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Theoretical Investigation on Functionalization of Alkanes by a Rhodium Complex Catalyst

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A theoretical study has been carried out for the detailed mechanism of Rh-catalyzed alkane borylation reaction with the density functional methods of B3LYP and B3PW91 and the MP2 methods. The pathway of the reaction has been shown to proceed via two steps: (a) formation of the reactive boryl intermediate; (b) C−H bond activation and B−C bond formation. Although the geometries and energetics derived from the three methods differ dramatically, they give a consistent prediction of the preference of the oxidative addition and reductive elimination pathway for the alkane functionalization by the Rh-complex catalyst.

Introduction

The catalytic functionalization of hydrocarbons remains a challenging problem in organometallics and organic synthesis.[1] Since the 1980s the possibility of transition metal-mediated C−H activation has intrigued many organic chemists and great progress has been made.[2,3] However, the subsequent reaction to generate functionalized hydrocarbon products did not occur until recently. In light of the versatile bonding capacities of the boron reagents and ligands,[4] coupled with their Lewis acidity, the boryl complexes have emerged as successful reagents or catalysts to fulfill the functionalization of hydrocarbons. As the first evidence for the stoichiometric borylation of alkanes, the late transition boryl complexes $Cp^*M(CO)_n(BR_2)$ (M = Fe, W, Ru; n = 2 or 3)[5] were shown to selectively functionalize the C−H bonds of alkanes at the primary sites under photoinduced conditions. Subsequently, the interesting result was reported by Hartwig et al. that irradiation of B_2pin_2 in pentene by the presence of $Cp^*Re(CO)_3$ results in a catalytic reaction, but once again light was required to drive the reaction.[6] Searching for thermally catalytic functionalization, in light of the thermal dative-ligand dissociation, Hartwig and co-workers found the complex $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ can accomplish the same transformation at 150 °C without the need of photochemical activation.[7] Indeed, before this discovery the $Cp^*(PMe_3)$-Ir(H)(Bpin) complex[8] had first shown thermally catalytic reactivity of B−C bond formation. Under thermal conditions, the precatalyst $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ is believed to lose the hexamethylbenzene ligand and form the intermediate $Cp^*RhH_2(Bpin)_2$, responsible for the reaction with alkane and diboronate reagents ($R_2B{-}BR_2$) to give H_2 and the organoborane product, whereas the catalyst Cp^* $(PMe_3)Ir(H)(Bpin)$ is believed to proceed via another route to lose the Cp* ligand and to couple with the boryl ligand.[9] The same products, H_2 and the organoborane compound, are generated. In both of these two cases, as proposed in these literature, the unsaturated and reactive boryl intermediates are requisite for the subsequent B−C bond formation. Therefore, it is logically believed that the boryl complexes are crucial for the catalytic process. Given the experimental evidence, a putative mechanism for the alkane borylation catalyzed by $Cp^*Rh(\eta^4\text{-}C_6Me_6)$ is proposed by Hartwig et al. as in Scheme 1. In terms of the reaction mechanism, the cycle of the catalytic process can be taken apart into two sequential reactions: the formation of the reactive boryl intermediate and the C−H functionalization involving C−H activation and B−C bond formation. The former involves the adduct of the boronate reagent and extrusion of H_2, resulting in the unsaturated boryl intermediate, while the latter is similar to the case of the stoichiometric borylation of alkanes. Recently we have reported a theoretical study of the mechanism of the stoichiometric borylation of alkanes.[10] Herein, we present

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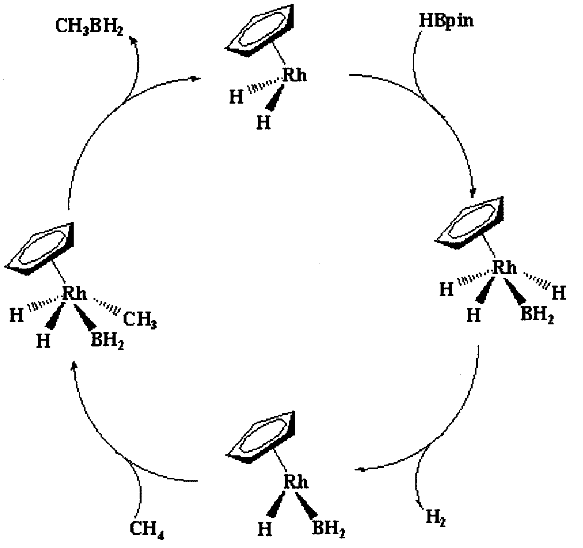
Scheme 1 Proposed Mechanism for the Alkane Borylation Catalyzed by the Rh Complex



an ab initio theoretical study on the catalytic reaction as well. In particular, the available catalytic properties are paid more intensive attention. As a model reaction in our study, the reaction of borane (BH_3) and methane (CH_4) with “CpRh” (Cp = C_5H_5) to form the products CH_3BH_2 and H_2 has been calculated using the MP2 and DFT methods.

Computational Details

All of the calculations on the model reaction were carried out by the Gaussian 98 program.[11] Methods based on the second-order Møller−Plesset (MP2)[12] and hybrid density functional theory (DFT)[13] were performed. In the case of the DFT methods, the Becke three-parameter exchange functional (B3) respectively in conjunction with the Lee−Yang−Parr (LYP) and Perdue−Wang (PW91) correlation functional[14] was employed. The transition states (TS) were optimized by using the STQN algorithm,[15] in which the final updated Hessian shows only one negative eigenvalue and was characterized by only one imaginary frequency for every unique TS. The intrinsic reaction coordinate (IRC) calculations were performed to confirm the TSs of the reactions. The basis set for the rhodium center is a modified version of the standard LANL2DZ basis set, where the outermost 5p functions have been replaced by the optimized (41) split basis sets from Couty and Hall.[16] All the geometries of the present study were fully optimized at the LANL2DZ* level. In addition, the energetics of the B3PW91 calculations, involving the zero-point vibrational energies (ZPE), were recalculated at the 6-31G(d,p) basis set for the carbon, hydrogen, and boron atoms.

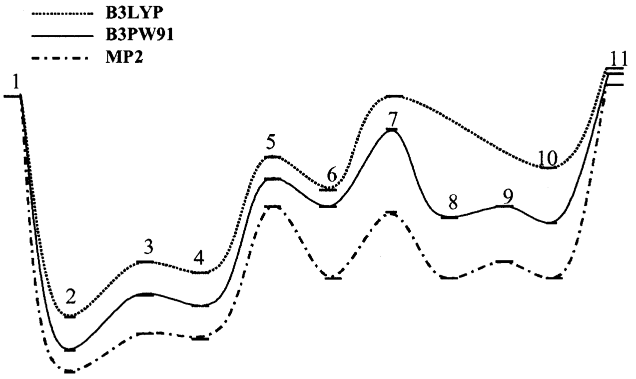


Figure 1. Potential energy surfaces of the catalytic reaction for the methane borylation.

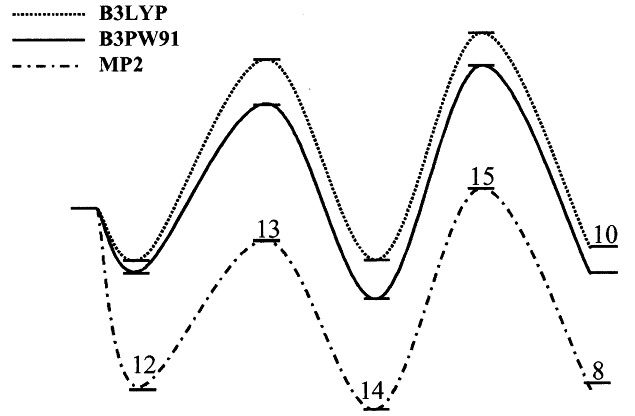


Figure 2. Potential energy surfaces of the *trans* pathway for the methane borylation.

Results and Discussion

Ab initio calculations on the catalytic reaction were carried out with the MP2 and B3LYP as well as the B3PW91 methods. The reason these methods were employed will be addressed later. As an accepted trend, the B3LYP method is believed to be a considerably accurate and efficient method to investigate the transition metal complex systems.[17] The potential energy surfaces (PES) are shown in Figure 1 and Figure 2, and the geometries of these stationary points are illustrated in Figure 3. The energetics of the reaction are shown in Table 1.

(a) Formation of the Reactive Boryl Intermediate. Without losing generality, we investigated the catalytic reaction starting from the dihydride complex $CpRhH_2$ intermediate (**1**), by which the borane reagent is attacked at the H−B bond and the trihydride complex is formed, followed by extrusion of H_2. The unsaturated 16e complex of **1** shows a pyramidal conformation with an H−Rh−H angle of 72.9−75.2° using each of the employed three methods. It is consistent with the result of $Cp(CO)_2Mn$[18] that the pyramidal conformation is of lower energy than the planar conformation in the

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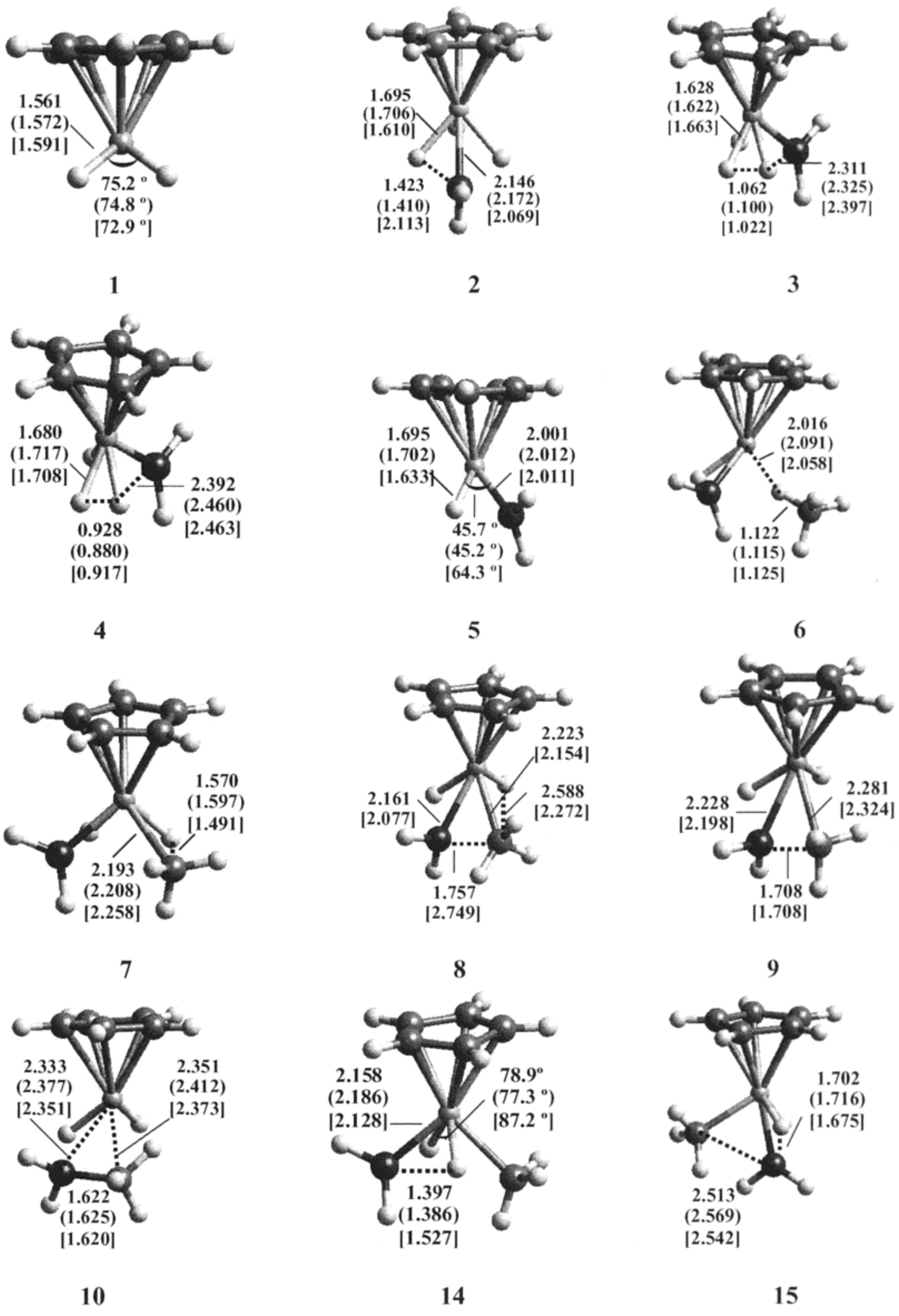

Figure 3. Geometric structures of the stationary points involved in the methane borylation catalyzed by the Rh complex. The first values are the results of the B3LYP method, the values in parentheses are the results of the B3PW91 method, and the values in square brackets are the results of the MP2 method.

ground state. Consequently, the pyramidal conformation makes formation of the adduct of the borane molecule facile. Indeed, the addition process to yield the 18e complex of **2** generates a favorable energy of 38.1, 43.6, and 46.8 kcal/mol related to the separated borane and **1**, with B3LYP, B3PW91, and MP2 methods at the LANL2DZ* level, respectively. Furthermore, no transition states were found for this process. In turn, the markedly exothermic binding energy of the borane molecule adduct to **1** confirms that the unsaturated complex **1** prefers the borane reagent to the alkanes to coordinate itself. The Lewis acidity of borane is responsible for the favored affinity by changing the electron density around the metal center. Geometrical analysis of **2**, derived from either the B3LYP or B3PW91 calculation, shows a strong interaction between the BH_2 ligand and its neighboring hydride ligands. It lengthens the distance between Rh and the coordinating hydrogen fragments by 0.13 Å with respect to that in **1**, and the distance of B and H is as close as 1.42 (B3LYP) or 1.41

Table 1. Energies of the Reactants, Intermediates, Transition States, and Products with the B3LYP, MP2 and B3PW91 Methods, with Respect to Those of the Reactants and 1[a]

	B3LYP	MP2	B3PW91	
compound	LANL2DZ*	LANL2DZ*	LANL2DZ*	LANL2DZ*/6-31G(d,p)
1+BH_3+CH_4	0.0	0.0	0.0	0.0
2	−38.1	−46.8	−43.6	−43.8
3	−28.0(10.1)	−40.9(5.9)	−34.0(9.6)	−32.9(10.9)
4	−28.8(−0.8)	−41.0(−0.1)	−34.2(−0.2)	−33.5(−0.6)
5	−11.4(17.4)	−18.3(22.7)	−14.5(19.7)	−13.4(20.1)
6	−15.6(−4.1)	−31.4(−13.1)	−19.0(−4.5)	−18.5(−5.1)
7	0.5 (16.1)	−20.5(10.9)	−5.7(13.3)	−5.3(13.2)
8		−30.3(−9.8)	−20.6(−14.9)	−20.8(−15.5)
9		−28.2(2.1)	−19.6(1.0)	−20.0(0.8)
10	−15.7(−16.2)	−30.2(−2.0)	−22.7(−3.1)	−24.2(−4.2)
11	5.3(21.0)	3.5(33.7)	4.3(27.0)	3.9(28.1)
12	−15.8(−4.4)	−31.8(−13.5)	−19.4(−4.9)	−18.7(−5.3)
13	−1.9(13.9)	−22.3(9.5)	−8.3(11.1)	−7.4(11.3)
14	−15.9(−14.0)	−32.4(−10.1)	−21.7(−13.4)	−23.1(−15.7)
15	−0.2(15.7)	−20.2(12.2)	−5.3(16.4)	−4.5(18.6)

[a] The values in parentheses are the differential energies relative to the former species.

Å (B3PW91), while the distance of B and Rh is as long as 2.15 (B3LYP) or 2.17 Å (B3PW91) (see Figure 3); these distances are fairly longer than those in the other species. These geometrical data imply that **2** can be described as the dihydridoborate complex, which has been observed in the complexes of $[(C_5H_5)_2Nb(BH_4)]$[19] and $[(C_5H_5)_2Nb(H_2BC_8H_{14})]$.[20] The structural characteristics of the dihydridoborate complex seem to arise from the boryl ligands, not from the metal center.

The species **2** is so stable that extrusion of H_2 from it should be expected to be a formidable process. However, the interaction of the boryl ligand with the lateral hydride leads to the dihydrogen complex **4**. The energy of **4** is 9.3 (B3LYP), 9.4 (B3PW91), and 5.8 (MP2) kcal/mol above that of the trihydride complex **2**, respectively. The existence of this η^2-H_2 intermediate (**4**) can be attributed to the presence of the Lewis acid boryl ligand attached to the metal center. The transition state **3** is close to the dihydrogen complex **4** either energetically or geometrically. The energy of **3** is only within 1 kcal/mol above that of **4**. This implies that the existence of **4** is relatively instable and short-lived. Nevertheless, the presence of the transient **4** is believed to drastically lessen the difficulty of extruding the H_2 moiety. Since elimination of H_2 from **4** needs an energy of only 17.4 (B3LYP), 19.7 (B3PW91), and 22.7 (MP2) kcal/mol in thermodynamics, while that directly from **2** would need an energy of 26.7 (B3LYP), 29.1 (B3PW91), and 28.5 (MP2) kcal/mol at least in thermodynamics and if the transition state existed in this pathway (directly from **2** to **5**), the activation energy should be higher than the thermodynamic energy. Our investigation shows that no transition states exist in the step of extrusion of H_2 from **4**. Then, the species of **4** functions as a "relay station" to facilitate the extrusion of H_2.

(b) C−H Functionalization. Although elimination of H_2 from **4** is unfavorable in thermodynamics, the reverse process seems improbable in the alkane solvents, because the affinity of alkanes to the unsaturated intermediate (**5**) is also much favored. The presence of the small acute H−Rh−B angle in the unsaturated 16e complex **5** shows a highly unsaturated coordination of the metal center. Therefore, the addition of alkane suffices this necessity. The η^2-methane agostic state of **6** shows a weak interaction between methane and the rhodium center. Usually this arises from a weak covalent dative bond,[21] which leads to lowering the energy by 4.1 (B3LYP), 4.5 (B3PW91), and 13.1 (MP2) kcal/mol. The relatively long distance of 2.02−2.09 Å between the metal center and the hydrogen atom that is attached to the metal center, coupled with the insignificantly elongated C−H distance, gives evidence for the above weak interaction.

On the basis of our previous work on the stoichiometric reaction of the C−H functionalization by ruthenium boryl complexes,[10] it is reasonable to believe that the C−H functionalization in this catalytic reaction is also along the oxidative addition route, where the methyl hydride complex is formed first as the transient intermediate. Therefore, we sought the methyl hydride complex using the B3LYP method. It is awe-inspiring that the intermediate like that in the stoichiometric reaction cannot be obtained as expected. Attempts of optimization starting from the analogous structures always result in the complex **10**, where the boron−carbon distance is as short as 1.62 Å, which strongly implies that the boron−carbon bond in this complex is already formed. The failure to obtain the methyl hydride intermediate would lead us to revise our preemptive concept of the oxidative addition mechanism to that of the σ-bond metathesis for this catalytic reaction. However, the finding of the transition state from **6** to form **10** is confusing, since the resulting transition state (**7**) does not show a four-center transition state, but a three-center transition state. Actually in this state the distance of the activated C−H bond is protracted to 1.57 Å, but no evidence shows any changes happen to the boryl ligand. In other words, the C−H activation involves only the Rh, C, and the relative H atoms. So far we are in a dilemma, because neither the oxidative addition nor the σ-bond metathesis pathway could be eliminated within our employed B3LYP method. As a tentative method to solve this problem, we used the MP2 method, which is completely different from the B3LYP method based on the density functional theory. Inter-

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estingly, we indeed succeeded in locating the methyl hydride complex, where the Rh−C distance is normally 2.15 Å and the Rh−B distance is 2.08 Å, but the boron−carbon distance is as large as 2.75 Å. For the sake of comparison, we used the B3PW91 method to reoptimize the complex as well. The result gives the compound **8**, as did the MP2 calculation. Thus, the existence of the methyl hydride intermediate **8** is confirmed by the MP2 and B3PW91 calculations, while the failure of the B3LYP calculation is only an exception. Now, the reason we onerously employed the three methods to investigate our system is apparent. However, so far we do not understand the cause of the failure to obtain the intermediate **8** using the B3LYP method. In addition, searching for the four-center transition state of the σ-bond metathesis by the MP2 and B3PW91 methods also failed. Therefore, the oxidative addition mechanism is established for the catalytic reaction of the alkane C−H bond functionalization by the Rh catalyst as well.

Nevertheless, the geometric structures of **8** derived from the MP2 and B3PW91 calculations are dramatically different. In particular, the boron−carbon distance of the MP2 calculation is 2.75 Å, while that of the B3PW91 calculation is only 1.76 Å. In our previous study of the stoichiometric reaction we discovered a three-center bond around the metal, boron, and carbon centers existing in the oxidative addition intermediate, which is denoted to facilitate the subsequent boron−carbon bond formation. It is apparent that the existence of the three-center bond is impossible in the MP2 result due to its too large boron−carbon distance, whereas the appropriate structure of the B3PW91 result implies that the three-center bond does exist around the rhodium, boron, and carbon centers. It is more helpful to compare the distances of the Rh−B and Rh−C bonds. The longer Rh−B distance by 0.08 Å and the longer Rh−C distance by 0.07 Å in the B3PW91 calculation compared with those in the MP2 calculation predict the weakened Rh−B and Rh−C bonds due to the formation the three-center bond among the Rh, C, and B atoms. Energetically, the formation of **8** in the B3PW91 calculations is exothermic by 1.6 kcal/mol, via the transition state **7**, with an energy barrier of 13.3 kcal/mol, relative to the "agostic" precursor **6**. Compound **8** in the MP2 calculations is 1.1 kcal/mol higher than **6**, overcoming the transition state **7** with the energy barrier of 10.9 kcal/mol. It is worthy of noting that the transition state **7** in the B3LYP calculations is 16.1 kcal/mol relative to the "agostic" precursor **6**, which is higher than the values of the MP2 and B3PW91 results.

As mentioned above, the product of the intra-arrangement process (**10**) confirms the B−C bond formation, where the B−C bond distance is about 1.62 Å, close to the value of the free CH_3BH_2 molecule, and the CH_3BH_2 fragment is already far away from the rhodium metal center (the Rh−C distance is about 2.35 Å, and the Rh−B distance is about 2.37 Å). The rapid formation of the B−C bond is demonstrated by our calculated result. The low activation energy of 1.0 and 2.1 kcal/mol for the B3PW91 and MP2 methods, respectively, is consistent with the experimental observations. In the transition state **9**, the B−C distance is 1.71 Å, either for the B3PW91 or MP2 calculation. The complex **10** is a little lower than the "agostic" state for the DFT calculations, but a little higher than the "agostic" state for the MP2 calculations.

The abstraction of the moiety containing the B−C bond is very endothermic (27.0, 21.0, and 33.7 kcal/mol for the B3PW91, B3LYP, and MP2 calculations, respectively). However, it can be compensated by the addition of the borane molecule to the coordinatively unsaturated complex **1** in the subsequent reaction cycle.

With respect to the asymmetric chemistry of the unsaturated complex **5**, the addition of the methane molecule to this complex leads to two alternative pathways, namely, the *cis* and *trans* pathways, which are dependent upon the mutual positions between the boryl and methyl ligands at *cis* or *trans* sites, respectively. It is believed that the product of the *trans* pathway is inert for the reductive elimination of the boryl and methyl ligands due to their *trans* sites.[22] However, our results show that the *trans*-intermediate **14** through the *trans* pathway is favored either kinetically or thermodynamically. **14** is more stable than the corresponding *cis*-isomer of **8** by 1 and 2 kcal/mol for the B3PW91 and MP2 calculations, respectively. The energy barrier of the *trans* pathway is also lower than that of the *cis* one. It should be noted that **14** could be obtained by the B3LYP method. The favorable stability of **14** is attributed to the dihydridoborate formation in terms of the shorter distance between the boron and the hydride ligands calculated by the DFT methods. In our previous work[10] we ascribed two different mechanisms as accounting for the two alternative pathways. In the case of the *cis* pathway, the methane reagent plays a role as an π-acceptor, which receives electron density from the metal center. Conversely, in the case of the *trans* pathway, it behaves as a σ-donor, which donates electron density to the metal center with the appropriate positions and orbital overlaps.

In terms of the reactive chemistry of **8** and the favorable stability of **14**, it is reasonable to postulate that the isomerization from **14** to form **8** could occur to fulfill the B−C bond formation. The energy profile is shown in Figure 2, and the structure of the transition state (**15**) is shown in Figure 3. The results show that the isomerization is fairly unfavorable with respect to the higher energy barriers (16.4, 15.7, and 12.2 kcal/mol for the B3PW91, B3LYP, and MP2 calculations, respectively). Then, it can be indicated that the *trans* pathway is unfeasible to achieve the B−C bond formation in the alkane functionalization catalyzed by the Rh complex of our investigations.

In generalization, the global reaction of the C−H functionalization with the reactants BH_3 and CH_4 is only a few kcal/mol endothermic (4.3, 3.5, and 5.3 kcal/mol for the B3PW91, B3LYP, and MP2 calculations, respectively), which is in line with the previous theoretical data.[23,24] Hence, catalysis is thermodynamically viable for this reaction, compared with the uncatalyzed reaction of BH_3 and CH_4, which was predicted via a four-center transition state with the activation energy of 23.5 kcal/mol at the B3LYP/6-311++G** level.[23] Herein, the catalyzed reaction by the rhodium catalyst

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shows an activation energy no higher than 16 kcal/mol (the values of the rate-determining step for the C−H cleavage). In addition, the formation of the reactive boryl complex **5** is thermodynamically favored. In particular, the existence of the dihydrogen complex **4** prompts the extrusion of H_2. To a certain degree, the success of the catalytic activity is accounted for by the feasible elimination of H_2 from the trihydride complex **2** to provide the reactive intermediate **5**.

Methodologically, both the DFT and MP2 methods propose the preference of the oxidative addition/reductive elimination mechanism, not the σ-bond metathesis, but they provide largely different energy profiles and the geometric structures. In the applicable cases, the B3PW91 and B3LYP calculations, which only differ in the correlation functionals, give comparable results of energies and structures, except for **8**. However, the results of the MP2 calculations deviate far away from those of the DFT calculations. In particular, in the intermediates **2** and **8**, the MP2 method failed to predict the structures with the conjugated boron−hydrogen and boron−carbon bonds, respectively. Our calculations employing the higher basis set of 6-31G(d,p) eliminate the possibility originating from the insufficient basis sets. Hence, these failures are probably attributed to the unsatisfactory electron−electron correlation correction inside the MP2 method. Moreover, the much higher binding energy in **6** with the MP2 method partially arises from the notorious basis set superposition error (BSSE), since the binding energy will be reduced by about 2.0 kcal/mol with the higher basis set of 6-31G(d,p). Hugely different binding energies of the precursor with the MP2 and DFT methods also can be found in the MCp(CO) (M = Co, Rh, and Ir) and methane systems.[25] However, the DFT methods are believed to produce more reasonable results compared with the MP2 method. Generally, regardless of the stationary points, their predicted energies are in the order B3LYP > B3PW91 > MP2. Compared with the accuracy and efficiency of the three methods, in our investigating system, the B3PW91 method is more reliable. Thus, the higher basis sets of 6-31G(d,p) are employed to produce the energies with the B3PW91 method. This shows that the relative energies are close to those at the LANL2DZ* level. It is well known that the DFT methods are insensitive to the basis sets.[17]

Conclusion

Our theoretical calculations using the DFT of the B3LYP and B3PW91 methods and the MP2 methods show that the catalytic reaction of methane functionalization by the rhodium complex catalyst is also along the oxidative addition/reductive elimination pathway. The rate-determining step is C−H bond scission, whereas B−C bond formation is a rapid process with a much lower barrier. Compared with the analogous stoichiometric reaction, the realization of the catalytic reaction is attributed to the feasible elimination of H_2 from the trihydride intermediate to generate the reactive boryl complex by the presence of the transient intermediate of the dihydrogen complex.

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