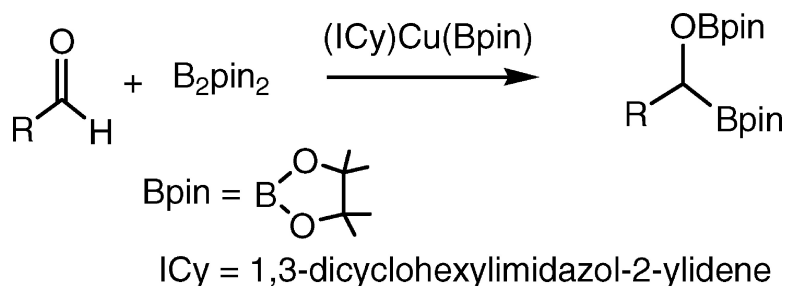


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DFT Studies on the Mechanism of the Diboration of Aldehydes Catalyzed by Copper(I) Boryl Complexes

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Abstract: The detailed mechanism for the diboration of aldehydes catalyzed by (NHC)Cu(boryl) complexes (NHC = N-heterocyclic carbene) was studied with the aid of DFT by calculating the relevant intermediates and transition states. The results show that the catalyzed diboration occurs through aldehyde insertion into Cu–B to give a Cu–O–C(boryl) species followed by σ -bond metathesis with a diboron reagent. It is the “electron-richness”, that is, the nucleophilicity of the Cu–boryl bond, which gives rise to a small insertion barrier and determines the direction of insertion. The results of our calculations also explain the formation of the product, observed experimentally, from the stoichiometric reaction of (IPr)Cu–Bpin (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with mesitylaldehyde. In the absence of a diboron reagent, the insertion intermediate having a Cu–O–C(boryl) linkage isomerizes to the thermodynamically preferred Cu–C–O(boryl) isomer via a boryl migration to the metal-bonded oxygen through an S_E2 -like transition state. We have also studied the catalyzed diboration of 2-pyridinecarboxaldehyde, which gives the unexpected reductive coupling product 1,2-di-2-pyridyl-1,2-bis(pinacolboroxy)ethane. The insertion intermediate, which contains a coordinated pyridyl group, isomerizes easily to a 1,2-dihydropyridine form, preventing its metathesis with a diboron reagent to give the expected diboration product as observed for other aldehyde substrates.

Introduction

Transition metal boryl complexes¹ 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} Recently, Sadighi and co-workers reported the diboration of aldehydes catalyzed by N-heterocyclic carbene-ligated copper boryl complexes, (NHC)Cu(boryl) (eq 1).⁷ Related diboration reactions of thiocarbonyls and ketimines catalyzed by the Wilkinson catalyst RhCl(PPh₃)₃ were also reported by Baker and Westcott et al.⁸ In the study of the diboration of aldehydes, it was found that the stoichiometric reaction of (IPr)Cu–Bpin (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with mesitylaldehyde gave (IPr)Cu–CHAr(OBpin) (Ar = 2,4,6-Me₃C₆H₂) **1**, a species containing a Cu–C σ bond (eq 2).⁷ The result of the

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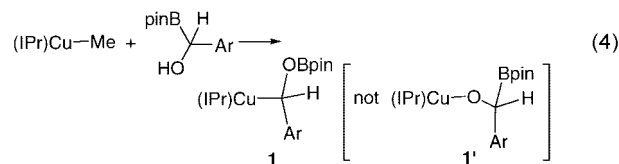
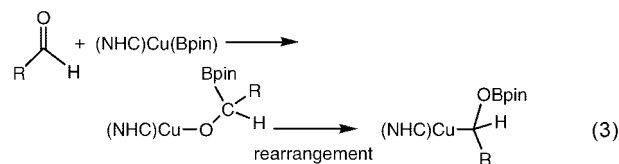
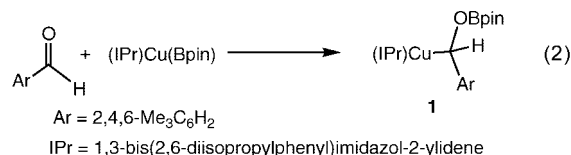
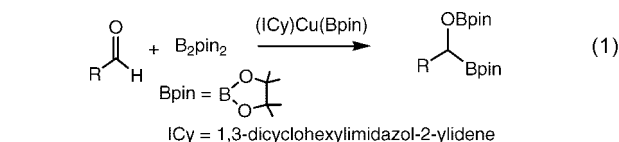
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stoichiometric reaction is intriguing. Earlier studies showed that CO₂ inserts into the Cu–Me bond of (IPr)Cu(Me) at room temperature to give (IPr)Cu(η^1 -O₂CCH₃), a species containing a Cu–O bond, rather than a Cu–C σ bond.⁹ In our theoretical study of the mechanism for the reduction of CO₂ to CO catalyzed by copper(I) boryl complexes, a reaction also reported by Sadighi and co-workers,¹⁰ we found that the Bpin ligand is

also nucleophilic, preferentially attacking the carbon atom of the coordinated CO₂ ligand, forming C–B and Cu–O bonds, rather than Cu–C and O–B σ bonds.¹¹ Clearly, there is a somewhat inconsistent picture regarding the insertion of a carbonyl unit into a Cu–B bond.

For the aldehyde insertion chemistry, we therefore also considered the possible rearrangement of a species containing a Cu–O σ bond to another species containing a Cu–C σ bond (eq 3). Following our discussions, Sadighi and co-workers carried out an additional experiment, reacting (IPr)CuMe with (Ar)(Bpin)(H)C(OH) (eq 4).⁷ It was originally anticipated that this would lead to the formation of the alternative regioisomer **1'** containing a [Cu–O–C–B] linkage because reaction of (IPr)CuMe with ROH was known to give (IPr)Cu(OR) and CH₄.¹² Instead, the reaction gave **1** as the observed product. The result of the additional stoichiometric reaction provides support for our proposal of the possible rearrangement. In this work, we set out to investigate the detailed reaction mechanism of the copper-catalyzed diboration of aldehydes with the aid of density functional theory (DFT) calculations. Our results explain the apparent inconsistency and have allowed us to examine the mechanism of the rearrangement. A clear understanding of the reaction mechanism should lead to more efficient synthetic strategies.

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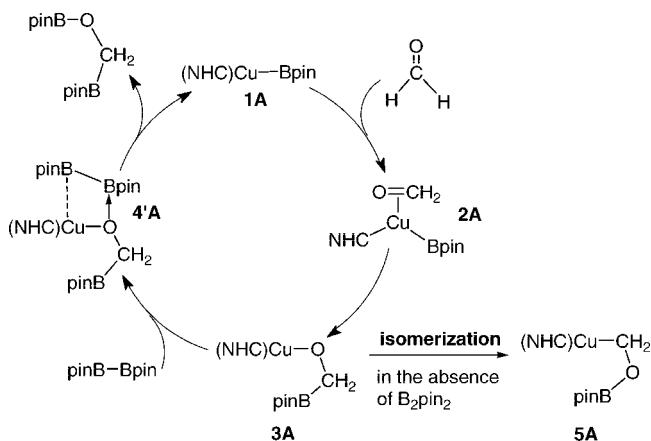


Computational Details

Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the Becke3LYP (B3LYP)¹³ functional. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequencies) or transition states (one

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Scheme 1



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. Intrinsic reaction coordinates (IRC)¹⁴ were calculated for the transition states to confirm that such structures indeed connect two relevant minima. The 6-311G* basis set¹⁵ was used for B and atoms in the O=C moiety of the aldehyde, while the 6-311G* Wachters–Hay basis set^{16,17} was used for Cu. The 6-31G basis set was used for other atoms. The effect of solvent was examined by performing single-point self-consistent reaction field (SCRF) calculations based on the polarizable continuum model (PCM)¹⁸ for several selected gas-phase-optimized species. Benzene was used as the solvent, corresponding to the experimental conditions, and the atomic radii used for the PCM calculations were specified using the UAKS keyword. The results show that the solvent effect is small. For example, without the solvation energies, the relative electronic energies of **1A**, **2A**, $\text{TS}_{\text{A}(2-3)}$, **3A**, $\text{TS}_{\text{A}(4-5)}$, **5A**, $\text{TS}_{\text{B}(2-3)}$, $\text{TS}_{\text{A}(5-1)}$, and $\text{TS}_{\text{A}(6-7)}$ are 0.0, -16.8, -3.8, -32.2, -4.2, -47.0, 17.7, -39.9, and -35.8 kcal/mol, respectively. With the solvation energies included, the relative solvation-corrected electronic energies are 0.0, -15.3, -4.2, -32.6, -5.0, -46.5, 18.6, -36.9, and -34.3 kcal/mol, respectively. All calculations were performed with the Gaussian 03 software package.¹⁹

Results and Discussion

In this paper, we examine the detailed reaction mechanism for the Cu-catalyzed diboration of aldehydes via DFT calculations, using the model catalyst [(NHC)Cu{Beg}] {NHC = 1,3-dimethylimidazol-2-ylidene; eg (ethyleneglycolato) = -OCH₂CH₂O-}, in which the substituents at N in the NHC carbene ligand and the methyl groups in the Bpin ligand were replaced by CH₃ and H, respectively. B₂eg₂ was used to model B₂pin₂, and formaldehyde was used as the model substrate.

On the basis of our calculations, the catalytic cycle shown in Scheme 1 is formulated. Diboration of aldehydes involves two important steps, that is, aldehyde insertion into the Cu–B bond of **1A** followed by metathesis between **3A** and B₂eg₂. The experimental observation from the stoichiometric reaction shown in eq 2 can be explained as follows. Aldehyde insertion into

the Cu–B bond of (IPr)Cu–Bpin gives (IPr)Cu–O–CHArBpin as the kinetic product, which isomerizes to the thermodynamically stable complex (IPr)Cu–CHAr(OBpin) in the absence of B₂pin₂.

In Figure 1, and the following figures that contain potential energy profiles, calculated relative free energies (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. In this paper, relative free energies are used to analyze the reaction mechanism. It should be noted here that the entropic contribution to the free energies based on the gas-phase calculations is overestimated for those steps involving substrate association or dissociation. Recent discussions on the overestimation can be found in the literature.²⁰ As one will see later, the important steps that affect the conclusions made in this study are not those involving substrate association or dissociation.

Figure 2 shows the optimized structures with selected structural parameters for the species involved in this catalytic cycle. In Figure 2, the calculated structures of the model complexes **1A** and **5A** are compared with their corresponding experimental ones. Calculated geometric parameters for **5A**, Cu–C = 1.934 Å, C–O = 1.485 Å, O–B = 1.324 Å, agree well with experimentally determined values for the (IPr)CuCH(Ph)OBpin complex, Cu–C = 1.947 Å, C–O = 1.464 Å, O–B = 1.352 Å, thus confirming that the basis sets are adequate for present study. The calculated C–O bond is slightly longer than the experimentally measured C–O bond, while O–B is slightly shorter, the errors being within 0.03 Å, which are acceptable.

In Figure 1, Path A gives the energy profiles relevant to the catalytic cycle shown in Scheme 1, while Path B shows the energy profile calculated for insertion of aldehyde into the Cu–B bond of **1A** directly giving **5A**, a model complex of (IPr)Cu–CHAr(OBpin). The energy profiles clearly show that insertion of aldehyde into the Cu–B bond of **1A** directly giving **5A** is much less favorable than formation of **5A** via the sequence of **1A** → **2A** → **3A** → **4A** → **5A** in Path A.

The first step in Path A is aldehyde coordination to the copper center of **1A** forming η^2 -aldehyde intermediate **2A**. From **2A**, the coordinated aldehyde inserts into the Cu–B bond to give **3A** with a barrier of 12.8 kcal/mol. The step **1A** → **3A** is exergonic by 17.0 kcal/mol. From **3A**, two pathways have to be considered. In the presence of a diboron reagent (e.g., B₂pin₂), which is the case for the catalytic reactions, coordination of B₂eg₂ to **3A** gives an adduct **4A'**, which has a B–O Lewis acid–base bond between one boron atom of B₂eg₂ and the metal-bonded oxygen. Through a σ -bond metathesis-like step via the transition state $\text{TS}_{\text{A}(4-1)}$, the catalyst **1A** is regenerated and diboration product Beg–OCH₂–Beg is formed with a relatively small barrier of 6.4 kcal/mol. The catalyzed diboration of formaldehyde is exergonic by 36.2 kcal/mol, and the aldehyde insertion (conversion of **2A** to **3A**) is the rate-determining step.

In the absence of B₂(OR)₄, which is the case for the stoichiometric reaction (eq 2), the kinetic product **3A** undergoes a structural rearrangement to give the slightly less stable intermediate, **4A**, with a very small barrier of 4.8 kcal/mol through a simple rotation of the CH₂Beg group around the

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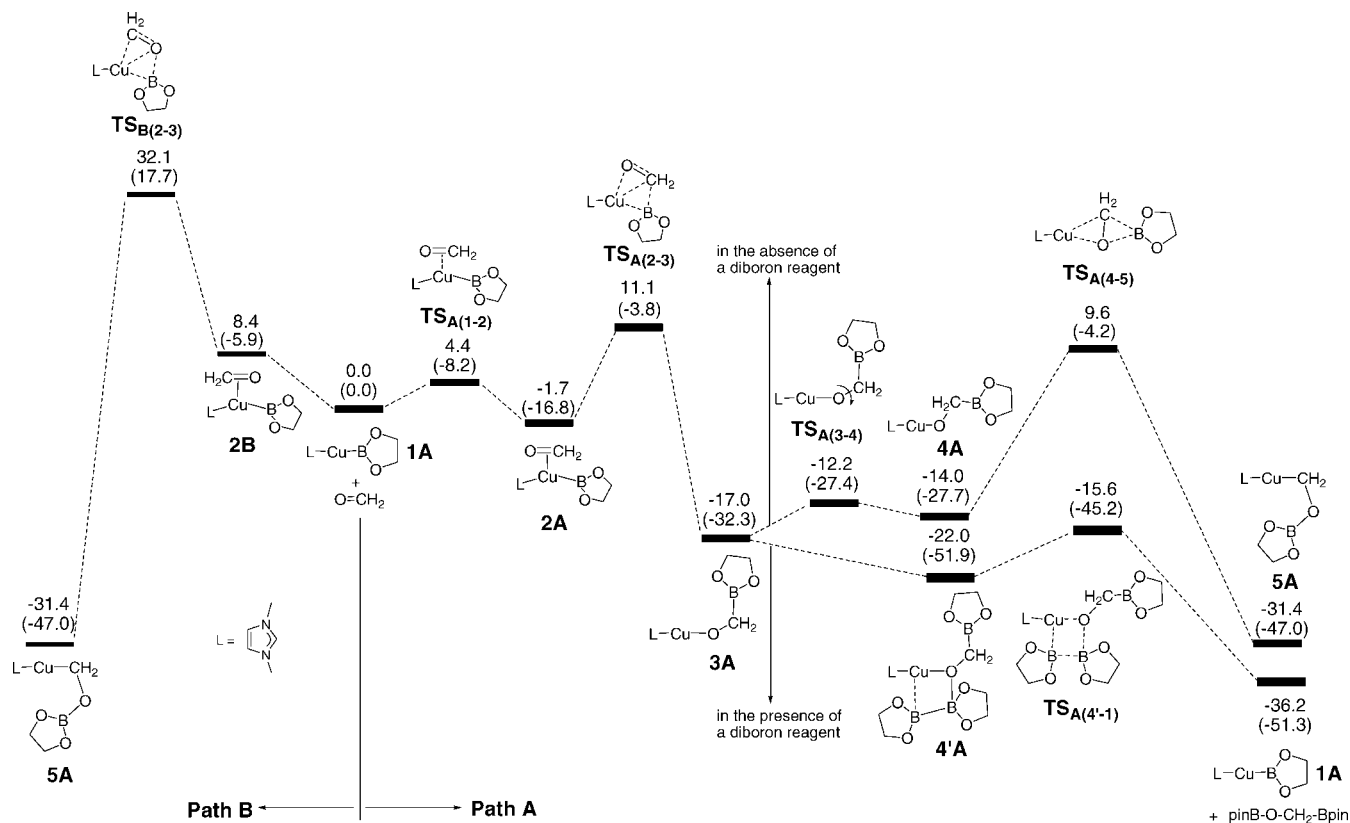


Figure 1. Energy profiles of Paths A and B calculated for the (NHC)Cu(boryl)-catalyzed diboration of aldehyde. Path A is the most favorable reaction pathway, and Path B is the insertion step for an alternative, but unlikely, reaction pathway. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

(NHC)Cu-O-CH₂Beg single bond. Through an S_E2-like transition state, TSA(4-5), 4A isomerizes to the thermodynamically preferred Cu-C-O-B isomer 5A with a barrier of 23.6 kcal/mol via a boryl migration to the metal-bonded oxygen. This S_E2-like TS is related to a similar process in the Cu-catalyzed CO₂ borylation reaction mechanism by which the boryl group migrates from C to O.¹¹

From Figure 1, we can see that, in the aldehyde insertion, the boryl ligand preferentially migrates to the carbon atom of the coordinated carbonyl moiety. This result is consistent with what we observed in our earlier studies of the insertion of CO₂ into a Cu-B bond, in which the metal-boryl bond (in essence, the boryl ligand) is a nucleophile.¹¹

Isolation of (IPr)Cu-CHAr(OBpin) (Ar = 2,4,6-Me₃C₆H₂) from the stoichiometric reaction of (IPr)Cu-Bpin with mesitaldehyde suggests that (IPr)Cu-CHAr(OBpin) could be involved in the catalytic cycle. Sadighi and co-workers found that the isolated complex (IPr)Cu-CHAr(OBpin) (Ar = 2,4,6-Me₃C₆H₂) was indeed able to promote the diboration of mesitylaldehyde with B₂pin₂, although the reaction was observed to be sluggish. Our calculations rule out the involvement of a species containing a Cu-C bond in the catalytic cycle. Therefore, it is necessary to explain how (IPr)Cu-CHAr(OBpin) is able to serve as a catalyst precursor for the diboration reaction. There must be a slow initiation step in which (IPr)Cu-CHAr(OBpin) reacts with B₂pin₂ or mesitylaldehyde in the first cycle to regenerate the active Cu-B species (IPr)Cu-Bpin. With this in mind, we examined the metathesis process with B₂eg₂ and the insertion of H₂C=O into the Cu-C bond in 5A, a model for (IPr)Cu-CHAr(OBpin). Figure 3 shows the relevant energy profiles. Metathesis of 5A with B₂eg₂ via TSA(5-1), with a barrier of 22.5

kcal/mol gives BegOCH₂Beg and 1A, a model for the catalytically active species (IPr)Cu-Bpin. The insertion of H₂C=O into the Cu-C bond of 5A, with a barrier of 24.7 kcal/mol, gives 7A, which is followed by a σ -bond metathesis with B₂eg₂, regenerating the active species 1A together with a reductive dimerization/coupling product, BegOCH₂CH₂OBeg. On the basis of our calculations on the model system, the metathesis between 5A and B₂eg₂ is the (slightly) more favorable of the two processes. When a realistic substrate, such as benzaldehyde, was used in the calculations, the preference for the metathesis process is even greater (vide infra). Thus, the metathesis pathway is likely to be important for the slow initiation step mentioned above.

The barriers for the two reactions shown in Figure 3 are much higher than the barriers (shown in Figure 1) associated with the favorable catalytic cycle in Scheme 1. These results explain the sluggishness observed when isolated complex (IPr)Cu-CHAr(OBpin) was used to catalyze the diboration reaction because catalyst initiation is very slow.

Comparing the energy profiles in Figures 1 and 3, we see that σ -bond metathesis between a Cu-O bond and a B-B bond (3A \rightarrow 4'A \rightarrow 1A, Figure 1) has a much lower reaction barrier than that between a Cu-C bond and a B-B bond (5A \rightarrow 1A, Figure 3). The lone pairs on the metal-bonded oxygen atom play an important role in lowering the 3A \rightarrow 1A barrier; thus, a Lewis acid-base adduct 4'A is formed by donation of one oxygen lone pair to the "empty" p orbital on one of the boron atoms of B₂pin₂, facilitating the metathesis process.

Important implications can also be derived by comparing the barriers of the two σ -bond metathesis processes (between a Cu-O bond and a B-B bond vs that between a Cu-C bond

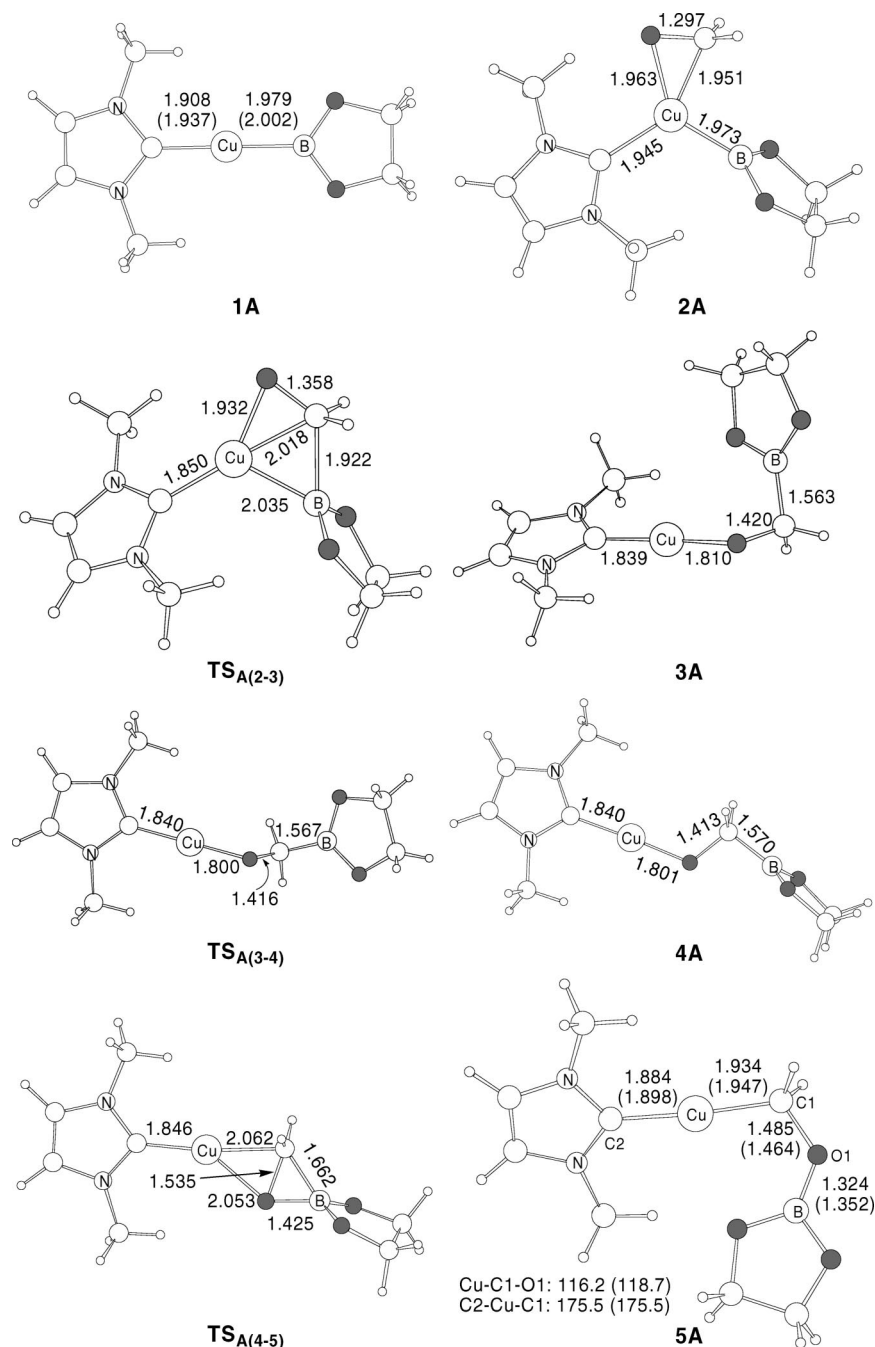


Figure 2. The optimized structures with selected structural parameters (bond lengths in angstroms and angles in degrees) for the species involved in the (NHC)Cu(boryl)-catalyzed diboration of aldehydes. Selected calculated structural parameters for the model compounds **1A** and **5A** are compared to the experimental values (in parentheses) for (IPr)Cu(Bpin) and (IPr)Cu[CH(Ph)OBpin] where IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

and a B–B bond) as well as the barriers of the two aldehyde insertion processes (insertion into a Cu–B bond vs a Cu–C bond). The σ -bond metathesis between a Cu–O bond and a B–B bond (**3A** \rightarrow **4'A** \rightarrow **1A**, Figure 1) is almost barrierless, while the corresponding process between a Cu–C bond and a B–B bond requires a barrier of 22.5 kcal/mol (**5A** \rightarrow **1A**, Figure 3). The very recently reported dramatic rate acceleration of the copper-catalyzed β -borylation of α,β -unsaturated carbonyl compounds upon addition of alcohols²¹ is likely to be related to the almost barrierless σ -bond metathesis between a Cu–O bond and a B–B bond. The alcohol additives allow Cu–OR to

be formed, and an almost barrierless σ -bond metathesis between the Cu(I) alkoxide and a diboron reagent, such as B₂pin₂, facilitates the regeneration of the active Cu–B species. The insertion of aldehyde into a Cu–B bond has a barrier of only 12.8 kcal/mol (**2A** \rightarrow **3A**, Figure 1), compared with the significantly higher barrier of 22.6 kcal/mol for the insertion into a Cu–C bond (**6A** \rightarrow **7A**, Figure 3), manifesting the importance of metal–boryl complexes in the catalytic reactions of various unsaturated organic substrates,^{1–6} and highlighting the extremely strong nucleophilicity of the boryl group.^{11,22}

Reaction of the Substrate 2-Pyridinecarboxaldehyde. Sadighi and co-workers also found that, in contrast to other aldehyde substrates, 2-pyridinecarboxaldehyde undergoes reductive cou-

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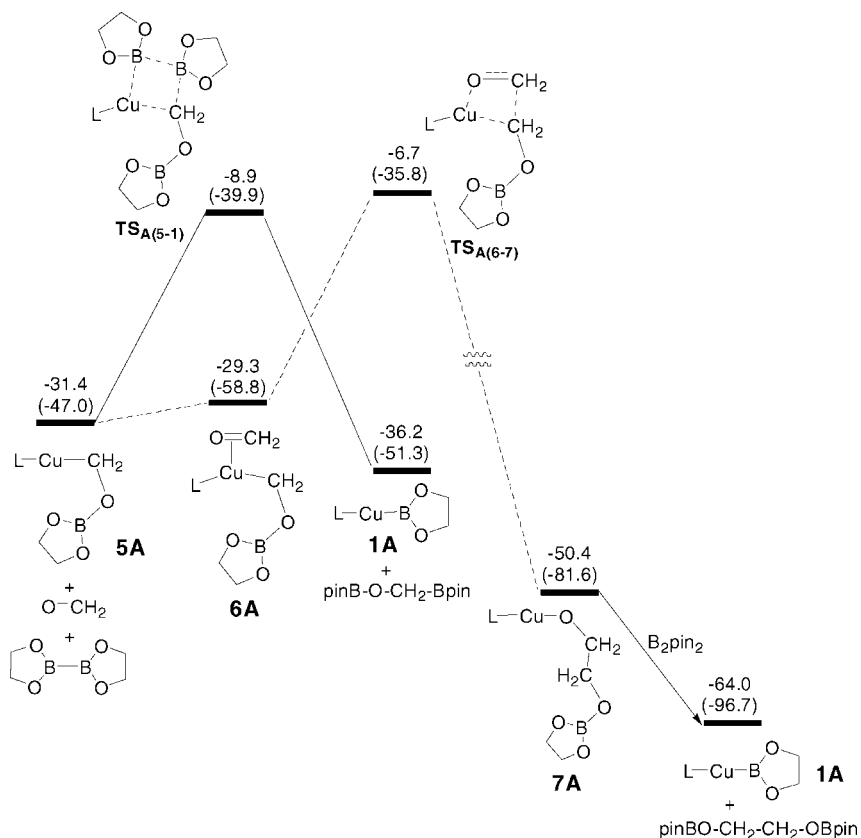


Figure 3. Energy profiles calculated for the possible (NHC)Cu(boryl) regeneration pathway from **5A**, a model for (IPr)Cu[CH(Ph)OBpin] where IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

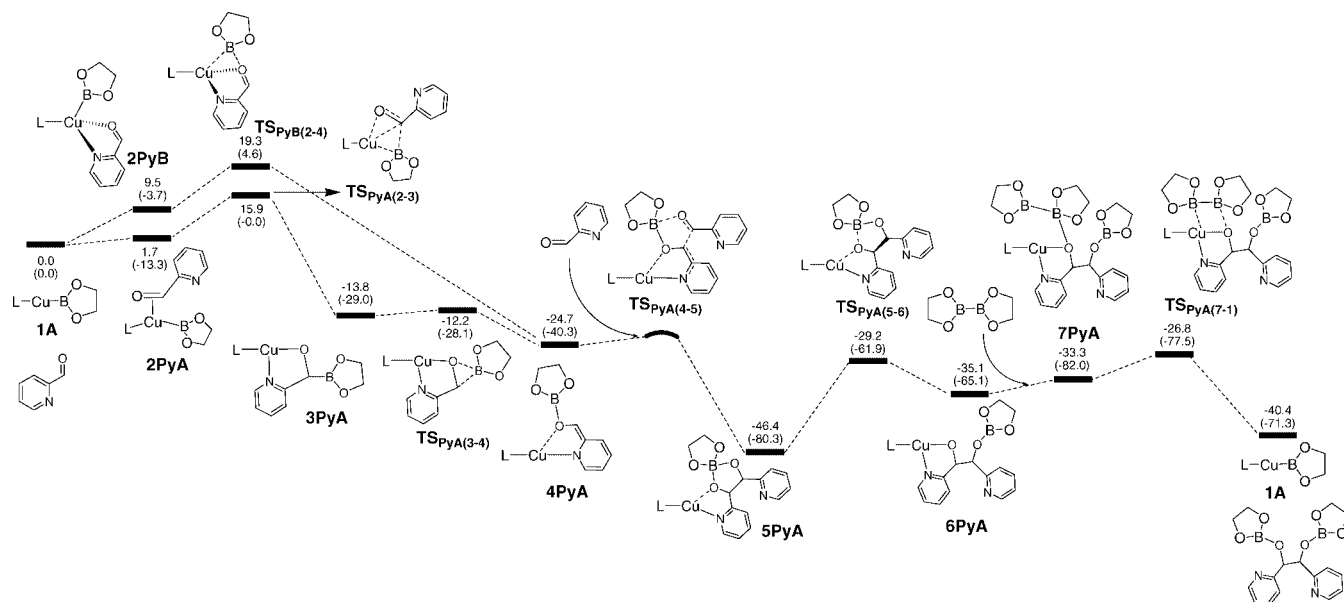


Figure 4. Energy profiles calculated for the (NHC)Cu(boryl)-catalyzed diboration of 2-pyridinecarboxaldehyde. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

pling to form 1,2-di-2-pyridyl-1,2-bis(pinacolboroxy)ethane as the major reaction product (eq 5) in the catalyzed diboration reaction.⁷ Our DFT calculations shed light on how the pyridyl group of the substrate facilitates the reductive coupling process. Figure 4 shows the relevant energy profiles, and Figure 5 shows the optimized structures with selected structural parameters for the species involved in this catalytic process.

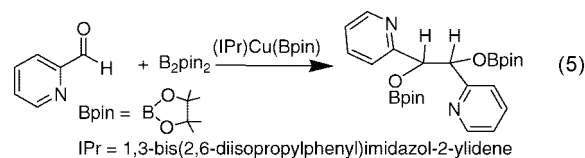


Figure 4 shows that, similar to other aldehydes, 2-pyridinecarboxaldehyde initially coordinates to the copper center of

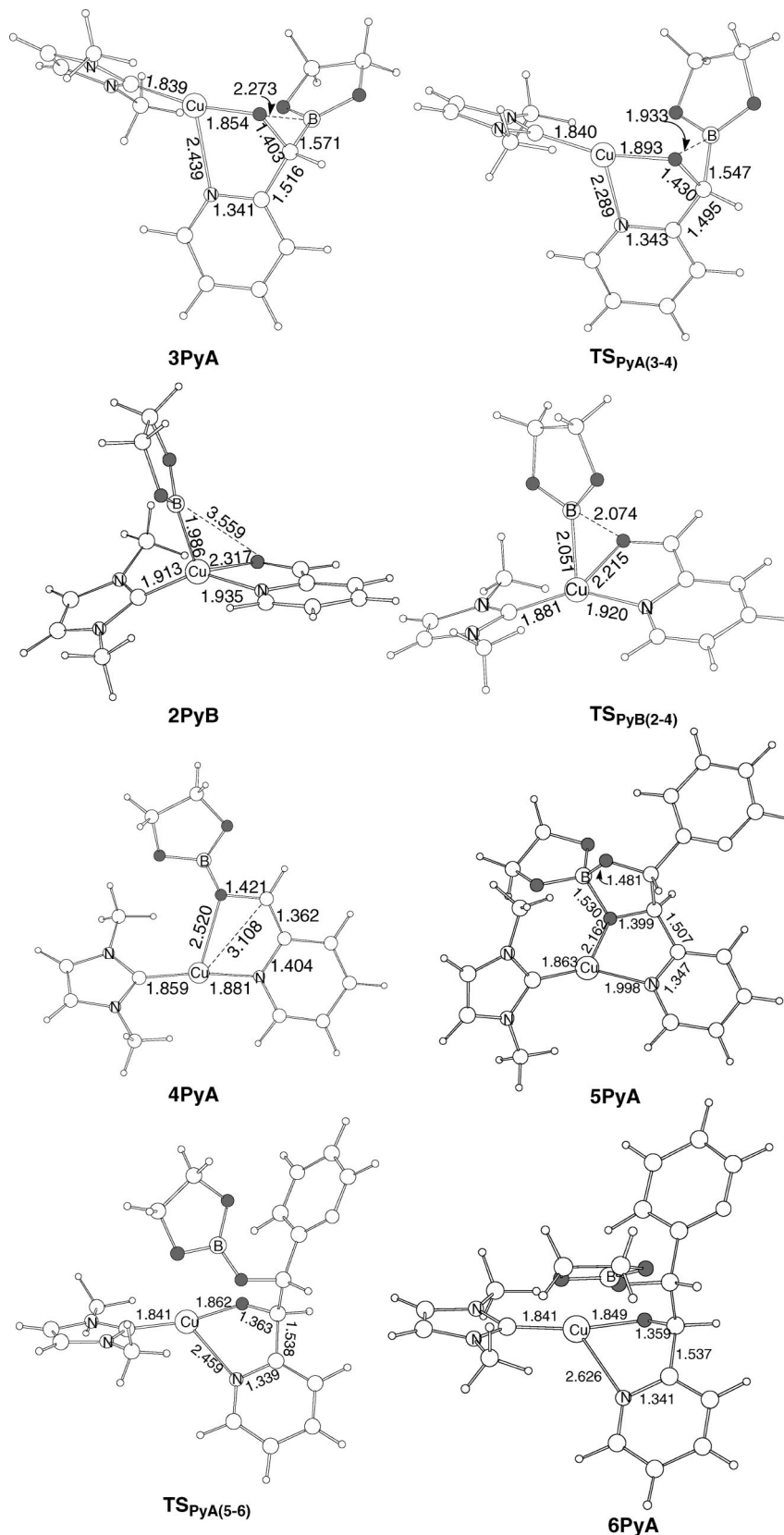
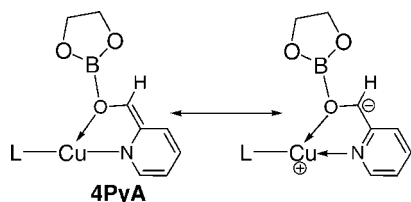


Figure 5. The optimized structures with selected structural parameters (bond lengths in Å) for selected species involved in the (NHC)Cu(boryl)-catalyzed diboration of 2-pyridinecarboxaldehyde.

1A, forming an η^2 -aldehyde intermediate **2PyA**. From **2PyA**, the coordinated 2-pyridinecarboxaldehyde inserts into the Cu–B bond to give **3PyA** with a barrier of 15.9 kcal/mol. In the insertion intermediate **3PyA**, the N atom of the pyridyl group

coordinates to the metal center. Because of the easily accessible 1,2-dihydropyridine form from a coordinated pyridine group,²³ the insertion intermediate **3PyA** quickly isomerizes to a more stable intermediate containing a 1,2-dihydropyridine ring, **4PyA**,

Scheme 2



with a very small barrier of 1.6 kcal/mol, via a boryl migration from the carbonyl carbon to the metal-bonded oxygen.

4PyA can further react with a second 2-pyridinecarboxaldehyde molecule via a [3 + 2] addition to give a very stable intermediate **5PyA**. Attempts to locate the [3 + 2] addition transition state were unsuccessful. Various starting structures were attempted. All of the calculations led to the very stable intermediate **5PyA**. These results suggest that the barrier for the [3 + 2] addition is too small to be located. The very small barrier indicates that **4PyA** is very reactive toward a second 2-pyridinecarboxaldehyde molecule. This is because **4PyA** has another resonance structure in which the O-bonded carbon carries a negative charge (Scheme 2).

5PyA can further isomerize to the less stable intermediate **6PyA** with a barrier of 17.2 kcal/mol. **6PyA** contains a Cu–O σ bond and a Cu–N dative bond. From **6PyA**, a metathesis with B_2eg_2 easily gives the reductive coupling product and regenerates the catalyst **1A**.

Figure 4 shows that **3PyA** rearranges to **4PyA** with almost no barrier and then undergoes the [3 + 2] reaction with another molecule of 2-pyridinecarboxaldehyde, again with virtually no barrier. This precludes metathesis of **3PyA** or **4PyA** with B_2eg_2 directly. It is interesting to note that **5PyA** is highly stable on the basis of the calculations (Figure 4). In the catalytic reactions, **5PyA** is expected to be present only in small amounts and therefore was not detected in the experiments, although **5PyA** corresponds to the deepest minimum in the energy profile (Figure 4). Here, we predict that it is a possible target for experimentalists to isolate in a stoichiometric reaction.

We also examined an alternative path leading to the formation of **4PyA**. This alternative path considers the coordination of 2-pyridinecarboxaldehyde to the metal center through both the carbonyl oxygen atom and the pyridine N atom (**2PyB**).²⁴ The calculation results show that this path from **2PyB** to **4PyA** via a boryl migration has a higher energy barrier than the normal insertion (**2PyA** to **3PyA**) (Figure 4).

We conclude here that the insertion intermediate **3PyA** isomerizes easily to **4PyA** via a boryl migration, due to the availability of a 1,2-dihydropyridine form of the coordinated

Table 1. Comparison of the Computed Barriers Using Formaldehyde and Benzaldehyde as the Substrate Molecules^a

	formaldehyde as the model substrate molecule		benzaldehyde as the substrate molecule	
	ΔE	ΔG (298K)	ΔE	ΔG (298K)
2A \rightarrow TS_{A(2-3)}	13.0	12.8	16.0	16.3
2A \rightarrow TS_{B(2-3)}	34.5	33.8	30.0	29.6
3A \rightarrow TS_{A(2-3)}	28.5	28.1	28.4	28.3
3A \rightarrow TS_{A(4-5)}	28.1	26.6	24.8	22.3
5A \rightarrow TS_{A(5-1)}	7.1	22.5	10.1	26.8
5A \rightarrow TS_{A(6-7)}	11.2	24.7	19.9	34.3

^a The relative electronic energies (ΔE) and the relative free energies ($\Delta G(298\text{ K})$) are given in kcal/mol.

pyridyl group in **3PyA**, preventing its metathesis with a diboron reagent to give the expected diboration product observed for other aldehyde substrates.

Comments on the Use of H_2CO as a Model Substrate. In the calculations, we used formaldehyde as a model substrate for the aldehydes employed in the experiments. It is necessary to examine whether the simple model is sufficient. Employing benzaldehyde as the substrate molecule, we optimized the species corresponding to **2A**, **TS_{A(2-3)}**, **3A**, **TS_{A(4-5)}**, **5A**, and **TS_{B(2-3)}** in Figure 1 and **TS_{A(5-1)}** and **TS_{A(6-7)}** in Figure 3. The geometries of these benzaldehyde-based species can be found in the Supporting Information. The reaction barriers relevant to these benzaldehyde-based species were compared against those relevant to the formaldehyde-based species (Table 1). Steric factors seem to contribute to the differences between the two sets of data presented in Table 1 (see discussion below).

From Table 1, we can see that the barrier for the aldehyde insertion into the Cu–B bond (**2A** \rightarrow **TS_{A(2-3)}**, Path A of Figure 1) increases by 3.5 kcal/mol in free energy from the formaldehyde-based models to the benzaldehyde-based models. The opposite, a decrease of 4.2 kcal/mol in free energy, is seen for the overall barrier in Path B of Figure 1 (**2A** \rightarrow **TS_{B(2-3)}**). The results suggest that the steric repulsion between the substituents at B and the phenyl group at the benzaldehyde carbon in the transition state **TS_{A(2-3)}** is significant, while in **TS_{B(2-3)}**, the steric repulsion between the NHC ligand and the phenyl group at the benzaldehyde carbon is not. Introduction of the phenyl group at the aldehyde carbon in **TS_{B(2-3)}** likely also makes the carbonyl oxygen even more nucleophilic, lowering the overall barrier, due to the fact that the phenyl group is capable of shifting π electron density onto the carbonyl unit. Despite the changes found in the barriers calculated for the aldehyde insertion steps when the realistic benzaldehyde substrate molecule was used in the calculations, the preference for Path A over Path B is still clear.

For **3A** \rightarrow **TS_{A(2-3)}**, use of the realistic benzaldehyde substrate does not affect the barrier much as the steric repulsion between the substituents at B and the phenyl group at the benzaldehyde carbon is present in both **3A** and **TS_{A(2-3)}**. For **3A** \rightarrow **TS_{A(4-5)}**, the benzaldehyde substrate reduces the barrier by 4.3 kcal/mol in free energy (Table 1), due to the fact that the steric repulsion between the substituents at B and the phenyl group at the benzaldehyde carbon is relatively less significant in the transition state **TS_{A(4-5)}**. In the formaldehyde-based model, **TS_{A(2-3)}** lies slightly higher in energy than **TS_{A(4-5)}**. With the benzaldehyde substrate, the energy difference increases and the trend does not change.

As expected, the realistic benzaldehyde substrate increases both the barriers of **5A** \rightarrow **TS_{A(5-1)}** and **5A** \rightarrow **TS_{A(6-7)}** (Table 1 and Figure 3), which are relevant to the slow initiation step

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with the isolated (IPr)Cu-CHAr(OBpin) discussed above, because of the previously mentioned steric effects. The barrier increase is much less significant for the metathesis $5A \rightarrow TS_{A(5-1)}$ than for the aldehyde insertion $5A \rightarrow TS_{A(6-7)}$, implying that the steric repulsion between the substituents at the aldehyde carbon and the eg group at B in $TS_{A(5-1)}$ is less significant than that between the substituents at the two aldehyde carbons in $TS_{A(6-7)}$. Using the formaldehyde model, the metathesis $5A \rightarrow TS_{A(5-1)}$ was calculated to be slightly more favorable than the insertion process $5A \rightarrow TS_{A(6-7)}$. With the realistic benzaldehyde substrate, the preference for the metathesis process is even greater.

The additional calculations based on the realistic benzaldehyde substrate and presented here indicate that the conclusions derived from the formaldehyde model are valid.

Conclusions

The detailed mechanism for the diboration of aldehydes catalyzed by (NHC)Cu(boryl) complexes has been investigated with the aid of DFT calculations. The results show that the catalyzed diboration occurs through aldehyde insertion into Cu–B to give a Cu–O–C–B linkage followed by a σ -bond metathesis with a diboron reagent. The “electron-richness”, that is, the nucleophilicity of the Cu–boryl bond, gives rise to a small insertion barrier and determines the direction of insertion. In the absence of a diboron reagent, the insertion intermediate having a Cu–O–C–B linkage isomerizes to the thermodynamically preferred Cu–C–O–B isomer via a boryl migration to the metal-bonded oxygen through an S_E2 -like transition state.

Different from other aldehydes, 2-pyridinecarboxaldehyde undergoes reductive coupling to form a 1,2-di-2-pyridyl-1,2-bis(pinacolboroxy)ethane in the catalyzed diboration reactions. Our calculations indicate that the Cu–O–C–B insertion intermediate also involves pyridine N-coordination. The availability of a 1,2-dihydropyridine form of the N-coordinated

pyridyl group makes the boryl migration to the metal-bonded oxygen very facile in the Cu–O–C–B insertion intermediate. The intermediate having the 1,2-dihydropyridine form derived from the boryl migration reacts readily with a second 2-pyridinecarboxaldehyde molecule, leading to the observed 1,2-dipyridyl-1,2-bis(pinacolboroxy)ethane product.

Main group organometallic compounds containing M–C bonds, such as Grignard reagents, are good nucleophiles due to their highly polarized M–C bonds. The high nucleophilicity of the Cu–B bond in (NHC)Cu(boryl) discussed in this paper seems counter-intuitive as the Cu–B bond is expected to have substantial covalent character. In the reactions catalyzed by (NHC)Cu(boryl), the copper metal center coordinates to an electrophilic substrate molecule, allowing the boryl ligand to function as a nucleophile, attacking the substrate. The results presented in this paper suggest that the metal-assisted nucleophilic attack does not require a highly polarized M–B bond. It is the high-lying Cu–B σ -bonding molecular orbital that makes the boryl ligands highly nucleophilic.

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Supporting Information Available: Tables giving Cartesian coordinates, electronic energies (E) for all of the calculated structures, and complete ref 19. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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