.0196(15)	O(1)−B(1)−Rh(1)	125.87(10)
B(1)−O(1)	1.3835(18)	O(2)−B(1)−Rh(1)	123.44(10)
B(1)−O(2)	1.3909(18)	O(1)−B(1)−O(2)	110.67(12)
Rh(1)−C(Cp)	2.2233(14)−2.3198(14)	H(1A)−Rh(1)−B(1)	71.0(8)
C(6)−O(1)	1.4533(16)	H(1A)−Rh(1)−P(1)	88.5(8)
C(7)−O(2)	1.4601(16)		
Rh(1)−H(1A)	1.50(2)		
B(1)···H(1A)	2.09(2)		

NMR spectroscopic data for the products are summarized in Table 1 and illustrated in the Supporting Information (Figures S8−S10).

Orange crystals of **2b**, from the large-scale preparation, were grown from hexane at room temperature. The crystal structure (Figure 2, Table 3) confirmed the identity of the product and showed a Rh−B distance of 2.0196(15) Å. The puckering of the boronate ring was indicated by the torsional angle B(1)−O(1)−C(6)−C(7) of −19.69(14)°. The B(1)−Rh(1)−P(1) angle is 88.82(4)°, close to the expected value for a pseudo-octahedral complex. The hydride was located in the difference map and was refined at a Rh(1)−H(1A) distance of 1.50(2) Å with an acute B(1)−Rh(1)−H(1A) angle of 71.0(8)°, leading to an H···B separation of 2.09(2) Å. The P(1)−Rh(1)−H(1A) angle is considerably larger at 88.5(8)°. Since the B(1)−Rh(1)−P(1) angle is so close to 90°, we see no steric reason for the acute B−Rh−H angle. These parameters are very similar to those determined by X-ray diffraction at 120 K for [Rh(Cl)(H)(Bpin)(P^iPr_3)$_2$], for which Rh−H = 1.47(2) Å, B−Rh−H = 70.0(8)°, and H···B = 2.02(2) Å.[52] However, Rh−H distances determined by accurate X-ray diffraction measurements are systematically underestimated by ca. 0.1 Å, although the direction of the bond can be obtained with reasonable accuracy.[52] In [Rh(Cl)(H)(Bpin)(P^iPr_3)$_2$], neutron diffraction data obtained at 20 K gave Rh−H = 1.571(5) Å and B−Rh−H = 67.8(2)°, resulting in an H···B separation of 2.013(5) Å.[52] DFT studies on [Rh(Cl)(H)(Bpin)(P^iPr_3)$_2$] showed evidence for a weak residual H···B interaction, although the structure is much closer to that of a formal hydrido−boryl complex than that of a σ-borane complex (e.g., *r*(B−H) = 1.35 Å in ref 14). Thus, given the strong similarity of the structural data for **2b** and [Rh(Cl)(H)(Bpin)(P^iPr_3)$_2$], a similar description seems appropriate.

Hartwig et al. reacted [Rh(η^5-C_5Me_5)(H)$_2$(Bpin)$_2$] with P(*p*-tol)$_3$ to form [Rh(η^5-C_5Me_5)(H)(Bpin){P(*p*-tol)$_3$}], a close analogue of **2b**. NMR spectroscopic data include a hydride resonance at δ −13.08 ($J_{RhH} = J_{PH} = 33.8$ Hz) and a J_{RhP} value of 179 Hz, as well as an ^{11}B resonance at δ 42.3.[23] They reported no NMR spectroscopic evidence for B···H interaction. The molecular structure of [Rh(η^5-C_5Me_5)(H)(Bpin){P(*p*-tol)$_3$}] was also determined by X-ray diffraction data at 183 K, which gave Rh−B = 2.029(4) Å, Rh−H = 1.42(3) Å, B−Rh−H = 78.5(12)°, and a resulting H···B separation of 2.23(3) Å.

We would anticipate that the degree of formal oxidative addition of the B−H bond will be enhanced by electron-rich metal centers. Comparison of the structures of **2b** and [Rh(η^5-C_5Me_5)(H)(Bpin){P(*p*-tol)$_3$}] show changes in the expected direction with a decrease in *r*(Rh−H), an increase in H···B, and a less acute B−Rh−H angle. The differences are on the order of 3σ in *r*(Rh−H), but 7σ in the B−Rh−H angle. DFT calculations[18] on the model complex [Rh(η^5-C_5H_5)(H)($BOCH_2CH_2O$)(PH_3)], where the C_5Me_5 was replaced by C_5H_5, Bpin by $BOCH_2CH_2O$, and P(*p*-tol)$_3$ by PH_3, gave Rh−B = 2.033 Å, Rh−H = 1.56 Å, B−Rh−H = 71.7°, and a resulting B···H separation of 2.14 Å. These values are indeed closer to the measurements on **2b** as expected by the reduction in electron-donating ability of the ligands. Importantly, there must be a continuum of structures available representing various degrees of oxidative addition, and the differences in structure between **2b** and [Rh(η^5-C_5Me_5)(H)(Bpin){P(*p*-tol)$_3$}], especially in the B−Rh−H angle, show this clearly. In **2b**, the B···H interaction is demonstrably stronger than in [Rh(η^5-C_5Me_5)(H)(Bpin){P(*p*-tol)$_3$}], although neither can be described as a σ-borane complex, and the lack of BH coupling in solution is significant.[53]

A hexane solution containing a mixture of **2b** and **3b**, formed by photoreaction of **1b** with HBpin at room temperature, was left at −18 °C, yielding orange crystals, which were also investigated by X-ray diffraction. The crystal structure reveals

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(53) Comparisons may be drawn to M(η^5-C_5R_5)(H)$_2$(Bcat′) (M = Nb, Ta; R = H, Me; cat′ = $O_2C_6H_4$ or $O_2C_6H_3$-3-^tBu). The Ta complexes are best described as boryl hydride complexes, while the dominant form of the niobium complexes is the dihydridoborate. However, isotopic perturbation of the ^1H resonance shows that the niobium complexes are in equilibrium with another species, either the boryl hydride complexes or Nb(H)(η^2-HBcat) (Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661. Lantero, D. R.; Ward, D. L.; Smith, M. R., III. *J. Am. Chem. Soc.* **1997**, *119*, 9699). A related situation exists for Rh and Ir compounds, where the former prefer a square-planar Rh^I hydridoborate structure, while the latter prefer an octahedral Ir^{III}(H)$_2$(BR_2) structure (Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399. Baker, R. T.; Ovenall, D. W.; Harlow, R. L.; Westcott, S. A.; Taylor, N. J.; Marder T. B. *Organometallics* **1990**, *9*, 3028. Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Lam, K. C.; Lin, Z. *Polyhedron* **2004**, *23*, 2665).

Table 4. NMR Spectroscopic Data [solvent C_6D_6, δ (J/Hz)] for Products of Photoreaction of 1a−1c with Silanes[a]

	5a $SiMe_2Et$	**6a** $SiMeEt_2$	**7a** $Si(OMe)_3$	**8a** $SiEt_2H$	**9a** $SiEt_3$	**10a** Si^iPr_3
^1H hydride	−14.5 dd, J_{PH} 33.1, J_{RhH} 32.1	−14.58 dd, J_{PH} 33.1, J_{RhH} 32.4	−14.06 t, J_{PH} 31.5, J_{RhH} 32.3	−14.6 dd, J_{PH} 33.5, J_{RhH} 32.1	−14.55 t, J_{PH} 32.3, J_{RhH} 31.5	−14.6 dd, J_{PH} 33.2, J_{RhH} 29.8
^1H Cp	5.10 s	5.11 s	5.22 s	5.10 s	5.14 s	5.12 s
$^{31}P\{^1H\}$	5.5 d, J_{RhP} 171	5.3 d, J_{RhP} 171	9.6 d, J_{RhP} 160	8.2 d, J_{RhP} 165	5.2 d, J_{RhP} 171	0.87 d, J_{RhP} 174
	5b	**6b**	**7b**	**8b**	**9b**[42]	**10b**[42]
^1H hydride	−13.38 dd, J_{PH} 29.3, J_{RhH} 30.2	−13.40 app t, J_{PH} 29.3, J_{RhH} 29.3	−12.99 dd, J_{PH} 28.3, J_{RhH} 29.1	−13.57 dd, J_{PH} 29.9, J_{RhH} 29.5	−13.49 app t, J_{PH} 29.1, J_{RhH} 29.1	−13.60 dd, J_{PH} 29.9, J_{RhH} 28.2
^1H Cp	5.07 s	5.08 s	5.21 s	5.13 s	5.10 s	5.10 t, $J_{RhH} = J_{PH}$ 0.5
$^{31}P\{^1H\}$	62.5 d, J_{RhP} 184	62.0 d, J_{RhP} 185	59.2 d, J_{RhP} 175	62.8 d, J_{RhP} 178	59.6, J_{RhP} 188	56.8, J_{RhP} 185
	5c	**6c**	**7c**	**8c**	**9c**	**10c**
^1H hydride	−15.24 ddq, J_{PH} 33.3, J_{RhH} 33.1 J_{FH} 2.8	−15.20 ddq, J_{PH} 33.3, J_{RhH} 32.8 J_{FH} 2.8	−14.52 ddq, J_{PH} 31.1, J_{RhH} 33.1, J_{FH} 2	−15.14 ddq, J_{PH} 33.3, J_{RhH} 32.8 J_{FH} 2.9	−15.14 ddq, J_{PH} 35.7, J_{RhH} 32.8 J_{FH} 2.9	−14.91 ddq, J_{PH} 33.2, J_{RhH} 30.7, J_{FH} 2.9
^1H Cp	4.72 s, 5.18 s, 5.30 s, 5.39 s	4.73 s, 5.20 s, 5.29 s, 5.41 s	4.93 s, 5.27 s, 5.42 s, 5.57 s	4.74 s, 5.06 s, 5.38 s, 5.43 s	4.76 s, 5.21 s, 5.28 s, 5.44 s	4.86 s, 5.21 s, 5.37 s, 5.40 s
$^{31}P\{^1H\}$	6.8 d, J_{RhP} 171	8.7 d, J_{RhP} 171	9.6 d, J_{RhP} 160	9.1 d, J_{RhP} 165	4.7 d, J_{RhP} 171	0.3 d, J_{RhP} 174

[a] Values of J_{RhH} were determined by recording $^1H\{^{31}P\}$ spectra; app = apparent.

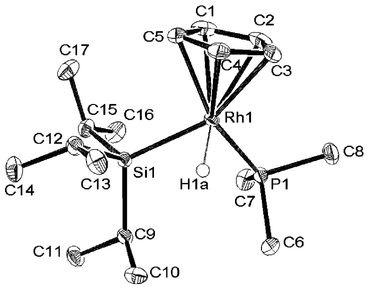

Figure 3. Molecular structure of **10a** (50% thermal ellipsoids, hydrogen atoms omitted except H1A).

that **2b** and **3b** had cocrystallized (Figure S4 and S5, Tables S1). The bond lengths and angles measured for **2b** in this structure are similar to those in the crystal structure described above, but are less well determined. The most notable feature of the structure of **3b** is a $\pi-\pi$ interaction between a phenyl ring of one phosphine and a phenyl ring of the other phosphine, with a centroid-to-centroid distance of 3.6069(17) Å and an angle between planes of 4.2°.

Reaction with $B_2(pin)_2$. The complex **1a** was irradiated in the presence of a 2-fold excess of B_2pin_2 in hexane solution. At room temperature, the product of B−B bond activation, [Rh(η^5-C_5H_5)$(Bpin)_2$(PMe_3)] (**4a**), was formed along with the bis(phosphine) complex **3a**, but this byproduct could be avoided by carrying out the photolysis at −10 °C. The reaction was taken to complete conversion to **4a**; elution of a hexane solution of the mixture through a silica column separated the boryl complex **4a** from boron-containing impurities. Final purification of **4a** was achieved by sublimation. The product **4a** exhibits a doublet at δ 14.7 with a J_{RhP} value of 177 Hz in the $^{31}P\{^1H\}$ NMR spectrum, downfield of **1a** (contrast to **2a**). Further evidence for the identity of the complex came from the ^1H and ^{13}C resonances of the Bpin groups, the ^{11}B NMR resonance at δ 45.1 to low field of that of B_2pin_2 at δ 34.4 (Figure S11, Supporting Information), and the parent ion in the mass spectrum. We also observed the characteristic upfield shift in the ^{13}C resonance of the quaternary carbons of the Bpin ligands. Crystals were grown from hexane as very thin plates, but the quality of the resulting diffraction data was low. Nevertheless, the data were consistent with the formulation.

The above procedure was also used for the photochemical reactions of complex **1b** and **1c** to give the B−B activation products [Rh(η^5-C_5H_5)$(Bpin)_2$(PPh_3)] (**4b**) and [Rh(η^5-C_5H_4-CF_3)$(Bpin)_2$(PMe_3)] (**4c**), respectively, with complete conversion. Selected NMR data for the boryl complexes are summarized in Table 1 and illustrated in the Supporting Information (Figures S11−S13); full data may be found in the Experimental Section. Hartwig et al. have reacted [Rh(η^5-C_5Me_5)(H)$(Bpin)_3$] with PEt_3 at 70 °C in cyclohexane, yielding the analogue [Rh(η^5-C_5Me_5)$(Bpin)_2$(PEt_3)], which exhibits an ^{11}B resonance at δ 42.3 and a doublet in the ^{31}P NMR spectrum with a J_{RhP} value of 169 Hz.[23]

The limiting factor in the synthesis of **4b** is the solubility of the precursor **1b** in inert solvents. We attempted to irradiate **1b** with B_2pin_2 in a variety of alternative solvents without success. Photolysis in chlorinated solvents yielded [Rh(η^5-C_5H_5)Cl_2(PPh_3)] (**11b**), which was crystallized from toluene. Details of the molecular structure are given in the Supporting Information.

Reactions with Tertiary and Secondary Silanes. Complex **1a** was irradiated in neat trialkyl or trialkoxy silanes $HSiR_3$ (R = Et, ^{i}Pr, OMe) or mixed trialkyl silanes $HSiMe_2Et$, $HSiMeEt_2$, and H_2SiEt_2, at room temperature, on an NMR scale (Table 4). The most thoroughly characterized reaction was that of **1a** with $^iPr_3SiH$. The reaction generated [Rh(η^5-C_5H_5)(Si^iPr_3)(H)(PMe_3)] (**10a**) in greater than 90% yield (by NMR spectroscopy) together with traces of [Rh(η^5-C_5H_5)$(Si^iPr_3)_2(H)_2$] (δ −14.5 d, J_{RhH} 30 Hz)[27] and another {Rh(η^5-C_5H_5)(PMe_3)} product that could not be identified. Complex **10a** exhibits a characteristic doublet of doublets in the ^1H NMR spectrum (δ −14.6, J_{RhH} 29.8 and J_{PH} 33.2 Hz) and a doublet in the ^{31}P NMR spectrum (δ 0.87, J_{RhP} 174 Hz). The {$^1H-^{29}Si$} correlation linked the isopropyl resonances to a ^{29}Si resonance at δ 52.1 with passive doublet couplings to rhodium and phosphorus of 14 and 33 Hz, respectively. We could not establish a correlation to the hydride resonance, implying that J_{SiH} for the hydride is very small, with a value less than 2 Hz. In contrast, [Rh(η^5-C_5H_5)$(Si^iPr_3)_2(H)_2$] exhibited a correlation from hydride to ^{29}Si at δ 52.1 with J_{RhSi} = 15 Hz.

Crystals of **10a** were grown from hexane, and the structure was determined (Figure 3, Table 5). The Rh−Si bond length is 2.3617(3) Å, and the Si−Rh−P angle is 99.224(11). The hydride was located, leading to a Rh−H bond length of 1.508(17) Å

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 10a

Rh(1)−P(1)	2.2251(3)	Si(1)−Rh(1)−P(1)	99.224(11)
Rh(1)−Si(1)	2.3617(3)	H(1A)−Rh(1)−P(1)	84.7(6)
Rh(1)−C(Cp)	2.2556(11)−2.3057(11)	H(1A)−Rh(1)−Si(1)	68.0(6)
Rh(1)−H(1A)	1.508(17)		
Si⋯H(1A)	2.278(18)		

and a Si⋯H distance of 2.278(17) Å. The H−Rh−P and H−Rh−Si angles are 84.7(6)° and 68.0(6)°, respectively. It is striking that these two angles are so different and that the very acute angle is associated with silicon despite the greater steric demand of the Si^iPr_3 group compared to the PMe_3 group. For comparison, Maitlis et al. determined the structure of $[Rh(\eta^5\text{-}C_5Me_5)(SiEt_3)_2(H)_2]$ by X-ray and neutron diffraction at 20 K. The neutron determination gave an average Rh−H bond length of 1.581(3) Å and an average Si⋯H distance of 2.27(6) Å.[54] Sabo-Etienne et al. have published several structures with both σ-disilane and hydride ligands and have highlighted the role of secondary Si⋯H interactions (SISHA interactions). Their importance has been demonstrated by structure determinations, NMR dynamics, and DFT calculations. These SISHA Si⋯H distances are typically close to 2.2 Å.[55] In conclusion, the structure of **10a** suggests the presence of some residual Si⋯H interaction, although there is negligible SiH coupling in the solution NMR spectrum.

Photochemical reaction of **1a** in the presence of the other silanes leads to formation of $[Rh(\eta^5\text{-}C_5H_5)(SiR_2R')(H)(PMe_3)]$ **5a**−**9a** assigned on the basis of NMR spectra as the major products (Table 4). Traces of the rhodium(V) hydride $[Rh(\eta^5\text{-}C_5H_5)(SiR_2R')_2(H)_2]$ are also formed. In addition, other minor products are observed in the $^{31}P\{^1H\}$ NMR spectrum that have no associated hydride resonances. These complexes have not been identified conclusively and hamper full characterization. In the case of $HSi(OMe)_3$, the reaction is as clean as for HSi^iPr_3. The value of J_{RhP} is 160 Hz for $[Rh(\eta^5\text{-}C_5H_5)\{Si(OMe)_3\}(H)(PMe_3)]$, compared to 171−174 Hz for the trialkylsilyl derivatives.

The irradiation of **1b** with $HSiEt_3$ and HSi^iPr_3 leading to $[Rh(\eta^5\text{-}C_5H_5)(SiR_3)(H)(PPh_3)]$ (R = Et, **9b**; R = ^{i}Pr, **10b**) has been reported previously, and the structure of **10b** has been determined.[42] The current experiments were conducted on an NMR scale in neat silane $HSiMe_2Et$, $HSiMeEt_2$, H_2SiEt_2, and $HSi(OMe)_3$ at −10 °C. In contrast to **1a**, photochemical reactions of triphenylphosphine complex **1b** lead to formation of single products, $[Rh(\eta^5\text{-}C_5H_5)(SiR_3)(H)(PPh_3)]$, with NMR spectra similar to the PMe_3 analogues (Table 4).

Irradiation at −10 °C of complex **1c** in the presence of neat silanes results in rhodium hydride silyl complexes as the major products. For instance, the reaction of **1c** in $HSiMeEt_2$ leads to formation of a single product, assigned on the basis of ^1H and ^{31}P NMR spectra as $[Rh(\eta^5\text{-}C_5H_4CF_3)(SiMeEt_2)(H)(PMe_3)]$ (**6c**). The hydride region of the ^1H NMR spectrum reveals a ddq pattern at δ −15.2 (J_{PH} 33.3, J_{RhH} 32.8, J_{FH} 2.8 Hz). The $^{31}P\{^1H\}$ spectrum shows a doublet at δ 8.5 (J_{RhP} 171 Hz), and a doublet is also observed in the ^{19}F NMR spectrum (δ −53.6. J 2.7 Hz).

NMR spectra are summarized in Table 4 and illustrated in the Supporting Information (Figures S14−S27).

Competition Reactions. To investigate the selectivity of reaction of the complex **1b** for the activation of E−H and B−B bonds, we conducted photochemical experiments in the presence of two or three of the substrates HBpin, $HSiEt_3$, $HSiMe_2Et$, HC_6F_5, and B_2pin_2 simultaneously. The results are summarized in Table 6.

Complex **1b** was irradiated in hexane in the presence of HBpin (10 equiv) and B_2pin_2 (10 equiv), and product formation was followed in situ by $^{31}P\{^1H\}$ NMR spectroscopy (Figure 4a). Integration (quantitative ^{31}P NMR and $^{31}P\{^1H\}$ gave identical results) shows a ratio of boryl hydride **2b** to bis-boryl **4b** complex of 1:3.2 after 30 min of photolysis, increasing to 1:4 after 90 min of photolysis, indicating a significant preference for B−B over B−H oxidative addition.

Formation of $[Rh(\eta^5\text{-}C_5H_5)(C_6F_5)(H)(PPh_3)]$ (**12b**) on irradiation of **1b** with HC_6F_5 was reported previously.[42] Irradiation of **1b** in C_6D_{12}, in the presence of HBpin and HC_6F_5, was followed by ^1H NMR spectroscopy in the hydride region. There is a very slight selectivity for B−H over C−H oxidative addition. A three-way competition reaction among HBpin, HC_6F_5, and $HSiMe_2Et$ is illustrated in Figure 4b and again shows only a slight selectivity. The choice of silane was governed by the need to avoid overlap of the hydride resonances. Finally, competition between HBpin and $HSiEt_3$ showed only a slight selectivity after short irradiation, although there was preference for Si−H oxidative addition on longer irradiation. Figure 4b also illustrates the absence of broadening of the hydride resonance of the boryl hydride complex **2b** compared to the aryl hydride and silyl hydride analogues, **12b** and **5b**.

The results of the competition reactions could reflect kinetic or thermodynamic selectivity. Since it would be possible, in principle, for the Rh(III) products to equilibrate, we carried out control experiments as follows: (a) **4b** + excess $HSiEt_3$; (b) **5b** + excess HBpin; (c) **5b** + B_2pin_2; (d) **2b** + $HSiEt_3$. The solutions were made up in C_6D_6 and followed by ^1H and ^{31}P NMR spectroscopy; they were left to stand at room temperature for at least 2 h, except for the first solution, which was heated to 75 °C. In no case, was any reaction observed. We can therefore exclude thermal equilibration of the final products. Photochemical equilibration of the final products was also excluded since the reactions were taken to relatively small conversion and the product distribution varied only slightly with photolysis time. Moreover, such Rh(III) species absorb very little light in the region $\lambda > 290$ nm.

It is more difficult to exclude equilibration between the Rh(I) reaction intermediates that may be involved in most of these reactions (Scheme 2). The intermediacy of η^2-arene complexes is already established in arene C−H bond activation.[34] Considering that η^2-silane and η^2-borane complexes are well known,[15,55,56] species of the type $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HE)(PPh_3)]$ (HE = HBpin, $HSiR_3$) are likely to act as intermediates in the reactions with HBpin and with silanes. The rate constant for conversion of $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_6H_6)(PMe_3)]$ to $[Rh(\eta^5\text{-}C_5H_5)(Ph)(H)(PMe_3)]$ at 263 K may be estimated to be ca. 50 s^{-1} from published data.[34] If we assume that the lifetime of species such as $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HSiEt_3)(PPh_3)]$ and $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_6HF_5)(PPh_3)]$ is of the same order, equilibration would become competitive if the rate constant for cross-reactions such as HBpin + $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}HSiEt_3)(PPh_3)]$ were greater than about 500 $dm^3\ mol^{-1}\ s^{-1}$. We conclude that the observed selectivity in the competition reactions represents either kinetic selection of $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)(S)]$ (S = hexane solvent) for substrates or

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Table 6. Results of Competition Reactions

	substrates				
	HBpin/B_2pin_2	HBpin/HC_6F_5	HBpin/HC_6F_5/$HSiMe_2Et$	HBpin/$HSiEt_3$	HBpin/$HSiEt_3$
conc rel to **1b**/eq	10:10	10:10	10:10:10	10:10	15:5
NMR method	$^{31}P\{^1H\}$	^1H	^1H	^1H	^1H
irradiation time/min	integrations[a] **2b**:**4b**:**1b**	integrations[a] **2b**:**12b**	integrations[a] **2b**:**12b**:**5b**	integrations[a] **2b**:**9b**	integrations[a] **2b**:**9b**
30	1:3.2:7.7	1:0.91	1:0.94:1.06		
60	1:3.8:2.6	1:0.89	1:0.99:1.07	1:1.07	
90	1:4.0:2.4	1:0.94	1:1.01:0.95		
120		1:0.97		1:2.5	1:0.64

[a] The error bars on relative integration are estimated as ±10%.

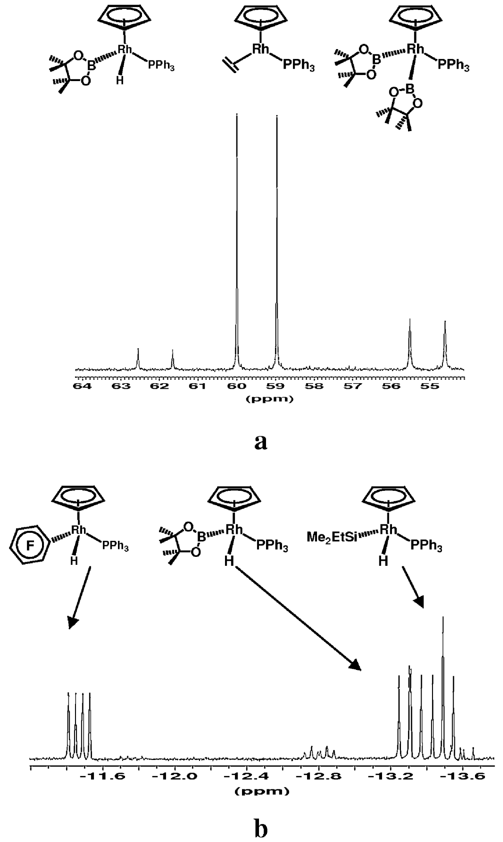


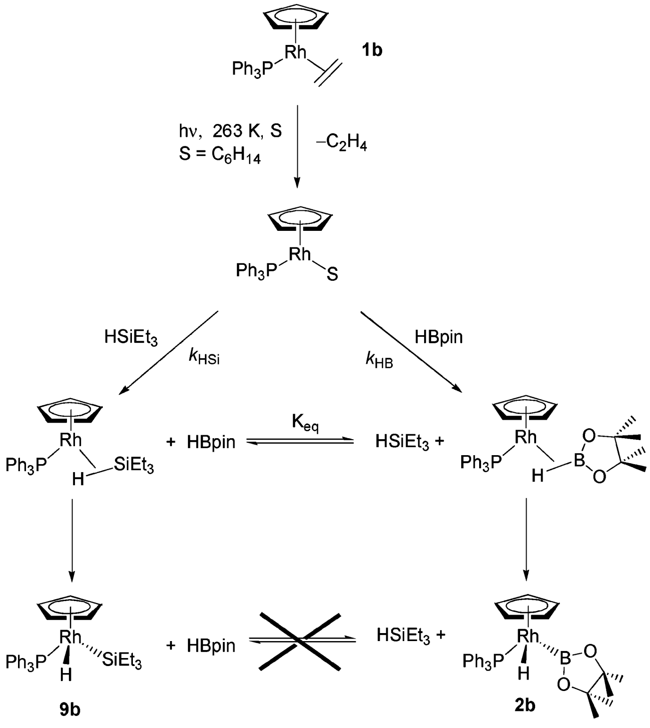
Figure 4. Competition reactions of **1b** after 30 min of photolysis: (a) ^{31}P NMR spectrum in hexane with HBpin and B_2pin_2; (b) hydride region of ^1H NMR spectrum in C_6D_{12} with C_6F_5H, HBpin, and $HSiMe_2Et$.

equilibration between Rh(I) intermediates (Scheme 2). It is worth mentioning that no such Rh(I) intermediate is anticipated in the case of B_2pin_2.

Comparisons of NMR Data. Comparison of the ^{31}P NMR spectra of the Rh(I) complexes **1a**, **1b**, and **1c** shows that J_{RhP} is 10 Hz higher for the PPh_3 complex than for the PMe_3 complexes, but the CF_3 group changes J_{RhP} by only 2 Hz when compared to **1a**. The changes in **3a**−**3c** are similar (Table 1). The NMR data for Rh(III) complexes $[Rh(\eta^5\text{-}C_5H_5)(X)(H)(PPh_3)]$ show that the values of J_{PH} for the PPh_3 complexes are consistently about 4 Hz lower than those of the PMe_3 complexes. In contrast, the values of J_{RhP} are consistently 10−15 Hz higher for the PPh_3 complexes than for the PMe_3 complexes. Furthermore, the values of J_{RhP} follow the order X (J/Hz) = SiR_3 (188−184) > $B(OR)_2$ (180) > $Si(OMe)_3$ (175) > H ~ C_6H_5 (166) > C_6F_5 (155).[57]

To our surprise, the CF_3 substituent on the Cp ring had a negligible effect on the values of J_{PH} and J_{RhP} (Tables 1 and 4). A recent DFT study of a broad range of complexes *trans*-$[Pt(T)(Cl)(PMe_3)_2]$ established the following order of *trans* influence based on the variation in the Pt−Cl bond length: T = $SiMe_3$ > Bpin > Bcat ≈ SiH_3 > H > C_6H_5.[58] Crystallographic data for $[Pt(Ph_2CH_2CH_2PPh_2)X_2]$ show the following mean Pt−P distances: X = Bcat 2.318(2) > X = Si^iPr_2H 2.304(3) > X = C_6F_5 2.276(3) Å.[59] Thus the Rh−P coupling constants reflect the σ-donor strengths of the X ligands (also related to their *trans* influence),[58] with larger values of J_{RhP} reflecting increased electron density at the metal center.

Scheme 2. Basis for Selectivity in an Illustrative Competition Reaction



Conclusions

Photochemical reactions of half-sandwich rhodium complexes $[Rh(Cp')(PR_3)(C_2H_4)]$ (R = Me, Ph; Cp′ = (η^5-C_5H_5), η^5-C_5H_4-CF_3) at room temperature in the presence of mono- and diboron

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(57) The dihydride complex $[Rh(\eta^5\text{-}C_5H_5)(H)_2(PPh_3)]$ gives a ^{31}P signal at δ 64.5 (d, J_{RhP} = 167 Hz) and ^1H resonances at δ 5.23 (s, 5H, C_5H_5), −13.27 (dd, 2H, J_{PH} = 35.1, J_{RhH} = 26.7 Hz). Campian, M. V.; Perutz, R. N. Unpublished data.

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reagents, HBpin and B_2pin_2, lead to formation of the boryl complexes along with byproducts. Lowering the photolysis temperature to −10 °C permitted the selective formation, in good yield, of the oxidative addition products of B−H and B−B bonds. Alternatively, pure boryl hydride complexes were formed by photolysis in liquid HBpin. To prevent the formation of C−H bond activation products, it is essential to avoid the presence of aromatic C−H bonds in the solvent or in the boronate esters. Thus, use of benzene as a solvent and/or HBcat as the borane resulted in mixtures of products. This observation appears to contrast with that for $[W(\eta^5\text{-}C_5H_5)_2H_2]$, which reacts photochemically with diboron dicatecholates even in benzene solution, although the selectivity of $\{W(\eta^5\text{-}C_5H_5)_2\}$ may have been dictated by the *tert*-butyl substituents on the catechol groups.[21]

Photolysis of $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)(C_2H_4)]$ in the presence of silanes leads to clean conversion to silyl hydride complexes. However, the photoreactions of $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)(C_2H_4)]$ and $[Rh(\eta^5\text{-}C_5H_4CF_3)(PMe_3)(C_2H_4)]$ generate the silyl hydride complexes cleanly only in certain cases, such as with HSi^iPr_3. Crystal and molecular structures of the complexes $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)(C_2H_4)]$ (**1b**), $[Rh(\eta^5\text{-}C_5H_4CF_3)(PMe_3)(C_2H_4)]$ (**1c**), $[Rh(\eta^5\text{-}C_5H_5)(Bpin)(H)(PPh_3)]$ (**2b**), $[Rh(\eta^5\text{-}C_5H_5)(Si^iPr3)(H)(PMe_3)]$ (**10a**), and $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (**3b**) were determined by single-crystal X-ray diffraction.

Comparisons of NMR coupling constants show that the values of the phosphorus−hydride coupling, J_{PH}, for the PPh_3 complexes are consistently lower than those of the PMe_3 complexes, while J_{RhP} is consistently higher. The values of J_{RhP} are also sensitive to the substituent X in Rh(III) complexes $[Rh(\eta^5\text{-}C_5H_5)(X)(H)(PPh_3)]$ and increase with the σ-donor strength of X. Surprisingly, the CF_3 group appears to exert no significant effect on the reactivity toward oxidative addition or on the NMR parameters of the products.

Competition reactions reveal that the photogenerated fragment, $\{Rh(\eta^5\text{-}C_5H_5)(PPh_3)\}$, is remarkably unselective. There is a slight preference for B−B over B−H oxidative addition, but no significant difference among B−H, Si−H, and C−H bond activation processes. The lack of selectivity originates either in very similar rate constants for reaction of $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)(\text{alkane})]$ with the substrates or in fast equilibration between Rh(I) intermediates of the type $[Rh(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^2\text{-HE})]$ (Scheme 2).

In conclusion, photoinduced B−H and B−B oxidative addition reactions are as straightforward as Si−H oxidative addition. It is striking that B−H and B−B oxidative additions are efficient at $\{Rh(\eta^5\text{-}C_5H_5)(PPh_3)\}$, whereas C−H oxidative addition yields stable products only for those arenes such as HC_6F_5 with exceptionally strong rhodium−carbon bonds in the product. The effectiveness of such reactions is often determined by the thermodynamic stability of the products[60] and points again to the strong σ-donor properties of the Bpin ligand.[20e,58]

Experimental Section

General Procedures. All operations were performed under a nitrogen or argon atmosphere, either on a high-vacuum line (10^{-4} mbar) using modified Schlenk techniques, on standard Schlenk (10^{-2} mbar) lines, or in a glovebox. Solvents for general use (THF, benzene, toluene) were of AR grade, dried by distillation over classical reagents, and stored under Ar in ampules fitted with Young's PTFE stopcocks. Deuterated solvents were dried by stirring over potassium and were distilled under high vacuum into small ampules with potassium mirrors.

Photochemical reactions, at room temperature, were performed in glass NMR tubes fitted with PTFE taps, using a 125 W medium-pressure mercury vapor lamp with a water filter (10 cm). UV−vis irradiations, at lower temperatures, were performed using a 300 W Oriel 66011 xenon lamp with a thermostatically controlled cooling system based on gaseous nitrogen boil-off obtained from a JEOL NMR spectrometer.

All NMR spectra were recorded on Bruker AMX500 spectrometers in glass tubes fitted with Young's PTFE stopcocks. All ^1H and ^{13}C chemical shifts are reported in ppm (δ) relative to tetramethylsilane and are referenced using the chemical shifts of residual protio solvent resonances (benzene, δ 7.16). The $^{31}P\{^1H\}$ and ^{11}B NMR spectra were referenced to external H_3PO_4 and $BF_3\cdot Et_2O$, respectively. In general, ^1H decoupling did not affect the ^{11}B spectra reported in this paper.

Mass spectra were recorded on a VG-Autospec spectrometer and are quoted for ^{11}B.

Syntheses and NMR Experiments. $[Rh(\eta^5\text{-}C_5H_5)(PR_3)(C_2H_4)]$ (R = Me, Ph) complexes were synthesized by literature procedures, but replacing TlCp by LiCp.[33,40] $Tl(\eta^5\text{-}C_5H_4CF_3)$ was synthesized by the literature method, via reaction of nickelocene with CF_3I followed by thallium ethoxide.[44]

$[Rh(\eta^5\text{-}C_5H_4CF_3)(C_2H_4)(PMe_3)]$, 1c. Complex **1c** was prepared by reaction of $Tl(\eta^5\text{-}C_5H_4CF_3)$ (1 g, 3 mmol) with $[RhCl(C_2H_4)(PMe_3)]_2$ (0.51 g, 1.3 mmol) in THF at 0 °C. The mixture was stirred for 3 h at 0 °C and was then allowed to warm to room temperature. The supernatant was decanted, and the solid residue was washed with hexane. The combined liquors were pumped to dryness, yielding a dark brown solid. The latter was extracted with hexane, forming a dark yellow solution, which was eluted through a 5 cm Celite column with hexane. The solution was pumped to dryness, and the resulting yellow solid was sublimed without heating onto a liquid-nitrogen-cooled finger (10^{-4} mbar). The product was washed off the finger with hexane and pumped down slowly, yielding yellow crystals. Yield: 0.72 g, 49%. The sample for analysis was recrystallized from hexane. Crystals for X-ray diffraction were grown by very slow sublimation in an ampule sealed under vacuum and left at room temperature in the dark. Anal. Calcd for $C_{11}H_{17}F_3PRh$: C, 38.84; H, 4.69. Found: C, 38.88; H, 5.04.

NMR (C_6D_6 300 K), ^1H: δ 5.18 (m, 2H, C_5H_4), 4.99 (m, 2H, C_5H_4), 2.8 (m, 2H, C_2H_4), 1.49 (m, 2H, C_2H_4), 0.71 (dd, J_{PH} = 9.6, J_{RhH} = 1.1 Hz, 9H, Me); $^{31}P\{^1H\}$: δ 6.9 (dq J_{RhP} = 198, J_{FP} = 2 Hz). ^{19}F: −54.4 (m); $^{13}C\{^1H\}$ NMR (75.4 MHz, toluene-d_8 300 K): δ 86.76 (m C_5H_4), 84.76 (s C_5H_4), 26.89 (dd J_{PC} = 16, J_{RhC} = 3 Hz, C_2H_4), 18.80 (d J_{PC} = 29.5 Hz, Me); $^{13}C\{^1H\}$ NMR (THF-d_8 300 K): 125.3 (q, J_{CF} = 267 Hz, CF_3), 93.6, q, J_{CF} = 38 Hz, CCF_3), 86.4 (s br, C_5H_4), 84.3 (s, C_5H_4), 25.8 (dd, J_{PC} = 17, J_{RhC} = 3 Hz, C_2H_4), 18.2 (d, J_{PC} = 29 Hz, Me). MS (EI, *m/z*) 340 (26%, M^+), 312 (100%, $M^+ - C_2H_4$), 293 (11%, $M^+ - C_2H_4 - F$), 236 (13%, $Rh(C_5H_4CF_3)^+$) 178 (69%, $Rh(PMe_3)^+$). HRMS *m/z*: exp 340.00753, calcd for $C_{11}H_{17}F_3PRH$ 340.00750, difference 0.03 mDa.

$[Rh(\eta^5\text{-}C_5H_5)(Bpin)(H)(PMe_3)]$, 2a. An 8 mm diameter NMR tube, fitted with a Young's tap, was charged with **1a** (55 mg) and HBpin (1.5 mL) and irradiated at −10 °C with the Oriel Xe arc (17 h), resulting in 100% conversion to **2a**. The excess HBpin was recovered by vacuum transfer on the high-vacuum line, leaving a brown oil. The oil was transferred to the glovebox, redissolved in toluene, and passed through a neutral alumina column (3 cm long, 1 cm diam) eluting with further toluene in order to remove boron-containing impurities. The eluent was pumped to dryness and redissolved in hexane to give a brown solid. In a smaller-scale reaction, an NMR tube was charged with a solution of complex **1a** (1−2 mg, 4−7 μmol) in neat HBpin (1 mL) and irradiated at ca.

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−5 °C for 15 h. All volatiles were removed under vacuum to give a dark orange solid. Further purification by sublimation onto a liquid-nitrogen-cooled finger at 35 °C at 10^{-4} mbar yielded a white solid, which darkened on standing. NMR (C_6D_6, 300 K), ^1H: δ 5.36 (s, 5 H, C_5H_5), 1.29 (d, 9 H $J_{PH} = 10.7$ Hz, $P(CH_3)_3$), 1.16 (s, 12H $BO_2C_6H_{12}$), −14.04 (dd, 1H, $J_{PH} = 33.7$ Hz, $J_{RhH} = 35.1$ Hz, RhH); $^{31}P\{^1H\}$: δ 12.4 (d, $J_{RhP} = 170.4$ Hz); $^{13}C\{^1H\}$: δ 87.5 (t, C_5H_5, $J_{PC} = J_{RhC} = 2$ Hz), 81.2 (s, $BO_2C_2(CH_3)_4$), 25.4 (s, $BO_2C_2(CH_3)_4$), 25.3 (s, $BO_2C_2(CH_3)_4$), 24.2 (dd, $J_{PC} = 32$, $J_{RhC} = 1$ Hz, $P(CH_3)_3$); $^{11}B\{^1H\}$: δ 45.4. MS *m/z*: 372 (4%), 369 (1%), 272 (2%), 244 (100%, $[Rh(C_5H_5)(PMe_3)]^+$). HRMS *m/z*: exp 372.09090, calcd for $C_{14}H_{27}BO_2PRh$ 372.08968, difference 1.2 mDa

[Rh(η^5-C_5H_5)(Bpin)$_2$(PMe$_3$)], 4a. An 8 mm diameter NMR tube, fitted with a Young's tap, was charged with **1a** (55 mg) in hexane and a ca. 2-fold excess of B_2pin_2 and irradiated at −10 °C with the Oriel Xe arc (37 h), resulting in 100% conversion to **4a**. The solution was pumped to dryness, leaving an orange-brown solid. The solid was transferred to the glovebox, redissolved in toluene, and eluted through a neutral alumina column (3 cm long, 1 cm diam) with toluene in order to remove boron-containing impurities; the eluent was pumped to dryness. Fractional sublimation (sample at 40 °C) onto a liquid-nitrogen-cooled finger initially removed excess B_2pin_2. On heating for longer periods, the product **4a** also sublimed; multiple sublimations yielded off-white **4a**. NMR (C_6D_6, 300 K), ^1H: δ 5.46 (s, 5 H, C_5H_5), 1.41 (dd, 9 H $J_{PH} = 10.6$ $J_{Rh-H} = 1.3$ Hz, $P(CH_3)_3$), 1.19 (s, 24 H, $BO_2C_6H_{12}$); $^{31}P\{^1H\}$: δ 14.8 (d, $J_{RhP} = 177$ Hz); $^{13}C\{^1H\}$: δ 89.7 (t, C_5H_5, $J_{PC} = J_{RhC} = 2.29$ Hz), 81.09 (s, $BO_2C_2(CH_3)_4$), 25.4 (s, $BO_2C_2(CH_3)_4$), 25.3 (s, $BO_2C_2(CH_3)_4$), 23.6 (dd, $J_{PC} = 32.0$, $J_{RhC} = 1.5$ Hz, $P(CH_3)_3$); ^{11}B: δ 45.1. MS, (EI, *m/z*: 498 (2%, M^+), 414 (3.8%, $M^+ - C_2Me_4$), 371 (25%, M^+ − Bpin), 244 (100%, $M^+ - B_2pin_2$).

[Rh(η^5-C_5H_5)(SiMe$_2$Et)(H)(PMe$_3$)], 5a. An NMR tube was charged with **1a** (1−2 mg, 4−7 μmol) and neat Me_2EtSiH (1 mL) and irradiated at room temperature for 10 h. All volatiles were removed under vacuum, giving a brown oil. NMR (C_6D_6, 300 K), ^1H: δ 5.10 (s, 5H, C_5H_5), 1.22 (t, 3 H, J_{HH} 7.9 Hz, CH_3), 1.02 (d, 9 H, $J_{PH} = 9.5$ Hz, $P(CH_3)_3$), 0.86 (m, 2 H, CH_2), 0.51(s, 3 H, CH_3), 0.48 (s, 3 H, $SiCH_3$), −14.5 (dd, 1 H, $J_{RhH} = 32.1$ Hz, $J_{PH} = 33.1$ Hz, RhH); $^{31}P\{^1H\}$: δ 5.5 (d, $J_{RhP} = 171$ Hz).

[Rh(η^5-C_5H_5)(SiMeEt$_2$)(H)(PMe$_3$)], 6a. The same procedure was followed as for **5a**. NMR (C_6D_6, 300 K), ^1H: δ 5.11 (s, 5 H, C_5H_5), 1.20 (t, 6 H, $J_{HH} = 7.7$ Hz, CH_3), 1.01 (d, 9 H, $J_{PH} = 10.8$ Hz, $P(CH_3)_3$), 0.88 (m, 4 H, CH_2), 0.43 (s, 3 H $SiCH_3$), −14.58 (dd, 1 H, $J_{RhH} = 32.4$, $J_{PH} = 33.1$ Hz, RhH); $^{31}P\{^1H\}$: δ 5.3 (d, $J_{RhP} = 171$ Hz).

[Rh(η^5-C_5H_5){Si(OMe)$_3$}(H)(PMe$_3$)], 7a. The same procedure was followed as for **5a**. NMR (C_6D_6, 300 K), ^1H: 5.22 (s, 5 H, C_5H_5), 3.61 (s, 9H, CH_3), 1.18 (dd, 9H, $J_{PH} = 10.5$, $J_{RhH} = 1$ Hz, $P(CH_3)_3$), −14.06 (dd, 1 H, $J_{PH} = 31.5$, $J_{RhH} = 32.3$ Hz, RhH); $^{31}P\{^1H\}$: δ 9.6 (d, $J_{RhP} = 160$ Hz).

[Rh(η^5-C_5H_5)(SiEt$_2$H)(H)(PMe$_3$)], 8a. The same procedure was followed as for **5a**. NMR (C_6D_6, 300 K), ^1H: δ 5.10 (s, 5 H, C_5H_5), 3.94 (d, 1H, $J_{HP} = 16$ Hz, SiH), 1.31 (m, 6 H, CH_3), 1.07 (d, 9 H $J_{PH} = 9.5$ Hz, $P(CH_3)_3$), 0.96 (m, 4 H, CH_2), −14.6 (dd, 1 H, $J_{PH} = 33.5$, $J_{RhH} = 32.1$ Hz, RhH); $^{31}P\{^1H\}$, δ 8.2 (d, $J_{RhP} = 165$ Hz).

[Rh(η^5-C_5H_5)(SiEt$_3$)(H)(PMe$_3$)], 9a. The same procedure was followed as for **5a**. NMR (C_6D_6, 300 K), ^1H: δ 5.14 (s, 5 H, C_5H_5), 1.27 (t, 9H, $J_{HH} = 7.8$ Hz, CH_3), 0.99 (d, 9H, $J_{PH} = 10.1$ Hz, $P(CH_3)_3$), 0.86 (m, 6H, CH_2), −14.55 (dd, 1H, $J_{PH} = 32.3$, $J_{RhH} = 31.5$ Hz, RhH) $^{31}P\{^1H\}$: δ 5.2 (d, $J_{RhP} = 171$ Hz).

[Rh(η^5-C_5H_5)(Si^{i}Pr$_3$)(H)(PMe$_3$)], 10a. The same procedure was followed as for **5a**. Slow evaporation of a hexane solution in the glovebox gave yellow crystals. NMR (C_6D_6, 300 K), ^1H: δ 5.12 (s, 5 H, C_5H_5), 1.23 (dd, 18H, $J_{HH} = 13.7$ Hz, CH_3), 1.13 (m, 3H, CH), 0.95 (d, 9H, $J_{PH} = 9.6$ Hz, $P(CH_3)_3$), −14.6 (dd, 1H, $J_{PH} = 33.2$, $J_{RhH} = 29.8$ Hz, RhH); $^{31}P\{^1H\}$: δ 0.87 (d, $J_{RhP} = 174$ Hz).

[Rh(η^5-C_5H_5)(Bpin)(H)(PPh$_3$)], 2b. A 15 mm diameter NMR tube, fitted with a Young's tap, was charged with **1b** (40 mg) and HBpin (5.5 mL) and irradiated with a medium-pressure Hg arc (6 h), resulting in 100% conversion to **2b**. The excess HBpin was recovered by vacuum transfer on a high-vacuum line, leaving a brown oil. The oil was transferred to a glovebox, redissolved in toluene, and passed through a neutral alumina column (3 cm long, 1 cm diam) eluting with further toluene in order to remove boron-containing impurities. The eluent was pumped to dryness and redissolved in hexane. Slow evaporation of the solution in the glovebox gave brown crystals of **2b**. In a smaller-scale reaction, a 5 mm diameter NMR was charged with **1b** (3 mg) and HBpin (ca. 1 mL) and irradiated similarly for 6 h. The HBpin was removed under vacuum and the residue was dissolved in hexane and cooled to −18 °C, yielding cocrystals of **2b·3b**. NMR (C_6D_6, 300 K), ^1H: δ 7.68−6.68 (m, 15H, C_6H_5), 5.33 (s, 5H, C_5H_5), 0.95 (s, 6H $BO_2C_6H_{12}$), 0.88 (s, 6H $BO_2C_6H_{12}$), −13.04 (dd, 1H, $J_{PH} = 29.6$, $J_{RhH} = 32.8$ Hz, RhH); $^{31}P\{^1H\}$: δ 62.5 (d, $J_{RhP} = 180$ Hz); $^{13}C\{^1H\}$: δ 134.4 (d, $J_{PC} = 11.9$ Hz, *o*-Ph), 132.5 (d, $J_{PC} = 9.6$ Hz, *m*-Ph), 131.6 (d, $J_{PC} = 2.8$ Hz, *p*-Ph), 89.2 (t, $J_{PC} = J_{RhC} = 2.5$ Hz, C_5H_5), 82.9 (s, $BO_2C_2(CH_3)_4$), 24.59 (s, $BO_2C_2(CH_3)_4$), 24.58 (s, $BO_2C_2(CH_3)_4$); $^{11}B\{^1H\}$: δ 44.8. MS (EI, *m/z*: 558 (3%, M^+), 430 (100%, M^+ − HBpin), 286 (26%), 183 (20%), 168 (7%). HRMS (FAB *m/z*): exp 581.1271 (M + Na^+), calcd for $C_{29}H_{33}BO_2NaPRh$ 581.1264, difference 0.7 mDa. Anal. Calcd for $C_{29}H_{33}BO_2NaPRh$: C, 62.39; H, 5.96. Found: C, 62.38; H, 5.97.

[Rh(η^5-C_5H_5)(Bpin)$_2$(PPh$_3$)], 4b. A 15 mm diameter NMR tube fitted with a Young's tap was charged with **1b** (15 mg) in hexane and B_2pin_2 (26 mg) and irradiated at −20 °C with the medium-pressure Hg arc (14 h), resulting in 100% conversion (by NMR spectroscopy) to **4b**. The solution was pumped to dryness, leaving an orange-brown solid. The solid was transferred to the glovebox, redissolved in toluene, and passed through a neutral alumina column (3 cm long, 1 cm diam) eluting with further toluene in order to remove boron-containing impurities. The eluent was pumped to dryness, and the excess B_2pin_2 was removed by sublimation to give an orange-brown solid. A smaller-scale reaction at room temperature gave a mixture of two products that were eluted through an alumina column with toluene to give **4b**. NMR (C_6D_6, 300 K), ^1H: δ 7.68−6.68 (m, 15H, Ph), 5.41 (s, 5H, C_5H_5), 1.07 (s, 6H $BO_2C_6H_{12}$), 1.04 (s, 6H $BO_2C_6H_{12}$); $^{31}P\{^1H\}$: δ 55.5 (d, $J_{RhP} = 182$ Hz); $^{13}C\{^1H\}$: δ 134.8 (d, $J_{PC} = 11.7$ Hz, *o*-Ph), 129.1 (d, $J_{PC} = 2.3$ Hz, *p*-Ph), 127.3 (d, $J_{PC} = 10.2$ Hz, *m*-Ph), 91.9 (t, $J_{PC} = J_{RhC} = 2.2$ Hz, C_5H_5), 81.35 (s, $BO_2C_2(CH_3)_4$), 25.21 (s, $BO_2C_2(CH_3)_4$), 25.14 (s, $BO_2C_2(CH_3)_4$); $^{11}B\{^1H\}$: δ 43.7. MS, (ESI, *m/z*: 707 (100%, M + Na^+), 579 (5%, M + Na^+ − Bpin), 501 (25%).

[Rh(η^5-C_5H_5)(SiMe$_2$Et)(H)(PPh$_3$)], 5b. An NMR tube was charged with **1b** (1−2 mg, 2−4 μmol) and neat Me_2EtSiH (1 mL) and irradiated at ca. −10 °C for 15 h. All volatiles were removed under vacuum to give a dark brown oil. NMR (C_6D_6, 300 K), ^1H: δ 7.68−6.68 (m, 15H, Ph), 5.07 (s, 5H, C_5H_5), 1.16 (t, 3H, $J_{HH} = 7.7$ Hz CH_3), 0.75 (m, 2H, CH_2), 0.3 (s, 3H, CH_3), 0.1 (s, 3H, CH_3), −13.38 (dd, 1H, $J_{PH} = 29.3$, $J_{RhH} = 30.2$ Hz, RhH); $^{31}P\{^1H\}$: δ 62.5 (d, $J_{RhP} = 184$ Hz).

[Rh(η^5-C_5H_5)(SiMeEt$_2$)(H)(PPh$_3$)], 6b. The same procedure was followed as for **5b**. NMR (C_6D_6, 300 K), ^1H: δ 7.68−6.68 (m, 15H, Ph), 5.08 (s, 5H, C_5H_5), 1.13 (m, 6H, CH_3), 0.89 (m, 2H, CH_2), 0.78 (2H, CH_2), 0.07 (m, 3H, CH_3), −13.4 (apparent t, 1H, $J_{PH} \sim J_{RhH} = 29.3$ Hz, RhH); $^{31}P\{^1H\}$: δ 62 (d, $J_{RhP} = 185$ Hz).

[Rh(η^5-C_5H_5){Si(OMe)$_3$}(H)(PPh$_3$)], 7b. The same procedure was followed as for **5b**. NMR (C_6D_6, 300 K), ^1H: δ 7.69−7.03 (m, 15H, Ph), 5.21 (s, 5H, C_5H_5), 3.4 (s, 9H, CH_3), −12.99 (dd, 1 H, $J_{PH} = 28.3$, $J_{RhH} = 29.1$ Hz, RhH); $^{31}P\{^1H\}$: δ 59.2 (d, $J_{RhP} = 175$ Hz).

[Rh(η^5-C_5H_5)(SiEt$_2$H)(H)(PPh$_3$)], 8b. The same procedure was followed as for **5b**. NMR (C_6D_6, 300 K), ^1H: δ 7.68−6.68 (m, 15H, Ph), 5.13 (s, 5H, C_5H_5), 3.82 (d, 1H, $J_{HP} = 15$ Hz, SiH), 1.31

Table 7. Summary of Crystallographic Data for 1b, 1c, 2b, 2b·3b, 10a, and 11b·$C_6H_5CH_3$

	1b	**1c**	**2b**	**2b·3b**	**10a**	**11b·$C_6H_5CH_3$**
formula	$C_{25}H_{24}PRh$	$C_{11}H_{17}F_3PRh$	$C_{29}H_{33}BO_2PRh$	$C_{70}H_{68}BO_2P_3Rh_2$	$C_{17}H_{36}PRhSi$	$C_{30}H_{28}Cl_2PRh$
fw	458.32	340.13	558.24	1250.78	402.43	593.30
temp (K)	115(2)	115(2)	110(2)	115(2)	110(2)	110(2)
cryst syst	monoclinic	orthorhombic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	19.6790(18)	10.7234(6)	10.7735(7)	12.0010(7)	8.6515(4)	13.5551(15)
b (Å)	9.6720(9)	14.3049(8)	10.9101(7)	14.0158(8)	10.4606(5)	10.2404(11)
c (Å)	21.451(2)	16.7704(10)	11.7832(7)	18.2082(11)	12.1019(6)	19.151(2)
α (deg)	90	90	77.068(1)	72.634(1)	74.981(1)	90
β (deg)	95.435(2)	90	77.854(1)	85.868(1)	71.512(1)	100.272(2)
γ (deg)	90	90	77.895(1)	89.726(1)	72.050(1)	90
volume (Å^3)	4064.6(7)	2572.5(3)	1300.29(14)	2915.0(3)	972.20(8)	2615.8(5)
Z	8	8	2	2	2	4
density (calcd) (Mg/m^3)	1.498	1.756	1.426	1.425	1.375	1.507
F(000)	1872	1360	576	1288	424	1208
no. of reflns collected	22 114	27 291	14 651	23 235	11 103	19 928
no. of ind reflns	7168	3743	7284	16 255	5479	4621
no. of ind reflns [$I > 2\sigma(I)$]	4455	3413	6836	11762	5285	3766
no. of data/ restraints/ params	7168/0/487	3743/0/160	7284/0/315	16 255/0/711	5479/0/194	4621/0/308
H atoms	riding + diff	riding + diff	riding + diff	riding + diff	riding + diff	riding
goodness-of-fit on F^2	0.930	1.033	1.060	0.996	1.049	1.019
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0349, wR2 = 0.0695	R1 = 0.0251, wR2 = 0.0645	R1 = 0.0223, wR2 = 0.0574	R1 = 0.0400, wR2 = 0.0838	R1 = 0.0158, wR2 = 0.0407	R1 = 0.0364, wR2 = 0.0833
R indices (all data)	R1 = 0.0786, wR2 = 0.0822	R1 = 0.0284, wR2 = 0.0662	R1 = 0.0243, wR2 = 0.0583	R1 = 0.0687, wR2 = 0.0960	R1 = 0.0166, wR2 = 0.0409	R1 = 0.0503, wR2 = 0.0887
max. diff peak and hole (e/Å^3)	0.807 and −0.757	1.117 and −0.360	0.830 and −0.567	1.111 and −0.543	0.549 and −0.240	1.165 and −0.945
CCDC no.	616691	616692	616693	616694	616695	616696

(t, 3H, J_{HH} = 7.7 Hz CH$_3$), 1.03−1.10 (m, 7H, CH$_3$ + 2CH$_2$), −13.57 (dd, 1 H, J_{PH} = 29.9, J_{RhH} = 29.5 Hz, RhH); $^{31}P\{^1H\}$: δ 62.8 (d, J_{RhP} = 178 Hz).

[Rh(η^5-C_5H_5)Cl_2(PPh_3)], 11b. An NMR tube was charged with **1b** (10 mg) in 1,2-dichloroethane and a 2-fold excess of B$_2$pin$_2$ and irradiated at room temperature with the medium-pressure Hg arc (5 h), resulting in 100% conversion to **11b**. All volatiles were removed to give an orange solid. The solid was transferred to the glovebox, redissolved in toluene, and eluted through a neutral alumina column with additional toluene in order to remove boron-containing impurities, followed by sublimation of B$_2$pin$_2$. Slow evaporation of the toluene solution in the glovebox gave orange crystals of **11b**. NMR (C_6D_6, 300 K), ^{1}H: δ 7.87−6.99 (m, 15H, Ph), 5.4 (s, 5H, C_5H_5); $^{31}P\{^1H\}$: δ 32.8 (d, J_{RhP} = 136 Hz).

[Rh(η^5-$C_5H_4CF_3$)(Bpin)(H)(PMe_3)], 2c. An NMR tube was charged with **1c** (1−2 mg, 2−4 μmol) and neat HBpin (∼1 mL) and irradiated at ca. −10 °C for 15 h. All volatiles were removed under vacuum to give a dark orange solid. NMR (C_6D_6, 300 K), ^{1}H: δ 5.75 (s, 1H, C_5H_4), 5.52 (s, 1H, C_5H_4), 5.31 (s, 1H, C_5H_4), 5.19 (s, 1H, C_5H_4), 1.23 (s, 6H, $BO_2C_2(CH_3)_4$), 1.25 (s, 6H, $BO_2C_2(CH_3)_4$), 0.95 (d, 9H, J_{PH} = 9.7 Hz, P(CH$_3$)$_3$), −14.58 (dd, 1H, J_{PH} = 34.6, J_{RhH} = 36.8 Hz, RhH); $^{31}P\{^1H\}$: δ 13.7 (d, J_{RhP} = 169 Hz); $^{13}C\{^1H\}$: δ 125.5 (q J_{CF} = 267, *C*F$_3$), 95.3 (qd, J_{CF} = 38, J_{CRh} = 3 Hz, *C*-CF$_3$), 90.0 (apparent sextet, *J* = 3 Hz C_5H_4), 89.6 (m, C_5H_4), 89.3 (s, C_5H_4), 85.6 (overlapping dq, J_{CRh} = 5, J_{CF} = 3 Hz, C_5H_4), 81.6 (s, $BO_2\mathit{C}_2(CH_3)_4$), 25.2 (s, $BO_2C_2(\mathit{C}H_3)_4$), 24.8 (s, $BO_2C_2(\mathit{C}H_3)_4$), 22.9 (dd, J_{PC} = 34, J_{RhC} = 2 Hz, P(*C*H$_3$)$_3$,); $^{11}B\{^1H\}$: δ 43.9; ^{19}F: δ −54.0 (s). MS, (EI, *m/z*): 440 (13%, M$^+$), 355 (1%, M$^+$ − C_6H_{13}), 312 (100%, M$^+$ − HBpin). HRMS: exp 440.077062, calcd 440.077680, difference 0.618 mDa.

[Rh(η^5-$C_5H_4CF_3$)(Bpin)$_2$(PMe_3)], 4c. An NMR tube was charged with a hexane solution of **1c** (0.01 g, 22.7 μmol) and a ca. 4-fold-excess of B$_2$pin$_2$ (0.02 g, 78.74 μmol) and irradiated at ca. −10 °C for 15 h. All volatiles were removed under vacuum to give a dark brown solid. NMR (C_6D_6, 300 K), ^{1}H: δ 5.76, 5.43 (s, 4 H, C_5H_4), 1.39 (d, 9 H J_{PH} = 12.7 Hz, P(CH$_3$)$_3$), 1.14 (s, 24 H ($BO_2C_6\mathit{H}_{12})_2$); $^{31}P\{^1H\}$: δ 19 (d, J_{RhP} = 176 Hz); $^{11}B\{^1H\}$: δ 43.8; ^{19}F: δ −53.5 (s).

[Rh(η^5-$C_5H_4CF_3$)($SiMe_2Et$)(H)(PMe_3)], 5c. An NMR tube was charged with **1c** (0.01 g, 23 μmol) and neat Me$_2$EtSiH (1 mL) and irradiated at at ca. −10 °C for 4 h. All volatiles were removed to give an orange-brown oil. NMR (C_6D_6, 300 K), ^{1}H: δ 5.39 (s, 1H, C_5H_4), 5.30 (s, 1H, C_5H_4), 5.18 (s, 1H, C_5H_4), 4.72 (s, 1H, C_5H_4), 1.13 (t, 3H, J_{HH} = 7.7 Hz, CH$_3$), 0.97 (dd, 9H J_{PH} = 12.7, J_{RhH} = 1.4 Hz, P(CH$_3$)$_3$), 0.77 (m, 2H, CH$_2$), 0.44 (s, 3H, CH$_3$), 0.39 (s, 3H, CH$_3$), −15.24 (ddq, 1H, J_{PH} = 33.5, J_{RhH} = 33.1, J_{FH} = 2.8 Hz, RhH); $^{31}P\{^1H\}$: δ 6.8 (d, J_{RhP} = 171 Hz); ^{19}F: δ −53.71 (s).

[Rh(η^5-$C_5H_4CF_3$)($SiMeEt_2$)(H)(PMe_3)], 6c. The same procedure was followed as for **5c**. NMR (C_6D_6, 300 K), ^{1}H: δ 5.41 (s, 1H, C_5H_4), 5.29 (s, 1H, C_5H_4), 5.20 (s, 1H, C_5H_4), 4.73 (s, 1H, C_5H_4), 1.12 (t, 6H, J_{HH} = 7.8 Hz, CH$_3$), 0.96 (d, 9H J_{PH} = 12.7 Hz, P(CH$_3$)$_3$), 0.79 (m, 4H, CH$_2$), 0.35 (s, 3H, CH$_3$), −15.2 (ddq, 1H, J_{PH} = 33.3, J_{RhH} = 32.8, J_{FH} = 2.8 Hz, RhH); $^{31}P\{^1H\}$: δ 8.7 (d, J_{RhP} = 171 Hz); ^{19}F: δ −53.6 (d, J_{FRh} = 3 Hz).

[Rh(η^5-$C_5H_4CF_3$){(SiOMe)$_3$}(H)(PMe_3)], 7c. The same procedure was followed as for **5c**. NMR (C_6D_6, 300 K), ^{1}H: δ 5.57 (s, 1H, C_5H_4), 5.42 (s, 1H, C_5H_4), 5.27(s, 1H, C_5H_4), 4.93 (s, 1H, C_5H_4), 3.52 (s, 9H, CH$_3$), 1.15 (d, J_{PH} = 10.7, 9H, P(CH$_3$)$_3$), −14.52 (ddq, 1H, J_{PH} = 31.1, J_{RhH} = 33.2, J_{FH} = 2 Hz, RhH); $^{31}P\{^1H\}$: δ 9.6 (d, J_{RhP} = 160 Hz); ^{19}F: δ −53.72 (s).

[Rh(η^5-$C_5H_4CF_3$)($SiEt_2H$)(H)(PMe_3)], 8c. The same procedure was followed as for **5c**. NMR (C_6D_6, 300 K), ^{1}H: δ 5.43 (s, 1H, C_5H_4), 5.38 (s, 1H, C_5H_4), 5.06 (s, 1H, C_5H_4), 4.74 (s, 1H, C_5H_4), 3.99 (d, 1H, J_{HP} = 16 Hz, SiH), 1.22 (t, 6H, J_{HH} = 7.7 Hz, CH$_3$), 1.02 (d, 9H, J_{PH} = 10.4 Hz, P(CH$_3$)$_3$), 0.94 (m, 4H, CH$_2$), −15.14 (ddq, 1H, J_{PH} = 33.3, J_{RhH} = 32.8, J_{FH} = 2.9 Hz, RhH); $^{31}P\{^1H\}$: δ 9.1 (d, J_{RhP} = 165 Hz); ^{19}F: δ −53.93 (s).

[Rh(η^5-$C_5H_4CF_3$)($SiEt_3$)(H)(PMe_3)], 9c. The same procedure was followed as for **5c**. NMR (C_6D_6, 300 K), ^{1}H: δ 5.44 (s, 1H, C_5H_4), 5.28 (s, 1H, C_5H_4), 5.21 (s, 1H, C_5H_4), 4.76 (s, 1H, C_5H_4), 1.21 (t, 6H, J_{HH} = 7.7 Hz, CH_3), 0.96 (dd, 9H, J_{PH} = 9.7, J_{RhH} = 1.0 Hz, $P(CH_3)_3$), 0.77 (m, 4H, CH_2), −15.14 (ddq, 1H, J_{PH} = 35.7, J_{RhH} = 32.8, J_{FH} = 2.9 Hz, RhH); $^{31}P\{^1H\}$: δ 4.7 (d, J_{RhP} = 171 Hz); ^{19}F: δ −53.4 (d, J_{FRh} = 3 Hz).

[Rh(η^5-$C_5H_4CF_3$)(Si^{i}Pr$_3$)(H)(PMe$_3$)], 10c. The same procedure was followed as for **5c**. NMR (C_6D_6, 300 K), ^1H: δ 5.40 (s, 1H, C_5H_4), 5.37 (s, 1H, C_5H_4), 5.21 (s, 1H, C_5H_4), 4.86 (s, 1H, C_5H_4), 1.1−1.21 (m, 21H, CH_3 + CH), 0.97 (dd, 9H, J_{PH} = 9.8, J_{RhH} = 1.0 Hz, $P(CH_3)_3$), −14.91 (ddq, 1H, J_{PH} = 33.2, J_{RhH} = 30.7, J_{FH} = 2.9 Hz, RhH); $^{31}P\{^1H\}$: δ 0.3 (d, J_{RhP} = 174 Hz); ^{19}F: δ −53.0 (d, J_{FRh} = 3 Hz).

Competition Reactions. An NMR tube was charged with **1b** (5 mg, 0.011 mmol), HBpin (10 eq, 15.8 μL), and Et_3SiH (10 equiv, 17.4 μL), all dissolved in hexane (−1 mL), and irradiated at −10 °C for a specified period. Several similar reactions were carried out with different combinations of reagents in competition (Table 6). In some cases, the reactions were followed by $^{31}P\{^1H\}$ NMR spectroscopy with no lock. Otherwise, all volatiles were removed under vacuum, C_6D_6 was added, and the ^1H NMR spectrum was recorded. The reactions followed by ^1H NMR were carried out in C_6D_{12} and those by ^{31}P NMR spectroscopy, in hexane.

X-ray Crystallography. Crystallographic data are listed in Table 7. Diffraction data were collected on a Bruker Smart Apex diffractometer with Mo Kα radiation (λ = 0.710 73 Å) using a SMART CCD camera. Diffractometer control, data collection, and initial unit cell determination were performed using “SMART” (v5.625 Bruker-AXS). Frame integration and unit-cell refinement was carried out with “SAINT+” (v6.22, Bruker AXS). Absorption corrections were applied using SADABS (v2.03, Sheldrick). Structures were solved by direct methods using SHELXS-97 (Sheldrick, 1997) and refined by full-matrix least squares using SHELXL-97 (Sheldrick, 1997).[61] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon were placed using a “riding model” and included in the refinement at calculated positions with the exception of the C_2H_4 hydrogen atoms in **1b** and **1c**. These hydrogen atoms and the hydrides were located on difference maps after all non-hydrogen atoms had been located and were refined isotropically.

The structure of **1b** was refined in $P2_1/n$ and showed two independent molecules in the asymmetric unit, which differed only by the orientation of one phenyl ring. An attempt to refine in a $P2_1/c$ cell with a reduced by a factor of 2 to 9.8395 Å and Z reduced by a factor of 2 resulted in a structure with unsatisfactory anisotropic displacement parameters.

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Supporting Information Available: Crystal and molecular structure of **1b**; intermolecular interactions for **2b**; crystal and molecular structure of **2b·3b**, including intramolecular $\pi-\pi$ interaction for **2b** and intermolecular interactions in **2b·3b**; crystal and molecular structure of **11b·$C_6H_5CH_3$**; intermolecular interactions for **11b·$C_6H_5CH_3$**; ^1H, ^{31}P, and (where appropriate) ^{11}B NMR spectra of **2a**−**2c**, **4a**−**4c**, **5a**−**5c**, **6a**−**6c**, **7a**−**7c**, **8a**−**8c**, **9a**, **9c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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