

Addition of Catecholborane to a Ruthenium–Alkyl: Evidence for σ -Bond Metathesis with a Low-Valent, Late Transition Metal

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Abstract: Addition of catecholborane to the low-valent $\text{CpRu}(\text{PPh}_3)_2\text{Me}$ complex led to formation of the corresponding ruthenium hydride and methylcatecholborane by a mechanism more characteristic of high-valent metal centers. Kinetic experiments conclusively showed that oxidative addition of the B–H bond did not occur. A stereochemical analysis of the reaction employing, (*R,R*)- and (*R,S*)- $\text{CpRu}(\text{DPPP})\text{Me}$ (DPPP = 1,2-bis(diphenylphosphino)propane) showed that epimerization of the ruthenium center was occurring before product formation and that the species undergoing epimerization never reformed starting material. The exchange reaction, therefore, involved an intermediate whose formation was rate determining. The observation of a primary deuterium isotope effect (1.62 ± 0.13) and the absence of exchange between $\text{CpRu}(\text{PPh}_3)_2\text{Me-}d_3$ and MeBcat provided strong evidence for weakening of the borane B–H bond during formation of the transition state leading to this intermediate. The electronic effect of varying the phosphine ligand suggested a buildup of positive charge at the metal center, consistent with an intermediate possessing a coordinated hydridoborate ligand. All of the data were consistent with a mechanism proceeding through a four-centered transition state that involves partial cleavage of the B–H bond during formation of the B–C bond. Epimerization occurred by dissociation of the resulting hydridoborate ligand to form a three-coordinate ruthenium cation. The intermediate resulting from this step was trapped as a THF complex of the cationic ruthenium center during reactions in this solvent. The unligated three-coordinate cation provided epimerized product, but was not on the pathway to exchange of the boron–hydrogen and ruthenium–methyl groups.

Introduction

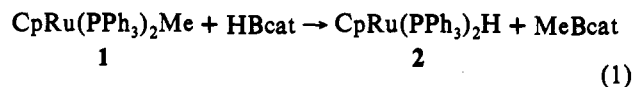
We present detailed evidence for a rare example of σ -bond metathesis^{1–5} involving a low-valent, late transition metal alkyl complex.⁶ The reactions of molecules containing H–H, C–H, and Si–H bonds across high-valent, early metal alkyl linkages are believed to involve four-centered transition states. This mechanism is characteristic of highly electrophilic d^0 systems, in part, because these metal centers cannot undergo oxidative addition and reductive elimination reactions. The presence of an intermediate preceding this transition state has been recently predicted by theoretical studies,⁷ although experimental work has not provided definitive evidence for or against its existence. The four-centered transition state in this process arises by cleavage of the substrate X–H bond in concert with the organometallic metal–carbon bond.

Our data provide strong evidence for the absence of oxidative and reductive steps in the exchange of a low-valent ruthenium-bound alkyl group with borane B–H bonds. Moreover, kinetic studies and an assessment of the electronic requirements of the transition state point to a mechanism involving simultaneous cleavage of the borane B–H bond and organometallic Ru–C bond. The observation of this mechanism, which is more characteristic of high-valent metal centers, implies that the pathways for reactions of borane B–H bonds with low- and high-valent metal

centers may not be as distinct as they are for reactions of H–H, C–H, and Si–H bonds. Sigma bond metathesis should now be considered for the carbon–boron bond formation step in metal-catalyzed hydroboration processes.^{8–11}

Results and Discussion

Addition of catecholborane (HBcat) to $\text{CpRu}(\text{PPh}_3)_2\text{Me}$ (**1**)¹² in arene solvent at room temperature led to quantitative formation of the hydride $\text{CpRu}(\text{PPh}_3)_2\text{H}$ (**2**)¹² and methylcatecholborane¹³ (MeBcat) in less than 30 min (eq 1).

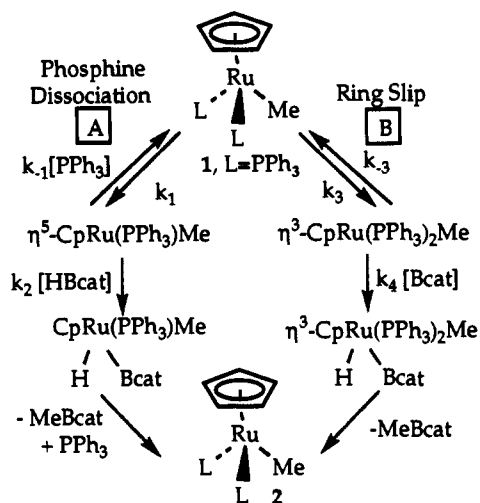


A comparison of the thermodynamic aspects of this process relative to those of hydrogenolyses deserves comment. Addition of H_2 across a metal–carbon bond is favorable due to the significantly greater strength of the metal–hydride bond relative to that of the corresponding metal–alkyl, while similar bond dissociation energies exist for the C–H bond formed and the H–H bond cleaved. It was not clear that a small difference in strength between the boron–carbon and boron–hydrogen linkages existed for the bonds being broken and formed in the exchange reaction reported here, since most studies report average B–H and B–R bond energies. Average B–H bond dissociation energies

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Scheme 1



(BDEs) for BH_3 have been measured to be 93 kcal/mol.¹⁴ A calculated value at the G-2 level for the first BDE of BH_3 was much higher, 105 kcal/mol.¹⁵ We have conducted a similar calculation for $\text{HB}(\text{OH})_2$ and found the B-H BDE to be 107 kcal/mol, indicating a minimal effect of oxygen substitution.¹⁶ An experimental value for the average BDE in BMe_3 was 87 kcal/mol,¹⁷ while our calculated value using the CBS-4 method¹⁸ for the first BDE of Me_3B was 102 kcal/mol and for $\text{MeB}(\text{OR})_2$ ($\text{R} = \text{alkyl}$), 111 kcal/mol. Although values for the first BDE differ significantly from those for average BDEs, it is clear that the first B-H and B-Me bond energies are similar to each other and allow the difference in metal-hydride and -alkyl linkages to provide the thermodynamic driving force.

We initially assumed that the exchange reaction was proceeding by oxidative addition and reductive elimination steps, as outlined in Scheme 1. This mechanism would be similar to those proposed as part of the cycle for catalytic hydroborations employing low-valent, late metal complexes.⁹ Moreover, this mechanism would be analogous to that documented for hydrogenolysis of low-valent, late metal alkyl complexes.¹⁹

1. Absence of an Unsaturated Intermediate. Oxidative addition to **1** would require preceding formation of a 16-electron intermediate by either phosphine dissociation or change in hapticity of the cyclopentadienyl ligand (Scheme 1). We have ruled out the possibility of phosphine dissociation and present data which argue strongly against a ring slip mechanism. The absence of either process makes these usual exchange mechanisms in Scheme 1 unlikely.

The overall transformation takes place faster than dissociation of phosphine from **1**. Exchange of free PPh_3 - d_{15} with coordinated PPh_3 in starting complex **1** required several days at 65 °C. In order to demonstrate that the borane does not induce phosphine dissociation, PPh_3 - d_{15} was added to the reaction, and no incorporation of labeled phosphine into starting material or product was observed.²⁰ As the absence of exchange predicts, addition of PPh_3 to the reaction solution did not alter the rate of the reaction.

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Although the possibility of a ring slip²¹ pathway is difficult to eliminate rigorously, our data argue strongly against this mechanism. The most definitive evidence against a ring slip was obtained by comparing the rate of reaction of **1** with its indenyl analog. Indenyl ligands are known to undergo changes from η^5 to η^3 bonding modes faster than the parent cyclopentadienyl complexes,²¹ and a common test for a ring slip mechanism is to compare the reaction rates for the cyclopentadienyl and indenyl systems.²² The indenyl analog of **1** has been prepared previously.²³ This compound reacted cleanly with catecholborane in a fashion analogous to reaction with **1** and produced the corresponding indenyl ruthenium hydride and methylcatecholborane. Although quantitative rate studies were not performed with the indenyl complex, the half-life for reaction was on the order of 2 h. Clearly this complex reacted more slowly with the same excess catecholborane in the presence of the same excess PPh_3 than did the parent complex **1**. The slower rate strongly suggests the absence of a ring slip mechanism. This conclusion is consistent with the absence of chemistry that requires a change in hapticity with the well-studied $\text{CpRu}(\text{PPh}_3)_2$ auxiliary.²⁴

In order to corroborate the absence of a ring slip, quantitative rate studies were performed with complex **1**. Reaction by pathway B of Scheme 1 would follow a rate law that predicts saturation behavior for k_{obs} at high $[\text{HBcat}]$. The reaction of catecholborane with **1** was clearly first order in metal complex under conditions of excess borane, and a linear $\ln k$ versus $\ln [\text{HBcat}]$ plot with a slope of 1.06 indicated strict first-order behavior in borane with respect to borane concentrations up to 0.33 (39 equiv).²⁵ An absence of saturation behavior at high $[\text{HBcat}]$ during quantitative rate studies with compound **1** also argues against a ring slip mechanism, albeit more weakly than the slower reaction rate with the indenyl system. In the absence of the indenyl analog, the lack of saturation behavior may be attributed either to the inability of $k_2[\text{HBcat}]$ to compete with k_{-1} or to a borane-induced ring slip.

These results were expected considering the absence of PPh_3 exchange with PPh_3 - d_{15} . The slow phosphine exchange rate relative to that of borane addition suggested the absence of any open coordination site, the implicit assumption being coordination of labeled phosphine would be at least competitive with B-H oxidative addition.

2. Presence of an Intermediate and Evidence for a Four-Centered Transition State. In order to use the stereochemical outcome of the reaction to probe the presence or absence of any intermediate, the exchange process was performed with the (*R*)-1,2-bis-(diphenylphosphino)propane analogs of **1** (Figure 1, **3a** and **3b** in Scheme 2). Replacement of the two triphenylphosphine ligands by this chelating ligand should not alter the reaction mechanism, since phosphine dissociation does not lie along the reaction coordinate. The presence of the chiral center on the ligand backbone and unsymmetric disposition of diphenylphosphino groups creates two diastereomers with the ruthenium as one stereocenter. Single diastereomers of [(*S*)- $\text{Ru}(\text{C}_5\text{H}_5)$](*R*)-prophos)Me (**3a**) and [(*R*)- $\text{Ru}(\text{C}_5\text{H}_5)$](*R*)-prophos)Me (**3b**) have been isolated previously and are appropriate for probing these three mechanisms.²⁶ Addition of catecholborane to **3a** or **3b** gave no epimerization of unreacted starting material, as determined by monitoring the reaction by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. However, the products showed a loss of stereochemistry at

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Scheme 2

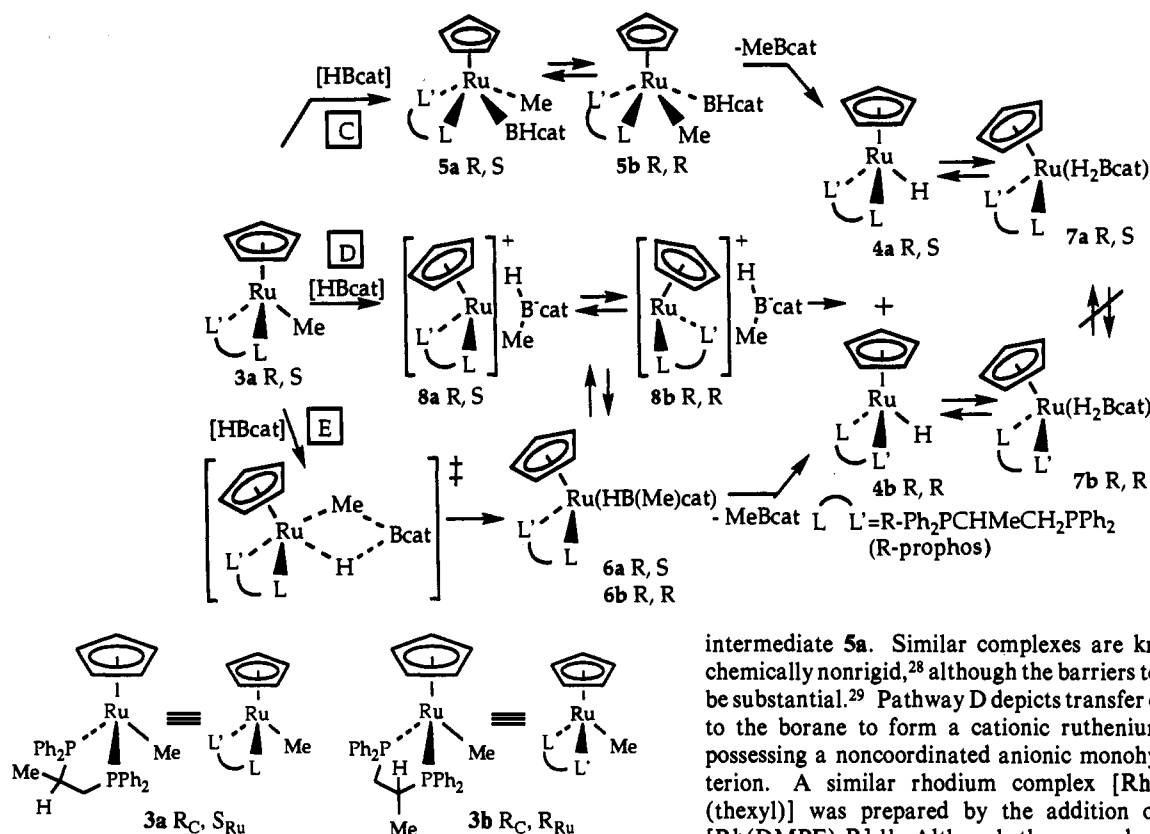


Figure 1. The diastereomers used to demonstrate the presence of an intermediate.

ruthenium. After 25–50% conversion, equal amounts of the two possible diastereomers **4a** and **4b** were formed from reaction with **3a** and a 1:13 mixture of **4a**:**4b** was formed from **3b**. The 1:2 equilibrium ratio of the two diastereomers was formed after several days in each case. The presence of *R,S* and *R,R* product hydrides but diastereomerically pure starting material throughout the course of the reaction indicated that there must be an intermediate in the reaction. Moreover, the absence of starting material reformed from the epimerized intermediate and the lack of an accumulation of the intermediate indicated that the formation of this intermediate must be rate determining.

The reproducible observation of two different nonequilibrium ratios of diastereomeric products demonstrated that the rate of product formation is competitive with the rate of epimerization of the intermediates. The diastereomeric nature of these intermediates implies that different epimerization rates for each species, constituting a nonunity equilibrium constant, are likely to exist. Moreover, the product-forming rates will be different for the energetically distinct diastereomers. As a result, the two diastereomeric starting materials will give different diastereomeric product ratios as long as the intermediates do not fully equilibrate. The differences in energy that account for the product ratios total less than 1.5 kcal/mol for $\Delta\Delta G^\ddagger$. Importantly, the presence of nonequilibrium diastereomeric mixtures of products also indicates that the excess catecholborane does not epimerize the hydride products on the reaction time scale.

3. Identification of the Intermediate. Three mechanisms that do not require the formation of an open coordination site from **1** are outlined as pathways C, D, and E in Scheme 2. Each pathway provides a means to epimerize the ruthenium center. Pathway C involves preequilibrium coordination of the borane to the metal center,²⁷ followed by hydride and alkyl exchange. Coordination of the borane would provide a five-coordinate

intermediate **5a**. Similar complexes are known to be stereochemically nonrigid,²⁸ although the barriers to epimerization can be substantial.²⁹ Pathway D depicts transfer of the methyl group to the borane to form a cationic ruthenium intermediate **8a** possessing a noncoordinated anionic monohydridoborate counterion. A similar rhodium complex $[\text{Rh}(\text{DMPE})_2][\text{BH}_2\text{R}(\text{hexyl})]$ was prepared by the addition of hexylborane to $[\text{Rh}(\text{DMPE})_2\text{R}]$.¹¹ Although the ground state for the three-coordinate ruthenium cation is bent, it is known to undergo inversion to epimerize the metal center.³⁰ Pathway E involves formation of a hydridoborate-coordinated intermediate without the intermediacy of an unsaturated ruthenium cation. This pathway requires simultaneous weakening of the ruthenium-carbon and boron-hydrogen linkages and is distinguished from pathway D by the direct involvement of the borane B-H bond during formation of the intermediate. Intermediate **6a** or **6b** could undergo epimerization by dissociation of the borate to generate **8a** or **8b**.

Pathways C, D, and E were distinguished, in part, by evaluation of the deuterium isotope effect. A secondary isotope effect would be expected for pathways C and D. Isotope effects concerning borane reagents are not well understood, and it was not clear if a hybridization change from sp^2 to sp^3 would provide a normal or inverse secondary effect. We have used ab initio calculations of the addition of hydride and methyl anion nucleophiles to a number of boranes to determine the expected direction of a secondary isotope effect. Ab initio vibrational frequencies of the starting materials and anionic products in these hypothetical reactions were calculated, and from these results equilibrium isotope effects were derived. Since full formation of the four-coordinate anionic species is likely to maximize the calculated secondary effect, the equilibrium values would be close to the maximum values expected for a kinetic effect in this case. The calculations revealed a normal isotope effect, in contrast to the inverse effect typical for sp^2 to sp^3 changes in C-H bonds.³¹ The normal effect resulted from a decreased B-H stretching vibration

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2 and 4a and 4b with deuteriocatecholborane in the absence of epimerization. The H/D exchange suggests that intermediates 7a and 7b, analogous to 6a and 6b but containing a dihydrido-catecholborate substituent, are accessible through a four-centered transition state possessing two bridging hydrides. Intermediates 7a and 7b are analogous to isolated hydridoborate complexes, including the closely related tetrahydridoborate complex CpRu(PPh₃)₂(BH₄),³² and their greater stability is substantiated by the observation of [CpRu(PPh₃)₂(THF)]⁺ by displacement of [H(Me)Bcat]⁻, but the lack of observable concentrations of this cation when the [H₂Bcat]⁻ anion must be displaced. It therefore seems likely that dissociation of the borate counterion to form three-coordinate ruthenium intermediates 8a and 8b allows epimerization. The weak bridging interaction in 6a and 6b allows a dissociation to generate 8a and 8b that is more rapid than for the dihydrido species 7a and 7b. The more facile formation of 8a and 8b from 6a and 6b allows inversion at ruthenium and is consistent with the observed rates of epimerization.

6. Relationship between Exchange and Epimerization. Oxidative addition of B-H bonds³⁸⁻⁴¹ and the formation of Lewis acid-base complexes²⁷ has been thought to be typical of the reactivity of low-valent, late metal complexes with boranes. The possibility of B-C bond formation in catalytic hydroborations with low-valent, late metal complexes by processes that are neither oxidative nor reductive^{8,42-44} has been suggested only recently.²⁰ This suggestion was put forth as a result of the observation of cationic rhodium complexes with noncoordinated hydridoborate anions upon apparent abstraction of rhodium hydride and methyl groups.^{11,20}

Our kinetic and stereochemical results in benzene solvent suggest that transient complexes of similar structure, 8a and 8b, are formed as a result of carbon-boron bond formation with the ruthenium system reported here. However, these species appear to lie on the pathway to epimerization at ruthenium and not directly on the pathway to formation of the boron-carbon bond. Our stereochemical experiments demonstrate the presence of an intermediate. However, the intermediate need not undergo epimerization itself. In this case it appears that the intermediate on the pathway to exchange forms a second species, an unligated three-coordinate cation, that undergoes epimerization. The results of kinetic isotope experiments demonstrate the weakening of the borane B-H bond at the transition state for formation of the intermediate on the reaction pathway. The absence of exchange between CpRu(PPh₃)₂Me-d₃ and MeBcat substantiates the importance of the boron-hydrogen bond during boron-carbon bond formation.

Conclusions

The B-C-bond-forming process described here and the C-H-bond-forming steps in hydrogenations provide an interesting mechanistic comparison since both are involved in an analogous step in reductive transformations. The hydrogenation process with low-valent complexes typically requires oxidative addition of hydrogen, either to create a hydride or to provide hydrogenolysis of the metal alkyl resulting from olefin insertion. The overall transformation discussed in the work presented here can be thought of as a boranalysis, involving reaction with a B-H rather than H-H bond. It is clear from this work that an oxidative step is not involved in the reaction of the borane B-H bond, in contrast

to the oxidative addition of H₂ typically involved in hydrogenolyses at low-valent late metal centers. The clear-cut formation of alkylboranes in a single, low-valent oxidation state makes it likely that complexes other than common hydrogenation catalysts will be able to promote hydroboration.

Experimental Section

General. Unless otherwise noted, all manipulations were carried out in an inert atmosphere glovebox or by using standard Schlenk or vacuum line techniques. ¹H NMR spectra were obtained on a GE QE 300-MHz or Ω 300-MHz Fourier transform spectrometer. ¹¹B and ³¹P NMR spectra were obtained on the Ω 300-MHz Fourier transform operating at 96.38 and 121.65 MHz, respectively. ¹H NMR spectra were recorded relative to residual protiated solvent. ³¹P{¹H} and ¹¹B NMR chemical shifts are reported in units of parts per million downfield from 87% H₃PO₄ and BF₃·OEt₂ as external standards. Sealed NMR tubes were prepared by attaching the sample tube via Cajon Ultra Torr adapters directly to a high-vacuum valve and were heated in Neslab constant temperature baths.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Catecholborane was distilled under vacuum prior to use. Methylcatecholborane was prepared by literature methods¹³ and distilled prior to use. Deuteriocatecholborane was prepared by literature methods,³⁶ employing NaBD₄ (98%) as the only hydride source, and was distilled prior to use. Pentane (tech grade) was distilled under nitrogen from purple sodium benzophenone ketyl made soluble by addition of tetraglyme to the still. Benzene, toluene, and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was vacuum transferred from CaH₂. Deuterated solvents for use in NMR experiments were dried as their protiated analogs, but were vacuum transferred from the drying agent.

Reaction of CpRu(PPh₃)₂Me (1), (Indenyl)Ru(PPh₃)₂Me, (R,S)-CpRu(prophos)Me (3a), or (R,R)-CpRu(prophos)Me (3b) with Catecholborane. For reactions involving compound 1 and its indenyl analog, 2.5–6.0 mg (3.6–8.6 μmol) of ruthenium complex was weighed into a vial in the drybox and dissolved in 0.7 mL of C₆D₆ to provide solutions between 5.1 and 12 mmol concentration. Catecholborane (10.0 μL, 94 mmol) was added by syringe. For complexes 3a and 3b, between 1.5 and 5.0 mg (2.4–8.0 μmol) of ruthenium complex was weighed into a vial and dissolved in 0.5 mL of benzene to provide solutions between 4.8 and 16 mmol concentration. To this solution was added 10 equiv of catecholborane. The resulting solutions were then transferred to an NMR tube for spectroscopic analysis.

Exchange of PPh₃-d₁₅ with CpRu(PPh₃)₂Me. In the drybox, 5.0 mg (0.71 μmol) of complex 1 was weighed into a vial and 0.6 mL of C₆D₆ was added. The benzene solution was added to a second vial containing 2.0 equiv of PPh₃-d₁₅. The resulting solution was transferred to an NMR tube which was sealed under vacuum. The resulting sample was monitored at room temperature for 24 h, and no exchange between labeled free phosphine and unlabeled coordinated phosphine was observed. Free PPh₃ and PPh₃-d₁₅ are easily resolved due to the large isotopic shift upon perdeuteration. Upon warming to 65 °C and monitoring over the course of 2 days, exchange was observed to produce two signals of equal intensity for free phosphine and two signals for coordinated phosphine after 1.5–2 days.

Reaction of CpRu(PPh₃)₂Me with Catecholborane in the Presence of PPh₃ and PPh₃-d₁₅. In the drybox, 9.2 mg (0.13 μmol) of complex 1 was weighed into a vial and 1.2 mL of C₆D₆ was added. To this solution was added 1.0 equiv of catecholborane. Into a second vial was weighed 2.0 equiv of PPh₃. The ruthenium solution was divided into two equal portions. One portion was placed directly into an NMR tube, and the other portion was added to the PPh₃ before placing it into a separate NMR tube. The two reactions were monitored by ³¹P{¹H} NMR spectroscopy and showed equivalent conversions to product after 0.5 h and 1 h. A similar experiment was conducted in the presence of PPh₃-d₁₅. Again, the reaction was monitored by ³¹P{¹H} NMR spectroscopy. Only signals due to free PPh₃-d₁₅ and 1-d₀ were observed. No resonance due to coordinated PPh₃-d₁₅ was observed. The four resonances due to free and coordinated labeled and unlabeled phosphine can be resolved as described for the exchange reaction above.

Attempted Exchange of Methylcatecholborane with CpRu(PPh₃)₂Me-d₃. In the drybox, 4.2 mg (5.95 μmol) of complex 1-d₃ was weighed into a vial and 0.6 mL of C₆H₆ was added. To this solution was added 0.8 μL (1 equiv) of methylcatecholborane. The resulting solution was transferred to an NMR tube, which was sealed under vacuum. The

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resulting sample was monitored at room temperature, 45 °C, and 75 °C, obtaining several NMR spectra over the course of 24 h in each case. No exchange between the ruthenium methyl group and the borane methyl group was detected. $^{31}\text{P}\{^1\text{H}\}$, ^{11}B , and ^2H NMR spectra were unchanged under these conditions. A similar experiment was conducted in THF solvent. No exchange was observed after 24 h at 55 °C.

Preparation of $\text{CpRu}[\text{P}(p\text{-F-C}_6\text{H}_4)_3]_2\text{Cl}$. A 250-mL three-necked round-bottom flask, equipped with a dropping funnel, reflux condenser, and nitrogen outlet, was charged with 0.499 g (1.58 mmol) of $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$. Into the dropping funnel was placed 0.082 g (0.31 mmol) of hydrated ruthenium trichloride and 0.192 mL (2.37 mmol) of freshly distilled cyclopentadiene. The apparatus was thoroughly purged with nitrogen. Nitrogen-saturated absolute ethanol was then cannulated into the reaction flask (10 mL) and into the dropping funnel (2.5 mL). The $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ was dissolved by heating. The dark brown ethanolic solution of ruthenium trichloride and cyclopentadiene was then added to the refluxing $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3$ solution over a period of 10 min. The reaction was refluxed for 1 h, over which time its color changed from dark brown to dark red-orange. The solution was then filtered quickly in air while hot and cooled at -10 °C overnight. The orange crystals, 0.23 g (88%), were collected on a sintered glass filter and washed with ethanol (4×6 mL) and hexanes (4×6 mL) and dried *in vacuo*: $^{31}\text{P}\{^1\text{H}\}$ NMR (THF) δ 38.58; ^1H NMR (C_6D_6) δ 4.02 (s, 5H), 6.58 (t, 8.5 Hz, 12H), 7.23 (m, 12H).

Preparation of $\text{CpRu}[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3]_2\text{Me}$. In a pear-shaped flask was suspended 0.202 g (0.24 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3]_2\text{Cl}$ in 10 mL of ether. To the stirred suspension was added 80 μL (0.24 mmol) of a 3 M solution of MeMgBr in ether. The reaction was left for 12 h at 20 °C, after which time less than 10% conversion to product had occurred, as determined by obtaining a ^{31}P NMR spectrum directly of the reaction mixture. At this time an additional 0.81 mL of the MeMgBr solution was added, and the reaction was complete within 2 h. At this time, the solvent was evaporated under reduced pressure. The resulting yellow residue was dissolved in toluene, filtered through a fritted-glass funnel, and placed into a vial. The toluene solution was layered with pentane and cooled for 12 h at -30 °C. The mother liquor was removed by pipet from the resulting yellow-orange solid. After drying under vacuum, 0.10 g (52%) of product was isolated: $^{31}\text{P}\{^1\text{H}\}$ NMR (THF) δ 54.65; ^1H NMR (C_6D_6) δ 0.70 (t, 5.7 Hz, 3H), 3.95 (s, 5H), 6.54 (m, 12H), 6.949 (m, 12H).

Preparation of $\text{CpRu}[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Me})_3]_2\text{Me}$. In a pear-shaped flask was suspended 0.35 g (0.43 mmol) of $\text{RuCl}[\text{P}(p\text{-MeC}_6\text{H}_4)_3]_2(\eta\text{-C}_5\text{H}_5)$ in 5 mL of ether, and to the suspension was added 0.14 mL (0.43 mmol) of methylmagnesium bromide. After 12 h the solvent was removed under reduced pressure, the product dissolved in toluene, and the resulting solution filtered through a fritted-glass funnel. The mother liquor was then placed into a vial, layered with pentane, and left for 12 h at -30 °C. The yellow-orange crystals (0.28 g, 80%) were collected by pipeting off the clear yellow mother liquor and drying under vacuum: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) δ 55.67; ^1H NMR (C_6D_6) δ 1.09 (t, 5.4 Hz, 3H), 2.07 (s, 18H), 4.50 (s, 5H), 6.77 (d, 7.8 Hz, 12H), 7.30 (m, 12H).

Kinetic Studies. Into a 1.0-mL volumetric flask was weighed 8.5 mmol of the appropriate ruthenium complex, which was then dissolved in toluene- d_8 , THF- d_8 , or CD_2Cl_2 . For each rate measurement, 0.40 mL of the 1.0-mL solution was added to a medium-walled NMR tube by syringe. To the sample was then added the appropriate amount of catecholborane or deuteriocatecholborane. For all relative rate studies, including isotope and solvent effect measurements, 10.0 μL of borane was added. The sample, attached via Cajon adapters directly to a high-vacuum valve, was then quickly brought out of the drybox and immersed in liquid nitrogen. The sample tube was evacuated while the solution was frozen, and the tube was flame sealed. Rate measurements were performed by ^1H NMR spectroscopy at 5 °C by cooling the probe to 5 °C, thawing the sample, and quickly placing it in the probe. Single-pulse experiments were performed, waiting at least 7 min between data collections to ensure an interval of $3T_1$. The cyclopentadienyl resonance of the starting material was integrated versus the methyl resonance of the toluene solvent as internal standard in order to obtain rate data. Reactions were monitored over three half-lives, except in the case of the $\text{CpRu}[\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3]_2\text{Me}$ complex. This reaction was monitored for 24 h, which amounted to ca.

two half-lives. The following pseudo-first-order rate constants were obtained at varying concentrations of borane: k , $[\text{HBcat}]$, $6.0 \times 10^{-5} \text{ s}^{-1}$, 0.094 mM; $8.8 \times 10^{-5} \text{ s}^{-1}$, 0.14 mM; $1.4 \times 10^{-5} \text{ s}^{-1}$, 0.23 mM; $2.4 \times 10^{-5} \text{ s}^{-1}$, 0.33 mM.

Secondary Equilibrium Isotope Effect Calculations. Equilibrium isotope effects are often described in terms of the effect of isotopic substitution on the vibrational zero-point energy. However, this approximation is generally insufficient. Instead, one must assess the effect of isotopic substitution on both the vibrational and rotational components of the molecular partition function as well as its effect on the vibrational energy levels.^{45,46} The isotope effect $K_{\text{H}}/K_{\text{D}}$ can then be calculated from the difference in free energy resulting from isotopic substitution or directly from the ratio of the partition functions.⁴⁶⁻⁴⁸ Predicted isotope effects are generally calculated within the rigid-rotor harmonic oscillator approximation,⁴⁶ as was done in this work. Model compounds were chosen that lack free torsional modes in order to avoid the difficulty of their poor approximation by the harmonic oscillator model. The low-frequency skeletal vibrations in the larger model compounds may be poorly described in the harmonic oscillator approximation. However, the errors incurred should roughly cancel for the deuterated and nondeuterated species, since the isotope effects are dominated by higher-frequency bond stretch and bend vibrations involving the substituted B-H bonds.

The two programs THERMO^{49,50} and QUIVER,⁴⁶ which assess the effect of isotopic substitution on the vibrational and rotational components of the molecular partition function and on the vibrational energy levels, were used for the isotope effect calculations in this work. As expected, the two programs yielded almost identical results for several examples tested. In both cases, frequencies were calculated using the Gaussian 93 package⁵¹ at the HF/6-31G* level⁵² and were scaled by the recommended factor of 0.8934.⁵³ All calculations were performed for a temperature of 278.16 K, and the following values were obtained: $\text{BH}_2\text{X} + \text{H}^-$ 1.15, $\text{BH}_2\text{X} + \text{CH}_3^-$ 1.08, $(\text{HO})_2\text{BX} + \text{H}^-$ 1.22, $(\text{HO})_2\text{BX} + \text{CH}_3^-$ 1.26, $\text{BF}_2\text{X} + \text{H}^-$ 1.22, $\text{BF}_2\text{X} + \text{CH}_3^-$ 1.14, $c\text{-}(\text{OCHCHO})\text{BX} + \text{H}^-$ 1.19, $c\text{-}(\text{OCHCHO})\text{BX} + \text{CH}_3^-$ 1.14, (catecholate) $\text{BX} + \text{H}^-$ 1.12, (catecholate) $\text{BX} + \text{CH}_3^-$ 1.08 (X = H, D).

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