Evidence of boron assistance for CO_2 activation during copper-catalyzed boracarboxylation of vinyl arenes: A synthetic model for cooperative fixation of CO_2

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ABSTRACT: In this comment, insights gained from density functional theory into the mechanism by which the Cu(I)-catalyzed boracarboxylation of vinyl arenes occurs with specific focus on the CO_2 insertion step are presented. Preliminary calculations indicated a potential non-covalent interaction between boron and CO_2 in the carboxylation transition state, implicating cooperative CO_2 activation. A study of boron Lewis acidity was conducted through substitution of sp^2 mono-boron substituents. An inverse correlation between boron valency deficiency (BVD) and the enthalpic barrier of CO_2 insertion into the β-borylbenzyl-Cu(I) bond was revealed, supporting Lewis acid/base cooperativity between boron and the proximal oxygen of CO_2 at the carboxylation insertion transition state. These findings suggest that future methodology development should consider strategic incorporation of similar Lewis acidic functionality to facilitate carboxylation of challenging substrates.

KEYWORDS: boracarboxylation; Lewis acid/base; cooperative activation

INTRODUCTION

Carbon dioxide as a C_1 synthon has been a focus of chemical research recently due to its large abundance and low cost as well as the prevalence of the carboxylic acid functionality in many synthetically and pharmaceutically interesting targets.[1,2,3,4] However, CO_2 remains an underutilized feedstock due to its inherent stability and lack of reactivity under practical conditions.[1a,1b] The need to identify conditions that will readily allow for CO_2 activation and functionalization has resulted in many transition metal systems aimed at carbon dioxide conversion in recent years.[4,5]

Understanding the mechanism by which CO_2 is activated by transition metal complexes is imperative to developing catalytic methods for CO_2 valorization. Thus, a great deal of attention has been given to the synthesis and characterization of carbon dioxide-appended metal complexes.[4,6] Given that the nature of binding depends heavily on the electronic state of the metal center, more nucleophilic late transition metals, such as copper and nickel, are generally required to activate the electrophilic carbon of CO_2. The first complex demonstrating binding through carbon was described by Aresta in 1975 with the characterization of $Ni(PCy)_2(\eta^2(C,O)\text{-}CO_2)$,[6a] Aresta's complex, and many other examples of η^2-(C,O) and η^2-(O,O) binding followed (Figure 1A).[6] A number of these discrete complexes have demonstrated stoichiometric and catalytic reactivity toward carboxylation.[6h,7] One example from Dong and colleagues demonstrated that Aresta's complex coupled with organozinc reagents allows catalytic access to organocarboxylates.[6h]

[insert Figure 1 here]

Highly reactive enzymes that catalyze small molecule activation have been of interest in developing synthetic analogs. One avenue of research in biomimetics focuses on the concept of second-sphere activation, a common motif in biological systems.[8] For instance, carbon monoxide dehydrogenase (CODH II),[9] which is responsible for carbon fixation in anaerobic bacteria, facilitates the reversible oxidation/reduction of CO/CO_2 through substrate activation by a histidine residue proximal to the Ni-Fe binding site (Figure 1B). With such inspiration, many have successfully demonstrated second sphere activation in discrete synthetic complexes, specifically the activation of CO_2.[10] In 2011, for example, Crabtree and Harazi employed an Ir(III)-PNP complex featuring a hydridic site at the metal and protic site in the ligand scaffold to reduce CO_2 to formate.[10a] Second-sphere activation of CO_2 can also be initiated through addition of exogeneous Lewis acid, such as in the case Re-CO_2 complex described by Berke or frustrated Lewis pair (FLP) reactivity described by Fontaine (Figure 1C).[10c,10d]

Valorization of CO_2 has also been expanded past C_1 product formation (eg., formate, carbon monoxide) to include the functionalization of more complex organic frameworks. Hydrocarboxylation of allenes, alkynes, aldehydes, etc. has been well documented using many synthetic methods.[5,11] However, hetero(element)carboxylation, in which the reducing element (or moiety) is not a hydride equivalent, has been studied to a lesser extent, and mechanistic understanding is limited. Only in recent years has this concept been expanded upon, with a handful of examples of boron- and silicon-based derivatizations.[Error! Bookmark not defined.,Error! Bookmark not defined.,Error! Bookmark not defined.] One notable example, reported in 2012 by Hou, demonstrated copper-catalyzed boracarboxylation of internal and terminal alkynes, generating a series of α,β-unsaturated boralactonates.[Error! Bookmark not defined.] In 2016, we extended hetero(element)carboxylation for the first time to sp^2-hydrocarbon substrates when we reported the catalytic boracarboxylation reaction to vinyl arenes using an ICyCu(I) complex (ICy = dicyclohexyl-2*H*-imidazolylidene) and bis(pinacolato)diboron (B_2pin_2) as the reductant (Figure 2).[Error! Bookmark not defined.a] The catalytic reaction demonstrated excellent regioselectivity, favoring installation of the carboxylate in the benzylic position, while maintaining mild conditions similar to those in the previously reported hetero(element)carboxylation systems (i.e. ambient temperatures, low CO_2 pressures, etc.). The boracarboxylation reaction is amenable to electron rich- and electron neutral substrates, providing good to excellent yields, and recently, methods to overcome the original electronic limitations were reported.[Error! Bookmark not defined.b]

[insert figure 2 here]

The proposed mechanism, based on past experimental and computational observations,[Error! Bookmark not defined.,Error! Bookmark not defined.] identifies carboxylation of the Cu(I)-benzyl-β-boryl intermediate as the rate determining step of the boracarboxylation reaction (Figure S2). Following 2,1-insertion of the vinyl arene into a Cu-Bpin bond, CO_2 associates at the Cu(I) center in apparent η^2-(C,O) fashion prior to insertion into the nucleophilic Cu(I)-benzyl bond.[Error! Bookmark not defined.,Error! Bookmark not defined.,Error! Bookmark not defined.] Our own computational analysis using density functional theory (DFT) revealed a close interaction between the boron and the proximal oxygen of the metal-bound CO_2 in the carboxylation transition state, a detail that had not been discussed in previous studies (cf., Figure 1d). Motivated by this observation as well as precedent that boron can facilitate carboxylative transformations cooperatively,[9,12,13,14] a computational analysis was initiated. Here, we present a computational study of the impact of boron electronic character on the CO_2 insertion barrier in the boracarboxylation of styrene.

METHODS

All calculations were performed using the Gaussian 09 package.[15] For ground state and transition state geometry optimizations, the M06 functional[16,17] and the Pople basis sets 6-311+G(d) for copper and 6-311G(d) for all other atoms were used,[18] applying a fine integral grid (75,302) to all calculations.[19] Normal-mode analyses were performed at the same level of theory, confirming that each optimized minimum or transition state has zero or one imaginary frequency, respectively. IRC analysis was used to confirm that transition states related to the appropriate reaction/product potential energy surface. Single-point self-consistent reaction field calculations (SCRF) were also performed with tetrahydrofuran solvation, the catalytic reaction solvent,[Error! Bookmark not defined.] specified using the SMD model.[20] Natural bond orbital (NBO) analysis was performed using the Gaussian NBO version 3.1[21] with the same level of theory. Natural bonding orbitals were visualized using NBOPro 6.0,[21] and Jmol visualization software was used for generation of 3D NBO plots.[22] NBO analysis allowed for the determination of boron valence deficiency (BVD) for each boron moiety. BVD was calculated by subtracting the electronic population of the boron atom from the formal valence of three.[23]

RESULTS AND ANALYSIS

Computational analysis of the reaction mechanism was conducted in 2017 by Lu and colleagues, wherein the effect of sterics of the ancillary N-heterocyclic carbene (NHC) and phosphine ligands employed in the catalytic reaction was explored.[Error! Bookmark not defined.] A steric dependence was observed in the CO_2 insertion into the Cu-benzyl bond, namely an inhibitory interaction between the proximal pinacol oxygen and the hydrogens on the NHC ligand. Although it was revealed that steric contributions of the ancillary ligands affect the CO_2 insertion energy barrier, there was no consideration for the role of the boron fragment. We viewed this as an important detail that was overlooked, thus we sought to identify how the electronic nature of the boron fragment may assist carboxylation.

The full ICy-ligated copper-benzyl complex with a slightly sterically reduced ethyleneglycato boron ester (eg-B) was used to locate the carboxylation transition state.[Error! Bookmark not defined.] The transition state structure revealed close contact between the boron and the proximal oxygen of the

CO_2 associated at Cu (Figure 3A). The distance ($r_{B\text{-}O}$ = 2.51 Å) falls within the Van der Waals radii range for these atoms (O=1.5 Å; B=1.8 Å),[24] suggesting the potential for a non-covalent interaction.

Natural bond orbital analysis (NBO), a powerful tool that provides information about electron density distribution in atoms and bonds of a molecular structure,[25,26] was utilized to understand the apparent interaction. NBO analysis revealed that the vacant acceptor p orbital on the boron ester moiety overlaps with the appropriately oriented donor oxygen lone pair orbital (Figure 3B). Consistent with this qualitative picture, a stabilization energy of 8.7 kcal/mol, obtained from NBO 2nd order perturbation analysis, was calculated for the interaction between the appropriately oriented lone pair of the CO_2 oxygen and the boron vacant p orbital. This encouraged us to explore the electronic variability at boron through modification of the ester functional group and determine the resulting energetic effect on donor/acceptor orbitals identified in the carboxylation transition state structure.

[insert Figure 3 here]

This study focuses on variability strictly at the boron center, thus removing steric contributions from the ancillary ligand without altering the electronic contribution significantly was deemed important. The use of the truncated IMe model ligand (IMe = dimethyl-2*H*-imidazolylidene) in place of ICy was shown to have minimal effects on the energetics of the system in previous computational studies.[Error! Bookmark not defined.] Gratifyingly, the enthalpic barrier of CO_2 insertion for both ICy and IMe model systems were comparable, differing by less than 1 kcal/mol (Figure S1). Thus, the remainder of the study was conducted using the IMe model system.

We identified three energetically feasible transition states for the carboxylation of copper-benzyl complex (structure **A**, Figure 4): 1) a cooperative pathway in which boron interacts with the proximal oxygen of CO_2 (structure **B**); 2) a non-cooperative pathway wherein the boron substituent is directed away from the metal center (structure **C**); and 3) an S_E^n-like pathway in which the copper center does not participate directly in C–C bond formation (structure **D**). The structure resulting from an S_E^n mechanism was considered based on a report of styrene carboxylation through the formation of a "masked" carbanion from boronic ester substituted substrates[27] as well as our own research using a stereochemical probe substrate (β-methylstyrene) that revealed the major and minor diastereomers (dr > 7:1) resulted from direct insertion and electrophilic substitution, respectively.[**Error! Bookmark not defined.**a] The cooperative insertion transition state is lower in energy in the gas phase while both insertion transition states, with THF solvation, are essentially isoenergetic. Attempts to identify ground-state and/or transition-state structures that feature competing boron-THF Lewis pairing were unsuccessful.[28] The S_E^n-derived transition state is less favorable than both insertion transition states, which is consistent with our previous experimental data. To explore the potential energetic impact of the Lewis-acid character on cooperative pathway (structure B), a series of boron moieties that spanned a range of Lewis acidic character were evaluated computationally (Figure 5).

[insert Figure 4 here]

[insert Figure 5 here]

The Lewis acidity of each boron center was assessed through its natural charge (NC) and boron valence deficiency (BVD), a parameter established by Plumley and Evanseck in 2009 in their study of boron Lewis acidity in a number of $H_3N–BX_3$ adducts.[23] BVD is defined as the ability of boron to accept electrons, analogous to the concept of Lewis acid/base theory,[29] and it is determined by subtracting the NBO computed natural valency of boron from its formal valence of three. This alternative description of the Lewis acidity of boron is necessary, as the electronegativity of substituents alone does not adequately describe the ability of boron to participate in non-covalent interactions (cf., Figure S3). Our analysis of the NBO results from the series of β-borylbenzyl-copper complex carboxylation transition states (Table 1) revealed a positive correlation close to unity (Figure 6A), confirming the direct relationship between BVD and the NC on boron and validating its use as a diagnostic tool.

BVD values were then compared to the enthalpic CO_2 insertion barrier (Figure 6B). A moderate correlation was observed in which the enthalpic barrier decreased with increasing BVD. Spanning a range of electronegativities from BH_2 to BF_2 (EN: H = 2.1; F = 4.1),[30] an overall change in enthalpy of 20 kcal/mol was observed.

[insert Table 1 here]

[insert Figure 6 here]

The correlation of BVD and the CO_2 insertion barrier was further examined using NBO 2nd order perturbation analysis to obtain stabilization energies, denoted $\Delta E^{(2)}_{i \rightarrow j*}$ or E(2). Donor/acceptor behavior was quantified through stabilization of the donor orbital upon overlap with an unoccupied orbital (ie., *i* = appropriately oriented lone pair of the CO_2 oxygen; j = vacant p orbital of boron). Stabilization energies of boron ester and amide derivatives were found to correlate well with BVD (Figure 7, black trace), and a rendering of donor/acceptor NBOs illustrates significant orbital overlap (cf., Figure 7). For example, there is a stronger stabilizing interaction (5 kcal/mol) between the donor/acceptor pair for B(eg) relative to analogous B(en) (en=ethylenediamino) (BVD = 1.24 and 1.02, respectively). Further, the interaction distance between the boron and the participating oxygen atom was examined (Figure 7, red trace). An inverse correlation was found for alkoxy and amido substituents obtained wherein decreasing BVD led to an increased distance ($r_{B\text{-}O}$) between the Lewis pair.[31] The decrease in the stabilization energy as the polarization of the B-X bond is reduced speaks to the importance of increased Lewis acidity at boron in promoting the delocalization of electron density from the CO_2 moiety, thereby providing a more electrophilic carbon to initiate insertion into the copper-benzyl bond.

[insert Figure 7 here]

PERSPECTIVES AND IMPLICATIONS

This computational study has evaluated the potential for an intramolecular Lewis donor/acceptor interaction to facilitate carboxylation of β-borylbenzyl-Cu(I) species relevant to catalytic boracarboxylation. We show that the enthalpic barrier of CO_2 insertion decreases with increasing electron deficiency at the boron center as quantified using NBO-determined boron valence deficiency. The kinetic benefit of an electron deficient boron suggests a more active role in which boron participates as a Lewis acid that promotes CO_2 insertion through the removal of electron density from the proximal oxygen, thereby yielding a more electrophilic carbon poised for metalation by copper. Interestingly, similar NHC-copper complexes are not viable catalysts for hydrocarboxylation of vinyl arenes.[32] The present study provides a conceptual framework for understanding how pinacolboryl- and other boron moieties could play a cooperative role in catalytic boracarboxylation.

Given the prevalence of Lewis-acid-assisted activation of C=O bonds in organometallic transformations,[33] most notably migratory insertion, we suggest that this concept might be extended to similar transition-metal-catalyzed carboxylation systems through strategic catalyst/reaction design.[6] A vast literature now exists on the preparation of a wide variety of boron containing compounds, which reinforces their importance in contemporary organic chemistry (cf., diboration reactions, Figure 8).[34] Compounds containing boron are also well studied as activators, co-catalysts, or stand-alone catalysts for synthetic transformations.[13] The Szymczak group, for example, demonstrated the usefulness of boron-appended ligand-metal complexes in several transformations, including alkyne hydrogenation[13a] and hydrazine activation[13h-i] (Figure 8, top right). These methods harness the Lewis-acidic properties of the pendent borane in the second sphere to cooperatively activate Lewis-basic compounds. Similar concepts have been extended to coupling through the introduction of a boronic ester adjacent to a Lewis-basic substituent that both promotes facile cross coupling through intramolecular chelation and neighboring group stabilization of challenging transition-state structures (Figure 8, bottom left).[14]

[Insert Figure 8 here]

Each of the synthetic methods described above, however, require pre-installation of the boron functionality as well as prior isolation. Only one example exists of a system that couples, in a single reaction, the introduction of a Lewis acid functional group with subsequent Lewis-acid-promoted proximal functionalization. Morken and coworkers proposed that a pinacolboryl substituent, introduced during alkene diboration, activates the second pinacolboryl substituent for transmetallation in a subsequent Pd-catalyzed arylation reaction (Figure 8, bottom center).[12] The computational study presented here supports a similar activating role for pinacolboryl substituent in the CO_2 insertion step, and is strikingly similar to the pathway for reversible CO_2 binding at carbon monoxide dehydrogenase (CODH II).[9] To the best of our knowledge, a similar biomimetic CO_2 activation pathway has yet to be discovered or rationally coupled to a transition-metal-catalyzed reaction. We believe such a pathway could create significant new opportunities for the improved installation of CO_2 in organic molecules, an important contemporary endeavor. Efforts are currently underway to demonstrate this concept experimentally both in copper-catalyzed boracarboxylation as well as other late-transition-metal carboxylation reactions where strategic incorporation of a boron functional group, or Lewis acid more generally, could allow selective functionalization.

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DECLARATION OF INTEREST

The authors declare no competing financial interest.

SUPPORTING INFORMATION

Associated correlation plots, computational data, and XYZ coordinates for all computed structures (PDF)

REFERENCES

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1. For selected reviews on chemical synthesis utilizing CO_2, see: (a) Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2. *Chem. Rev.* **2014**, *114*, 1709-1742. (b) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using Carbon Dioxide as a Building Block in Organic Synthesis. *Nat. Commun.* **2015**, *6*, 5933-5948. (c) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kuhn F. E. Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution of a Global Challenge? *Angew. Chem. Int. Ed.* **2011**, *50*, 8510-8537. (d) Peters, M.; Muller, T. E. Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain. *ChemSusChem*, **2011**, *4*, 1216-1240. (e) Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365-2387. (f) Gooßen, L. J.; Rodriguez, N.; Gooßen, K. Carboxylic Acids as Substrates in Homogeneous Catalysis. *Angew. Chem., Int. Ed.* **2008,** *47*, 3100-3120. (g) Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternburg, A.; Bardow, A.; Leitner, W. Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment. *Chem. Rev.* **2018**, *118*, 434-504. (h) Burkhart, M. D.; Hazari, N.; Tway, C. L.; Zeitler, E. L. Opportunities and Challenges for Catalysis in Carbon Dioxide. *ACS Catal.* **2019**, *9*, 7937-7965.
2. Patai, S. *The Chemistry of Acid Derivatives;* Wiley: New York, 1992.
3. Maag, H. *Prodrugs of Carboxylic Acids;* Springer: New York, 2007.

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4. For selected reviews on transition metal-catalyzed carboxylation using CO$_2$, see: (a) Huang, K.; Sun, C. L.; Shi, Z. J. Transition-Metal-Catalyzed C-C Bond Formation through the Fixation of Carbon Dioxide. *Chem. Soc. Rev.* **2011***, 40,* 2435-2452. (b) Tsuji, Y.; Fujihara, T. Carbon Dioxide as a Carbon Source in Organic Transformation: Carbon-Carbon Bond Forming Reactions by Transition-Metal Catalysts. *Chem. Commun.* **2012**, *48*, 9956-9964. (c) Zhang, L.; Hou, Z. M. *N*-Heterocyclic Carbene (NHC)-Copper-Catalysed Transformations of Carbon Dioxide. *Chem. Sci.* **2013***, 4*, 3395-3403. (d) Yueng, C. S.; Dong, V. M. Making C-C Bonds from Carbon Dioxide via Transition-Metal Catalysis. *Top. Catal.* **2014**, *57*, 1342-1350. (e) Yu, D.; Teong, S. P.; Zhang, Y. Transition Metal Complex Catalyzed Carboxylation Reactions with CO$_2$. *Coord. Chem. Rev.* **2015**, *293*, 279-291. (f) Wang, S.; Du, G.; Xi, C. J. Copper-Catalyzed Carboxylation Reactions using Carbon Dioxide. *Org. Biomol. Chem*. **2016**, *14*, 3666−3676. (g) Wu, X.; Zheng, F. Synthesis of Carboxylic Acids and Esters from CO$_2$. *Top. Curr. Chem.* **2017**, *375*, 1-60. (h) Zhang, L.; Hou, Z. Transition Metal Promoted Carboxylation of Unsaturated Substrates with Carbon Dioxide. *Curr. Opin. Green Sust. Chem.* **2017**, *3*, 17-21. (i) Yang, Y.; Lee, J. Toward Ideal Carbon Dioxide Functionalization. *Chem. Sci.* **2019**, *10*, 3905-3926.

5. Tortajada, A.; Juliá-Hernández, F.; Börjesson, M.; Moragas, T.; Martin, R. Transition-Metal-Catalyzed Carboxylation Reactions with Carbon Dioxide. *Angew. Chem. Int. Ed.* **2018**, *57*, 15948-15982.

6. For selected works on the activation of carbon dioxide at transition metal complexes, see: (a) Aresta, M.; Nobile, C. F. New Nickel-Carbon Dioxide Complex: Synthesis, Properties, and Crystallographic Characterization of (carbon dioxide)-bis(tricyclohexylphosphine) Nickel. *Jour. Chem. Soc. Chem. Comm.* **1975**, *15*, 636-637. (b) Alvarez, R.; Carmona, E.; Gutierrez-Puebla, E.; Marín, J. M.; Monge, A.; Poveda, M. L. Synthesis and X-Ray Crystal Structure of [Mo(CO$_2$)$_2$(PMe$_3$)$_3$(CNPr^i)]: the First Structurally Characterized Bis(Carbon Dioxide) Adduct of a Transition Metal. *J. Chem. Soc. Chem. Commun.* **1984**, 1326-1327. (c) Aresta, M.; Gobetto, R.; Quaranta, E.; Tommasi, I. A Bonding-Reactivity Relationship for Ni(PCy$_3$)$_2$(CO$_2$): A Comparative Solid-State-Solution Nuclear Magnetic Resonance Study (^{31}P, ^{13}C) as a Diagnostic Tool to Determine the Mode of Bonding of CO$_2$ to a Metal Center. *Inorg. Chem.* **1992**, *31*, 4286-4290. (d) Komiya, S.; Akita, M.; Kasuga, N.; Hirano, M.; Fukuoka, A. Synthesis, Structure and Reactions of a Carbon Dioxide Complex of Iron(0) Containing 1,2-bis(diethylphosphino)ethane Ligands. *J. Chem. Soc. Chem. Commun.* **1994**, 1115-1116. (e) Hirano, M.; Akita, M.; Tani, K.; Kumagai, K.; Kasuga, N. C.; Fukuoka, A.; Komiya, S. Activation of Coordinated Carbon Dioxide in Fe(CO$_2$)(depe)$_2$ by Group 14 Electrophiles. *Organometallics*. **1997**, *16*, 4206-4213. (f) Gong, J. K.; Wright, C. A.; Thorn, M.; McCauley, K.; McGill, J. W.; Sutterer, A.; Hinze, S. M.; Prince, B. *Adv. Chem. Conv. Mitigating CO$_2$*; Elsevier Science: Amsterdam, **1998**, vol. 114, p 491. (g) Yin, X.; Moss, J. R. Recent Developments in the Activation of Carbon Dioxide by Metal Complexes. *Coord. Chem. Rev.* **1999**, *181*, 27-59. (h) Yaung, C. S.; Dong, V. M. Beyond Aresta's Complex: Ni- and Pd-Catalyzed Organozinc Coupling with CO$_2$. *J. Am. Chem. Soc.* **2008**, *130*, 7826-7827. (i) Grice, K. A. Carbon Dioxide Reduction with Homogenous Early Transition Metal Complexes: Opportunities and Challenges for Developing CO$_2$ Catalysis. *Coord. Chem. Rev.* **2017**, *336*, 78-95. (j) Mascetti, J. Metal Coordination of CO$_2$. *Encyclopedia of Inorganic and Bioinorganic Chemistry*. **2014**, 1-17. (k) Chiou, T.; Tseng, Y.; Lu, T.; Weng, T.; Sokaras, D.; Ho, W.; Kuo, T.; Jang, L.; Lee, J.; Liaw, W. [Ni^{III}(OMe)]-mediated Reductive Activation of CO$_2$ Affording a Ni(κ^1-OCO) Complex. *Chem. Sci.* **2016**, *7*, 3640.

---

7. (a) Shook, R. L.; Borovik, A. S. Role of the Secondary Coordination Sphere in Metal-Mediated Dioxygen Activation. *Inorg. Chem.* **2010**, *49*, 3646-3660. (b) Wodrich, M. D.; Hu, X. Natural Inspirations for Metal-Ligand Cooperative Catalysis. *Nat. Rev. Chem.* **2018**, *2*, 1-7.

8. Kraatz, H.-B.; Metzler-Nolte, N. *Concepts and models in bioinorganic chemistry*. Wiley-VCH: Weinheim, 2006.

9. (a) Jeoung, J. H.; Dobbek, H. Carbon Dioxide Activation at the Ni,Fe-Cluster of Anaerobic Carbon Monoxide Dehydrogenase. *Science*. **2007**, *318*, 1461-1464. (b) Amara, P.; Mouesca, J.; Volbeda, A.; Fontecilla-Camps, J. C. Carbon Monoxide Dehydrogenase Reaction Mechanism: A Likely Case of Abnormal CO_2 Insertion to a $Ni\text{-}H^-$ Bond. *Inorg. Chem.* **2011**, *50*, 1868-1878.

10. For selected works on the synthetic manipulation of second coordination sphere interactions: (a) Schmeier, T. J.; Dobereiner, G. E.; Crabtree, R. H.; Hazari, N. Secondary Coordination Sphere Interactions Facilitate the Insertion Step in an Iridium(III) CO_2 Reduction Catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 9274-9277. (b) Feller, M.; Gellrich, U.; Anaby, A.; Diskin-Posner, Y.; Milstein, D. Reductive Cleavage of CO_2 by Metal-Ligand-Cooperation Mediated by an Iridium Pincer Complex. *J. Am. Chem. Soc.* **2016**, *138*, 6445-6454. (c) Oren, D.; Diskin-Posner, Y.; Avram, L.; Feller, M.; Milstein, D. Metal-Ligand Cooperation as Key in Formation of Dearomatized Ni^{II}-Pincer Complexes and in Their Reactivity toward CO and CO_2. *Organometallics*. **2018**, *37*, 2217-2221. (d) Jiang, Y.; Blacque, O.; Fox, T.; Berke, H. Catalytic CO_2 Activation Assisted by Rhenium Hydride/$B(C_6F_5)_3$ Frustrated Lewis Pairs—Metal Hydrides Functioning as FLP Bases. *J. Am. Chem. Soc.* **2013**, *135*, 7751-7760. (e) Courtemanche, M.; Légaré, M.; Maron, L.; Fontaine, F. A Highly Active Phosphine-Borane Organocatalyst for the Reduction of CO_2 to Methanol Using Hydroboranes. *J. Am. Chem. Soc.* **2013**, *135*, 9326-9329. (f) Courtemanche, M.; Légaré, M.; Maron, L.; Fontaine, F. Reducing CO_2 to Methanol Using Frustrated Lewis Pairs: On the Mechanism of Phosphine-Borane-Mediated Hydroboration of CO_2. *J. Am. Chem. Soc.* **2014**, *136*, 10708-10717. (g) Parks, D. J.; Piers, W. E. Tris(pentafluorophenyl)boron-Catalyzed Hydrosilation of Aromatic Aldehydes, Ketones, and Esters. *J. Am. Chem. Soc.* **1996**, *118*, 9440-9441. (h) Chen, D.; Gau, M. R.; Dobereiner, G. E. Palladium and Platinum Complexes and Their Lewis Acid Adducts. Experimental and Computational Study of Thermodynamics and Bonding. *Organometallics.* **2015**, *34*, 4069-4075. (i) Becica, J.; Dobereiner, G. E. The Roles of Lewis Acid Additives in Organotransition Metal Catalysis. *Org. Biomol. Chem.* **2019**, *17*, 2055-2069.

11. (a) Williams, C. M.; Johnson, J. B.; Rovis, T. Nickel-Catalyzed Reductive Carboxylation of Styrene using CO_2. *J. Am. Chem. Soc.* **2008**, *130*, 14936-14937. (b) Fujihara, T.; Xu. T.; Samba, K.; Terao, J.; Tsuji, Y. Copper-Catalyzed Hydrocarboxylation of Alkynes using Carbon Dioxide and Hydrosilanes. *Angew. Chem. Int. Ed.* **2011**, *50*, 523-527. (c) Greenhalgh, M. D.; Thomas, S. P. Iron-Catalyzed, Highly Regioselective Synthesis of α-Aryl Carboxylic Acids from Styrene Derivatives and CO_2. *J. Am. Chem. Soc.* **2012**, *134*, 11900-11903. (d) Shirakawa, E.; Ikeda, D.; Masui, S.; Yoshida, M.; Hayashi, T. Iron-Copper Cooperative Catalysis in the Reactions of Alkyl Grignard Reagents: Exchange Reaction with Alkenes and Carbometalation of Alkynes. *J. Am. Chem. Soc.* **2012**, *134*, 272-279. (e) Li, S.; Ma, S. Quadri-Synergetic Effect for Highly Effective Carbon Dioxide Fixation and Its Application to Indoloquinolinone. *Adv. Synth. Catal.* **2012**, *354*, 2387-2394. (f) Ohishi, T.; Nishiura, M.; Hou, Z. Carboxylation of Organoboronic Esters Catalyzed by N-Heterocyclic Carbene Copper(I) Complexes. *Angew. Chem. Int. Ed.* **2008**, *47*, 5792-5795. (g) Zhang, L.; Cheng, J.; Ohishi, T.;

Hou, Z. Copper-Catalyzed Direct Carboxylation of C-H Bonds with Carbon Dioxide. *Angew. Chem. Int. Ed.* **2010**, *49,* 8670-8673.

12. Mlynarski, S. N.; Schuster, C. H.; Morken, J. P. Asymmetric Synthesis from Terminal Alkenes by Cascade of Diboration and Cross-Coupling. *Nature*. **2014**, *505*, 386-390.

13. For selected works involving boron-containing catalysts that facilitate organic transformations, see: (a) Tseng, K. T.; Kampf, J. W.; Szymczak, N. K. Modular Attachment of Appended Boron Lewis Acids to a Ruthenium Pincer Catalyst: Metal-Ligand Cooperativity Enables Selective Alkyne Hydrogenation. *J. Am. Chem. Soc.* **2016**, *138*, 10378-10381. (b) Bisht, R.; Chattopadhyay, B. Formal Ir-Catalyzed Ligand Enabled Ortho and Meta Borylation of Aromatic Aldehydes via in Situ-Generated Imines. *J. Am. Chem. Soc.* **2016**, *138,* 84-87. (c) Li, W.; Werner, T. $B(C_6F_5)_3$-Catalyzed Michael Reactions: Aromatic C-H as Nucleophiles. *Org. Lett.* **2017**, *19*, 2568-2571. (d) Li, H. L.; Kuninobu, Y.; Kanai, M. Lewis Acid-Base Interaction-Controlled *ortho*-Selective C-H Borylation of Aryl Sulfides. *Angew. Chem. Int. Ed.* **2017**, *56*, 1495-1499. (e) Karunananda, M. K.; Mankad, N. P. Cooperative Strategies for Catalytic Hydrogenation of Unsaturated Hydrocarbons. *ACS Cat.* **2017**, *7*, 6110-6119. (f) Lawson, J. R.; Melen, R. L. Tris(pentafluorophenyl)borane and Beyond: Modern Advances in Borylation Chemistry. *Inorg. Chem.* **2017**, *56*, 8627-8643. (g) Rao, B.; Kinjo, R. Boron-Based Catalysts for C-C Bond-Formation Reactions. *Chem. Asian. J.* **2018**, *13*, 1279-1292. (h) Yang, L.; Uemura, N.; Nakao, Y. meta-Selective C-H Borylation of Benzamides and Pyridines by an Iridium-Lewis Acid Bifunctional Catalyst. *J. Am. Chem. Soc.* **2019**, *141*, 7972-7979. (i) Nichols, B. R.; Akhmedov, N. G.; Petersen, J. L.; Popp, B. V. Access to a Pair of Ambiphilic Phosphine-Borane Regioisomers by Rhodium-Catalyzed Hydroboration. *Dalton Trans*. **2018**, *47*, 8456-8465. (h) Kiernicki, J. J.; Norwine, E. E.; Zeller, M.; Szymczak, N. K. Tuning Ligand Field Strength with Pendent Lewis Acids: Access to High Spin Iron Hydrides. *Chem. Commun.* **2019**, *55*, 11896-11899. (i) Tutusaus, O.; Ni, Chengbao, N.; Szymczak, N. K. A Transition Metal Lewis Acid/Base Triad System for Cooperative Substrate Binding. *J. Am. Chem. Soc.* **2013**, *135*, 3403-3406.

14. (a) Sandrock, D. L.; Jean- Gérard, L.; Chen, C.; Dreher, S. D.; Molander, G. A. Stereospecific Cross-Coupling of Secondary Alkyl β-Trifluoroboratoamides. *J. Am. Chem. Soc.* **2010**, *132*, 17108-17110. (b) Ohmura, T.; Awano, T.; Suginome, M. Stereospecific Suzuki-Miyaura Coupling of Chiral α-(Acylamino)benzylboronic Esters with Inversion of Configuration. *J. Am. Chem. Soc.* **2010**, *132*, 13191-13193. (c) Endo, K.; Ohkubo, T.; Hirokami, M; Shibata, T. Chemoselective and Regiospecific Suzuki Coupling on a Multisubstituted sp^3-Carbon in 1,1-Diborylalkanes at Room Temperature. *J. Am. Chem. Soc.* **2010**, *132*, 11033-11035. (d) Lee, J. C. H.; McDonald, R.; Hall, D. G. Enantioselective Preparation and Chemoselective Cross-Coupling of 1,1-diboron Compounds. *Nature Chemistry*. **2011**, *3*, 894-899.

15. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,

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M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, Fox, D. J. *Gaussian 09*, revision D.01, Gaussian, Inc., Wallingford CT, 2009.

16. The M06 functional was chosen for geometry optimizations after consideration of benchmarking results for a comparatively similar NHC-copper(I) system; see, Collins, L. R.; Rajabi, N. A.; Macgregor, S. A.; Mahon, M. F.; Whittlesey, M. K. Experimental and Computational Studies of the Copper Borate Complexes [(NHC)Cu(HBEt$_3$)] and [(NHC)Cu(HB(C$_6$F$_5$)$_3$)]. *Angew. Chem. Int. Ed.* **2016**, *55*, 15539-15543.
17. Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Account.* **2008**, *120*, 215-241.
18. (a) Krishman, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72,* 650. (b) Clark, T.; Chandrasekhar, J.; Schleyer, P. V. R. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21 G basis set for first-row elements, lithium to fluorine. *J. Comp. Chem.* **1983**, *4*, 294.
19. For DFT method benchmarking studies, see the Supporting Information.
20. Marenich, A. V; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B.* **2009**, *113*, 6378–6396.
21. (a) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 3.1*. **1998**, Theoretical Chemistry Institute, University of Wisconsin, Madison. (b) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E., Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. *NBO 6.0*. **2013**, Theoretical Chemistry Institute, University of Wisconsin, Madison. (c) Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 6.0: Natural Bond Orbital Analysis Program. *J. Comp. Chem.* **2013**, *34*, 1429-1437.
22. Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/
23. Plumley, J. A.; Evanseck, J. D. Periodic Trends and Index of Boron Lewis Acidity. *J. Phys. Chem. A.* **2009**, *113*, 5985-5992.
24. Batsanov, S. S. Van der Waals Radii of Elements. *Inorganic Materials*. **2001**, *37*, 871-885.
25. F. Weinhold and C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective* (Cambridge University Press, 2005), 760pp.
26. Weinhold, F.; Landis, C. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective.* Cambridge University Press: 2005.
27. Grigg, R. D.; Rigoli, J. W.; Van Hoveln, R.; Neale, S.; Schomaker, J. M. Beyond Benzyl Grignards: Facile Generation of Benzyl Carbanions from Styrenes. *Chem. Eur. J.* **2012,** *18*, 9391-9396.
28. Sadighi and coworkers previously prepared and characterized similar β-borylbenzyl-Cu(I)NHC complexes; however, their work was done in pentane solvent and no studies were reported addressing the Lewis acidic character of the boron moiety. Laitar, D. S.; Tsui, E. Y.;

Sadighi, J. P. Copper(I) β-Boroalkyls from Alkene Insertion: Isolation and Rearrangement. *Organometallics* **2006**, *25*, 2405-2408.

29. Lewis, G. N. Acids and Bases. *Journal of the Franklin Institute*. **1938**, *226*, 293-313.
30. Pauling, L. The Nature of the Chemical Bond. IV. The Energy of Single Bonds and The Relative Electronegativity of Atoms. *J. Am. Chem. Soc.* **1932**, *54*, 3570-3582.
31. Examination of Lewis pair interaction distance for hydrocarbyl and halo substituents showed no correlation to BVD nor E(2). We attribute this to the fact that the Lewis pair interaction distance is much shorter in these transition states thus reflecting significant structural changes at the boron fragment at the transition state.
32. Hydrocarboxylation of styrene was demonstrated stoichiometrically using a Cu(I)NHC; however, no reports of Cu(I)-catalyzed hydrocarboxylation of vinyl arenes have been reported to the best of our knowledge, see: Sirokman, G. (N-Heterocyclic-Carbene)Copper(I)-Catalyzed Carbon-Carbon Bond Formation Using Carbon Dioxide. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA. May 2007.
33. (a) Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. Homogeneous CO Hydrogenation: Ligand Effects on the Lewis Acid-Assisted Reductive Coupling of Carbon Monoxide. *Organometallics*. **2010**, *29*, 4499-4516. (b) Wang, C.; Xi, Z. Co-operative Effect of Lewis Acids with Transition Metals for Organic Synthesis. *Chem. Soc. Rev.* **2007**, *36*, 1395-1406 and references therein.
34. For diboration of unsaturated substrates, see these reviews and selected works: (a) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A.; Westcott, S. A.; Marder, T. B. Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse. *Chem. Rev.* **2016**, *116*¸ 9091-9161. (b) Xu, L.; Zhang, S.; Li, P. Boron-Selective Reactions as Powerful Tools for Modular Synthesis of Diverse Complex Molecules. *Chem. Soc. Rev.* **2015**, *44*, 8848-8858. (c) Palau-Lluch, G.; Sanz, X.; La Cascia, E.; Civit, M. G.; Miralles, N.; Cuenca, A. B.; Fernández, E. Organocatalytic Functionalisation through Boron Chemistry. *Pure Appl. Chem.* **2015**, *87(2)*, 181-193. **Alkynes**: (d) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. Platinum(0)-Catalyzed Diboration of Alkynes. *J. Am. Chem. Soc.* **1993**, *115*, 11018−11019. (e) Morgan, J. B.; Morken, J. P. Catalytic Enantioselective Hydrogenation of Vinyl Bis(boronates). *J. Am. Chem. Soc.* **2004**, *126*, 15338-15339. (f) Yoshida, H.; Kawashima, S.; Takemoto, Y.; Okada, K.; Ohshita, J.; Takaki, K. Copper-Catalyzed Borylation Reactions of Alkynes and Arynes. *Angew. Chem. Int. Ed.* **2012**, *51*, 235-238. **Alkenes**: (g) Coombs, J. R.; Morken, J. P. Catalytic Enantioselective Functionalization of Unactivated Terminal Alkenes. *Angew. Chem. Int. Ed.* **2016**, *55*, 2636-2649. (h) Zhang, L.; Huang, Z. Synthesis of 1,1,1-Tris(boronates) from Vinylarenes by Co-Catalyzed Dehydrogenative Borylations-Hydroboration. *J. Am. Chem. Soc.* **2015**, *137*, 15600-15603. **Dienes**: (i) Burks, H. E.; Kliman, L. T.; Morken, J. P. Asymmetric 1,4-Dihydroxylation of 1,3-Dienes by Catalytic Enantioselective Diboration. *J. Am. Chem. Soc.* **2009**, *131*, 9134-9135. **Imines**: (j) Mann, G.; John, K. D.; Baker, R. T. Platinum-Catalyzed Diboration Using a Commercially Available Catalyst: Diboration of Aldimines to α-Aminoboronate Esters. *Org. Lett.* **2000**, *2*, 2105-2108. (k) Hong, K.; Morken, J. P. Catalytic Enantioselective One-pot Aminoborylation of Aldehydes: A Strategy for Construction of Nonracemic α-Amino Boronates. *J. Am. Chem. Soc.* **2013**, *135*, 9252-9254.

Tables:

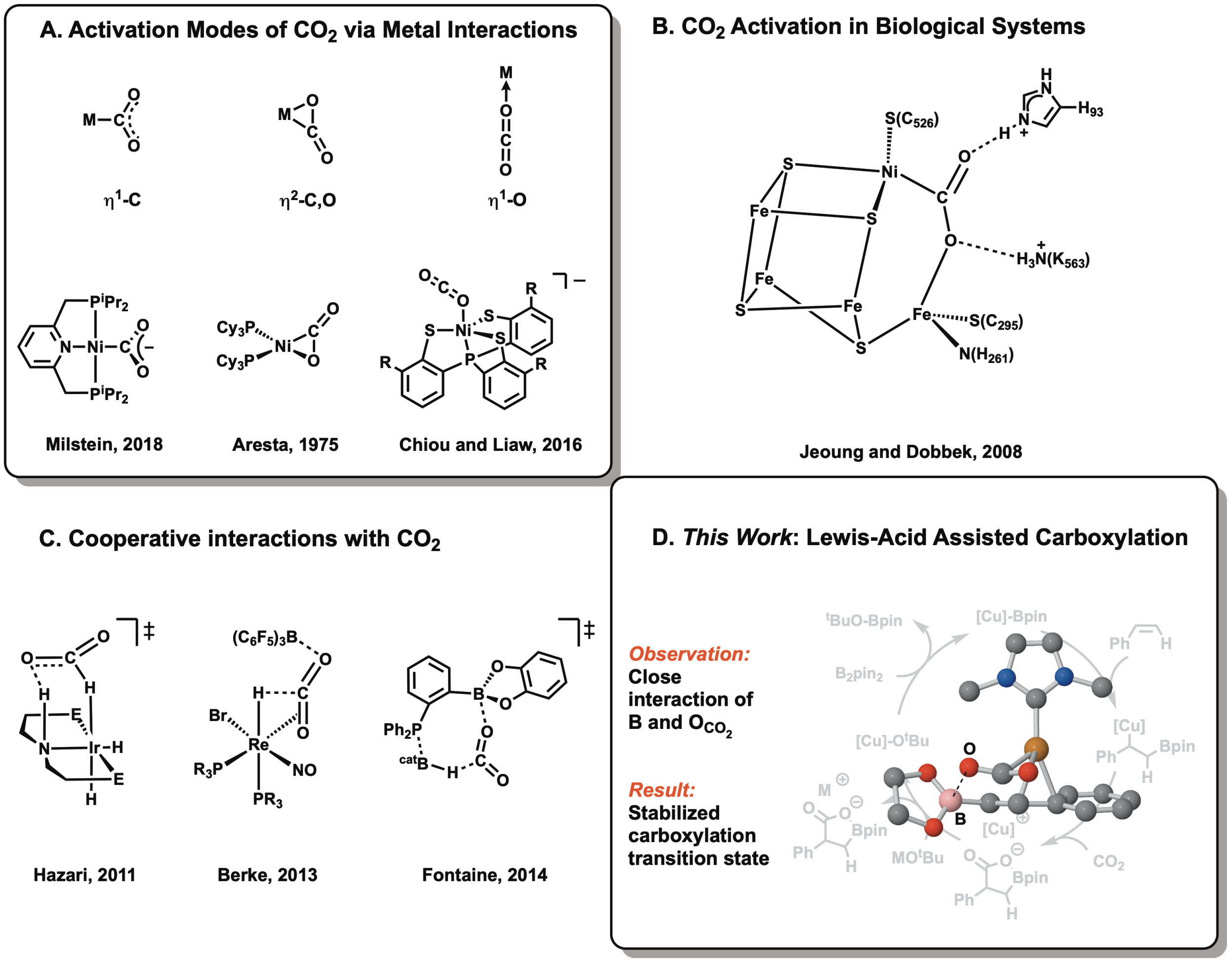
Table 1. Boron valence deficiency (BVD), natural charge (NC), CO_2 insertion enthalpy, and the distance between the boron atom and the appropriate oriented oxygen atom on CO_2 in the transition state ($r_{B—O}$).

Boron Fragment ($-BX_2$)	BVD[a]	Charge (*e*) on Boron[b]	$\Delta H^{\ddagger}_{smd}$ (kcal/mol)	$r_{B—O}$ (Å)
$-(F)_2$	1.33	1.30	2.56	1.93
$-(OMe)_2$	1.27	1.24	7.23	2.45
$-OCH_2CH_2O-$	1.24	1.20	6.75	2.49
$-O(CH)_2O-$	1.23	1.19	6.60	2.45
$-(OH)_2$	1.22	1.18	5.99	2.48
$-NH(CH_2)_2NH-$	1.04	1.02	8.16	2.75
$-(Ph)_2$	1.03	1.00	4.52	2.03
$-(CH_3)_2$	0.99	0.96	9.42	2.09
$-(NH_2)_2$	0.98	0.95	9.55	2.92
$-NH(CH)_2NH-$	0.94	0.92	10.26	2.90
$-(Cl)_2$	0.72	0.64	15.92	2.06
$-(H)_2$	0.40	0.39	22.66	1.90

[a] Boron valence deficiency determined by subtracting the NBO-calculated valence of boron at the transition state from the formal valence of boron (3). [b] Natural charge obtained from NBO analysis.

Figures:

Figure 1.



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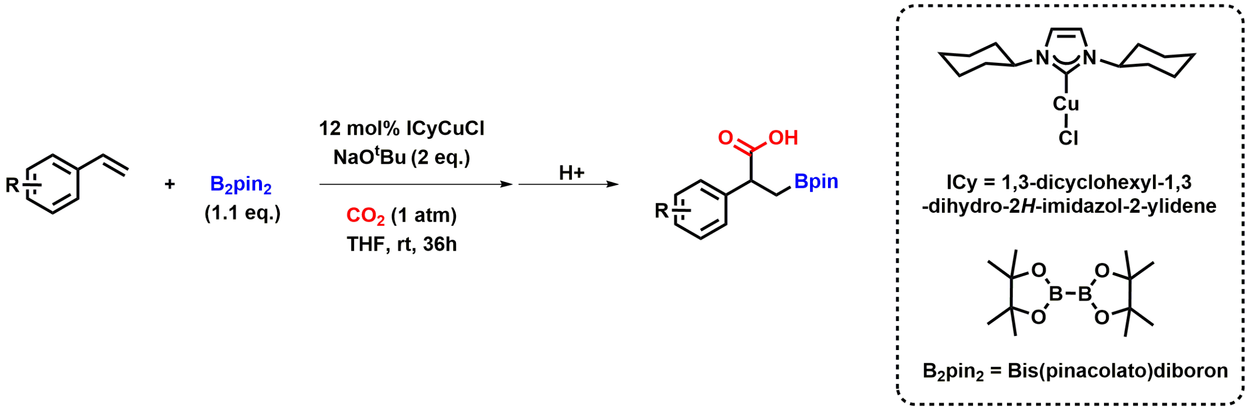

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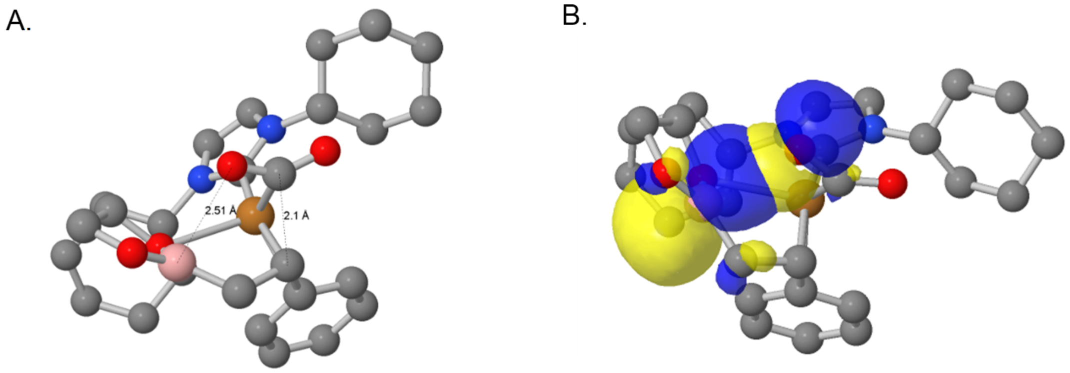

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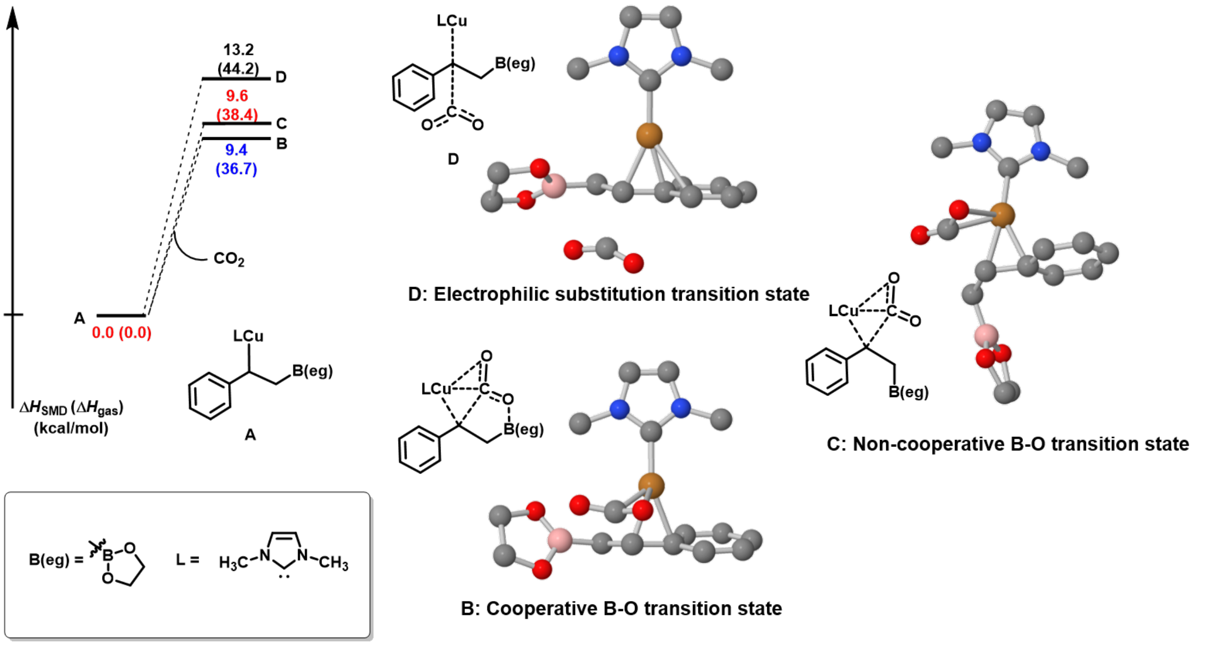

13.2
(44.2)
D
9.6
(38.4)
C
9.4
(36.7)
B
CO₂
A
0.0 (0.0)
ΔH_SMD (ΔH_gas)
(kcal/mol)
LCu
B(eg)
A
D
D: Electrophilic substitution transition state
C: Non-cooperative B-O transition state
B: Cooperative B-O transition state
B(eg) =
L =
H₃C–N N–CH₃

Figure 5:

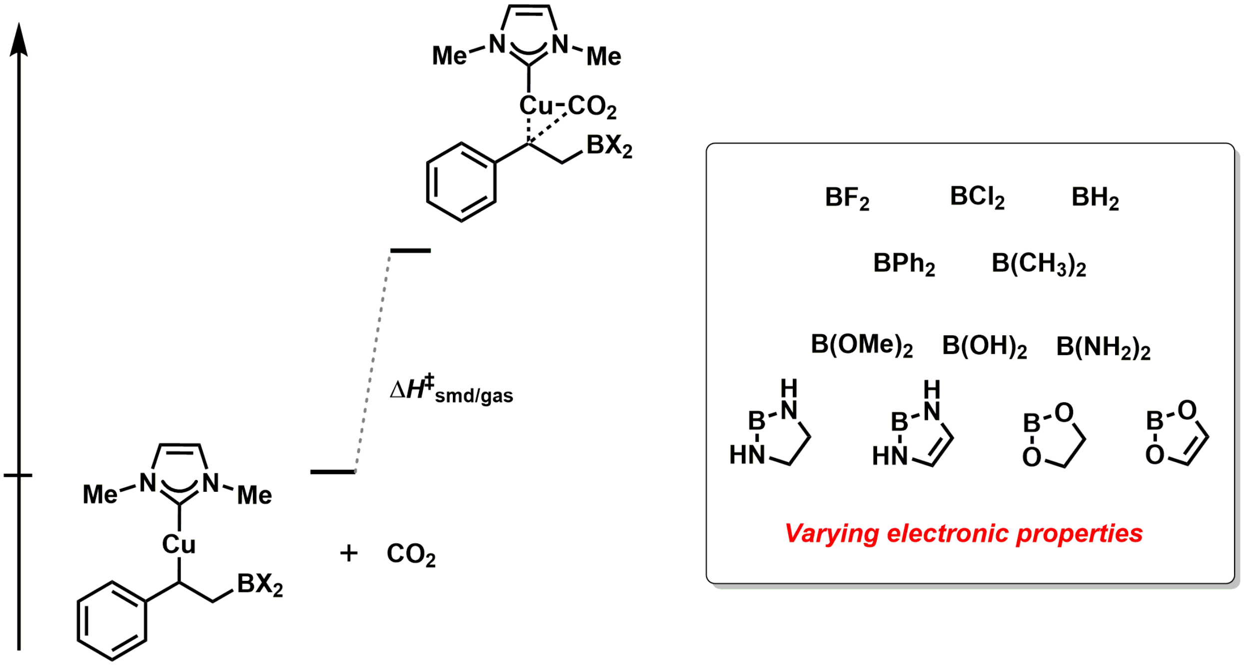
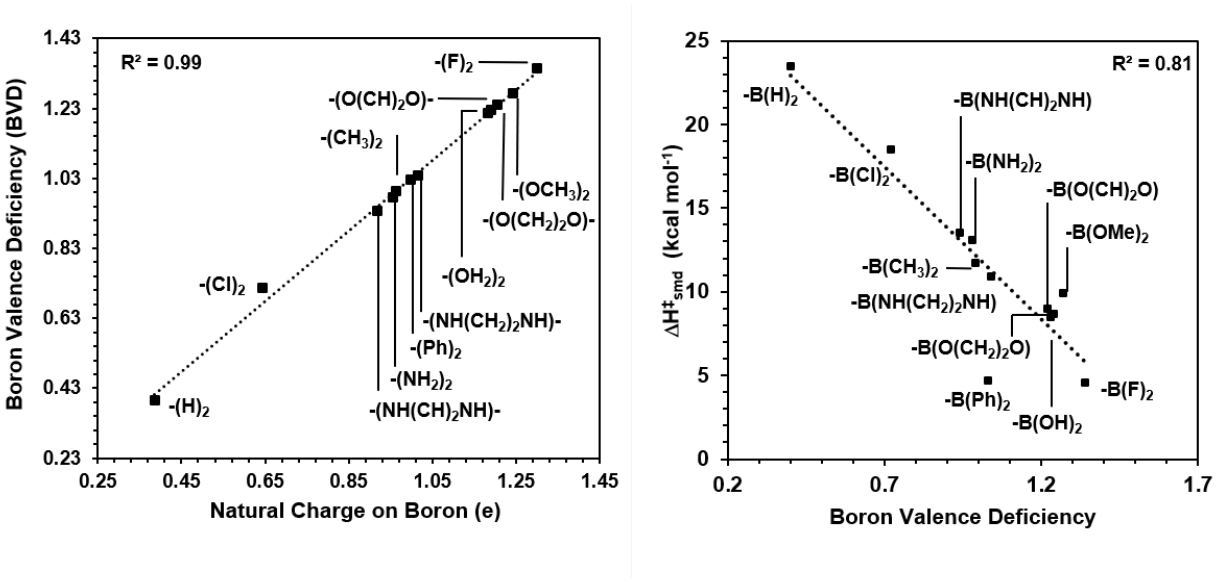

Me–N N–Me
Cu-CO₂
BX₂
ΔH‡smd/gas
Me–N N–Me
Cu
BX₂
+ CO₂
BF₂
BCl₂
BH₂
BPh₂
B(CH₃)₂
B(OMe)₂
B(OH)₂
B(NH₂)₂
H
B-N
HN
H
B-N
HN
B-O
O
B-O
O
Varying electronic properties

Figure 6:



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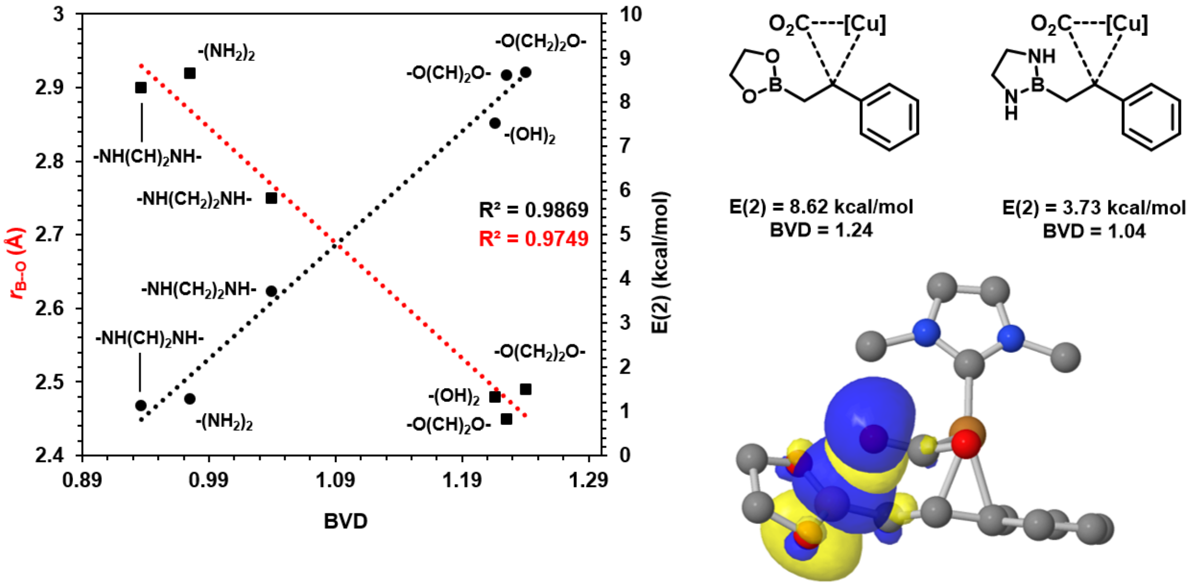

Figure 8:

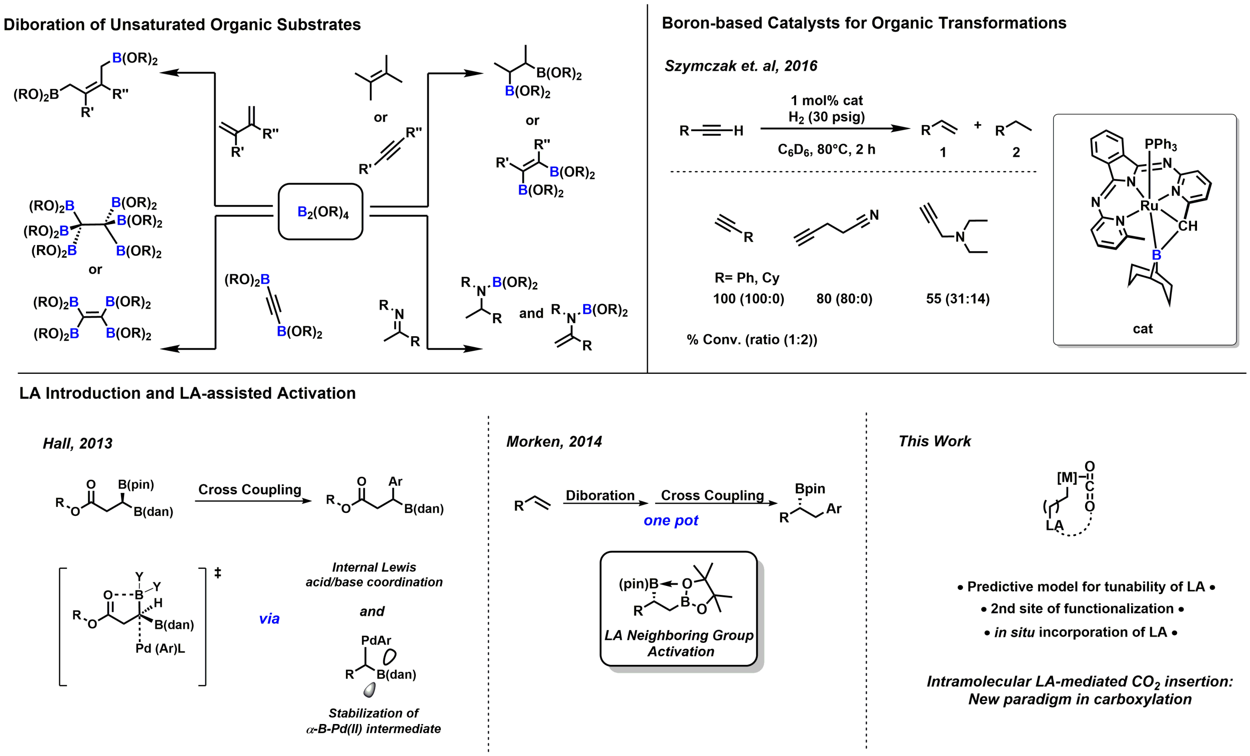

Figure captions:

Figure 1. A) Common CO_2 activation modes and examples of CO_2-ligated metal complexes. B) Active site of anaerobic carbon monoxide dehydrogenase from *C. hydrogenoformans*. C) Examples of transition metal and frustrated Lewis pair cooperative binding of CO_2 leading to activation/functionalization. D) *This work:* DFT-derived transition state structure suggesting Lewis acid-assisted carboxylation during Cu-catalyzed boracarboxylation of vinyl arenes.

Figure 2. The Cu(I)-catalyzed boracarboxylation of vinyl arenes.

Figure 3. A) Computed molecular structure of $ICyCu^{I}$-benzyl carboxylation transition state, illustrating an interaction between the boron atom of the ethyleneglycato (eg) boron ester and the proximal oxygen of CO_2. B) Relevant natural bond orbitals illustrating a non-covalent Lewis acid-base interaction. Hydrogen atoms are omitted for clarity.

Figure 4. Energetically feasible transition states for CO_2 insertion in the carboxylation reaction pathway as well as the respective gas- and solvent-phase $\Delta H^{\ddagger}$ values.

Figure 5. Reaction coordinate for carboxylation of β-borylbenzyl-Cu(I) species and the various boron substituents employed.

Figure 6. A) Natural charge on boron in each computed CO_2 insertion transition state structure and the associated boron valence deficiency. B) The effect of boron valence deficiency on the enthalpic barrier of CO_2 insertion in boracarboxylation mechanism.

Figure 7. Stabilization energies from NBO analysis of analogous oxygen- and nitrogen- containing boron fragments (black trace) and the relationship to the corresponding B-O interaction distances (red trace). Molecular structures featuring computed NBO interaction O(lp) → B(lp*) in IMeCu(CH(Ph)CH_2B(eg)) is shown on right. Hydrogens omitted for clarity.

Figure 8. **Top left:** A representative example of diboration reactions using diboron(4) compounds. **Top right:** A ligand-appended Lewis acid moiety participates in hydrogenation of alkyne substrates. **Bottom left:** Selective cross coupling that combines the concepts of intramolecular Lewis acid/base chelation and stabilizing neighboring effect of second boron substituents. **Bottom center:** Rare example of a one-pot diboration/cross-coupling through neighbor group activation. **Bottom right:** Generalized depiction of carboxylation chemistry using intramolecular Lewis-acid activation of CO_2.