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Understanding the Reactivity Difference of Metal Boryl Complexes toward Alkanes and Arenes: A Density Functional Study on the Functionalizations of Methane and Benzene by $CpM(CO)_n(BO_2C_2H_2)$ (M = Fe, Ru, W)

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Reaction mechanisms of the methane and benzene functionalizations (borylation) by $CpFe(CO)(BO_2C_2H_2)$ and $CpW(CO)_2(BO_2C_2H_2)$ have been investigated with the aid of B3LYP density functional theory calculations. The results show that the functionalizations by the Fe boryl complex favor a one-step mechanism with an oxidatively added transition state, while the functionalizations by the tungsten boryl complex only proceed by a two-step mechanism. The significant barrier difference between the functionalizations of methane and benzene by the Fe complex and the small barrier difference between the functionalizations by the W complex from our calculations are in good agreement with the experimental observation in a series of photochemical reactions of the transition-metal boryl complexes with alkanes and arenes. $Cp^*W(CO)_3Bcat'$ ($Bcat' = B\text{-}1,2\text{-}O_2C_6H_2\text{-}3,5\text{-}Me_2$) has comparable reactivity toward both alkanes and arenes, while the iron boryl complexes $Cp'Fe(CO)_2Bcat$ ($Cp' = Cp, Cp^*$; $Bcat = B\text{-}1,2\text{-}O_2C_6H_4$) are very reactive toward the aromatic C−H bonds of arenes and are unreactive toward the alkane C−H bonds. The distinct barriers between the functionalizations of methane and benzene by the Fe complex can be explained by the significant stabilization interaction between the “empty” boron p orbital of the boryl group and the π orbitals of the benzene ring in the oxidatively added transition state for the iron−benzene system. The types of B···C interactions become unimportant in the functionalization of benzene by the tungsten boryl complex because the functionalization proceeds via a two-step mechanism. For the purpose of comparison, a mechanistic study on the functionalizations of methane and benzene by the model complex $CpRu(CO)(BO_2C_2H_2)$ has also been done.

Introduction

The selective transformation of inert C−H bonds to other functional groups with effective strategies poses hard challenges. However, the potential of organometallic chemistry for functionalization of unreactive C−H bonds has been highlighted.[1−4] Hartwig et al. recently reported the photochemical reactions of transition-metal boryl complexes of the formula $Cp'M(CO)_nB(OR)_2$ (M = Fe, Ru ($n = 2$), W ($n = 3$); Cp′ = Cp, Cp*) with alkanes to form alkylboronate esters,[5] which are common reagents in organic synthesis. The metal boryl complexes reacted exclusively at the terminal C−H position of alkanes. A series of elegant experiments on $Cp^*W(CO)_3Bcat'$ ($Bcat' = B\text{-}1,2\text{-}O_2C_6H_2\text{-}3,5\text{-}Me_2$) by Hartwig et al. indicated that the mechanism involved initial photochemically induced CO loss to form a 16-electron fragment that reacts more quickly with alkane solvent than it recoordinates CO. Two plausible mechanistic pathways were proposed for the reactions of the resulting 16-electron fragment with alkanes (Scheme 1). One is a two-step mechanism which is the oxidative addition of alkane to the 16-electron fragment to form a W(IV) complex, followed by reductive elimination to form the alkylboronate ester product and metal hydride $Cp^*W(CO)_2H$, which will eventually recombine with CO to form $Cp^*W(CO)_3H$. The other is a one-step mechanism, which is σ-bond metathesis via a four-center transition state. The two-step mechanism is generally preferred for late-transition-metal systems,[6−8] while the one-step mechanism is chosen by early-transition-metal systems.[9−11]

[†] The University Grant Committee Area of Excellence Scheme (Hong Kong).

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Scheme 1

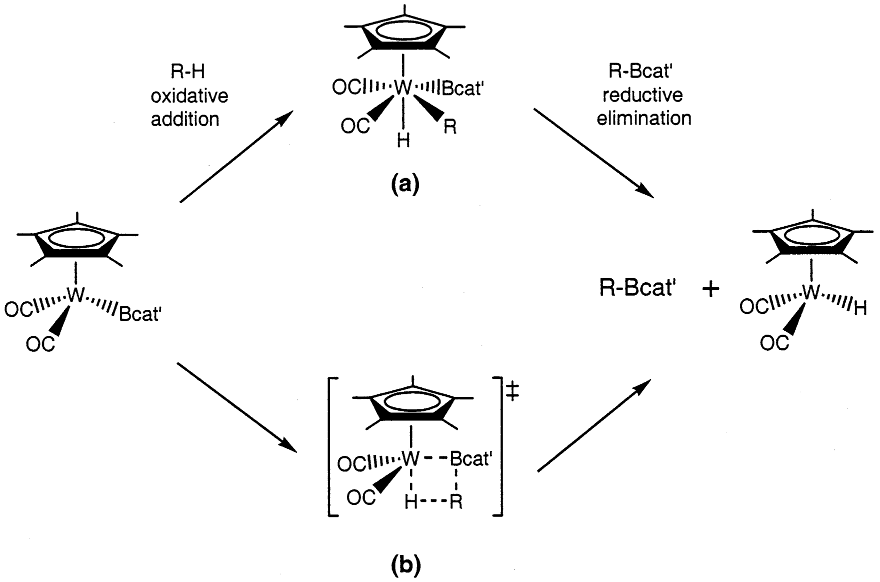
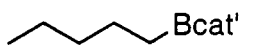
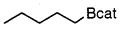
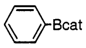
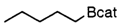
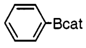
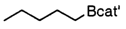
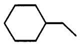
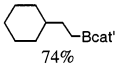
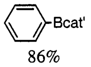
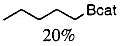


Table 1. Photochemical Reactions of Transition Metal Boryl Complexes with Hydrocarbons

Entry	Compound	Substrate	% Yield of products
1	Cp*Fe(CO)₂Bcat'		 20%
2	Cp*Fe(CO)₂Bcat		 <1%
			 99%
3	CpFe(CO)₂Bcat		 <1%
			 100%
4	Cp*W(CO)₃Bcat'		 85%
			 74%
			 86%
5	Cp*W(CO)₃Bcat		 20%

Extensive studies of the photochemical reactions of the metal−boryl complexes with various hydrocarbons[5,12] (see Table 1) show that the tungsten complexes Cp*W(CO)$_3$Bcat′ are reactive toward both alkanes and arenes (see entry 4). However, the reactivities of the iron boryl complexes are distinctly different toward the two types of substrates; these complexes are very reactive toward the aromatic C−H bonds of arenes and are unreactive toward the alkane C−H bonds (entries 1−3).

From Table 1, one may wonder why complex Cp*W(CO)$_3$Bcat (entry 5), containing unsubstituted catecholate, gives a much lower yield in the formation of pentylboronate ester than the catecholate-substituted complex Cp*W(CO)$_3$Bcat′. The lower yield has been explained as follows. Without the methyl protecting groups, the C(sp^2)−H bonds in the Bcat unit are dominantly activated, leading to the poor reactivity of the Bcat-containing complexes toward the alkane C−H bonds. The use of Bcat′ in the tungsten complex (entry 4) is to protect the C(sp^2)−H bonds in the boryl unit from being activated. The poor yields of the iron complexes toward pentane (entries 2 and 3) might also be due to the fact that the activation of the C(sp^2)−H bonds in the Bcat and Cp units dominates. With the methyl protecting groups (entry 1), Cp*Fe(CO)$_2$Bcat′ shows a bit of reactivity toward pentane. Although many factors affect the yields of the alkane functionalizations, the distinct reactivities of the Fe boryl complexes, but comparable reactivities of the W boryl complexes, toward alkanes and arenes still can be clearly observed.

In view of the interesting experimental observations and the importance of alkane borylations, we are prompted to systematically study the mechanistic pathway for the functionalizations of methane and benzene by the 16-electron model complexes CpW(CO)$_2$(BO$_2$C$_2$H$_2$) and CpFe(CO)(BO$_2$C$_2$H$_2$). We are interested in knowing whether there are electronic factors behind the reactivity difference. If so, what are they? We wish to study how the metal centers and the substrates affect the mechanistic pathway: i.e., whether a one-step mechanism with a four-center transition state or a two-step mechanism with an oxidatively added intermediate will be the most favorable pathway. As stoichiometric photochemical reactions of transition-metal boryl complexes are crucial discoveries in the development of catalytic functionalizations by transition-metal boryl complexes, elucidating the mechanisms could help us to understand the complicated catalytic borylations of hydrocarbons reported very recently.[13−21]

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Computational Details

Density functional theory calculations at the Becke3LYP (B3LYP) level[22] have been carried out to perform the geometry optimizations for all reactive species in the functionalizations. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). The effective core potentials (ECPs) of Hay and Wadt with Couty and Hall's modified version of the LANL2DZ basis set[23] have been chosen for transition metals, and the standard 6-31G basis set[24] was used for all other atoms. To increase the accuracy, polarization functions have been added for the B and O atoms (ξ_d(B) = 0.6 and ξ_d(O) = 0.8) in the $BO_2C_2H_2$ ligand and the C and H atoms (ξ_p(H) = 1.0 and ξ_d(C) = 0.8) which are directly coordinated to the metal center and involved in the functionalizations.

All calculations were performed with the use of the Gaussian 98 package[25] on Silicon Graphics Indigo^2 workstations and PC Pentium IV computers. The electron density analysis was carried out with MOPLOT 2.4.[26]

Result and Discussion

As mentioned in the Introduction, the functionalizations of methane and benzene by the 16-electron model complexes $CpM(CO)_n(BO_2C_2H_2)$ (M = Fe, Ru, W) will be studied. The validity of using $BO_2C_2H_2$ to model the catechol groups has been tested previously.[27] The reactions start with the formation of the σ complexes $CpM(CO)_n(BO_2C_2H_2)(\eta^2\text{-H}-R)$ (R = CH_3, C_6H_5), followed by either a two-step mechanism (OA/RE), with the formation of oxidatively added M(IV) intermediates, or a one-step mechanism, giving the borylated σ complexes $CpM(CO)_nH[\eta^2\text{-H}-CH_2B(BO_2C_2H_2)]$ for the methane functionalization and borylated π complexes $CpM(CO)_nH[\eta^2\text{-}C_6H_5(BO_2C_2H_2)]$ for the benzene functionalization. For convenience, the reactive species in the functionalizations of methane and benzene will be labeled as **MMe** and **MPh** followed by the boldface designation $\boldsymbol{\sigma_{CH}}$ to denote the initial σ complexes $CpM(CO)_n(BO_2C_2H_2)(\eta^2\text{-H}-R)$ and $\boldsymbol{\sigma_{CH'}}$ and $\boldsymbol{\pi_{CC'}}$ for the borylated methane σ complexes $CpM(CO)_nH[\eta^2\text{-H}-CH_2(BO_2C_2H_2)]$ and borylated benzene π complexes $CpM(CO)_nH[\eta^2\text{-}C_6H_5(BO_2C_2H_2)]$, respectively. **TS** stands for transition states for the one-step mechanism, while **TS1**, **TS2**, and **INT** are the transition states and M(IV) intermediates for the two-step mechanism.

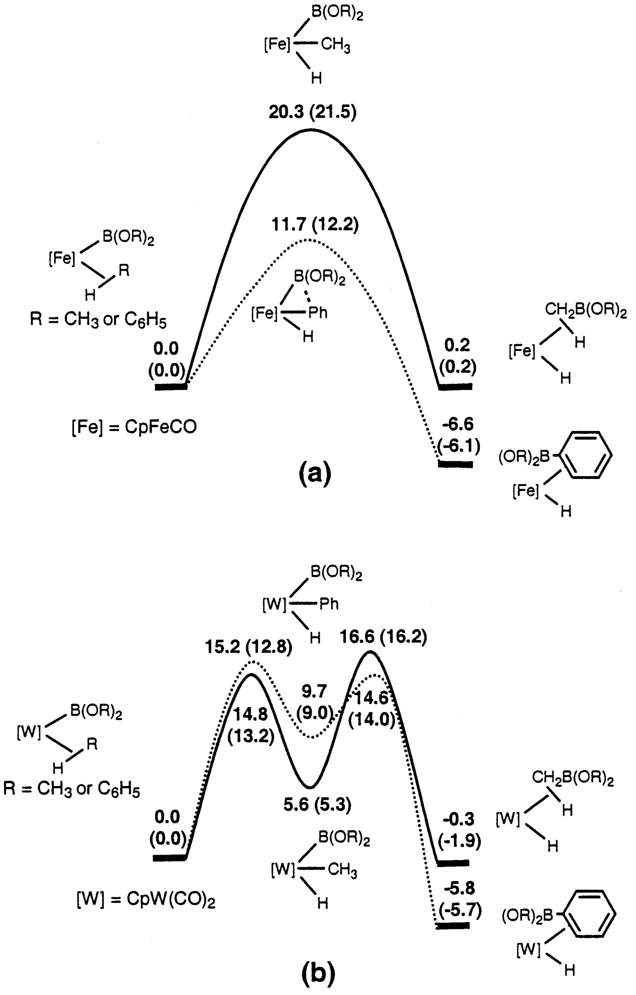

Figure 1. Relative reaction energies together with the relative free energies (in parentheses) related to the functionalizations of methane and benzene by (a) $CpFe(CO)B(OR)_2$ and (b) $CpW(CO)_2B(OR)_2$ ($(OR)_2 = O_2C_2H_2$). The relative energies are given in kcal/mol.

Mechanistic Pathways of the Functionalizations of Methane and Benzene by the 16-Electron Fragments $\mathbf{CpFe(CO)(BO_2C_2H_4)}$ and $\mathbf{CpW(CO)_2(BO_2C_2H_4)}$. The relative reaction energies and relative free energies (in parentheses) related to the functionalizations of methane and benzene by $CpM(CO)_n(BO_2C_2H_4)$ (M = Fe, W) are shown in Figure 1. The relative reaction energies do not differ too much from the relative free energies because no ligand dissociation or association is considered here. For the Fe complex, the methane and benzene functionalizations proceed via

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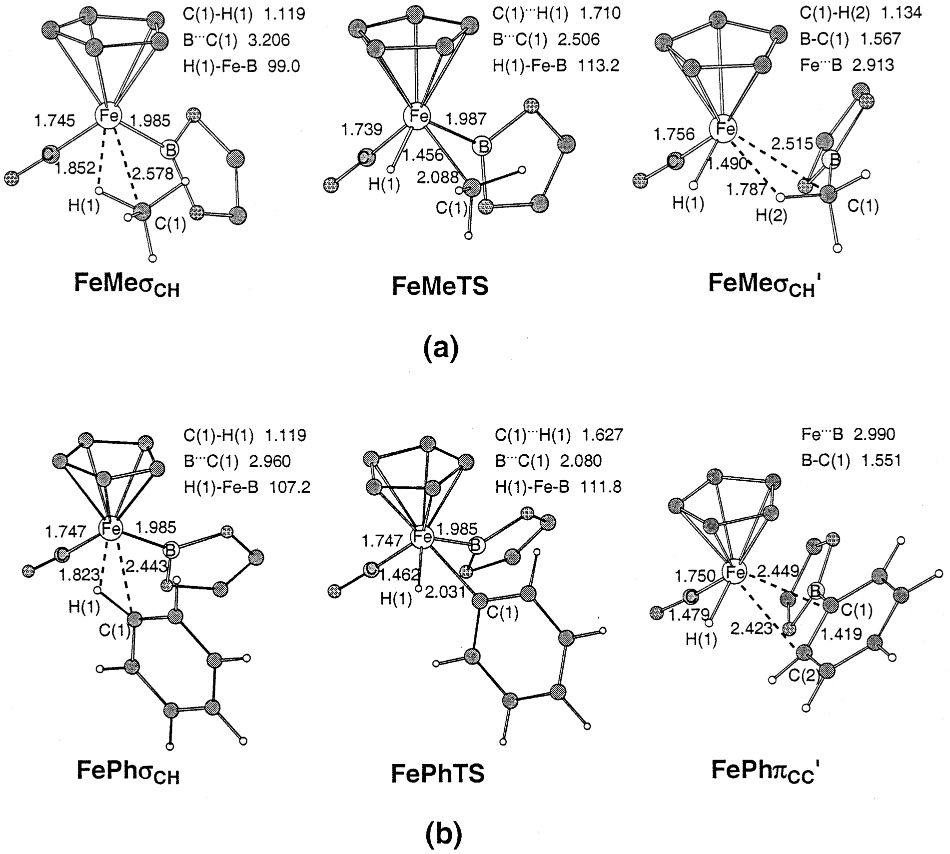

Figure 2. Selected structural parameters of the optimized species in the functionalizations of (a) methane and (b) benzene by $CpFe(CO)(BO_2C_2H_2)$. The bond distances are given in Å and angles in deg.

a one-step mechanism, while the functionalizations by the W complex go through a two-step mechanism with the formation of W(IV) intermediates. These results are related to the fact that Fe does not favor a high oxidation state. However, the more electron-rich W metal center has a greater tendency for a higher oxidation state. For both the Fe and W complexes, functionalizations of benzene require smaller barriers than the functionalizations of methane. However, the barrier for the benzene functionalization by the Fe complex is significantly lower than the methane functionalization, while the barrier for the benzene functionalization by the W complex is only slightly lower than the methane functionalization, in which the difference in the former is 8.6 (9.3) kcal/mol and in the latter is only 1.4 (2.2) kcal/mol. The significant barrier difference between the two Fe systems and the small barrier difference between the two W systems are in good agreement with the experimental observation in which $Cp^*W(CO)_3Bcat'$ has comparable reactivity with alkane and arene solvents, while the iron boryl complexes are very reactive toward the aromatic C−H bonds of arenes and are unreactive toward the alkane C−H bonds.

The 1.4 (2.2) kcal/mol barrier difference between the functionalization of methane and benzene by the W complex can be used to understand the experimental results on the reaction of $Cp^*W(CO)_2(PXy_3)[Bcat(Me)_2]$ and $Cp^*W(CO)_2(PMe_3)[Bcat(Me)_2]$ with toluene in which only the $C(sp^2)$−H bonds are activated.[5a] The calculations show that the activation of $C(sp^2)$−H is more favorable by 1.4 (2.2) kcal/mol than that of $C(sp^3)$−H. The 15−17 kcal/mol reaction barriers calculated for the two W systems (see Figure 1b) indicate that the reactions of the W complex with arenes or alkanes can occur easily at room temperature. This is supported by the experimental fact that both benzene and pentane can undergo the functionalization reaction individually. However, the 1.4 (2.2) kcal/mol barrier difference is large enough to cause discrimination against the $C(sp^3)$−H activation when both $C(sp^3)$−H and $C(sp^2)$−H are present in a reaction system. Therefore, it is not too surprising that toluene functionalization occurs only at the aromatic C−H bonds, while both benzene and pentane can undergo functionalization if they are separated.

Structural Details and Electron Density Analysis. The selected structural parameters of the species, which correspond to the stationary points of Figure 1, are shown in Figures 2 and 3. The two Fe systems proceed only via a one-step mechanism. The transition state **FeMeTS** in the functionalization of methane is a four-legged piano-stool structure (Figure 2a). Long C(1)···H(1) (1.710 Å) and C(1)···B (2.506 Å) distances indicate the absence of four-center character in the transition state. This mechanism provides another example of having a one-step pathway with an oxiditively added species as the transition state.[28] For the transition state **FePhTS** in the functionalization of benzene, relatively short C(1)···H(1) (1.627 Å) and C(1)···B (2.080 Å) distances can be found. A significantly short C(1)···B distance implies the existence of a B···C(1) interaction.

Figure 4 shows the Laplacian plots of the electron

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(28) Lam, W. H.; Jia, G.; Lin, Z.; Lau, C. P.; Eisenstein, O. Unpublished results.

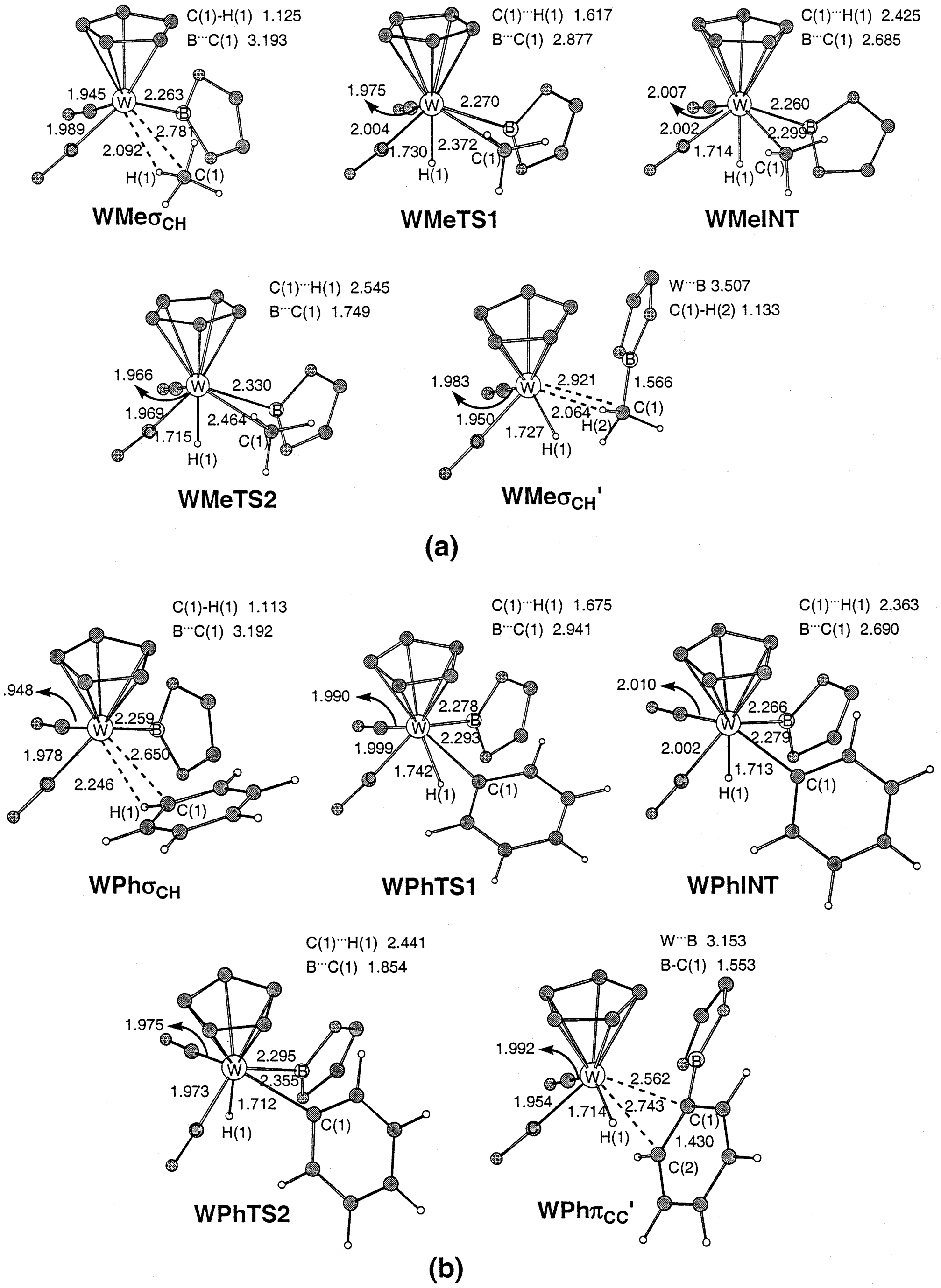
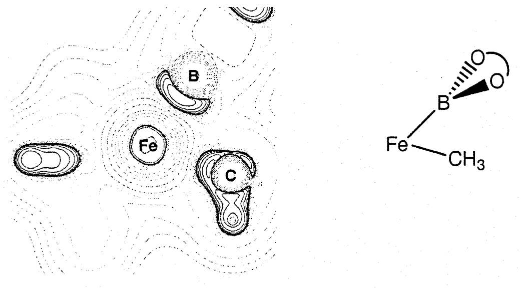


Figure 3. Selected structural parameters of the optimized species in the functionalizations of (a) methane and (b) benzene by CpW(CO)$_2$(BO$_2$C$_2$H$_2$). The bond distances are given in Å and angles in deg.

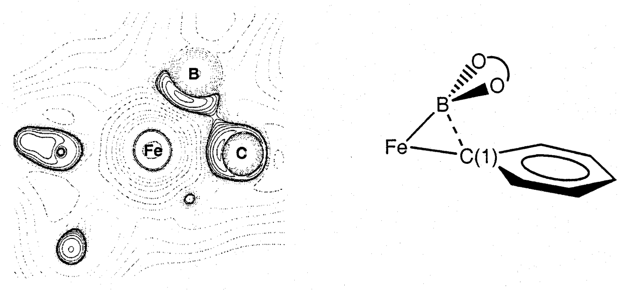
density, $-\nabla^2\rho$, for the transition states **FeMeTS** and **FePhTS** in a plane defined by the metal center, the B atom in the boryl ligand, and the C(1) atom in the methyl/phenyl group. In the contour plots, solid lines denote $-\nabla^2\rho > 0$, where the electron density is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron density is locally depleted. The Laplacian plot for the transition state **FePhTS** shows the existence of a B···C(1) interaction (see Figure 4b), as electron density concentrations can be found between the C(1) atom in the phenyl group and the B atom in the boryl ligand. The Laplacian plot for **FeMeTS** does not show the type of B···C(1) interaction (see Figure 4a). The results from the Laplacian plots provide further support to the claims that a one-step process with an oxidatively added transition state is found in the two Fe systems and that the B···C(1) interaction is important in **FePhTS**.

For the two W systems, only a two-step mechanism is adopted. The first step involves R−H bond oxidative addition to the W metal center to give W(IV) intermediates. The long C(1)···H(1) distances in **WMeTS1** (1.617 Å) and **WPhTS1** (1.675 Å) suggest that the C−H bonds of the entering methane and benzene substrates have completely broken in the transition states. The W(IV) intermediates **WMeINT** and **WPhINT** adopt a capped four-legged piano stool structure in which the hydride ligand caps the tetragonal face formed by the four legs (C(1)···H(1) = 2.425 Å (**WMeINT**) and 2.363 Å (**WPhINT**); C(1)···B = 2.685 Å (**WMeINT**) and 2.690 Å



FeMeTS

(a)



FePhTS

(b)

Figure 4. Plots of the Laplacian of electron density for the transition states (a) **FeMeTS** and (b) **FePhTS** in a plane defined by the metal center, the B atom in the boryl ligand, and the C(1) atom in the phenyl or methyl group.

(**WPhINT**)). The second step is the reductive eliminations of methylboronate ester and phenylboronate ester. In the transition states **WMeTS2** and **WPhTS2**, the methyl and the phenyl groups approach closer to the boryl ligand, having a C(1)···B distance of 1.749 Å in **WMeTS2** and 1.854 Å in **WPhTS2**.

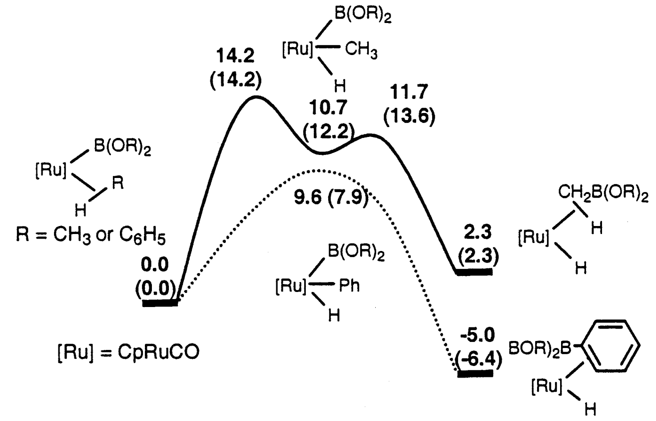


Figure 5. Relative reaction energies together with the relative free energies (in parentheses) related to the functionalizations of methane and benzene by CpRu(CO)B(OR)$_2$ ((OR)$_2$ = $O_2C_2H_2$). The relative energies are given in kcal/mol.

Comment on the Reactivity Difference toward Methane and Benzene among the Transition-Metal Boryl Complexes. From the electronic structure analysis, we can see that the functionalizations by the iron boryl complex only favor a one-step mechanism with an oxidatively added transition state. For the functionalization of benzene, the B···C interaction can be found between the boryl ligand and the phenyl group in the transition state **FePhTS**. The "empty" p orbital of the electrophilic boron center allows the B···C interaction. Apparently, the perpendicular π orbitals of the benzene ring further increase the interaction. As iron does not favor a high oxidation state, the strong B···C interaction between the "empty" p orbital of boron and the π orbitals of benzene stabilizes the oxidatively added transition state, giving a much smaller barrier for the functionalization of benzene. The metathesis processes of $L(PH_3)FeR(\eta^2\text{-}H{-}CH_3) \rightarrow L(PH_3)Fe(CH_3)(\eta^2\text{-}H{-}R)$ (L = Tp, Cp; R = H, CH_3) studied previously were found to proceed by a one-step mechanism through a four-center transition state having significant metal−hydrogen interaction in the transition states.[28] There are no four-center transition states for the two Fe systems studied here. In the metathesis processes, it is the hydrogen atom which shuttles between the η^2-H−CH_3 and η^2-H−R ligands. Therefore, the spherical nature of the 1s hydrogen orbital in the metathesis processes is better suited to stabilize a four-center transition state.[10]

The functionalizations by the tungsten boryl complex only favor a two-step mechanism, no matter whether methane or benzene acts as a substrate. The long C(1)···B distance in the W(IV) intermediates (**WMeINT**, 2.685 Å; **WPhINT**, 2.690 Å) suggest that no B···C(1) interaction exists. Because there is no significant B···C(1) interaction in the intermediates, the difference in the heights of the barriers simply reflects the difference between metal−C(sp^3) and metal−C(sp^2) interactions. One may wonder why there is a relatively lower stability of **WPhINT** in comparison to **WMeINT**. Examining the structural details of the two intermediates, we feel that the more crowded ligand environment in **WPhINT** might be responsible.

In summary, the distinct barriers in the two Fe systems can be explained by the significant stabilization interaction between the "empty" boron p orbital of the boryl group and the perpendicular π orbitals of the benzene ring in the oxidatively added transition state for the Fe phenyl system. For the tungsten systems, the functionalizations of methane and benzene proceed by a two-step mechanism. The intermediates formed do not possess the type of B···C interactions, leading to only a small difference between the barriers of functionalizations of the methane and benzene substrates.

Comparison with the Ru Analogues. The functionalization of pentane by Cp*Ru(CO)$_2$Bcat′ has also been reported previously. Irradiation of the Ru complex in neat pentane solvent gave pentylboronate ester in 40% yield.[5] However, the data on photochemical reaction of Cp*Ru(CO)$_2$Bcat′ with benzene has not been reported. To find out whether the reactivity difference exists in the functionalizations of alkanes and arenes by the Ru complex, a mechanistic study on the functionalizations of methane and benzene by the 16-electron fragment CpRu(CO)($BO_2C_2H_2$) has also been carried out. The energetics related to the functionalizations of methane and benzene by CpRu(CO)($BO_2C_2H_2$) is shown in Figure 5. Interestingly, a paradoxical situation is obtained for the two Ru systems where the functionalization of methane proceeds via a two-step mechanism, while the

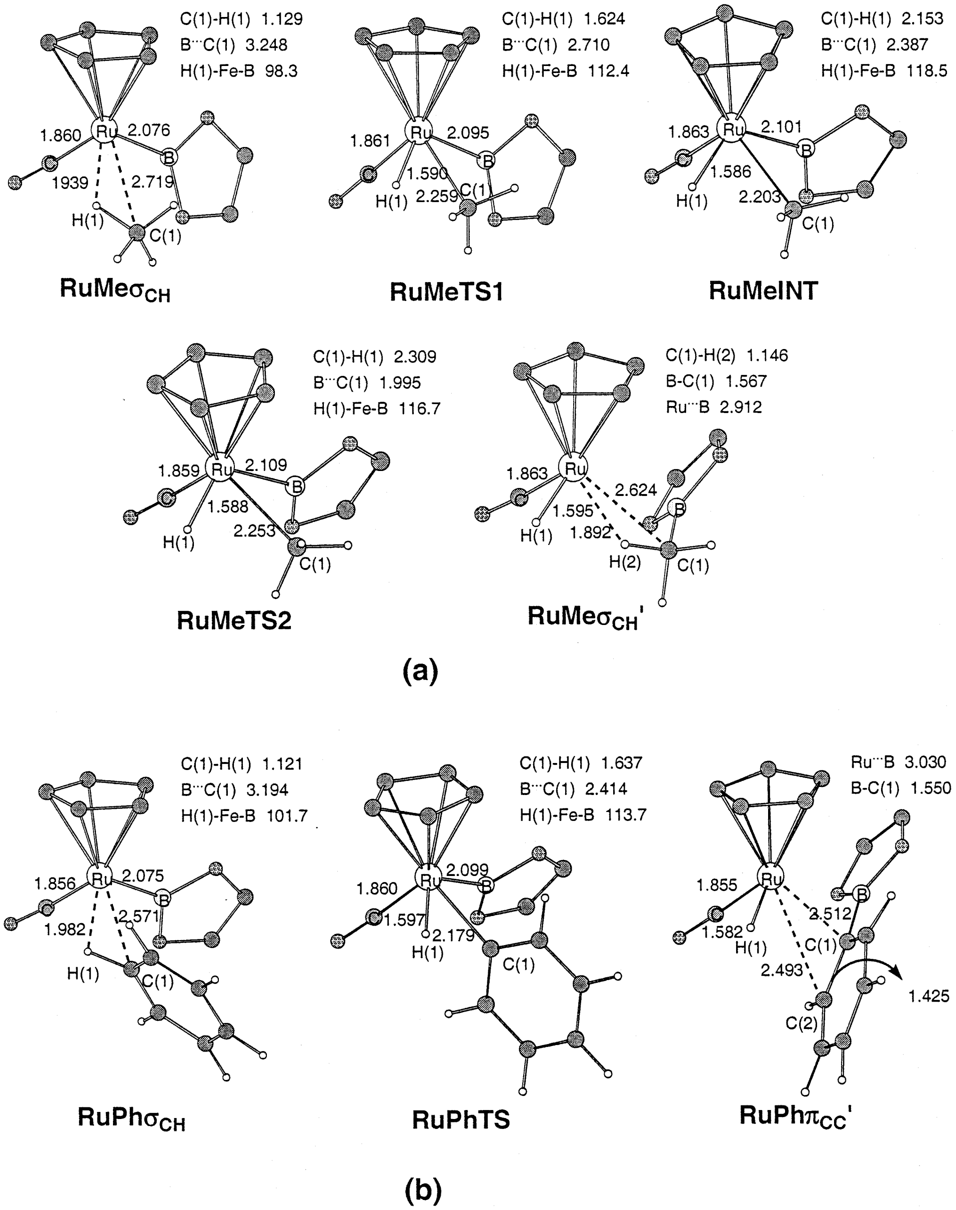


Figure 6. Selected structural parameters of the optimized species in the functionalizations of (a) methane and (b) benzene by CpRu(CO)($BO_2C_2H_2$). The bond distances are given in Å and angles in deg.

functionalization of benzene goes through a one-step mechanism. The selected structural parameters of the species, which correspond to the stationary points of Figure 5, are shown in Figure 6. For the functionalization of methane, a long C(1)···H(1) distance (1.624 Å) can be found in the oxidative addition transition state **RuMeTS1**. The methyl group approaches closer to the boryl ligand in the reductive elimination transition state **RuMeTS2**, having a C(1)···B distance of 1.995 Å. For the functionalization of benzene, long C(1)···H(1) (1.637 Å) and C(1)···B (2.414 Å) distances in **RuPhTS** suggest it is an oxidatively added transition state.

The special feature behaved by the two Ru systems can be easily understood because Ru is located in the second period of the periodic table. A change of the ligand environment around the metal center could alter the preference of mechanistic pathway. The barrier for the benzene functionalization is 4.6 (6.3) kcal/mol lower than that for the methane functionalization. As the barrier difference between the functionalizations of methane and benzene by the Ru complex is not as distinct as by the Fe complex, we predict that the reactivity difference of the Ru complex toward alkanes and arenes is not as distinct as that of the Fe complex. The results, however, show that the Ru boryl complex should be more reactive toward the aromatic C−H bonds of arenes than toward the alkane C−H bonds. Experiments show the reactivity difference exists in the analogous Ru boryl complex Cp*Ru(CO)$_2$BS$_2$Tol (BS$_2$-Tol = B-1,2-$S_2C_6H_3$-4-Me). The photochemical reaction of Cp*Ru(CO)$_2$BS$_2$Tol with pentane gives less than a 1% yield of C_5H_{11}BS$_2$Tol. However, the reaction with benzene-d_6 gives a 57% yield of Ph BS$_2$Tol.[5a]

Summary

Theoretical calculations on the methane and benzene functionalizations by CpM(CO)$_n$($BO_2C_2H_2$) (M = Fe, Ru, W) have been systematically carried out. The results show that the functionalizations by the Fe boryl complex favor a one-step mechanism with an oxidatively added transition state, while the functionalizations by the tungsten boryl complex only proceed by a two-step mechanism.

The significant barrier difference between the two Fe systems and the small barrier difference between the two W systems from our calculations are in good agreement with the experimental observation in which Cp*W(CO)$_3$Bcat′ has comparable reactivity toward both alkanes and arenes, while the iron boryl complexes are very reactive toward the aromatic C−H bonds of arenes and show unreactive toward the alkane C−H bonds. The distinct barriers between the functionalizations of methane and benzene by the Fe complex can be explained by the significant stabilization interaction between the "empty" boron p orbital of the boryl group and the π orbitals of the benzene ring in the oxidatively added transition state for the iron−benzene system. The types of B···C interactions become unimportant in the functionalization of benzene by the tungsten boryl complex because of the two-step reaction mechanism.

For the Ru systems, a one-step mechanism with an oxidatively added transition state and a two-step mechanism with an oxidatively added intermediate are both possible. On the basis of the calculated barrier difference between the functionalizations of methane and benzene, we predict that the reactivity difference of the Ru boryl complex toward alkanes and arenes should be smaller than that of the iron boryl complexes.

This paper discusses the reactivity difference between functionalizations of alkanes and arenes by transition-metal boryl complexes. More challenging issues include how the boryl groups' steric and electronic properties affect alkane functionalizations and why the reagents selectively cleave the primary C−H bond. Further theoretical and experimental studies are necessary to understand these important aspects.

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