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Understanding the Higher Reactivity of B_2cat_2 versus B_2pin_2 in Copper(I)-Catalyzed Alkene Diboration Reactions

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DFT calculations have been carried out to study the reactivity difference of B_2cat_2 and B_2pin_2 in the diboration reaction of alkenes catalyzed by carbene-ligated copper(I) complexes. The higher reactivity of B_2cat_2 versus B_2pin_2 in this reaction results largely from the enhanced electrophilicity/Lewis acidity of the former, which significantly lowers the barrier in the product-forming transmetalation step. Transmetalation reactions of B_2cat_2 and B_2pin_2 with (NHC)Cu−OMe have also been investigated, and the relative barriers are much closer than with analogous Cu−R systems.

Introduction

Transition metal boryl complexes[1] play important roles in catalyzed boration processes such as hydroboration, diboration, dehydrogenative borylation, and other B−X addition reactions to unsaturated organics[2–30] as well as the catalyzed borylation of C−H bonds in alkanes and arenes.[5,6] In these metal boryl complexes, Bcat and Bpin are among the most popular boryl ligands as a result of their applicability to catalytic processes and the commercial availability of HBcat, HBpin, B_2cat_2, and B_2pin_2 (cat = catecholato = 1,2-$O_2C_6H_4$; pin = pinacolato = $OCMe_2CMe_2$). Although the boron centers in both of the boryl ligands bear vicinal diol substituents, Bcat and Bpin display different bonding characteristics and reactivities. For example, it was found that reaction of $(PPh_3)_2Pt(Bpin)_2$with B_2cat_2 gave $(PPh_3)_2Pt(Bcat)_2$ and B_2pin_2,[7] suggesting stronger Pt−B bonding interactions in $(PPh_3)_2Pt(Bcat)_2$. In our recent theoretical study, Bcat was found to exert a weaker trans influence than Bpin.[8] We noted that the geometrical requirement resulting from the presence of sp^2 carbons, and the aromatic ring capable of removing electron density from the oxygens, causes the B−O bonds in Bcat to be weaker than those in Bpin. The weaker

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B−O bonds in Bcat make the pair of electrons in the σ bond with the metal center less electron-releasing. In the experimentally determined (both X-ray and neutron diffraction) structures of $[(P^iPr_3)_2RhHCl(Bcat)]$ and $[(P^iPr_3)_2RhHCl(Bpin)]$,[1i] the orientations of the boryl ligands with respect to the equatorial plane of a distorted-trigonal-bipyramidal (DTBP) structure were found to differ significantly. Bcat is roughly coplanar with this plane, whereas Bpin lies nearly perpendicular to it. Our theoretical study[1i] of this system showed that, in general, boryl ligands in such DTBP systems prefer a perpendicular orientation. However, the electron-accepting abilities of the "empty" and mutually orthogonal BO_2 σ^* and BO_2 π^* orbitals of Bcat are closer to one another when compared with those of Bpin. This intrinsic bonding feature of Bcat makes the energy difference between the perpendicular and coplanar structures smaller for a given Bcat complex than for its Bpin analogue, stabilizing the observed coplanar form for $[(P^iPr_3)_2RhHCl(Bcat)]$, wherein the steric effects of P^iPr_3 are significant.

Following from our report of Au-catalyzed diboration of styrenes,[9a] Pérez, Fernandez, and their co-workers recently investigated the diboration of styrene catalyzed by N-heterocyclic carbene-ligated copper and silver complexes.[9b–d] In the copper-catayzed diboration reactions (eq 1), they found that with a slight excess of B_2cat_2, the reactions gave good yields of the 1,2-diboration product, and under the same conditions, the use of B_2pin_2 gave little diboration product, the major product being the linear monoalcohol after oxidative workup.[9b] The reactivity difference observed suggested that further theoretical studies of the different behaviors of B_2cat_2 and B_2pin_2 were warranted. In this paper, we provide a deeper insight into how the subtly different electronic structures of Bcat and Bpin affect their reactivities, which is expected to be useful in the development of new systems for the catalytic diboration and other borylation reactions of unsaturated substrates.

Computational Details

Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the Becke3LYP (B3LYP)[10] functional. Frequency calculations at the same level of

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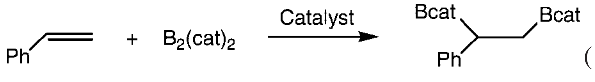


(1)

Catalyst = (NHC)Cu(I) complex

theory have also been performed to identify all of the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K, which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Transition states were located using the Berny algorithm. Intrinsic reaction coordinates (IRC)[11] were calculated for the transition states to confirm that such structures indeed connect two relevant minima. The 6-311G* Pople basis set[12] was used for B and alkenic C atoms in the alkene substrates, while the 6-311G* Wachters−Hay basis set[13] was used for Cu. For all other atoms, the 6-31G basis set was used.[14] To examine the basis set dependence, we also employed a larger basis set to carry out single-point energy calculations for several selected structures. In the large basis set, 6-311G* was used for B and alkenic C atoms in the alkene substrates, while the 6-311G* Wachters−Hay basis set was used for Cu and the 6-31G* basis set was employed for all other atoms. The results show that the basis set dependence is insignificant. For example, using the smaller basis set, the relative energies of **2Bcat**, $\mathbf{TS}_{\mathbf{Bcat(2-3)}}$, **3Bcat**, and $\mathbf{TS}_{\mathbf{Bcat(3-1)}}$ (Figure 1a) are −12.2, 4.1, −27.8, and −25.0 kcal/mol, respectively. Using the larger basis set, the relative energies are −11.8, 4.2, −28.0, and −23.9 kcal/mol, respectively. Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden 3.7 program written by Schaftenaar.[15] All of the DFT calculations were performed with the Gaussian 03 package.[16]

Results and Discussion

On the basis of their experimental and theoretical studies, Pérez, Fernandez, and co-workers found that the copper(I) boryl complex (NHC)Cu(boryl) is the active species in the catalytic diboration reactions. They also proposed that the diboration reactions proceed via a mechanism of olefin insertion followed by a metathesis step. As we mentioned in the Introduction, the objective of this paper is to investigate theoretically the reactivity difference of B_2cat_2 and B_2pin_2. Therefore, density functional theory (DFT) calculations were carried out on the catalytic processes shown in Scheme 1 to obtain the energetic difference between the Bcat and Bpin systems. In the DFT calculations, we used the model complexes $[(NHC)CuB(OR)_2]$ {NHC = 1,3-dimethylimidazol-2-ylidine; $B(OR)_2$ = Bcat or Bpin}, in which the substituents at N in the NHC carbene ligand were replaced by CH_3. Thus, 1,3-dimethylimidazol-2-ylidine was used to model the NHC ligand. We also explored the use of Beg (eg = ethyleneglycolato = OCH_2CH_2O) as a model for Bpin. Importantly, in the present study, this is a reasonably good model, although this cannot always be expected to be the case, especially where steric interactions may be important. Ethene was used as the model olefin substrate.

Figures 1a and 1b show the energy profiles of the diboration reactions of ethene with B_2cat_2 (a) and B_2pin_2 (b) catalyzed by the carbene-ligated copper boryl complexes **1Bcat** and **1Bpin**, respectively. In the figures, calculated relative free energies at 298.15 K (kcal/mol) and relative electronic energies (kcal/mol, in parentheses) are presented. The relative free energies and relative electronic energies are similar in cases where the number of reactant and product molecules is equal, for example, one-to-one or two-to-two transformations, but differ significantly for one-to-two or two-to-one transformations because of the entropic contribution. The relative free energies are used to analyze the reaction mechanism in this paper. Figures 2 and 3 show the optimized structures with selected structural parameters for the species involved in Figures 1a and 1b. In Figures 2 and 3, the calculated structures of B_2cat_2, **1Bpin**, and B_2pin_2 are compared with their corresponding experimental ones. The calculated geometric parameters for **1Bpin**, Cu−B = 1.98 Å, B−O = 1.40 Å, agree well with experimentally determined values for (IPr)Cu(Bpin) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[28a] Cu−B = 2.00 Å, B−O = 1.40 Å, thus confirming that the basis sets are adequate for the present study. The experimental structure of B_2cat_2 was also well reproduced.[17] For B_2pin_2, the B−B bond was reasonably reproduced but the calculated B−O bonds are noticeably longer than the experimentally measured ones.[18] We note that the experimental B−O distance in B_2pin_2 is unexpectedly short in view of the fact that the related diboron compounds $B_2[R,R\text{-}O_2CH(CO_2Me)CH(CO_2Me)]_2$, $B_2(S\text{-}O_2CH_2CHPh)_2$, and $B_2(R,R\text{-}O_2CHPhCHPh)_2$ all show much longer B−O bonds, in the range of 1.36–1.37 Å.[30e] We wonder whether the crystallographic value, determined at ambient temperature, might be a result of some unresolved disorder in the pinacolate moiety, as the Bpin rings are unusually planar in this structure.

As shown in Figure 1, an ethene substrate molecule initially coordinates to the copper center of an active copper(I) boryl forming a metal-η^2-alkene intermediate **2Bcat** or **2Bpin**. From the intermediate, the coordinated ethene undergoes an insertion into the Cu−B bond to give the carbene-ligated copper borylalkyl complex **3Bcat** or **3Bpin**, which is then followed by a metathesis step to give the diboration product and regenarate the catalyst **1Bcat** or **1Bpin**.

From the energy profiles, we can see that the insertion barriers for both Bcat and Bpin systems are similar. The difference between the two insertion barriers is only 2.9 kcal/mol, in favor of the insertion into a Cu−Bpin bond. A recent study of ours shows that insertion of an alkene substrate molecule into a Cu−B bond in a copper(I) boryl complex involves nucleophilic attack of the boryl ligand on the coordinated alkene.[19] The slightly smaller barrier for the insertion into a Cu−Bpin bond studied here suggests that the nucleophilicity of the Bpin ligand is somewhat greater than that of the Bcat ligand, consistent with the greater trans influence of Bpin.

The different reactivity of B_2cat_2 and B_2pin_2 cannot be explained by the difference in the insertion barriers. Instead, the factor that affects the different reactivity of B_2cat_2 and B_2pin_2 in the diboration reactions must then be related to the metathesis step. Indeed, the energy profiles shown in Figures 1a and 1b show distinct differences between the barriers for the metathesis step in the two reactions. The metathesis involving B_2cat_2 has a much smaller barrier (18.4 kcal/mol) than the one involving B_2pin_2 (26.3 kcal/mol). These results are in excellent agreement with the experimental observation that B_2cat_2 is an efficient reagent for the Cu(I) boryl-catalyzed diboration of alkenes, whereas B_2pin_2 is not.

The metathesis steps [**3Bcat** + B_2cat_2 → **1Bcat** + (Bcat)-CH_2CH_2(Bcat) and **3Bpin** + B_2pin_2 → **1Bpin** + (Bpin)-CH_2CH_2(Bpin)] involve B−B and Cu−C bond breaking and B−C bond formation. The Cu−C bonds in both **3Bcat** and **3Bpin** have the same bond distance. It is also roughly true for the B−C bonds in the diboration products. The B−B bond in B_2cat_2 is slightly shorter than that in B_2pin_2, suggesting a stronger B−B bond in B_2cat_2 than in B_2pin_2, *vide infra*. Despite this, the metathesis reaction of **3Bcat** with B_2cat_2 is still easier than that of **3Bpin** with B_2pin_2.

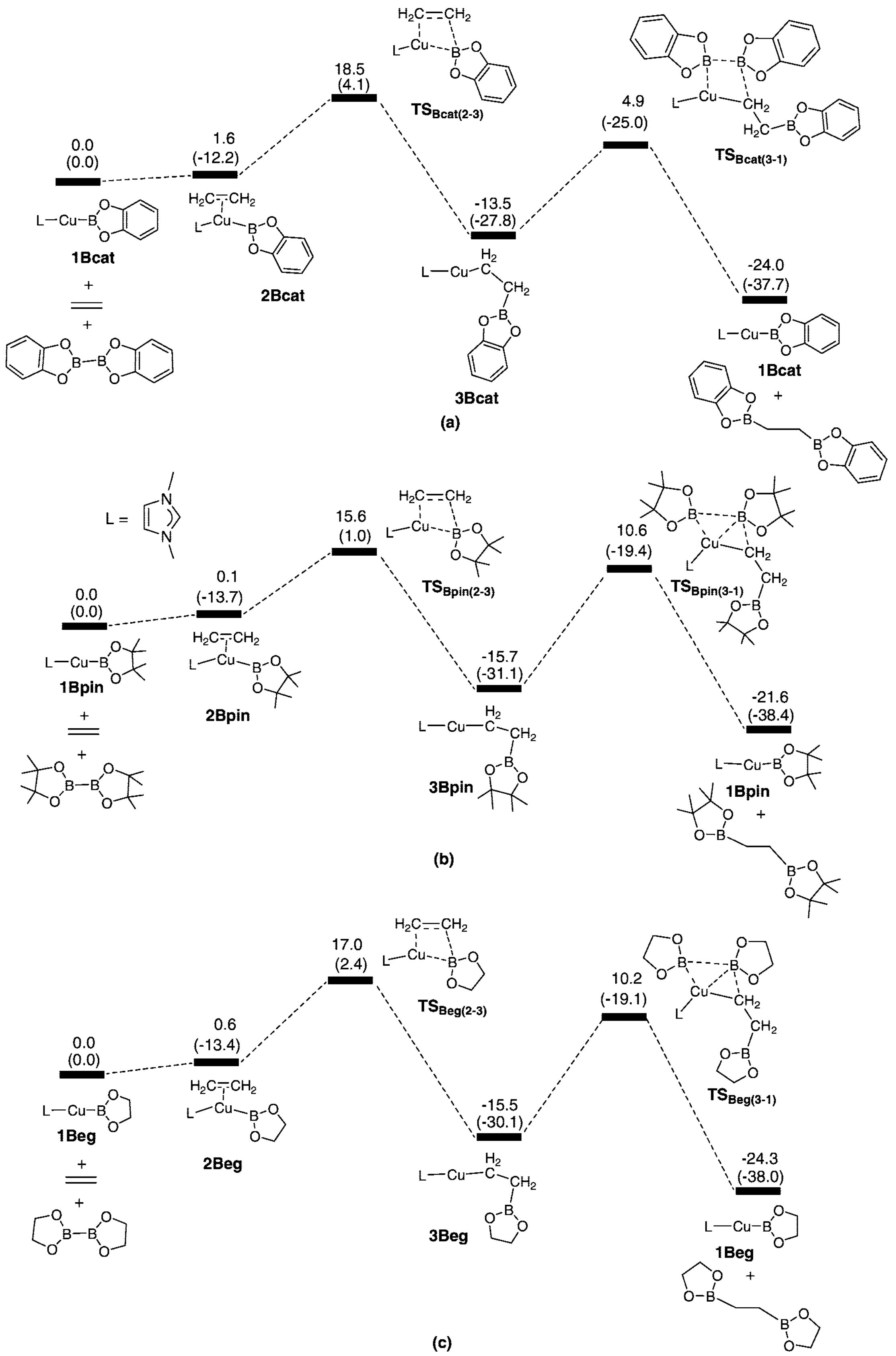
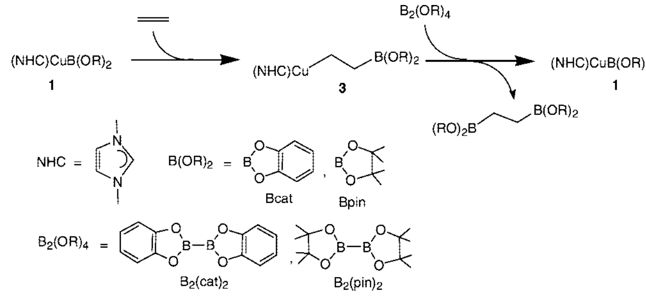


Figure 1. (a) Energy profile calculated for the diboration reaction of ethene with B_2cat_2 catalyzed by the model complex (NHC)CuBcat (**1Bcat**). (b) Energy profile calculated for the diboration reaction of ethene with B_2pin_2 catalyzed by the model complex (NHC)CuBpin (**1Bpin**). (c) Energy profile calculated for the diboration reaction of ethene with B_2eg_2 catalyzed by the model complex (NHC)CuBeg (**1Beg**). The calculated relative free energies and electronic energies (in parentheses) are given in kcal/mol.

We believe that there are two factors that favor the metathesis of **3Bcat** + B_2cat_2 → **1Bcat** + $(Bcat)CH_2CH_2(Bcat)$ over that of **3Bpin** + B_2pin_2 → **1Bpin** + $(Bpin)CH_2CH_2(Bpin)$. The first one is related to the fact that B_2cat_2 has a lower energy LUMO

Scheme 1



than B_2pin_2 does, making B_2cat_2 a much better electrophile or Lewis acid. In fact, we note that while B_2cat_2 binds 4-picoline reversibly, yielding crystallographically characterized mono- and, indeed, bis-adducts, we observed no evidence for interaction between B_2pin_2 and 4-picoline by solution ^{11}B NMR spectroscopy.[20] This is entirely consistent with the enhanced Lewis acidity/electrophilicity of B_2cat_2 compared with B_2pin_2. In this regard, we also note that the dithiocatecholato diboron compound $B_2(1,2\text{-}S_2C_6H_4)_2$ showed even greater Lewis acidity than B_2cat_2 and therefore may prove especially effective in Cu-catalyzed alkene diborations and related reactions, and this is under investigation. The LUMO of B_2cat_2 and B_2pin_2 corresponds to the unoccupied B−B π-bonding orbital. The B_2pin_2 LUMO is destabilized by stronger antibonding interactions with the all-in-phase combination of the O(p_z) orbitals as a result of the strong B−O bonding interaction in B_2pin_2 (Figure 4). B_2cat_2 has weaker B−O bonds than B_2pin_2 and consequently has a stronger B−B bond and a lower LUMO. The calculated B−B bond energy in B_2cat_2 (112.5 kcal/mol) is greater by 7.4 kcal/mol than that in B_2pin_2 (105.1 kcal/mol). The bond energies were evaluated by calculating the reaction energies of $B_2(OR)_4 \rightarrow 2\ B(OR)_2$ [$(OR)_2$ = Bpin, Bcat]. Figure 4shows the HOMOs and LUMOs for **3Bcat**, B_2cat_2, **3Bpin**, and B_2pin_2. The HOMO of **3Bcat** or **3Bpin** is the Cu−C σ bonding orbital. Comparing the HOMOs and LUMOs of **3Bcat** and B_2cat_2, we note that the gap between the HOMO of **3Bcat** and the LUMO of B_2cat_2 is smaller than the gap between the LUMO of **3Bcat** and the HOMO of B_2cat_2. Similar findings are obtained for **3Bpin** and B_2pin_2. These results suggest that the metathesis process of a Cu−C bond with a B−B bond involves a nucleophilic attack of the electron rich Cu−C bond on the electron-deficient diboron reagent. From Figure 4, we also see that the gap (3.3360 eV) between the HOMO of **3Bcat** and the LUMO of B_2cat_2 is considerably smaller than that (5.0392 eV) between the HOMO of **3Bpin** and the LUMO of B_2pin_2, due to the fact that the LUMO of B_2cat_2 (−1.2789 eV) is much lower in energy than that of B_2pin_2 (0.6852 eV), supporting the notion that B_2cat_2 is a much better electrophile.

The second factor is that the weaker B−O bonds in B_2cat_2, when compared with those in B_2pin_2, minimize the structural reorganization energies during the nucleophilic attack of the Cu−C bond on the diboron reagent, and thus lower the metathesis barrier. The nucleophilic attack causes a change in hybridization of the attacked boron center from sp^2 to approximately sp^3 in the transition state. The weaker B−O bonds in B_2cat_2 facilitate the structural reorganization. In the calculated transition state structures, both the B$\cdots$B and B$\cdots$C bond distances in $\mathbf{TS_{Bcat(3-1)}}$ (Figure 2) are respectively shorter than those in $\mathbf{TS_{Bpin(3-1)}}$ (Figure 3). The B−O bonds associated with the attacked boron center in $\mathbf{TS_{Bcat(3-1)}}$ are much longer than those associated with the spectator boron center. The difference is very small in $\mathbf{TS_{Bpin(3-1)}}$. These structural features suggest

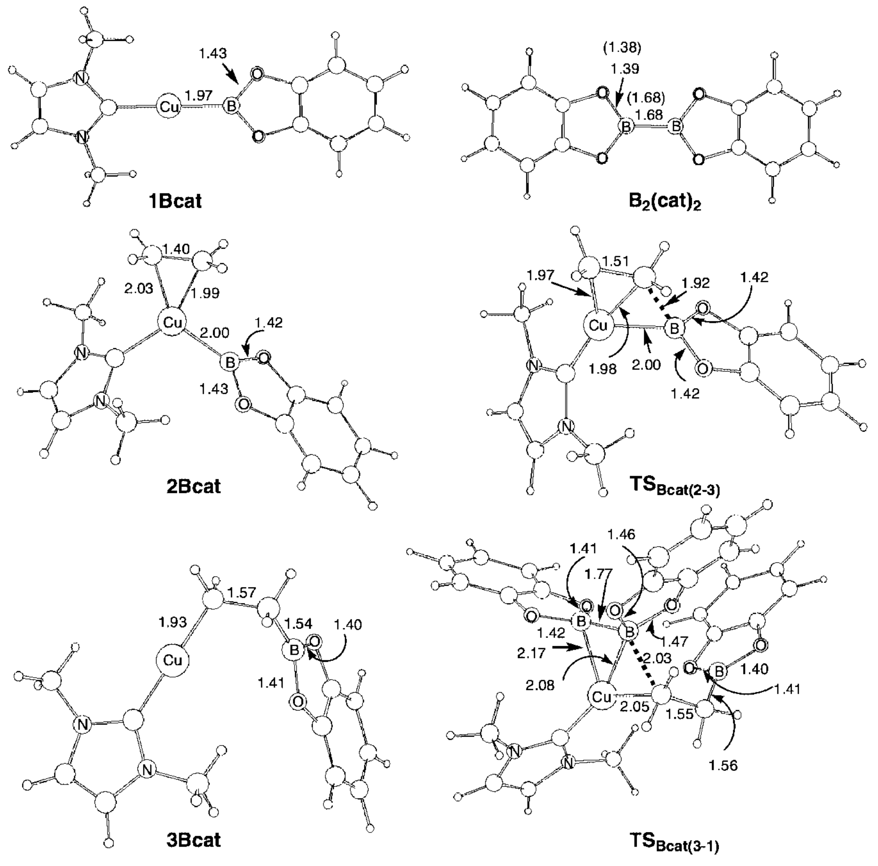


Figure 2. Optimized structures with selected structural parameters (distances in Å) for the species shown in Figure 1a. Selected calculated structural parameters for B_2cat_2 are compared to its experimental structural parameters (in parentheses).

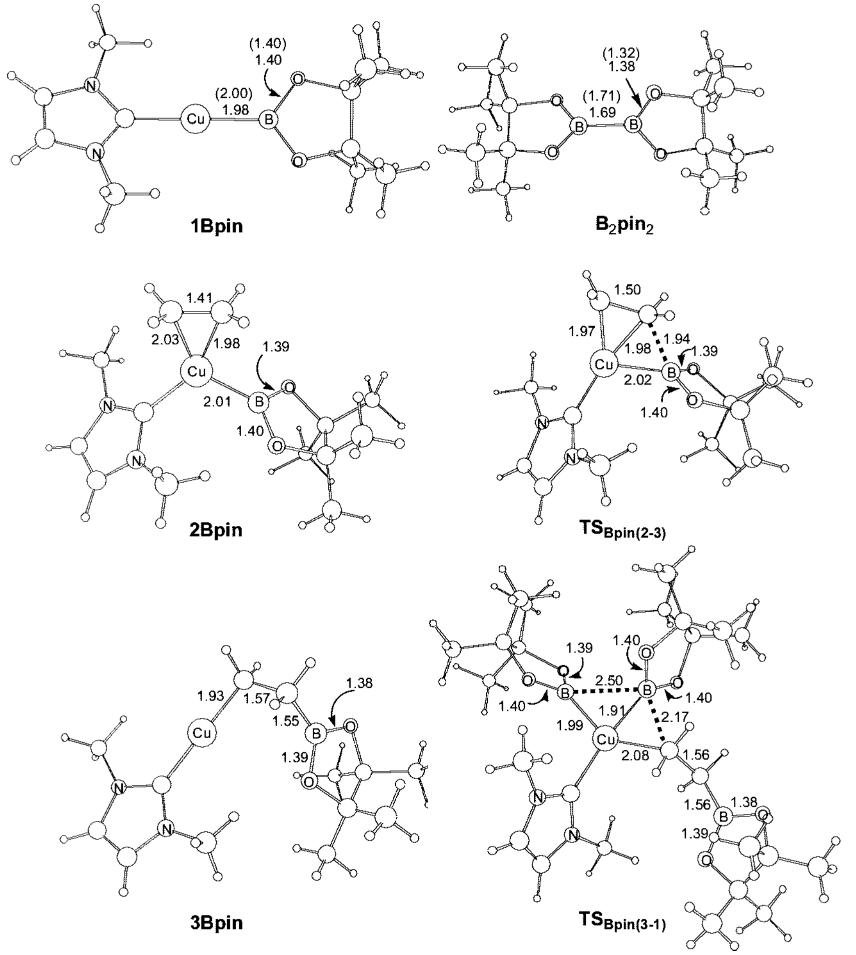


Figure 3. Optimized structures with selected structural parameters (distances in Å) for the species shown in Figure 1b. Selected calculated structural parameters for the model complex **1Bpin** and B_2pin_2 are compared to the experimental structural parameters (in parentheses) of (IPr)Cu(Bpin) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and B_2pin_2, respectively.

that the B—O bonds in B_2cat_2 are much less rigid than the B—O bonds in B_2pin_2. To support further the structural reorganization argument above, we carried out an energy-decomposition analysis[21] of the two metathesis barriers, shown in Scheme 2. Thus, the barrier for a given metathesis is the sum of two deformation energies and one binding energy between the two deformed species. Scheme 2 shows that the deformation energy of the copper complex **3Bcat** is 21.3 kcal/mol and the deformation energy of B_2cat_2 is 28.5 kcal/mol, both of which are respectively much smaller than that of **3Bpin** (48.6 kcal/mol) and that of B_2pin_2 (78.8 kcal/mol).

More comments are necessary on the structures of the metathesis transition states $\mathbf{TS_{Bcat(3-1)}}$ (Figure 2) and $\mathbf{TS_{Bpin(3-1)}}$ (Figure 3). In $\mathbf{TS_{Bcat(3-1)}}$, despite being significantly stretched, the B—B bond remains unbroken. The transition state involves mainly the pyramidalization at the attacked boron center. In contrast, $\mathbf{TS_{Bpin(3-1)}}$ resembles oxidative addition of the B—B bond to Cu. In the transition state structure, the "central" B—Cu bond length is only 1.91 Å, significantly shorter than in **1Bpin** itself, and the B—B bond is basically broken. $\mathbf{TS_{Bpin(3-1)}}$ provides another example of *one-step* metathesis having an oxidatively added transition state.[22] In the metathesis reactions of $L_nMR + R'{-}H \rightarrow L_nMR' + R{-}H$, if the metal center under consideration cannot easily attain a formally higher oxidation state, the oxidatively added species having the metal center in the formally higher oxidation state can become a transition state.[22] Highly electron-releasing ligands can stabilize a metal center in high oxidation states. $\mathbf{TS_{Bpin(3-1)}}$ is an oxidatively added transition state, while $\mathbf{TS_{Bcat(3-1)}}$ is not, consistent with the notion that Bpin is more electron-releasing than Bcat. The DFT calculations of Pérez, Fernandez, and their co-workers on $[(NHC)Cu]^+ + B_2cat_2$ suggest that no oxidative addition processes take place at copper,[9b] consistent with our finding in the Bcat system. In a recent study, Vastine and Hall classified various types of transition states for the metathesis reactions through analysis of the electron density together with the bond/ring critical points within Bader's atom-in-molecule theory.[23,24] Even though a similar analysis was not performed here, we can easily assign $\mathbf{TS_{Bcat(3-1)}}$ (Figure 2) and $\mathbf{TS_{Bpin(3-1)}}$ (Figure 3) as classes **C** (σ-CAM: σ-complex-assisted metathesis[25]) and **E** (OATS/OHM: oxidatively added transition state[22]/oxidative migration[26]) on the basis of the relevant bond distances in the two calculated transition structures.

Beg (eg = ethyleneglycolato) and B_2eg_2 have been widely employed as models for Bpin and B_2pin_2, respectively.[5n,p,w,6e,19,27] It is interesting to see how well the model reproduces the results obtained with the real Bpin and B_2pin_2. Figure 1c shows the energy profile for the diboration of ethene with B_2eg_2. Remarkably, the results calculated with the models are similar to those obtained with the real Bpin and B_2pin_2. The insertion barrier in Figure 1c is slightly higher than that in Figure 1b, likely due to the poorer nucleophilicity of the Beg ligand versus Bpin, while for the metathesis step, the two barriers in Figure 1b and Figure 1c are almost the same (difference = 0.6 kcal/mol), suggesting that the flexibility of B_2pin_2 is well reproduced by B_2eg_2. The results suggest that Beg and B_2eg_2 are good models for Bpin

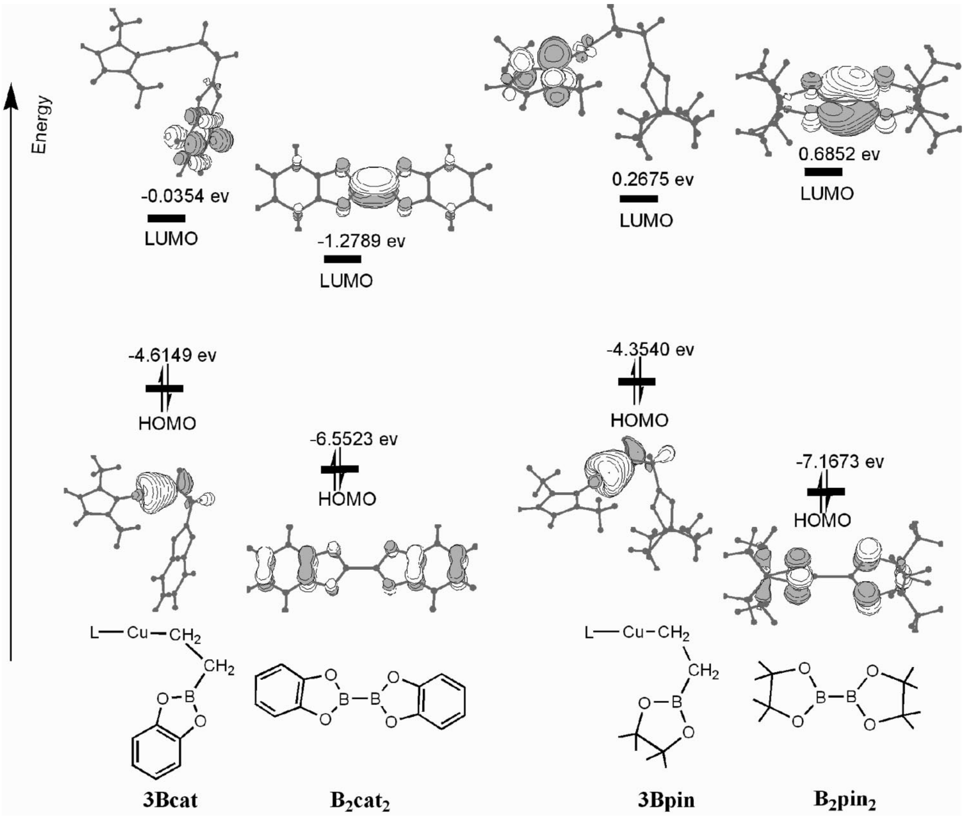


Figure 4. Frontier molecular orbitals calculated for the model complex (NHC)CuCH$_2$CH$_2$(boryl) (**3Bpin** and **3Bcat**), B$_2$cat$_2$, and B$_2$pin$_2$. The orbital energies are given in eV.

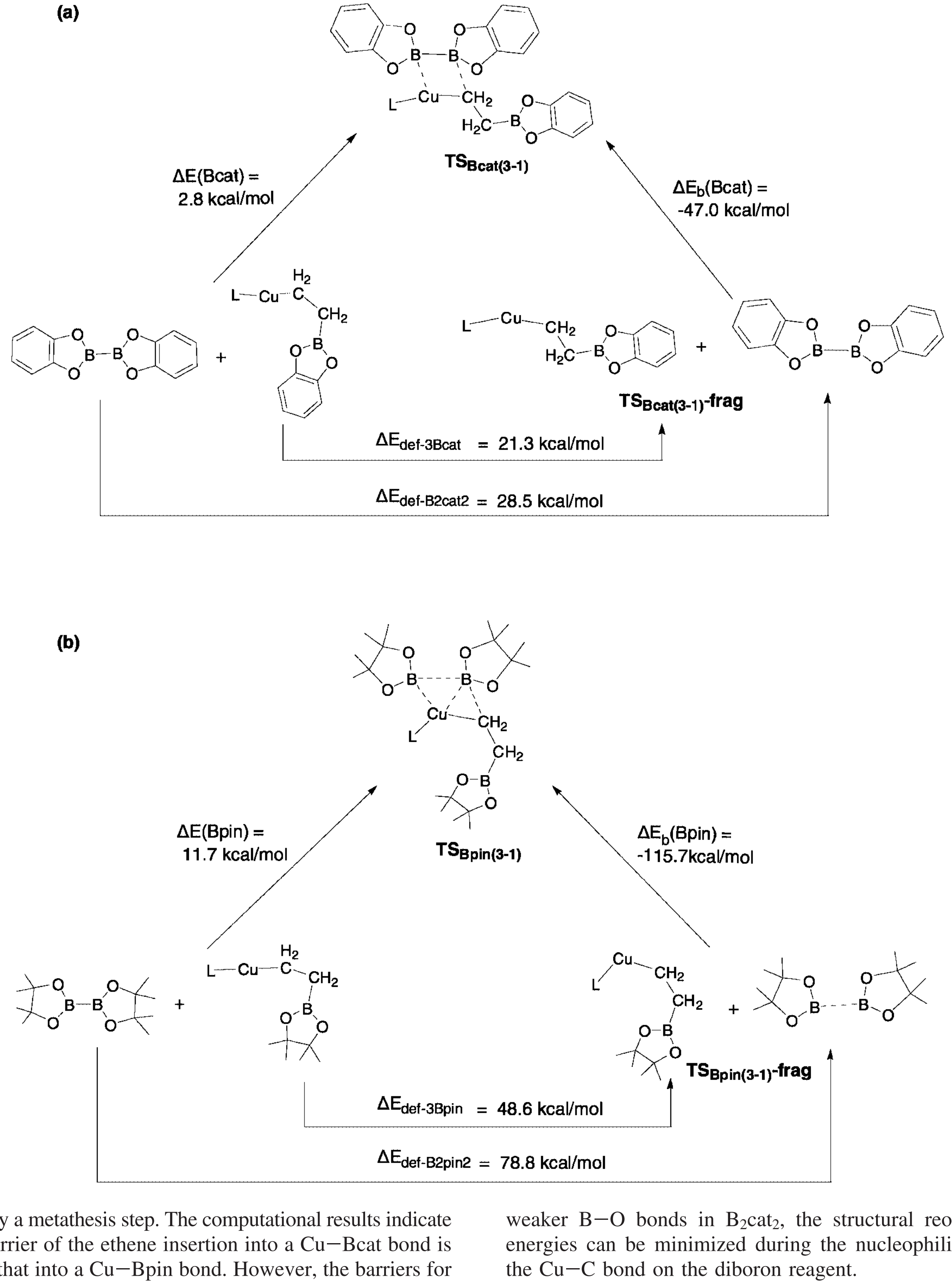
and B$_2$pin$_2$, respectively, at least in this system. This is important, and indeed gratifying, insofar as the use of eg in place of pin greatly reduces computation times. However, it should be noted that there may be increased steric interactions for B$_2$pin$_2$ when larger NHC ligands are employed in the real catalyst systems, and this would be expected to increase the barrier for the metathesis step. In other systems, especially when the metal center has much higher coordination numbers, it will be important to test the validity of using eg as a model for pin, particularly in cases where severe steric interactions might prove important.

It is worth mentioning that, unlike the diboration of alkenes discussed above, Cu(I)-catalyzed diboration of aldehydes[28a] and borylation of α,β-unsaturated carbonyl compounds[28b–f] proceed cleanly when B$_2$pin$_2$ is used as a diboron reagent in these reactions. Hosomi did employ B$_2$cat$_2$ in two examples of Cu-catalyzed borylation of α,β-unsaturated ketones,[28b] but there is insufficient experimental data to allow a meaningful comparison with his results using B$_2$pin$_2$. Cu(I)-catalyzed borylations of carbonyl compounds are also believed to follow a related reaction mechanism, i.e., insertion followed by metathesis. The intermediates formed from the insertion step are, most likely, copper(I) alkoxides. When Cu(I) alkoxides undergo metathesis with B$_2$cat$_2$ or B$_2$pin$_2$, the reaction barriers are expected to be very small. As was found earlier in our study of the mechanism of the Cu(I)-catalyzed reduction of CO$_2$ to CO,[29] the presence of additional lone pair electrons on the alkoxide ligands makes the metathesis step very facile. To examine the dependence of the copper alkoxide metathesis reactions on the nature of the diboron compound, we carried out calculations on the metathesis reactions of (NHC)CuOCH$_3$, a model complex for copper(I) alkoxide intermediates, with B$_2$cat$_2$ and B$_2$pin$_2$. Figure 5 shows that both metathesis reactions have similar and very small barriers. The transition state structures for the two metathesis reactions also resemble each other (Figure 6). Binding of B$_2$cat$_2$ to (NHC)Cu(OMe) is much more favorable than binding of B$_2$pin$_2$, again in keeping with our experimental observations on Lewis base binding to the two diboron reagents (*vide supra*). Both adducts **4Bcat** and **4Bpin** show strong bonding between the alkoxide oxygen and one boron center. However, we note the drastic difference in geometry around the other boron center. In **4Bpin**, the Cu···B nonbonded distance is much longer and the related Bpin is rotated in such a way as to make its binding to Cu especially weak. In both the adducts, the non-O-bonded Bcat and Bpin groups are quite far away from the metal centers. Therefore, it is expected that rotation of Bcat or Bpin along the B−B bond is very facile and the rotation barrier is very small. At the level of theory used in this study, the structure of **4Bpin** shown in Figure 6 was located as a minimum. We do not exclude the possibility of obtaining different minimum structures having different orientations of the non-O-bonded Bpin group when different levels of theory are employed in view of the fact that the rotation barrier is very small. Despite this, the relative energies obtained should be reliable because they are normally less sensitive to the levels of theory used. Therefore, the energetic results should not be affected regardless of what the exact orientations of the Bpin and Bcat groups in the adducts might be.

Conclusions

Employing DFT calculations, we have studied the reactivity difference of B$_2$cat$_2$ and B$_2$pin$_2$ in the diboration reactions of ethene catalyzed by the carbene-ligated copper(I) boryl complexes (NHC)Cu(boryl). The catalyzed ethene diboration reactions proceed via a mechanism involving olefin insertion

Scheme 2



followed by a metathesis step. The computational results indicate that the barrier of the ethene insertion into a Cu−Bcat bond is similar to that into a Cu−Bpin bond. However, the barriers for the metathesis steps are distinctly different. The metathesis barrier with B_2cat_2 used as the diboration reagent is significantly smaller than that with B_2pin_2 used as the diboration reagent. The results are consistent with the experimental observation that B_2cat_2 is an excellent reagent in the Cu(I) boryl-catalyzed diboration of alkenes, while B_2pin_2 is not.

Because B_2cat_2 has weaker B−O bonds than B_2pin_2, it has a lower energy LUMO (the unoccupied B−B π-bonding orbital). The lower energy LUMO makes B_2cat_2 a much better electrophile/Lewis acid, facilitating the metathesis process that involves nucleophilic attack of the electron-rich Cu−C bond on the electron-deficient diboron reagent. In addition, because of the weaker B−O bonds in B_2cat_2, the structural reorganization energies can be minimized during the nucleophilic attack of the Cu−C bond on the diboron reagent.

In contrast, B_2cat_2 and B_2pin_2 are not expected to show a large reactivity difference in the Cu(I)-catalyzed diboration reactions of aldehydes, or the reduction of CO_2 to CO, for example. The metathesis process in this case involves a Cu−O(alkoxide) bond rather than a Cu−C bond. Our calculations show that the metathesis between a Cu−O bond and a B−B bond has a very small barrier regardless of whether the diboron reagent is B_2cat_2 or B_2pin_2.

It is interesting to note here that both B_2cat_2 and B_2pin_2 were used as diboron reagents in Pt-catalyzed diborations of alkenes, alkynes, dienes, and α,β-unsaturated carbonyl compounds.[7,30] We expect that these reactions proceed via a mechanism

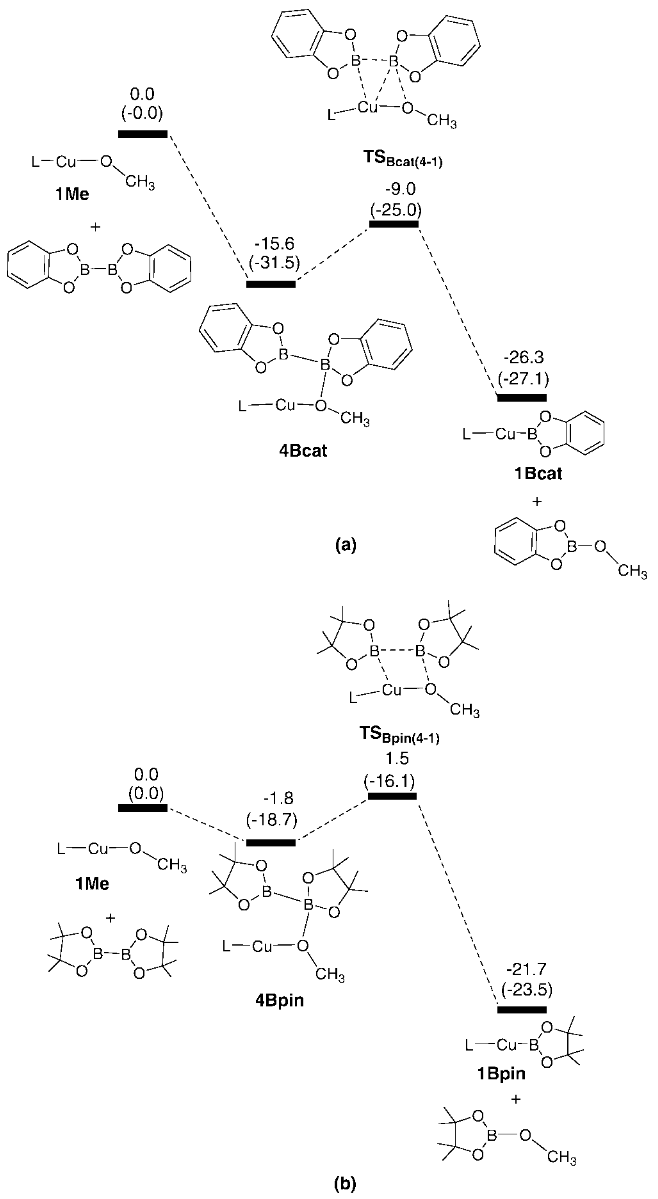


Figure 5. (a) Energy profile calculated for the metathesis reaction of the model complex (NHC)Cu(OMe) (**1OMe**) with B_2cat_2. (b) Energy profile calculated for the metathesis reaction of the model complex **1OMe** with B_2pin_2. The calculated relative free energies and electronic energies (in parentheses) are given in kcal/mol.

involving oxidative addition of the diboron reagents to the Pt(0) metal center. No metathesis is involved, and the reactivity difference of B_2cat_2 and B_2pin_2 is relatively small.

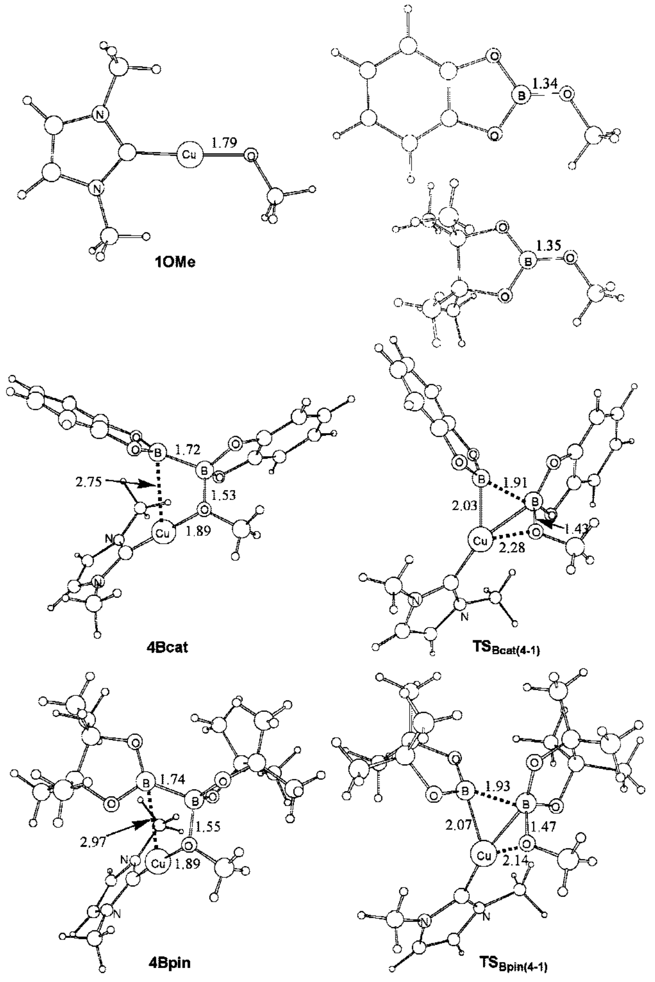


Figure 6. Optimized structures with selected structural parameters (distances in Å) for the species shown in Figures 5a and 5b.

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Supporting Information Available: Complete ref 16, tables giving Cartesian coordinates and electronic energies for all of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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