Abstract: The detailed reaction mechanism for the reduction of CO\textsubscript{2} to CO catalyzed by (NHC)Cu(boryl) complexes (NHC = N-heterocyclic carbene) was studied with the aid of DFT by calculating the relevant intermediates and transition state structures. Our DFT calculations show that the reaction occurs through CO\textsubscript{2} insertion into the Cu–B bond to give a Cu–OC(=O)–boryl species (i.e., containing Cu–O and C–B bonds), and subsequent boryl migration from C to O, followed by \(\alpha\)-bond metathesis between pinB–Bpin \((\text{B} \equiv \text{Bpin})\), \(\\text{pin} = \text{pinacolate} = \text{OCMe}_{2}\text{CMe}_{2}\text{O}\) and (NHC)Cu(Obpin). The overall reaction is exergonic by 38.0 kcal/mol. It is the nucleophilicity of the Cu–B bond, a function of the very strong \(\alpha\)-donor properties of the boryl ligand, rather than the oxophilicity of boron, which determines the direction of the CO\textsubscript{2} insertion process. The boryl migration from C to O, which releases the product CO, is the rate-determining step and involves the "vacant" orbital on boron. The (NHC)Cu(boryl) complexes show unique activity in the catalytic process. For the analogous (NHC)Cu(alkyl) complexes, the CO\textsubscript{2} insertion into the Cu–C bond giving a copper acetate intermediate occurs with a readily achievable barrier. However, the elimination of CO from the acetate intermediate through a methyl migration from C to O is energetically inaccessible.

Introduction

Transition metal boryl complexes\(^1\) have attracted considerable interest because of their role in catalyzed hydroboration, diboration, dehydrogenative borylation, and other B–X addition reactions to unsaturated organics,\(^2-^4\) as well as the catalyzed borylation of C–H bonds in alkanes and arenes.\(^5\) A recent report by Sadighi and co-workers shows that N-heterocyclic carbene-ligated copper boryl complexes catalyze oxygen abstraction from CO\textsubscript{2} in solution under mild conditions, that is, the reduction of CO\textsubscript{2} to CO, with high turnover numbers and frequencies (eq 1).\(^6\) Reduction of CO\textsubscript{2} to CO is important because CO\textsubscript{2} is naturally very abundant and CO is industrially useful.\(^7\) It is known that CO\textsubscript{2} can easily insert into an M–E bond (where E = C, H, N, O, P, Si, or other metal),\(^8\) but it is difficult to break the O=CO bond due to its high bond strength. Why do the copper boryl complexes show such a distinctive catalytic activity in the oxygen abstraction from CO\textsubscript{2}? Clearly, there are important implications of this oxygen abstraction for many reactions catalyzed by metal boryl complexes. We decided to study the reaction mechanism in detail. A deep understanding of the reaction mechanism will also lead to more practical systems for the reduction of CO\textsubscript{2}.

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\text{CO}_2 + \text{B}_2\text{pin}_2 (\text{NHC})\text{Cu(Bpin)} \rightarrow \text{CO} + (\text{pinB})_2\text{O} \quad (1)
\]


Computational Details

Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the Becke3LYP (B3LYP) functional. Frequency calculations at the same level of 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) were calculated for the transition states to confirm that such structures indeed connect two relevant minima. The 6-311G* Pople basis set was used for B and atoms in the CO2 moiety, while the 6-311G* Wachters–Hay basis set was used for Cu. The 6-31G* basis set was used for all other atoms. To examine the basis set dependence, we also employed a larger basis set, 6-311G* for Cu, B, and atoms in the CO2 moiety and 6-31G* for all other atoms, to carry out single-point energy calculations for several selected structures. Additional calculations show that the basis set dependence is small. For example, using the smaller basis set, the relative energies of TS\textsubscript{Bpin}–3, TS\textsubscript{Bpin}–4, TS\textsubscript{Bpin}–5, Bpin, and TS\textsubscript{Bpin}–6 (Figure 1a) are 6.7, −23.7, −1.3, −31.4, −43.6, and −31.7 kcal/mol, respectively. Using the larger basis set, the relative energies are 5.9, −24.9, −2.1, −32.6, −43.7, and −32.6 kcal/mol, respectively. Partial atomic charges were calculated on the basis of natural bond orbital (NBO) analyses. All calculations were performed with the Gaussian 03\textsuperscript{18} software package.

Results and Discussion

The careful experiments carried out by Sadighi and co-workers allowed them to formulate the catalytic cycle shown in Scheme 1.\textsuperscript{16} In this paper, we examine the detailed reaction mechanism via DFT calculations and show evidence for an unexpected mechanism of insertion. The model catalyst \([\text{Cu} (\text{Bpin})_2]\) \{\text{NHC} = 1,3-dimethylimidazol-2-ylidene; \text{OR} = \text{OCH}_2\text{CH}_2\text{O}\} was used, in which the substituents at \(N\) in the NHC carbene ligand and the methyl groups in the Bpin ligand were replaced by \(\text{CH}_3\) and \(\text{H}\), respectively. Thus, 1,3-dimethylimidazol-2-ylidene was used to model 1,3-dicyclohexylimidazol-2-ylidene (ICy), while \(\text{B} (\text{OCH}_2\text{CH}_2\text{O})_2\) was used to model Bpin\(_2\).

Based on our DFT calculations, the catalytic cycle shown in Scheme 2 was found to be the most favorable. Figure 1a shows the relevant energy profile. 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. 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 compounds 1Bpin and 5Bpin are compared to their corresponding experimental ones.\textsuperscript{4} The calculated geometries reproduce well the important structural parameters. The first step is the CO\(_2\) coordination to the copper center forming a metal–\(\eta^2\)-carbonyl intermediate 2Bpin. From 2Bpin, the coordinated CO\(_2\) then inserts into the M–B bond to give 3Bpin with a barrier of 3.8 kcal/mol. The small barrier suggests that CO\(_2\) coordination activates the O=CO bond significantly. The step 1Bpin \(\rightarrow\) 3Bpin is exergonic by 5.7 kcal/mol, and the overall barrier is 16.0 kcal/mol. Intermediate 3Bpin then isomerizes to the more stable intermediate, 4Bpin, with a very small barrier of 2.4 kcal/mol through a simple rotation of the \((\text{O})\text{Bpin}\) group around the \(\text{C}–\text{O}\) single bond.\textsuperscript{16} A CO molecule is released from 4Bpin with a barrier of 22.0 kcal/mol via a boryl migration from the carbonyl carbon to the metal-bonded oxygen giving 5Bpin. Coordination of a pinB\(_2\) Bpin molecule to 5Bpin gives 6Bpin. Through a \(\sigma\)-bond metathesis–like transition state, TS\textsubscript{Bpin}–1, the catalyst 1Bpin is regenerated and pinB\(_2\)–Bpin is formed from intermediate 6Bpin with a barrier of 14.3 kcal/mol. The overall reaction is exergonic by 38.0 kcal/mol, and the conversion of 4Bpin to 5Bpin is the rate-determining step. The DFT results thus show that the Cu-catalyzed reduction of CO\(_2\) to CO occurs through CO\(_2\) insertion into Cu–B forming a Cu=O–C=B linkage, and boryl migration from C to O, followed by a \(\sigma\)-bond metathesis between pinB–Bpin and (NHC)Cu(OBpin). The boryl migration, which releases the product CO, is the rate-determining step.
The experiments by Sadighi and co-workers show that the reaction turnover frequency is very low when bulkier NHC ligands, such as IPr ($\text{IPr} = 1,3$-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene), are employed. Although, on the basis of the model calculations, the catalyst regeneration step is not rate-determining, strong repulsion between a very bulky NHC ligand and B$_2$pin would increase significantly the energy of the transition state structure, $\text{TS}_{\text{Bpin}(6-1)}$, making the barrier of the $\text{Bpin} \rightarrow \text{Bpin}$ step comparable to that of the rate-determining step. Thus, using the bulky IPr ligand results in low turnover frequencies.

From Figure 1a, we see that the CO$_2$ insertion step leads to the formation of the Cu–O and C–B bonds in 3Bpin. When the CO$_2$ molecule adopts a different orientation in the insertion step, the insertion could give 3′Bpin with a Cu–C–O–B linkage (Figure 1b), an isomer of 3Bpin, having Cu–C and O–B bonds. Attempts to locate a metal–$\eta^2$-carbonyl intermediate ($\text{2′Bpin}$) similar to 2Bpin but having a different CO$_2$ orientation were not successful. Clearly, 2′Bpin does not correspond to a local minimum. To estimate roughly the energy of 2′Bpin, we partially optimized a structure in which the Cu–C(CO$_2$) bond was fixed at 1.999 Å, a distance taken from 2Bpin. The partially optimized structure is highly unstable and lies 12.9 kcal/mol higher in energy than does 2Bpin. The assumed 2′Bpin structure apparently lies even higher in energy.

**Figure 1.** Energy profiles calculated for the (NHC)Cu(boryl)-catalyzed CO$_2$ reduction to CO: (a) the most favorable reaction pathway and (b) an alternative, but unlikely, reaction pathway. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

**Scheme 1**

**Scheme 2**
than TS\textsubscript{Bpin(2-3)}, the transition state for the CO\textsubscript{2} insertion from 2Bpin. We can conclude that insertion from the assumed 2Bpin is not favored. The B(Bpin)–O(\eta\textsuperscript{2}-O=CO) distance in the calculated 2Bpin structure is 3.383 Å (see Figure S1 in the Supporting Information), suggesting a repulsive interaction between the Cu–B bond and the oxygen from the \eta\textsuperscript{2}-coordinated CO\textsubscript{2} (see below). One might wonder whether insertion giving 3Bpin with a Cu–C–O–B linkage would be possible with the bulkier “real” NHC ligand and a B(OCMe\textsubscript{2}-CMe\textsubscript{2}O) ligand. We do not expect this to be the case. Examining the structures of 2Bpin and TS\textsubscript{Bpin(2-3)} shown in Figure 2, we do not expect a significant repulsive interaction, between the

Figure 2. The optimized structures with selected structural parameters (bond length in Å) for the species involved in the most favorable reaction pathway of the (NHC)Cu(boryl)-catalyzed CO\textsubscript{2} reduction. Selected calculated structural parameters for the model compounds 1Bpin and 5Bpin are compared to the experimental structural parameters (in parentheses) of (IPr)Cu(Bpin) and (IPr)Cu(OBpin) where IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.
coordinated CO\(_2\) and the substituents from the NHC and Bpin ligands, which could change our conclusion regarding the CO\(_2\) insertion based on the model ligands.

Examining the bonding characteristics of the HOMO (Figure 3) calculated for 2Bpin, we found that there exists significant bonding character among the metal center, the boron atom, and the CO\(_2\) carbon. In the HOMO, the back-bonding interaction between the Cu–B σ-bond and the CO\(_2\) carbon can be seen clearly. In other words, the Cu–B σ-bond is involved in a bonding interaction with an empty π* orbital on the \(\eta^3\)-CO\(_2\) ligand in 2Bpin, which is mostly carbon-based. An NBO charge analysis on 2Bpin shows that there is an electron transfer of 0.53e from metal fragment to the CO\(_2\) moiety, suggesting that the back-bonding interaction is significant in 2Bpin. The absence of such a Cu–B → C back-bonding interaction in 2Bpin explains the failure to locate it. Attempts to locate a transition state directly connecting 1Bpin and 3Bpin also failed, likely due to the transition state being too high in energy to be found. Interestingly, in contrast to what we see here, in an early study by Morokuma and co-workers,\(^{17}\) a Cu(I)-to-\(\eta^2\)-acetylene back-bonding interaction was found to be mainly from a predominantly metal-centered orbital. In 2Bpin, the Cu–B σ-bonding molecular orbital lies higher in energy than the metal d orbitals, making the Cu–B → C back-bonding interaction more important.

To obtain 3Bpin, in which the Cu–C and B–O bonds are formed, one might also consider an adduct, which has a B–O Lewis acid–base bond between the boron center of the boryl ligand in the catalyst and one terminal oxygen of CO\(_2\), as a starting species. The calculations show that such an adduct is not a local minimum, suggesting that the Lewis acid–base attraction is very weak. The calculations suggest that the high-energy Cu–B σ-bond, as evidenced by its dominant contribution to the HOMO shown in Figure 3, determines the mode of the CO\(_2\) insertion and that there is no involvement of the “empty” orbital on boron, which interacts strongly with the two oxygens of the pinacolate.

During the attempts to locate the possible transition state structures discussed above, we instead found a new transition structure connecting 3Bpin and 3Bpin with a barrier of 21.4 kcal/mol from 3Bpin to 3Bpin (Figure 1b). Interestingly, 3Bpin easily isomerizes with CO elimination to give 5Bpin (Figure 1b). Although the 3Bpin → 5Bpin conversion is very feasible, the reaction pathway via 3Bpin is unlikely because, once formed, 3Bpin is immediately transformed into 4Bpin and does not have a chance to undergo the isomerization to 3Bpin. One would have to consider a very high overall barrier (29.4 kcal/mol, from 4Bpin → 3Bpin → TS\(_{Bpin(3\rightarrow 3)}\) → 3Bpin) if the reaction pathway proceeds via 3Bpin.

Experimentally, Sadighi and co-workers also found that CO\(_2\) can insert into the Cu–Me bond of a (IPr)Cu(Me) complex at room temperature to give \((\text{IPr})\text{Cu}(\eta^1\text{-O}_2\text{CCH}_3)\),\(^{18}\) Whereas the predicted (NHC)CuOC(=O)Bpin (4Bpin) intermediate extrudes CO very readily, the known (IPr)Cu(\(\eta^1\text{-O}_2\text{CCH}_3\)) has not been observed to do so. We thus examined the difference in reactivities between the Cu–boryl and Cu–alkyl complexes. DFT calculations on the reaction of [(NHC)CuMe] (NHC = 1,3-dimethylimidazol-2-ylidene) with CO\(_2\) were also carried out. Figure 4 shows the energy profile, and Figure 5 shows the optimized structures with selected structural parameters for the species involved. In Figure 5, the calculated structures of the model compounds 1Me and 3Me are also compared to their corresponding experimental ones.\(^{18}\) The optimized structures are again in good agreement with the experimental structures.

Figure 4 shows that the CO\(_2\) insertion into the Cu–C bond of 1Me gives 2Me with a barrier of 25.6 kcal/mol (\(\Delta G^\ddagger\)). Through an isomerization, 3Me, a model for the insertion product obtained in the experiment,\(^{18}\) is formed. From Figure 4, we see that 3Me cannot release CO through a methyl group migration from C to O, due to the very high barrier (103.6 kcal/mol) for such a process. The computational results are consistent with the experimental observation that (NHC)-Cu(Me) does not promote the reduction of CO\(_2\) to CO.

Comparing the energy profiles in Figures 1a and 4, we find that the overall barrier (\(\Delta G^\ddagger = 16.0 \text{ kcal/mol}\)) of the CO\(_2\) insertion step in the (NHC)Cu(boryl)-catalyzed CO\(_2\) reduction is smaller than that (\(\Delta G^\ddagger = 25.6 \text{ kcal/mol}\)) in the assumed (NHC)Cu(Me)-promoted CO\(_2\) reduction. The insertion barrier is also noticeably smaller than those calculated for the CO\(_2\)

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The optimized structures with selected structural parameters (bond length in Å) for the species involved in the assumed (NHC)Cu(Me)-complexes are compared to the experimental structural parameters (in parentheses) of (IPr)Cu(Me) and (IPr)Cu(O\textsubscript{2}CCH\textsubscript{3}) where IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidine.

Comparing the boryl and the methyl migrations, both of which would release CO, we found that the former has a much smaller barrier. For the latter, the transition state is energetically inaccessible. In the transition state TS\textsubscript{Bpin(4-5)} for the boryl migration (Figure 2), the boron center in the boryl ligand is tetra-coordinated, suggesting that the “empty” orbital of the boryl ligand assists the migration significantly. The presence of the “empty” orbital avoids exceeding the octet in the transition state of the C–O bond breaking and formation process. In contrast, in the transition state TS\textsubscript{Me(3-4)} for the methyl migration (Figure 5), the carbon center of the migrating methyl group has to adopt a five-coordinate geometry, and, as a result, the C–C and C–O distances are very long. The absence of an “empty” orbital forces the carbon center to exceed the octet, leading to the very long distances calculated for C–C (bond breaking) and C–O (bond forming) in the transition state structure. In the transition state structure TS\textsubscript{Me(3-4)}, the C–C bond is almost broken, while the C–O bond is far from being formed. The barrier (103.6 kcal/mol) calculated for the methyl migration can be considered to be the energy required to break the C–C σ-bond.

**Conclusions**

The detailed reaction mechanism for the reduction of CO\textsubscript{2} to CO catalyzed by (NHC)Cu(boryl) complexes has been investigated with the aid of DFT calculations. The computational results show that the catalyzed reduction occurs through CO\textsubscript{2} insertion into Cu–B to give a Cu–O–C–B linkage, and boryl migration from C to O, followed by a σ-bond metathesis between pinB–Bpin and (NHC)Cu(0Bpin). The boryl migration from C to O, which releases the product, CO, is the rate-determining step.

Our calculations show that the “electron richness” of the Cu–boryl bond, due to the low electronegativity of boron, gives rise to a small CO\textsubscript{2} insertion barrier because the back-bonding interaction between the Cu–B σ-bond and the CO\textsubscript{2} carbon is significant. Therefore, we believe that the back-bonding interaction of the Cu–boryl σ-bond versus the Cu–Me σ-bond to the CO\textsubscript{2} carbon explains the smaller barrier found in the CO\textsubscript{2} insertion into the Cu–B bond. The greater back-bonding interaction of the Cu–boryl σ-bond is apparently related to the low electronegativity of boron in the boryl ligand. The lower electronegativity of boron, as compared to carbon, makes the Cu–B σ bond “electron-rich”, in turn increasing the back-donation ability. In other words, the boryl ligand is a much stronger σ-donor than the methyl group, as we found previously.\( ^{19} \)\( ^{20} \)

To test whether the “electron-richness” argument is justified, we also performed calculations on the insertion of CO\textsubscript{2} in the Cu–B bond of the new model complex (NH\textsubscript{3})Cu(boryl) having NH\textsubscript{3} as the auxiliary ligand, instead of the NHC, as the latter are considered to be strongly trans-influencing.\( ^{20} \)\( ^{20} \) The CO\textsubscript{2} insertion barrier with this new model complex is ca. 10 kcal/mol greater than that with the (NH\textsubscript{3})Cu(boryl) model complex.

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*(All references are cited at the bottom of the text.)*
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Supporting Information Available: Tables giving Cartesian coordinates, electronic energies ($E$), free energies ($G$), and zero point energies ($ZPE$) for all of the calculated structures, and complete refs 8b and 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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