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# DFT Studies of β-Boryl Elimination Processes: Potential Role in Catalyzed Borylation Reactions of Alkenes

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DFT calculations on the model system $[(PH_3)(CO)(Cl)Ru-CH_2CH_2\overline{B(OCH_2CH_2O})]$ provide insight into the process by which a boryl group, at the β-position of a metal-bound alkyl moiety, can be transferred to the metal center. Implications of this pathway with regard to catalytic processes such as hydroboration, dehydrogenative borylation, diboration, and addition of other B−X bonds to alkenes are noted.

## Introduction

Transition metal boryl complexes[1] have attracted considerable interest because of their role in catalyzed hydroboration, diboration, dehydrogenative borylation, and other B−X addition reactions to unsaturated organics[2−4] as well as the catalyzed borylation of C−H bonds in alkanes and arenes.[5,6] A number of theoretical studies of M−B bonding have appeared[7−12] including our recent report on the role of σ- and π-effects on the exceptionally strong *trans*-influence of boryl ligands and a comparison of the *trans*-influence of boryls with those of hydride as well as C-, Si-, and Sn-based σ-donor ligands.[13] One important reaction of such ligands is the migratory insertion of alkenes. Thus, insertion of alkenes into M−H bonds is often reversible, leading to a host of catalytic processes.[14] Insertion of alkenes into M−B bonds in boryl complexes has also been established[15] and is critical to a variety of processes such as alkene diboration[16] and other B−X additions such as silylboration and stannylboration reactions[17] as well as the dehydrogenative borylation[18] of alkenes to vinylboronate esters, a process that involves alkene insertion into M−B followed by β-hydride elimination.[17f] Until very recently, however, direct evidence for the reversibility of the alkene insertion into M−B had not been reported.

In 2005, Marciniec et al. described a novel catalytic synthesis of vinylboronate esters via “*trans*-borylation”, i.e., the transfer of a boronate moiety from one alkene (e.g., vinyldioxaborolane) to another (e.g., styrene) (eq 1).[19a] Mechanistic insight and the ability to distinguish this pathway from a cross-metathesis alternative were obtained from an elegant deuterium labeling study using perdeuterostyrene (Scheme 1). The direct implication of this work was the reversibility of the alkene insertion

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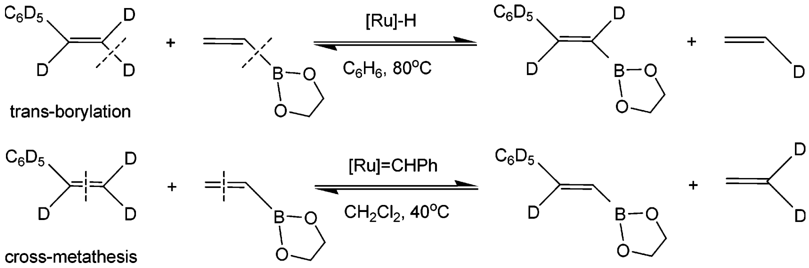
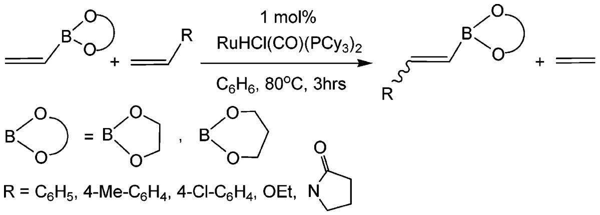
**Scheme 1. *trans*-Borylation and Cross-Metathesis of Styrene-$d_8$ with Vinyldioxaborolane**

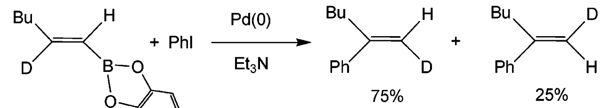


into a Ru−B bond, which provided clear evidence for the $\beta$-boryl elimination reaction. Insertion of a vinylboronate ester into a Pd−aryl bond followed by $\beta$-boryl elimination was proposed in 1981 by Miyaura and Suzuki[19b] to account for the results of the labeling study shown in eq 2. As the $\beta$-boryl elimination pathway has potential implications for many catalyzed borylation reactions, we decided to examine the potential surface for the process and the nature of the transition state in a model ruthenium system.

Similar to *trans*-borylation, *trans*-silylation,[20] i.e., the transfer of a silyl moiety from one alkene to another (eq 3), has also been observed, indicating the reversibility of alkene insertion into M−Si, which is potentially important for dehydrogenative silylation[21] and hydrosilylation reactions.[22] In this paper, we report the initial results of our theoretical studies on the *trans*-borylation as well as the *trans*-silylation reactions.



(1)



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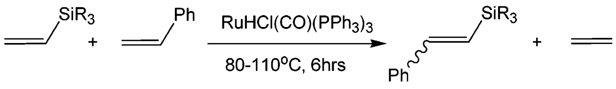

(3)

$R_3$ = $Me_3$, $Me_2Ph$, $(OEt)_3$

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## Computational Details

Geometry optimizations have been performed via density functional theory (DFT) calculations using the B3LYP functional.[23] Frequency calculations at the same level of theory have also been performed to confirm the characteristics of all the optimized structures as minima or transition states. The effective core potentials (ECPs) of Hay and Wadt with a double-$\zeta$ valence basis set (Lanl2DZ)[24] were used to describe Ru, Os, Si, P, and Cl atoms, while the standard 6-31G basis set was used for C, B, O, N, and H atoms.[25] Polarization functions were added for H($\zeta$(p)=1.10) and C($\zeta$(d)=0.600) that are directly bonded to the metal center and for N($\zeta$(d)=0.864), B($\zeta$(d)=0.388), P($\zeta$(d)=0.340), Cl($\zeta$(d)=0.514), Si($\zeta$(d)=0.262), and O($\zeta$(d)=1.154) of the boryl ligands or boryl substituents.[26a] The f-polarization functions were also added for Ru($\zeta$(f)=1.235) and Os($\zeta$(f)=0.886).[26b] All calculations were performed with the Gaussian 03 software package.[27] The bond energies for various Ru−X and C−X bonds (where X = H, $BOCH_2CH_2O$, and $SiMe_3$) were evaluated by eqs 4 to 7, and the results are listed in Table 1, which will be discussed below. The calculated bond energies are consistent with the previously calculated results by Hartwig and Rablen et al.[7,28] Evaluation of bond energies using eqs 4 to 7 should provide acceptable results when we are mainly interested in relative bond energies.

**Table 1. Ru−X and C−X (X = H, $B(OR)_2$, and $SiMe_3$) Bond Energies**

| | Ru−Si | Si−C | Ru−B | B−C | Ru−H | H−C |
|---|---|---|---|---|---|---|
| bond energies (kcal/mol) | 51.4 | 82.4 | 70.9 | 105.3 | 67.2 | 102.4 |

In our DFT calculations, we used $PH_3$ as a model for $PCy_3$. One reviewer was therefore concerned that the strong $\sigma$-donating property of $PCy_3$ may not be well modeled. To study how the $\sigma$-donating property affects the results, we performed calculations using $PMe_3$ for the species shown in Figure 1. In the $PH_3$ models, the relative electronic energies of **2A**, **TS$_{2A-3A}$**, **3A**, **3A1**, **TS$_{3A1-4A}$**, and **4A** are 0.0, 15.7, 3.6, −7.4, 12.8, and −1.8 kcal/mol, respectively. In the $PMe_3$ models, the relative energies are 0.0, 17.4, 2.7, −7.1, 13.1, and −1.2 kcal/mol, respectively. Thus, the largest energy difference is only 1.7 kcal/mol. The results show that a strong $\sigma$-donating phosphine ligand does not affect the relative energies significantly, suggesting that the results derived from the $PH_3$ models are qualitatively valid. The results imply that the use of $PCy_3$ makes the first phosphine dissociation from the five-coordinate precatalyst **1** even more facile, facilitating the catalytic reactions (see discussion below for more details).

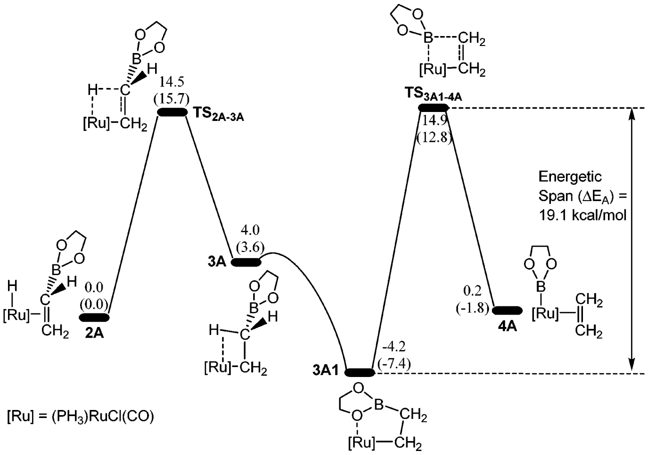

**Figure 1.** Energy profile calculated for the proposed *trans*-borylation reaction pathway. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

$$CH_3CH_2B(OR)_2 \rightarrow CH_3C^{\bullet}H_2 + B^{\bullet}(OR)_2 \tag{4}$$

$$CH_3CH_2SiMe_3 \rightarrow CH_3C^{\bullet}H_2 + Si^{\bullet}Me_3 \tag{5}$$

$$CH_3CH_2SiMe_3 \rightarrow CH_3C^{\bullet}HSiMe_3 + H^{\bullet} \tag{6}$$

$$PH_3Cl(CO)Ru(X)(\eta^2\text{-}CH_2{=}CH_2) \rightarrow PH_3Cl(CO)Ru^{\bullet}(\eta^2\text{-}CH_2{=}CH_2) + X^{\bullet} \tag{7}$$

where X = H, $B(OR)_2$, and $SiMe_3$; $B(OR)_2 = B(\overline{OCH_2CH_2O})$.

## Results and Discussion

On the basis of their experimental findings, Marciniec et al. proposed a mechanism to account for the "*trans*-borylation" reaction as shown in Scheme 2. The precatalyst **1** undergoes a ligand exchange to produce **2**. From **2**, the coordinated vinylboronate inserts into the Ru−H bond, followed by a $\beta$-boryl elimination to give **4** (**2** → **3** → **4**). A ligand exchange then occurs to give **4′**, having a substituted alkene as a ligand. From **4′**, the coordinated, substituted alkene inserts into the Ru−B

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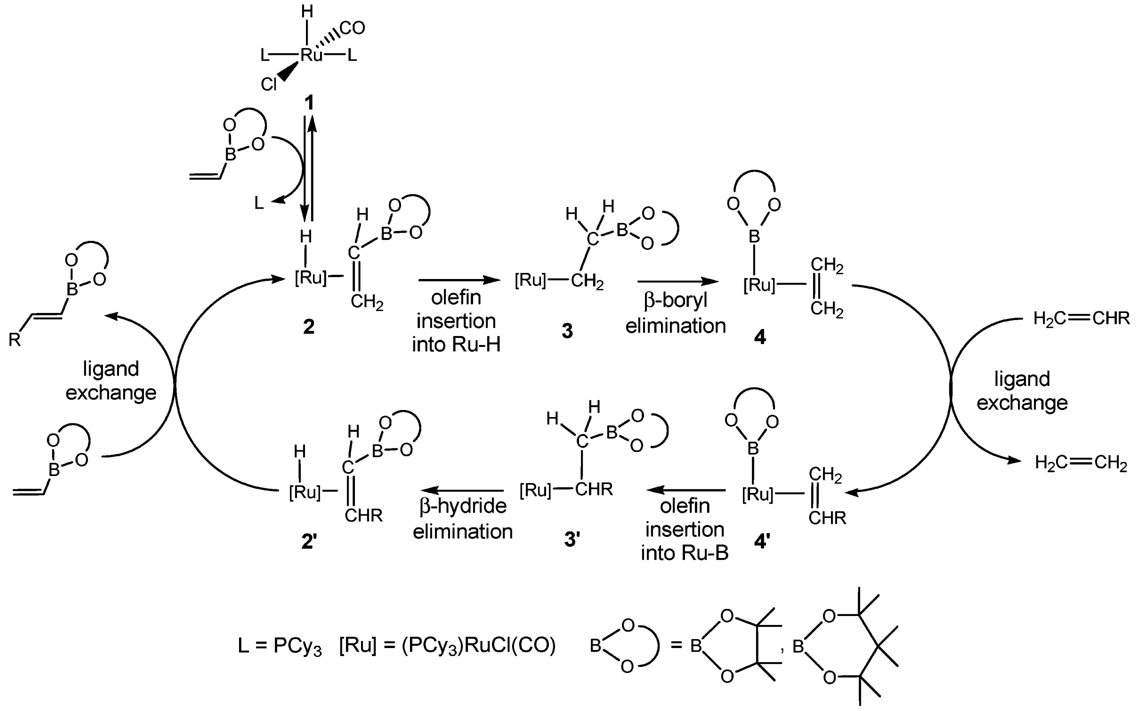
**Scheme 2. Proposed Mechanism for the "*trans*-Borylation" Reaction**



bond, followed by $\beta$-hydride elimination to give the functionalized vinylboronate derivative as a $\pi$-bound ligand (**4′** → **3′** → **2′**). The **4′** → **3′** → **2′** process can be viewed as the reverse process of **2** → **3** → **4** when R = H. Therefore, we focus our discussion on the **2** → **3** → **4** process.

**Mechanistic Aspects of the "*trans*-Borylation" Reaction.** To examine the structural and energetic aspects of the proposed reaction mechanism, DFT calculations have been carried out using the model complex $(PH_3)RuCl(CO)(\eta^2\text{-}CH_2{=}CH(B(OCH_2CH_2O))$, **2A**. Figure 1 shows the energy profile for the **2A** → **3A** → **4A** process. The relative free energies and electronic energies (in parentheses) are shown. Structural details of selected intermediates and transition states are shown in Figure 2. To take into account the effect of entropy, we use free energies in our discussion. In **2A**, $PH_3$ was used to model the phosphine ligands and $B(OR)_2$ $\{(OR)_2 = OCH_2CH_2O\}$ for the boryl ligands.

From Figure 1, we can see that the vinylboronate insertion into the Ru−H bond in **2A** via the transition state $\mathbf{TS_{2A-3A}}$ affords the formally 16-electron complex **3A** with a Ru−H−C agostic interaction. The barrier for the vinylboronate insertion is 14.5 kcal/mol, while the reverse process, the $\beta$-hydride elimination, has a smaller barrier of 10.5 kcal/mol. Rotation of the $-CH_2B(OR)_2$ group around the C−C single bond gives the stable intermediate **3A1**, a structural isomer of **3A**. A dative bonding interaction from a boryl group oxygen atom to Ru (Ru−O) stabilizes the unsaturated Ru center in **3A1**. The calculated Ru−O distance is 2.236 Å, which is close to the experimental value (2.275 Å) found in the complex $Ru(CH{=}CH{-}[BOC_6H_4O])Cl(CO)(PPh_3)_2$.[29] We were unable to locate the rotational transition state connecting **3A** and **3A1** because of the flatness of the potential energy surface near the transition state. We expect that the rotational barrier is small. Figure 1 shows that the barrier for the $\beta$-boryl elimination is 19.1 kcal/mol from **3A1** to **4A**, while the reverse process, alkene insertion into the Ru−B bond, has a smaller barrier of 14.7 kcal/mol.

The structures of the transition states for the vinylboronate insertion into the Ru−H bond ($\mathbf{TS_{2A-3A}}$) and the $\beta$-boryl group elimination ($\mathbf{TS_{3A1-4A}}$) together with those of **2A** and **4A** are shown in Figure 2. From Figures 1 and 2, **2A** and **4A** have similar stability, suggesting that the total bond strength of the Ru−H and C−B bonds is comparable to that of the Ru−B and C−H bonds.[7,28] Indeed, the calculated total bond energies (Table 1) of Ru−H + C−B and Ru−B + C−H are 172.5 and 173.3 kcal/mol, respectively. Interestingly, $\mathbf{TS_{2A-3A}}$ and $\mathbf{TS_{3A1-4A}}$ also have similar stability. The comparable stability of **2A** and **4A** as well as $\mathbf{TS_{2A-3A}}$ and $\mathbf{TS_{3A1-4A}}$ and the relatively low barriers for the forward and reverse processes of **2A** ↔ **3A1** and **4A** ↔ **3A1** (the reversibility of the two steps) guarantee the successful *trans*-borylation because the *trans*-borylation involves both the forward process **2A** → **3A1** → **4A** and the reverse process **4A** → **3A1** → **2A**. Here, the total barrier for the *trans*-borylation reaction is the energy difference between the highest and the lowest points of the catalytic cycle as shown in Figure 1. The energy difference was defined as the energetic span in the catalytic cycle.[30] The energetic span of the *trans*-borylation ($\Delta E_A$) is 19.1 kcal/mol. The overall reaction, $CH_2{=}CHB(OR)_2 + CH_2{=}C(H)Ph \rightarrow PhHC{=}CHB(OR)_2 + CH_2{=}CH_2$ (eq 1), is slightly exothermic by −1.4 kcal/mol, providing a small driving force for the *trans*-borylation to occur, and indeed, we might expect an equilibrium to be attained.

In Figure 2, we note that the phosphine ligand moves from a position *trans to the alkene* into a position *trans* to the developing C−H bond, and then back to one *trans to the new alkene* during the **2A** → **3A** → **3A1** → **4A** process. The change in the positions avoids a direct *trans*-arrangement of the phosphine ligand with respect to the strong *trans*-influencing ligand, hydride, alkyl, or boryl.[13]

In Scheme 2, the precatalyst **1** undergoes a ligand exchange to produce the 16-electron complex **2**, which starts the *trans*-borylation catalytic cycle. Because precatalyst **1** is a 16-electron

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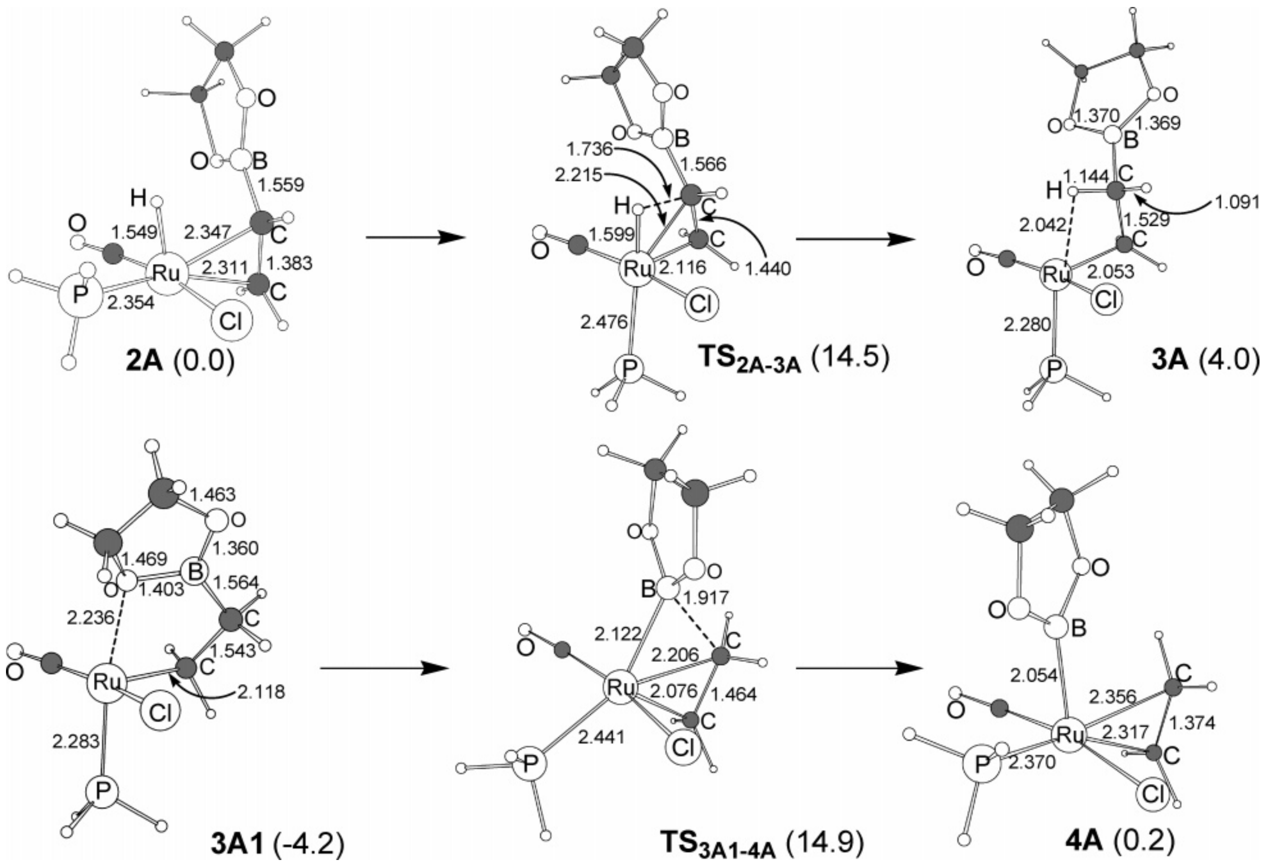

**Figure 2.** Optimized structures for the species shown in Figure 1. The relative free energies (kcal/mol) are given in parentheses. Bond lengths are given in angstroms.

species, one may consider the possibility of having the vinylboronate directly coordinate to the precatalyst **1** without losing a phosphine ligand. In the real catalyst system, we do not expect such a possibility to occur. The actual phosphine employed is $PCy_3$, which is very bulky. In the Grubbs Ru-metathesis systems, which have two *trans* $PCy_3$ ligands or one N-heterocyclic carbene (NHC) ligand *trans* to a $PCy_3$ ligand, studies have shown that the catalytically active species is a 14-electron intermediate formed via dissociation of one of the $PCy_3$ ligands from a five-coordinate, 16-electron Ru(II) complex.[31]

**Ruthenium−Alkene Bonding.** Calculations were performed on three model alkene complexes (Figure 3), bearing H, CN, and $NH_2$ substituents. Interestingly, the bond distances of the three coordinated C═C double bonds are not very sensitive to the donor/acceptor properties of the different substituents, whereas the bond distances between Ru and the alkene carbons are sensitive, suggesting that the alkene($\pi$)-to-metal($d_\sigma$) $\sigma$-donation dominates in the Ru(II)−alkene bonding interactions,[32] as has also been recognized and analyzed in Pd(II)−alkene complexes.[33] The coordinated alkene in each of the three Ru(II)−alkene complexes lies roughly perpendicular to the equatorial plane (Figure 3). In **4A**, the coordinated ethene binds unsymmetrically to the metal center, likely related to the steric effect of the boryl ligand, which weakens the metal−carbon bond adjacent to it. In **4B**, the electron-withdrawing CN substituent shifts $\pi$-electron density from the $CH_2$ carbon toward the cyano-substituted carbon;[34,35] therefore, the Ru−CH(CN) bond is shorter than the Ru−$CH_2$ bond. Compared to the corresponding Ru−C bond in **4A**, however, the Ru−CH(CN) bond in **4B** is longer, indicating that the overall effect of the electron-withdrawing CN substituent is to reduce the alkene($\pi$)-to-metal($d_\sigma$) $\sigma$-donation ability. In **4C**, the very strong $\pi$-electron-donating $NH_2$ substituent makes the $CH_2$ carbon very rich in $\pi$-electron density, giving a substantially shorter bond for Ru−$CH_2$ versus Ru−CH($NH_2$). The substantially longer Ru−CH($NH_2$) bond when compared with the Ru−$CH_2$ bond in **4C** suggests that the vinylamine ligand resembles an allyl anion three-center, four-electron $\pi$-system, in which the $\pi$-electron density on the central atom (i.e., the substituted carbon) is substantially depleted, such that the vinylamine HOMO is predominantly localized on the $CH_2$ group,[35] leading to unsymmetrical $\eta^2$-alkene binding. Further support for the claim that the alkene($\pi$)-to-metal($d_\sigma$) $\sigma$-donation dominates the Ru(II)−alkene bonding can be found from the Mulliken population analysis of the coordinated alkenes in **4A**, **4B**, and **4C**. The calculated charges on the coordinated alkenes in **4A**, **4B**, and **4C** are +0.24, +0.15, and +0.37, respectively, indicating that the alkene ligands lose electrons upon coordination. Very unsymmetrical $\eta^2$-alkene coordination of electron-donor-substituted alkenes was also found and discussed for $[CpFe(CO)_2(CH_2{=}CHX)]^+$ (X = OEt, $NMe_2$).[34]

**Nature of the *β*-Boryl Elimination.** It is worth examining whether or not the "empty" p orbital on the three-coordinate boron atom of the boryl ligand plays an important role in the

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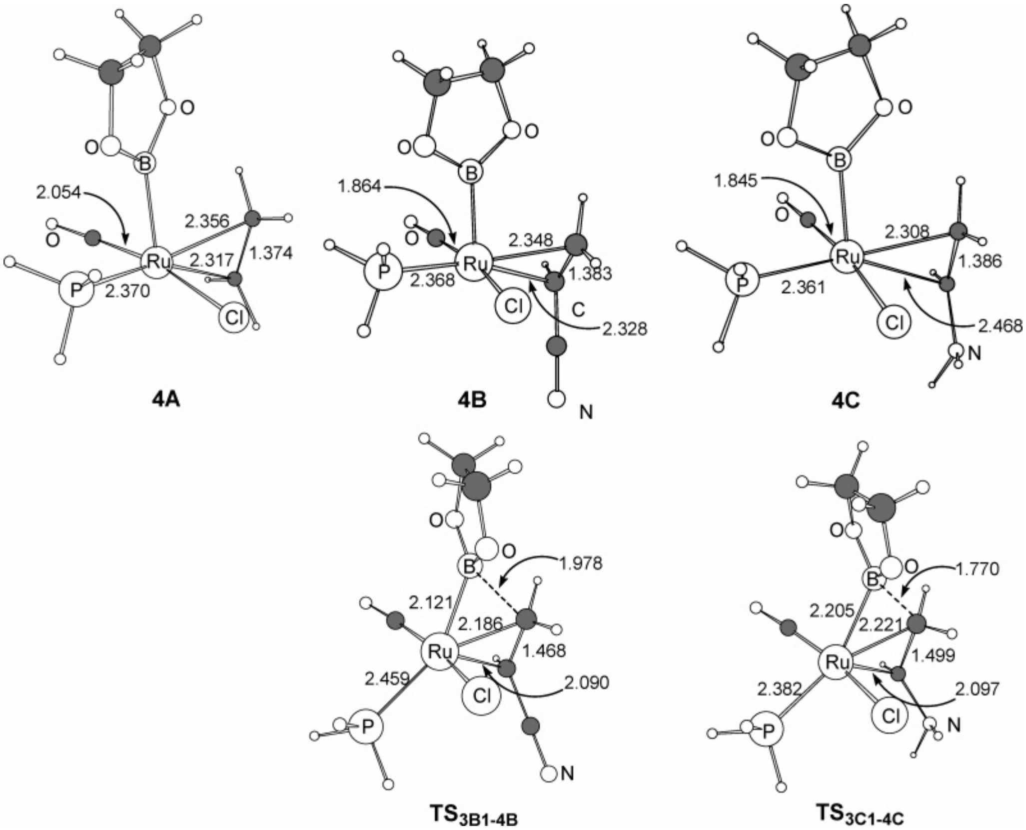

**Figure 3.** Optimized structures for $(PH_3)(Cl)(CO)Ru(B(OR)_2)(\eta^2\text{-}CH_2{=}C(H)R')$ ($R' = CN$, H, and $NH_2$) and their boryl migration transition states.

$\beta$-boryl elimination. The $p_\pi$ orbital on the boron atom could interact with an occupied metal $d_\pi$ orbital and/or O-lone pair $p_\pi$ orbitals.[1,7−10,13] We can make the following conjecture: during the boryl migration process, if the "empty" p orbital on the boron atom is important, it would accept an electron pair from the alkene $\pi$-system, and hence, an alkene ligand having an electron-donating substituent (e.g., $R' = NH_2$) would promote the boryl migration process and an alkene ligand having an electron-withdrawing substituent (e.g., $R' = CN$) would retard the migration. For the reverse process, $\beta$-boryl elimination, if the "empty" p orbital on the boron atom is important, an electron-withdrawing substituent would have a promoting effect and an electron-donating substituent would inhibit the elimination.

We therefore examined the alkene insertion processes (the reverse processes of the $\beta$-boryl elimination) in the complexes $(PH_3)(Cl)(CO)Ru(B(OR)_2)(\eta^2\text{-}CH_2{=}C(H)R')$ ($R' = H$ (**4A**), CN (**4B**), and $NH_2$ (**4C**)). Figure 4 compares the energy profiles of the insertion processes in the three complexes. We refer to the alkene insertion into the Ru−B bond as boryl migration, and similarly, the alkene insertion into the Ru−H bond as hydride migration. Because the coordinated alkene in **4A**, **4B**, and **4C** is roughly perpendicular to the equatorial plane, we expect that there are orientational isomers in $(PH_3)(Cl)(CO)Ru(B(OR)_2)(\eta^2\text{-}CH_2{=}C(H)R')$ with respect to the orientation of the coordinated alkene when R′ is not a hydrogen atom. We consider isomers **4B** and **4C** only, as we are mainly interested in analyzing how substituents with different electronic properties affect the insertion barriers from which we can delineate the nature of the boryl elimination process. Different regioselectivities would lead to different *trans*-borylation products. However, the main purpose of the present study is to emphasize the importance of the reversibility of boryl migration/$\beta$-boryl elimination, together with the relatively low barriers for these processes. Alkene ligands in **4B** and **4C** were not studied experimentally in the *trans*-borylation reactions,[19a] but were employed here to study substituent effects on the insertion barriers. The issue of regioselectivity in alkene insertions into metal−boryl bonds has been addressed by us very recently.[35]

The barriers for the boryl migration processes (**4A** → $\mathbf{TS_{3A1-4A}}$) increase in the order $R' = CN$ (14.5) < H (14.8) < $NH_2$ (19.0) (kcal/mol), while the barriers for the $\beta$-boryl elimination (**3A1** → $\mathbf{TS_{3A1-4A}}$) decrease in the order $R' = CN$ (24.1) > H (19.2) > $NH_2$ (12.4) (kcal/mol), as shown in Figure 4. Even though there will be enhanced ground state stabilization of the alkene complex for donor-substituted **4C** versus **4A**,**B**, if the boron p orbital played a critical role in the alkene insertion process, we would expect considerable transition state stabilization as well. However, given the substantially *increased* barrier calculated for **4C**, the role of the "empty" p orbital on boron must not be extremely important in the $\beta$-boryl elimination/boryl migration processes.

**Effect of the Metal Center.** In this section, we examine the effect of the metal center. Using the model complex **2D** with a more electron-rich osmium metal center, we calculated the corresponding energy profile, shown in Figure 5, which resembles that of Figure 1. The barrier for the $\beta$-hydride elimination is 16.5 kcal/mol from **3D1** to $\mathbf{TS_{2D-3D}}$. The barriers for the alkene insertion into the Os−H and Os−B bonds are slightly higher than those for alkene insertion into the Ru−H and Ru−B bonds, respectively, consistent with earlier findings that alkene insertion into an M−R bond is kinetically and thermodynamically less favorable when the metal(d)-to-alkene-($\pi^*$) back-bonding interaction is more significant.[36] The energetic span ($\Delta E_D$) of the *trans*-borylation reaction is 20.5 kcal/

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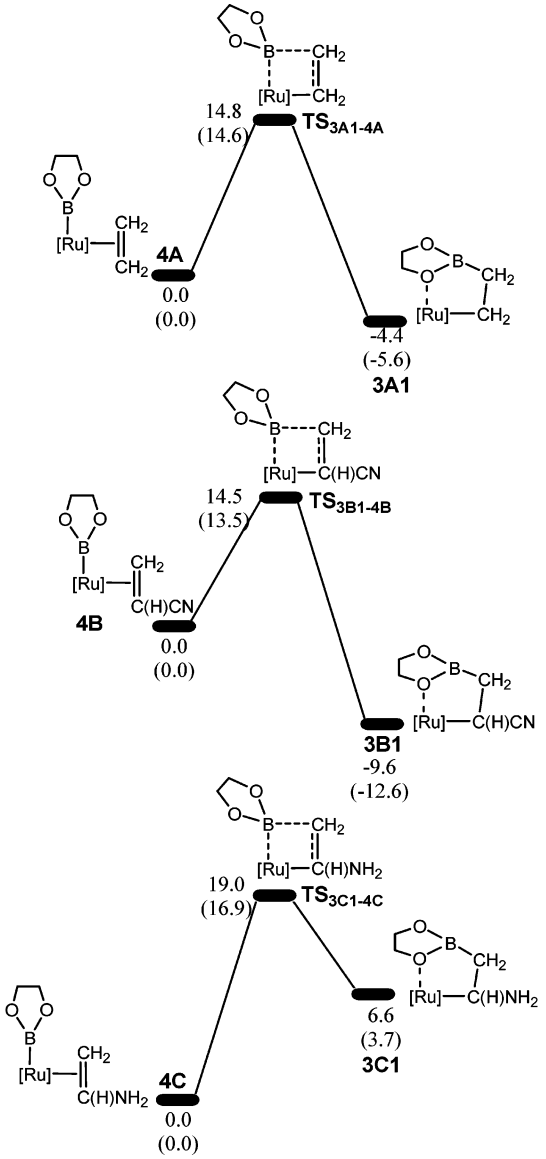

**Figure 4.** Energy profiles calculated for the boryl migration processes in $(PH_3)(Cl)(CO)Ru(B(OR)_2)(\eta^2\text{-}CH_2{=}C(H)R')$ (R′ = CN, H, and $NH_2$). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

mol, which is slightly higher than that found in **2A** for the less electron-rich ruthenium metal center. The results suggest that the corresponding Os complex is also capable of catalyzing *trans*-borylation, although it is expected to show somewhat lower catalytic activity when compared with the Ru analogue.

***trans*-Silylation.** As mentioned in the Introduction, similar to *trans*-borylation, *trans*-silylation can occur with the ruthenium catalyst $RuHCl(CO)(PPh_3)_3$.[20] For comparison, we calculated the energy profile for the key aspects of the *trans*-silylation reaction with the model complex $(PH_3)RuCl(CO)(\eta^2\text{-}CH_2{=}CHSiMe_3)$, **2E**, shown in Figure 6. The barriers and the energetic span are comparable to those calculated for the related processes in the *trans*-borylation reaction. One noticeable difference is that **3E1** is less stable than **3E** due to lack of the Ru−O interaction in the boryl systems studied above. Another noticeable difference is that **4E** is significantly more stable than **2E**. The calculated bond energies (Table 1) of Ru−H + C−Si and Ru−Si + C−H are 149.6 and 153.8 kcal/mol, respectively, explaining the relatively higher stability of **4E** versus **2E**.

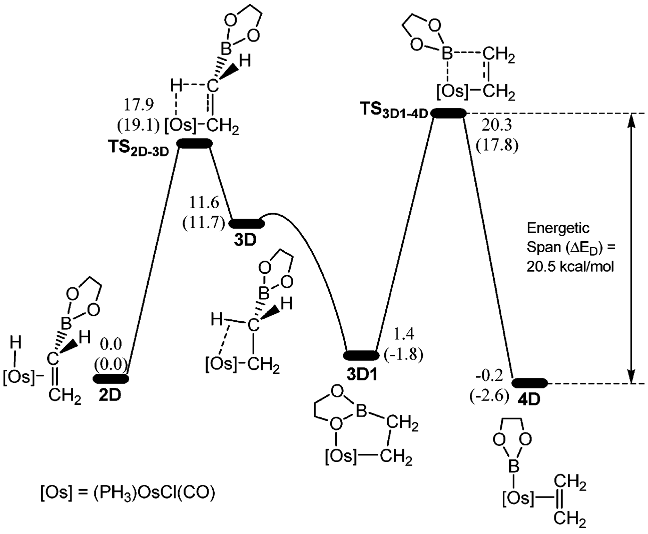

**Figure 5.** Energy profile calculated for *trans*-borylation catalyzed by $Os(H)(PH_3)_2Cl(CO)$, **1D**. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

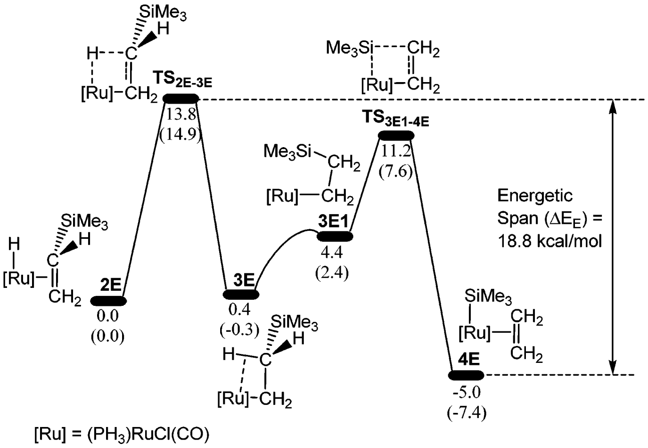

**Figure 6.** Energy profile calculated for *trans*-silylation. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

**General Comments.** On the basis of the above results, we can see that the barriers of the β-elimination processes for the hydride, boryl, and silyl groups together with their reverse processes are comparable, guaranteeing the successful *trans*-borylation and *trans*-silylation reactions. The bond energies calculated for various Ru−X and C−X bonds (where X = H, $B(OR)_2$, $SiMe_3$) with eqs 4 to 7 are given in Table 1. With the relatively weak Ru−Si and C−Si bonds, we do not expect large barriers for the β-silyl elimination and silyl migration processes. For the β-hydride elimination and hydride migration processes, the spherical property of the 1s valence orbital of the migrating hydrogen allows effective orbital overlap with both the metal center and the β-carbon in the transition state,[37] giving relatively low barriers for the elimination and migration processes, although the Ru−H and C−H bonds are relatively strong (Table 1). In the β-boryl elimination and boryl migration processes, as we have shown, the "empty" p orbital on boron is not important. Examining the frontier MOs for **4A**, **4B**, **4C**, **3A1**, **3B1**, and **3C1**, we found that the Ru−B and C−B σ-bonding orbitals contribute significantly to those orbitals lying just below the filled Ru-"$t_{2g}$" frontier orbitals, although we cannot assign specific orbitals to the Ru−B and C−B bonds due to the extensive orbital mixing. Therefore, we postulate that the boryl

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(37) (a) Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636. (b) Sakaki, S.; Ohkubo, K. *Organometallics* **1989**, *8*, 2970.

migration is a process involving nucleophilic attack of the boryl ligand on the coordinated alkene carbon that is nearest to the boron, similar to what we observed for the insertion reactions of $CO_2$ and alkenes into the Cu−B bond in Cu boryl complexes.[35,38] The Ru−B bond can be considered to be a strong nucleophile because of the very electropositive nature of the boron center, which makes the Ru−B $\sigma$-bond nucleophilic. Similarly, for the reverse process, $\beta$-boryl elimination, we can also consider the C−B bond and the Ru center as a strong nucleophile and electrophile, respectively, because of the high-lying C−B $\sigma$-bond orbital and low-lying empty d orbital of the unsaturated Ru center. Despite the high bond energies (Table 1), the Ru−B and C−B bonds are both "reactive" nucleophiles, leading to the relatively low barriers of the $\beta$-boryl elimination and boryl migration processes.

It is interesting to note that there are relatively few examples of $\beta$-alkyl elimination reported in the literature,[39] probably related to the large bond strength, the low nucleophilicity, and the strong directionality of an $sp^3-sp^3$ C−C $\sigma$-bond. Further investigations are necessary in order to gain a better insight into these processes.

## Conclusion

The mechanism of the Ru-catalyzed *trans*-borylation, the transfer of a boronate moiety from one alkene to another, has been investigated by DFT calculations. The computational results support the proposed mechanism, which involves (i) insertion of a coordinated vinylboronate into the Ru−H bond of the catalyst (hydride migration), followed by a $\beta$-boryl elimination; (ii) ligand substitution of the coordinated alkene by a substituted alkene; and (iii) insertion of the coordinated substituted alkene into the Ru−B bond (boryl migration), followed by a $\beta$-hydride elimination to give a new vinyl boronate.

The reversibility of the boryl migration versus $\beta$-boryl elimination, the silyl migration versus $\beta$-silyl elimination, and hydride migration versus $\beta$-hydride elimination involved in the catalytic cycle together with the relatively low barriers for these processes guarantee the successful *trans*-borylation and *trans*-silylation reactions. The studies into the nature of the boryl migration and the $\beta$-boryl elimination allow us to conclude that the "empty" p orbital on boron of the boryl ligand is not important in either the boryl migration or the $\beta$-boryl elimination processes. The high nucleophilicity of the Ru−boryl $\sigma$-bond promotes the boryl migration, and the relatively weak C−B $\sigma$-bond with respect to a C−C $\sigma$-bond facilitates the $\beta$-boryl elimination. Thus, the nucleophilicity of boryl ligands (more specifically, the electron-rich nature of metal−boryl bonds) is an important aspect of their reactivity.[38]

Although the $\beta$-boryl elimination may be an "invisible" back reaction in many borylations that involve boryl migration to coordinated alkene, it may prove to be a complicating factor in other cases, in addition to $\beta$-hydride eliminations. The ease with which the $\beta$-boryl elimination takes place in the Ru system,[19a] and its apparent participation in the arylation of vinylboronates,[19b,c] implies that this little-documented reaction may be much more widespread than previously considered. This should certainly be born in mind when considering any catalytic mechanism that involves the formation of a $\beta$-boryl-substituted alkyl moiety, including, for example, the hydrogenation of alkene-1,2-bisboronates[16q] and the dehydrogenative borylation of alkenes.[18]

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**Supporting Information Available:** Complete ref 27 and tables giving Cartesian coordinates and electronic energies for all the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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