Synthetic and Catalytic Studies of Group 11 N-Heterocyclic Carbene Complexes

By David S. Laitar

B.S. Chemistry, University of Notre Dame, 2001

Submitted to the Department of
Chemistry in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY IN
INORGANIC CHEMISTRY

At the

Massachusetts Institute of Technology

May, 2006
[June 2006]

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Abstract

This thesis presents the synthesis, structure and reactivity of two-coordinate Group 11 metal complexes, supported by N-heterocyclic carbene (NHC) ligands. The NHC ligand was found to stabilize monomeric, terminal fluoride complexes of copper, silver and gold, the last representing the first isolable gold(I) fluoride. These complexes were shown to be reactive synthons for new metal complexes.

The ability of the NHC ligand to support unusual coordination environments for these metals inspired us to explore the chemistry of copper(I) bonded to various main group elements, leading to the development of new catalytic reactions. The first well-characterized copper(I) boryl complex was synthesized and shown to react with a variety of unsaturated organic substrates. This complex reacts rapidly with CO_2 to form CO and a copper(I) borate complex. The boryl complex may be regenerated by treatment of the borate complex with the bis(pinacolato)diboron, (pin)B–B(pin), giving the stable byproduct (pin)B–O–B(pin). The use of a copper(I) alkoxide precatalyst and stoichiometric diboron reagent results in catalytic reduction

of CO_2, with high turnover numbers (1000 per Cu) and frequencies (100 per Cu in 1 hour) depending on supporting ligand and reaction conditions. Carbon dioxide also inserts into the Cu–Si bond of a copper silyl complex. The resulting complex evolves CO to give a copper siloxide complex.

Mesitaldehyde inserts cleanly and selectively into the Cu–B bond of (NHC)CuB(pin), to form a B–O and a copper–carbon bond. This complex reacts with bis(pinacolato)diboron to regenerate (NHC)CuB(pin) and produce an aldehyde diboration product, in which a diboron reagent has been added across the C=O bond of mesitaldehyde. A copper boryl complex with a smaller NHC supporting ligand proved to be a much more effective diboration catalyst and a wide range of aldehydes react cleanly with bis(pinacolato)diboron.

The insertion of alkenes into an (NHC)copper(I) boryl affords isolable β-boroalkyl complexes in high yields; competition experiments using substituted styrenes show that electron-donating substituents slow the reaction. Although the insertion products are stable at ambient temperature, a β-hydride elimination/reinsertion sequence affords a rearranged α-boroalkyl complex on heating.

Thesis Supervisor: Joseph P. Sadighi

Title: Assistant Professor of Chemistry

Acknowledgements

First, I would like to thank my advisor Professor Joseph Sadighi. Over the years, I have learned a large amount of chemistry from Joseph. He taught me not only how to make a specific reaction work, but also more broadly how to turn a specific reaction into a research project. His unwavering enthusiasm and thoughtful suggestions, particularly when my projects weren't cooperating, were essential to my successes. I also thank him for always treating me with respect, something that is not a guarantee when working for an assistant professor.

I would also like to thank Professor Richard Schrock for being my thesis chair, and Professor Stephen Lippard for being on my committee. I was privileged to be Professor Daniel Nocera's teaching assistant for two semesters in 5.04, and have a much greater respect for the words "first principles" and "perturbation" as a result. I would also like to thank all of the other chemistry faculty members that I have come in contact with during graduate school.

My graduate research was greatly aided by two staff scientists. Dr. Peter Müller has taught me an incredible amount of crystallography and is a good friend. Also, Dr. David Bray has readily and cheerfully answered all of my NMR questions.

I am grateful to Professor Seth Brown for doing an excellent job in preparing me for graduate school and for his continued advice. Professor Angel Pu, a former postdoc in the Brown group, has continued to be a close friend, and I greatly appreciate all of the support that she has given me throughout my graduate school career.

I have learned a lot from my fellow lab mates in the Sadighi group, and would like to thank all past and present members for making my experience in lab enjoyable. In particular, I would like to thank Charles Hamilton for being a good roommate and friend. It is quite an achievement that we are still friends after seeing each other almost constantly for four years.

Jennifer Akana has helped me get through the day with entertaining conversations and the occasional corny joke. I was privileged to supervise a terrific undergraduate, Emily Tsui, and I thank her for her patience and her willingness to try my sometimes hare-brained suggestions. I also thank Greg Sirokman for attempting to broaden my musical tastes.

Sze-Sze Ng and William Neeley are great friends and I thank them for all of the dinners, movies, and nights out on the town that we have shared.

Lastly, I would like to thank my parents. All that I have accomplished in my life is the result of their love and support.

Preface

Parts of this thesis have been adapted from articles co-written by the author. The following articles were reproduced in part with permission from the American Chemical Society:

Laitar, D. S.; Mathison, C. J. N.; Davis, W. M.; Sadighi, J. P. "Copper(I) Complexes of a Heavily Fluorinated β-Diketiminate Ligand: Synthesis, Electronic Properties and Intramolecular Aerobic Hydroxylation." *Inorg. Chem.* **2003**, *42*, 7354–7356.

Laitar, D. S.; Müller, P.; Sadighi, J. P.; Gray, T. G. "A Carbene-Stabilized Gold(I) Fluoride: Synthesis and Theory." *Organometallics* **2005**, *24*, 4503–4505.

Laitar, D. S.; Müller, P.; Sadighi, J. P. "Efficient Homogeneous Catalysis in the Reduction of CO_2 to CO." *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197.

Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. "Copper(I) β-Boroalkyls from Alkene Insertion: Isolation and Rearrangement" *Organometallics* **2006**, *25*, 2405–2408.

Respective Contributions

Much of the work in described in this thesis was the result of collaborative efforts:

Dr. Joseph P. Sadighi first synthesized (IPr)CuCl, and Mr. Neal P. Mankad first synthesized (IPr)CuO*t*-Bu, two starting materials that were critical for much of the work in this thesis.

Research for the chapter titled "Insertion of Aldehydes into Cu–B bonds: a Stoichiometric and Catalytic Study" was done in collaboration with Ms. Emily Y. Tsui. In the methodology part of that chapter, many of the initial reactions and optimizations were performed by Ms. Tsui. Also, many of the compounds in Table 1 of that chapter were synthesized by her and are noted as such. Single crystals of α-[(pinacol)boroxy]-(2,4,6-trimethyl) benzyl(pinacol)boronate used in an X-ray diffraction study performed by the author were grown by Ms. Tsui.

Ms. Tsui also identified the regiochemistry of the insertion of styrene into the Cu–B bond of (IPr)CuB(pin) in the chapter titled "Copper(I) β-Boroalkyls from Alkene Insertion: Isolation and Rearrangement."

Dr. Thomas Gray performed all of the DFT calculations in the group 11 metal fluoride chapter.

Mr. Casey J. N. Mathison discovered that the heavily fluorinated β-diketimines in the Appendix could be synthesized through use of an Aza-Wittig reaction.

Dr. Peter Müller helped model disordered solvent molecules in several crystal structures presented in this thesis and was instrumental in solving the crystal structure of (IPr)CuOB(pin), which was a pseudo-merohedral twin, in Chapter 2.

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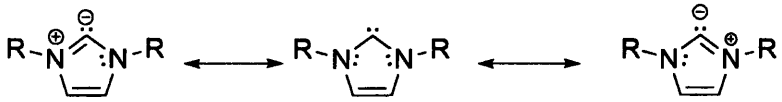
Introduction

The first N-heterocyclic carbene (NHC) metal complexes were reported independently by Wanzlick and Öfele in 1968.[1] Since the discovery that many imidazole-derived N-heterocyclic carbenes are stable, isolable compounds in their free form,[2] the use of these ligands in organometallic chemistry has dramatically increased.[3] N-Heterocyclic carbenes are neutral 2-electron donors, often compared to electron-rich phosphines in their donor strength (Scheme 1).[4] DFT calculations on NHC group 11 metal complexes show that these ligands primarily interact with a metal center through strong σ-donation, and to a lesser extent through a π-interaction.[5]

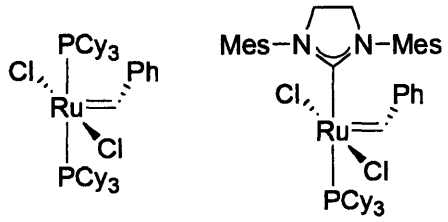
Scheme 1. Resonance forms of imidazole-based N-heterocyclic carbene compounds.



N-Heterocyclic carbene ligands in catalysis

One of the earliest and most effective uses of NHCs in catalysis was in ruthenium catalyzed olefin metathesis. The replacement of one phosphine ligand in $(Cy_3P)_2Cl_2Ru{=}CHR$ with an NHC ligand dramatically improved both the reactivity and stability of the ruthenium alkylidene in metathesis reactions (Figure 1).[6–8] The (NHC)-supported catalyst showed higher activity than the bisphosphine analogue for the ring-opening metathesis polymerization of unstrained and even sterically hindered olefins.[9] This catalyst was also effective in the ring-closing metathesis of sterically hindered dienes to form tri- and even tetra-substituted olefins.[10]

Figure 1. 1st and 2nd generation of the Grubbs catalyst.



[Ref 6]

Mes = 2,4,6-trimethylphenyl

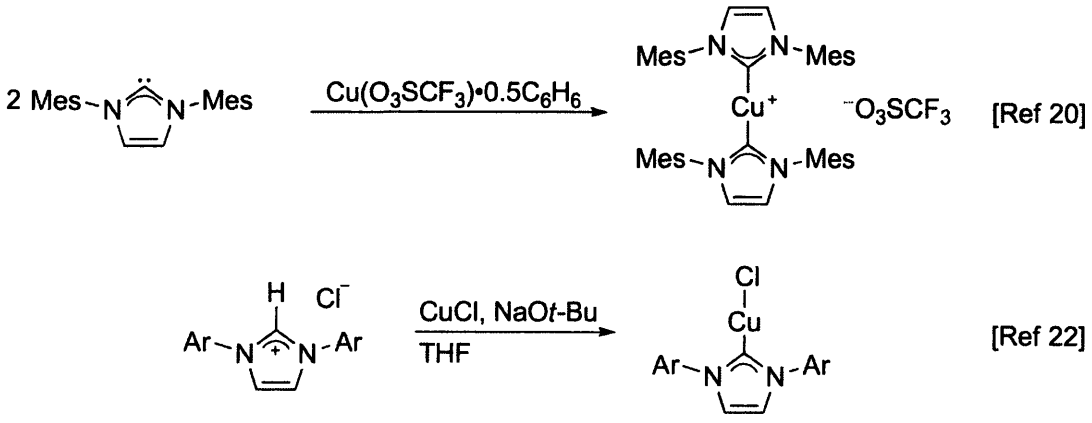
A similar, though somewhat less dramatic effect was observed when N-heterocylic carbene ligands were used in place of sterically demanding electron-rich phosphine ligands to support cross-coupling catalysts. These catalysts possess high thermal stability, and their activity is often comparable to that of phosphine-supported systems.[3] Herrmann and co-workers reported the first use of (NHC)metal catalysts in this context, demonstrating that biscarbene palladium complexes were active catalysts for the Heck reaction.[11] Shortly thereafter, the groups of Herrmann[12] and Nolan[13] reported that (NHC)palladium complexes are effective catalysts for Suzuki-Miyaura coupling reactions. Since then, (NHC)metal catalysts have been used in an array of cross-coupling reactions including the Kumada,[14] Sonogashira,[15] Stille[16] and Negishi[17] couplings. N-Heterocyclic carbenes have also been used as supporting ligands for a variety of other C–C bond-forming reactions,[18] notably the three-component reductive coupling of aldehydes, allenes, and silanes,[18a] and in carbon-heteroatom bond-forming reactions such as the Buchwald-Hartwig amination.[19]

The stoichiometric and catalytic reactivity of N-heterocyclic carbene copper complexes

The first (NHC)copper(I) complex, reported in 1993, was $[(NHC)_2Cu][O_3SCF_3]$, a homoleptic two-coordinate complex (Scheme 2).[20] A year later, the first mono(carbene)copper complexes were reported, and were synthesized by *N*-alkylation of *C*-bound (azolyl)copper(I) complexes.[21] Sadighi, Buchwald and coworkers later reported that mono(carbene)copper

complexes can be prepared by reaction of *in-situ*-generated free carbenes with copper(I) salts.[22] N-Hetercyclic carbene complexes of copper(I) are typically two-coordinate; however, when the carbenes are incorporated into chelating ligands, including *N*-(2-pyridyl)carbenes (Danopoulos),[23] *N*-(α-hydroxyalkyl)carbenes (Arnold),[24] and tris(carbene) pincers (Meyer),[25] higher coordination numbers are observed. The bridging of an NHC ligand across two copper centers has also been reported.[26] Although much more rare, (NHC)copper(II) complexes are also found in the literature.[27]

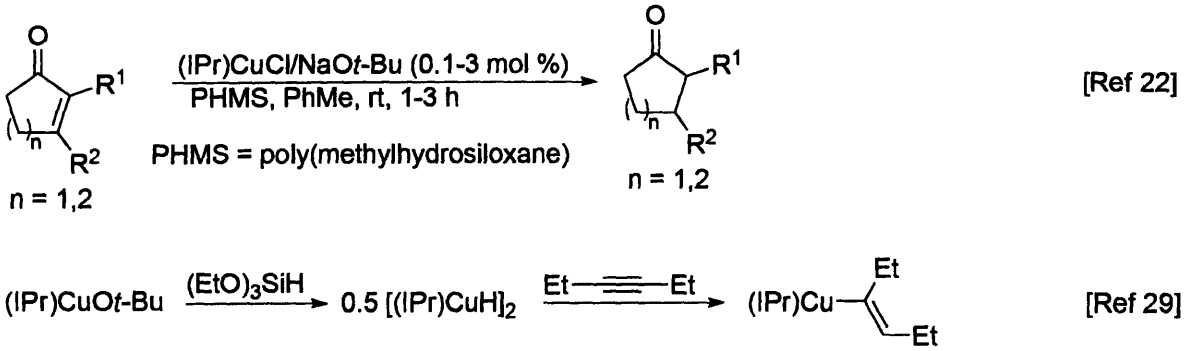
Scheme 2. Synthesis of (NHC)copper(I) complexes.



The first catalytic use of an (NHC)copper complex was reported by Jurkauskas, Sadighi and Buchwald, who used (IPr)CuCl, in combination with sodium *tert*-butoxide, as a precatalyst for the conjugate hydrosilylation of α,β-unsaturated carbonyl compounds (Scheme 3).[22] They reported that [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) chloride, [(IPr)CuCl], was an effective precatalyst in the presence of sodium *tert*-butoxide for the conjugate reduction of α,β-unsaturated carbonyl compounds with silanes. Nolan and coworkers later showed that (NHC)copper(I) complexes were also suitable catalysts for the 1,2-hydrosilylation of ketones.[28] Sadighi and coworkers examined certain intermediates in this catalytic cycle: They prepared

(IPr)CuO*t*-Bu from (IPr)CuCl in good yield and showed that it reacts with triethoxysilane to form a dimeric copper hydride complex, $[(IPr)CuH]_2$, which was isolated and structurally characterized. This hydride reacts cleanly with alkyne to give a well-defined copper vinyl product.[29] This reactivity with alkynes is in stark contrast with phosphine ligated copper hydrides, which react with alkynes to give hydrogenation[30] or reductive coupling products[31] rather than well defined insertion products.

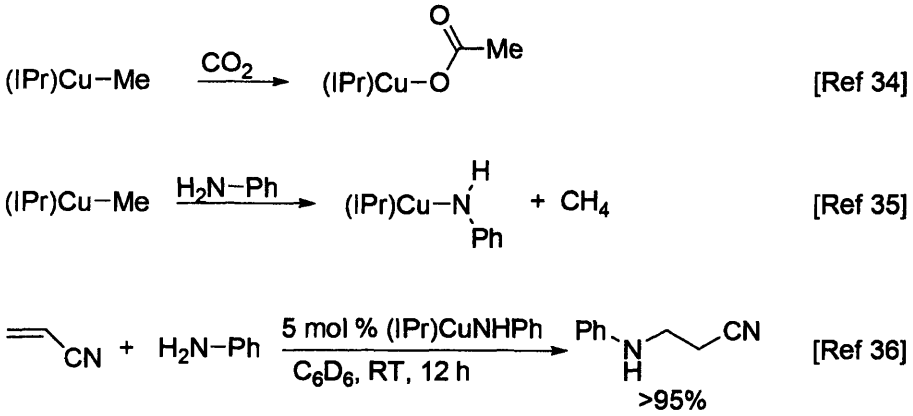
Scheme 3.



Subsequently, Díaz-Requejo, Pérez and coworkers found (IPr)CuCl to be a very effective catalyst for the transfer of carbenes from diazo compounds to olefins, alcohols, and amines without substantial formation of olefinic byproducts through diazo coupling.[32] The very low background reactivity between the (NHC)copper complex and ethyl diazoacetate helps account for the suppression of this normally important side-reaction. A complex with a more weakly coordinating anion $[(IPr)Cu][B(Ar^f)_4]$ [Ar^f = 3,5-bis(trifluoromethyl)phenyl] is a competent catalyst for carbene transfer from ethyl diazoacetate to the C–H bonds of unactivated alkanes.[33]

N-Heterocyclic-carbene ligated copper alkyl complexes have also been used in a variety of stoichiometric and catalytic processes (Scheme 4). Sadighi and coworkers reported that the two-coordinate, (IPr)CuMe reacts with CO_2 to form (IPr)CuOAc.[34] The acetate group in the solid-state structure of (IPr)CuOAc coordinates in a κ^1-binding mode. Calculations on a model complex, using density functional theory (DFT), indicate that the binding of acetate in a κ^1- versus a κ^2-fashion is approximately thermoneutral. The minimal energetic cost in going from a bidentate to a monodentate binding mode highlights the abiltiy of the NHC ligand to engender low-coordination numbers. Gunnoe and coworkers reported that weakly acidic compounds such as aniline, phenol, and phenylacetylene react with (IPr)CuMe to form methane and copper anilide, phenoxide, and acetylide complexes.[35] These copper anilide and phenoxide complexes are active catalysts for the Michael addition of N–H and O–H bonds to electron-poor olefins.[36] N-Heterocyclic-carbene supported copper alkyl complexes may also be intermediates in the catalytic alkylation of allylic phosphonates with dialkyl zinc or Grignard reagents.[27d,27f,37]

Scheme 4.

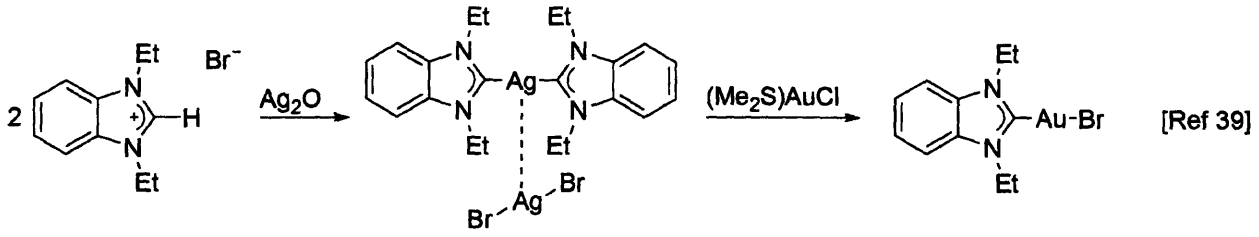


N-Heterocyclic carbene silver complexes: useful carbene transfer agents

The first silver complex of an N-heterocyclic carbene was synthesized by Arduengo and coworkers in 1993.[20] The chemistry of (NHC)silver complexes lay dormant until the discovery

by Wang and Lin in 1998 that such complexes readily transfer the NHC ligand to other metal centers (Scheme 5).[38] This method for the synthesis of new (NHC)metal complexes avoids the handling of free carbenes, which can be air- and moisture-sensitive, and is particularly useful when thermal instability precludes isolation of the free carbene. The wide range of interesting structures that (NHC)silver complexes adopt in the solid state has recently been reviewed.[39] Calculations using DFT indicate that (NHC)silver complexes have the weakest metal-carbene bond of the group 11 metals.[5] While this feature makes them useful as carbene transfer agents, it is undesirable for catalytic systems, and only two reports using (NHC)silver catalysts are found in the literature: Peris, Fernandez and coworkers found an (NHC)silver complex to be an effective catalyst for the diboration of alkynes and internal alkenes,[40] and Díaz-Requejo and Pérez used (NHC)silver complexes to catalyze carbene transfer from ethyl diazoacetate to the C–H bonds of cyclohexane.[41]

Scheme 5.

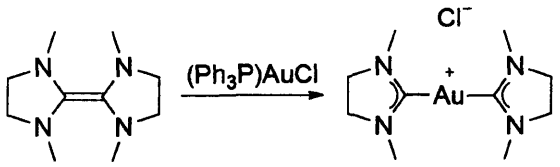


The stoichiometric and catalytic reactivity of N-heterocyclic carbene gold complexes

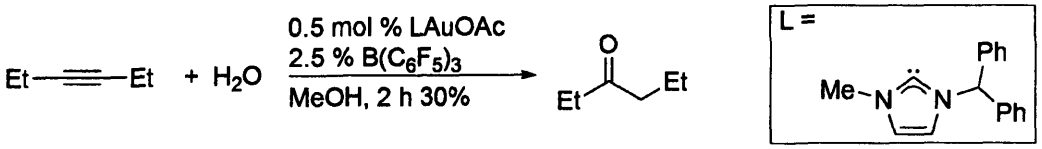
Gold complexes of N-heterocyclic carbenes have been known for more than a quarter of a century.[42] Lappert and coworkers prepared an (imidazolinylidene)gold complex through cleavage of the C=C bond in a tetraaminoalkene by $(Ph_3P)AuCl$ (Scheme 6).[43] Other (NHC)gold complexes have been prepared by a range of methods, including addition of free carbenes to gold complexes,[44] transfer of carbenes from (NHC)silver complexes to gold precursors,[38] and

alkylation or protonation of gold azolyl complexes.[45] Herrmann and coworkers reported that effective (NHC)gold catalysts for the hydrolysis of alkynes to ketones.[46] Cationic (NHC)gold complexes also catalyze carbene transfer from ethyl diazoacetate to unactivated aromatic C–H bonds.[47]

Scheme 6.



[Ref 43]



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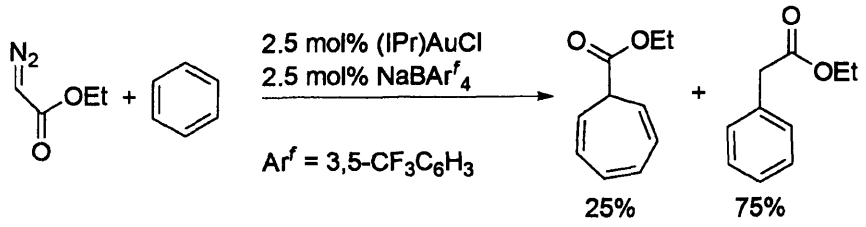


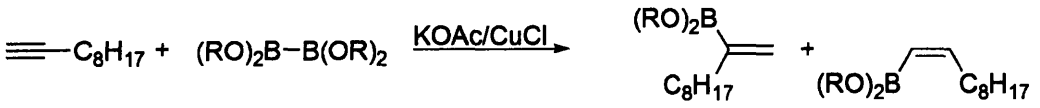
[Ref 47]

Research project goals

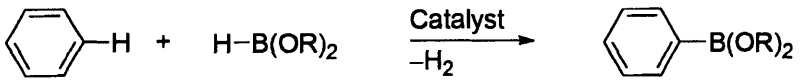
Since NHC ligands stabilize reactive copper alkyl and hydride complexes in low-coordination geometries, we set out to synthesize other (NHC)copper complexes expected to display interesting reactivity, such as the fluorides of the monovalent group 11 metals.[49] This effort led to the synthesis of the first well-defined copper(I) boryl complex. Copper boryl complexes were proposed as intermediates in the reaction of alkynes and α,β-unsaturated ketones with diboron reagents in the presence of copper(I) chloride and potassium acetate;[48] however, well-characterized copper boryl complexes had not been reported.

Metal boryl complexes have a very rich chemistry (Scheme 7).[49] For example, certain metal boryl complexes are catalysts for the borylation of C–H bonds in unactivated aromatic and alkyl hydrocarbons.[50] Metal boryl complexes are also intermediates in the metal-catalyzed hydroboration of alkenes and alkynes.[51] In the closely related diboration of alkenes and alkynes,[52] it is difficult to study the insertion of olefins into M–B bonds due to rapid β-hydride elimination from metal alkyl intermediates. We felt that a d^{10}-copper center would facilitate the study of olefin insertion, permitting isolation of the β-boroalkyl insertion product. We were also interested in studying the reactivity of a copper boryl complex towards substrates, such as carbon dioxide and aldehydes, whose reactions with metal boryl complexes had not been described.

Scheme 7.



[Ref 48]



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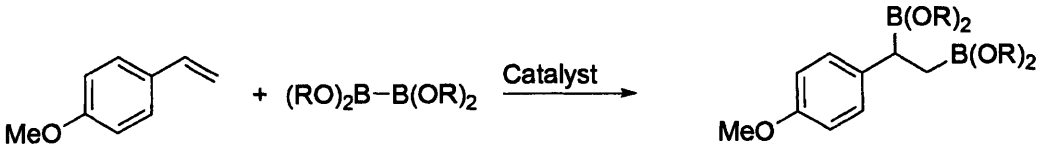

[Ref 51]

My first research goal was the synthesis of low-coordinate copper complexes designed to catalyze electrophilic heteroatom transfer reactions. A key feature of these complexes was the use of anionic, heavily fluorinated chelate ligands. The synthetic and reactivity studies of several

of these ligands and complexes are presented in the Appendix. We achieved advances in ligand synthesis, and described a new mode of reactivity in the aerobic oxidation of copper(I) diketiminates. The catalytic goals of this effort remain elusive, due in part to the tendency of these complexes to form dimers, except in the case of extremely bulky ligands that also shut down the desired reactivity. At the same time, the difficulty in incorporating certain fluorinated organic moieties into some of the desired ligands underscored how useful new C–F bond-forming methodologies could be. The (NHC)metal fluorides were first synthesized to explore their utility for this purpose. However, the strong tendency of NHC ligands to induce low coordination geometries through their electronic properties as well as through steric bulk, and the demonstrated ability of the NHC ligand to stabilize a complex with filled metal-ligand π^* orbitals, suggests that these ligands might in the future prove useful in the role for which our β-diketiminates were developed: supporting reactive oxo and imido complexes.

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Chapter 1

Carbene-Stabilized Group 11 Fluorides: Synthesis, Reactivity and Theory

Parts of this chapter have been adapted from:

Laitar, D. S.; Müller, P.; Sadighi, J. P.; Gray, T. G. "A Carbene-Stabilized Gold(I) Fluoride: Synthesis and Theory." *Organometallics* **2005**, *24*, 4503–4505.

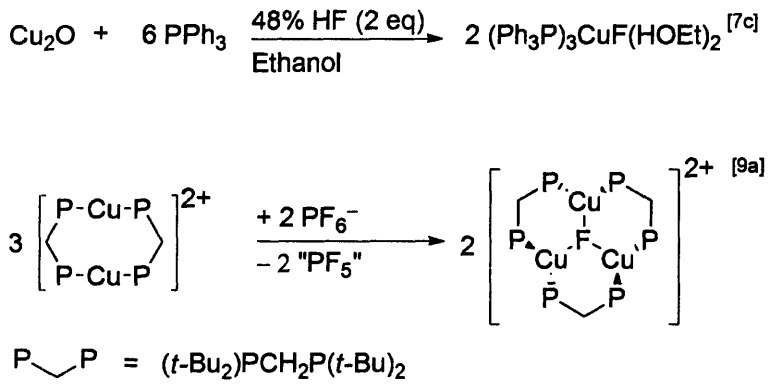
Fluoride complexes of the late transition metals raise interesting questions in bonding and display unusual reactivity. The fluoride ion, according to hard/soft acid-base theory,[1] is mismatched with the cations formed by late transition metals in low oxidation states. Its π-donating ability, moreover, can lead to destabilizing interactions with filled d-orbitals.[2–5] The resulting metal–fluorine bonds tend to be labile and reactive.[3] Such complexes have excited considerable synthetic interest, greatly intensified in recent years,[4] and have been studied in the context of C–F bond cleavage[5] and formation.[6]

Despite the attention paid to late transition metal fluoride complexes, low-valent fluoride complexes of group 11 are rare, with only a small number of examples found in the literature. The first copper(I) fluoride complex, $(Ph_3P)_3CuF$, isolated as ethanol or methanol adducts, was prepared by reaction of aqueous HF with Cu_2O in the presence of triphenylphosphine in alcohol solvent (Scheme 1).[7] This complex has found use as a precatalyst for several organic transformations, notably the aldol reaction of silyl ketene acetals with ketones.[8] The only other structurally characterized copper(I) fluoride complex was prepared by abstraction of fluoride from the PF_6^- counter ion of a dicationic diphosphinomethane copper(I) dimer to give a trigonal planar μ_3-fluorido complex.[9a]

In contrast to CuF and AuF, which are unstable to disproportionation, AgF is a stable salt, and as a result, silver(I) fluoride complexes are common. The complexes are typically polynuclear, with fluoride bound to two, three or six silver atoms.[10] The presumably monomeric $[(p\text{-tol})_3P]_3AgF$ has also been reported, but full characterization is lacking.[10a] Perhaps the most mismatched of all transition-metal fluorides, gold(I) fluoride was once thought impossible to prepare.[11] Only recently detected in the gas phase, AuF has been studied as a discrete

molecule,[12] and as noble gas[13a,b] and CO[13c] adducts. Prior to this work, no gold(I) fluoride complexes had been isolated.

Scheme 1. Previously synthesized copper(I) fluoride complexes.



N-Heterocyclic carbene (NHC) ligands,[14] particularly of the type developed by Arduengo and co-workers,[15] appeared ideally suited to the stabilization of low-valent late transition metal fluoride complexes. Such ligands have found recent use in the synthesis of new copper,[16] silver,[17] and gold complexes,[18] and the nature of the bonding between NHCs and group 11 metals has been investigated theoretically.[19] The possibility that a reactive copper(I) fluoride might catalyze the conversion of aryl halides to aryl fluorides, a transformation that currently lacks generality,[4c] was an exciting one. Copper catalysts have been used for cross coupling C–X bond formations,[20] including halide exchange reactions.[21] More generally, we expected these fluoride complexes to be versatile synthons for new and previously unattainable complexes, given the strong bond formed to fluorine by many main group elements.

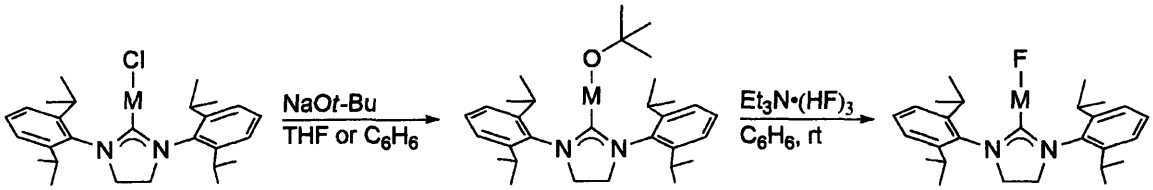
This report describes the synthesis of a series of group 11 fluoride complexes, including the first isolable fluoride of gold(I), supported by NHC ligands. Density functional calculations of the Au–F interaction find substantial splitting of the metal d-orbital energies through d-π/p-π interactions as well as through the σ-bonding interaction. A considerable negative charge on

fluorine leads to weak hydrogen-bonding interactions with the C–H bonds of dichloromethane. Although these group 11 fluorides showed only modest activity for the conversion of iodoarenes to fluoroarenes, they react efficiently with several silyl reagents to form a silicon–fluorine bond and new inorganic complexes.

Synthesis and reactivity of group 11 metal fluoride complexes

The metal chloride complexes, (SIPr)MCl [SIPr = 1,3-bis(2,6-diisopropylphenyl) imidazolin-2-ylidene, M = Cu, Ag, Au], were converted to the *tert*-butoxide complexes (SIPr)MO*t*-Bu (**1a–c**) in high yield by reaction with one equivalent of NaO*t*-Bu (Scheme 2).[22] An analogous route has been used to prepare a different (NHC)copper(I) alkoxide complex.[16d] Silver(I) and gold(I) alkoxides are quite rare, and only a small number of phosphine-stabilized complexes have been reported.[23,24]

Scheme 2. Synthesis of group 11 metal fluorides.



M = Cu, 94% (**1a**)
Ag, 86% (**1b**)
Au, 93% (**1c**)

M = Cu, 78% (**2a**)
Ag, 89% (**2b**)
Au, 48% (**2c**)

Addition of one equivalent of HF, in the relatively benign form of triethylamine tris(hydrofluoride) (Et_3N•3HF), to benzene solutions of **1a–c** resulted in the formation of colorless precipitates. The products after filtering, washing, and drying *in vacuo* were identified by ^1H NMR spectroscopy as metal(I) fluoride complexes (**2a–c**). These products typically contained small amounts of *tert*-butanol, which were removed by washing the crude products

with copious amounts of benzene, or by heating the crude products under vacuum. Crude samples of **2c** contained small amounts of an unidentified byproduct complex, which must be removed by recrystallization to obtain analytically pure product. The use of $Et_3N{\bullet}3HF$ to generate late transition-metal fluorides by protonolysis of a suitable precursor is well-established;[6a,25] however, no reports describe the isolation of silver(I) fluoride complexes by this method or the isolation of gold(I) fluoride complexes by any method. It is worth noting that treatment of $(Ph_3P)AuCl$ with AgF leads to the formation of $\{[(Ph_3P)Au]_3O\}^+ [H_2F_3]^-$, and that the gold(I)–oxo bonds do not react with the dihydrotrifluoride anion to form gold(I)–fluoride bonds.[26]

In the solid state, complexes **2a–c** are stable indefinitely when protected from light. In contrast to complexes **2a** and **2b** which are also stable indefinitely in CD_2Cl_2 solution, substantial decomposition of **2c** was observed after 1 day (~25%), forming a mixture of unidentified byproducts as judged by ^1H NMR spectroscopy. The ^{19}F NMR spectra of **2a–c** in CD_2Cl_2 each show a single resonance for the fluoride, observed at –238.8 ppm for **2a**, –243.4 ppm for **2b,** and –247.0 ppm for **2c**. Complexes **2b** and **2c** are both judged to be monomeric in solution based on coupling between fluorine and a spin-active nucleus: In the ^{19}F NMR spectrum of **2b**, the fluorine resonance is split into a doublet by dipolar coupling to silver ($^1J_{Ag-F}$ = 143 Hz),[27] and in the ^{13}C NMR spectrum of **2c**, the resonance for the gold-bound carbon is split into a doublet by coupling to fluorine ($^2J_{C-F}$ = 61 Hz). The IR spectra of **2a** and 2**c** show strong bands, absent from the spectrum of (SIPr)MCl, at 543 cm^{-1} (M = Cu) and 500 cm^{-1} (M = Au) which are similar to the frequencies estimated for Cu–F (ω_e = 623 cm^{-1}) and Au–F ($\omega_e \approx$ 500 cm^{-1}) in the gas phase.[28] Definitive assignment of the Ag–F stretching frequency could not be made due to overlap with vibrations that arise from the SIPr ligand.

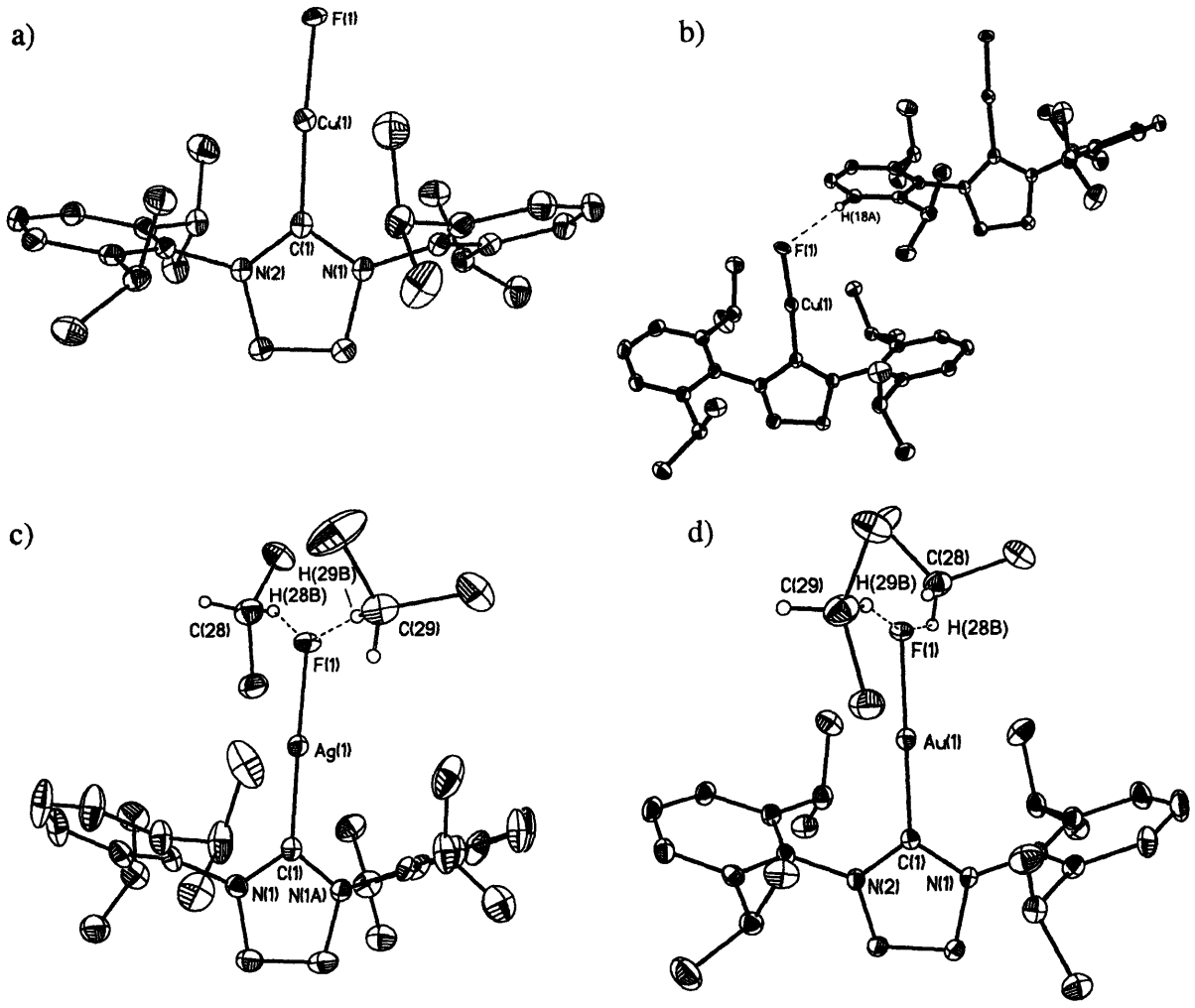


Figure 1. X-ray crystal structures of (M = Cu, Ag, Au) shown as 50% ellipsoids: (a) the solid-state structure of (SIPr)CuF; (b) the extended structure of (SIPr)CuF; (c) the solid-state structure of (SIPr)AgF•($2CH_2Cl_2$); (d) the solid-state structure of (SIPr)AuF•($2CH_2Cl_2$). All hydrogen atoms (calculated), except solvent hydrogens and H(18A) in (b), and disorder are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (deg) for **2a–c**.

M =	Cu	Ag	Au
M–F(1)	1.8426(10)	2.0682(13)	2.0281(17)
M–C(1)	1.8685(19)	2.064(2)	1.956(3)
F(1)–H(28B)		2.193	2.287
F(1)–H(29B)		2.190	2.243
C(1)–M–F(1)	176.19(6)	175.24(6)	177.22(9)

Single crystals of **2a–c** were grown by vapor diffusion of hexanes or pentanes into concentrated CH_2Cl_2 solutions. Analysis by X-ray diffraction (Figure 1) revealed monomeric structures, with nearly linear coordination geometries, in the solid state. Relevant bond lengths and angles for complexes **2a–c** are listed in Table 1. The metal–fluoride bond lengths of complexes **2a–c**, 1.8426(10) Å (**2a**), 2.064(2) Å (**2b**), and 2.0281(17) Å (**2c**) are substantially longer than those determined for M–F in the gas phase (M = Cu (1.745 Å), Ag (1.983 Å), Au (1.918 Å)).[28] In the solid-state structures of **2b** and **2c**, two CH_2Cl_2 molecules are found, with calculated positions of solvent C–H bonds closely approaching the fluoride of each complex. Similar hydrogen-bonding interactions have also been observed by Grushin and co-workers for the dimeric $[(Cy_3P)Pd(Ph)F]_2$.[29] Instead of a hydrogen-bonding interaction with dichloromethane, as found in the solid state structures of **2b** and **2c**, a weak interaction between fluoride and the *meta*-hydrogen (H_{meta}–F = 2.43 Å) of an adjacent ligand *N*-aryl group occurs in the solid-state structure of **2a** (Figure 1b). In the solid-state structure of **2c** the closest separation between Au centers, 8.1779(3) Å, is much more than twice the van der Waals radius of Au (1.66 Å) and falls well outside those observed for complexes with aurophilic Au–Au interactions.[30]

To understand the gold–fluorine interactions in **2c**, we have carried out density functional calculations on the model complex **A**, in which the *N*-aryl groups of **2c** are replaced by hydrogen. Implicit solvation by CH_2Cl_2 was included in all calculations through the polarizable

continuum model of Tomasi and collaborators.[31] Geometry optimizations converged to potential-energy minima having all-real calculated vibrational frequencies. Figure 2 gives an orbital energy level diagram, with images of selected molecular orbitals.

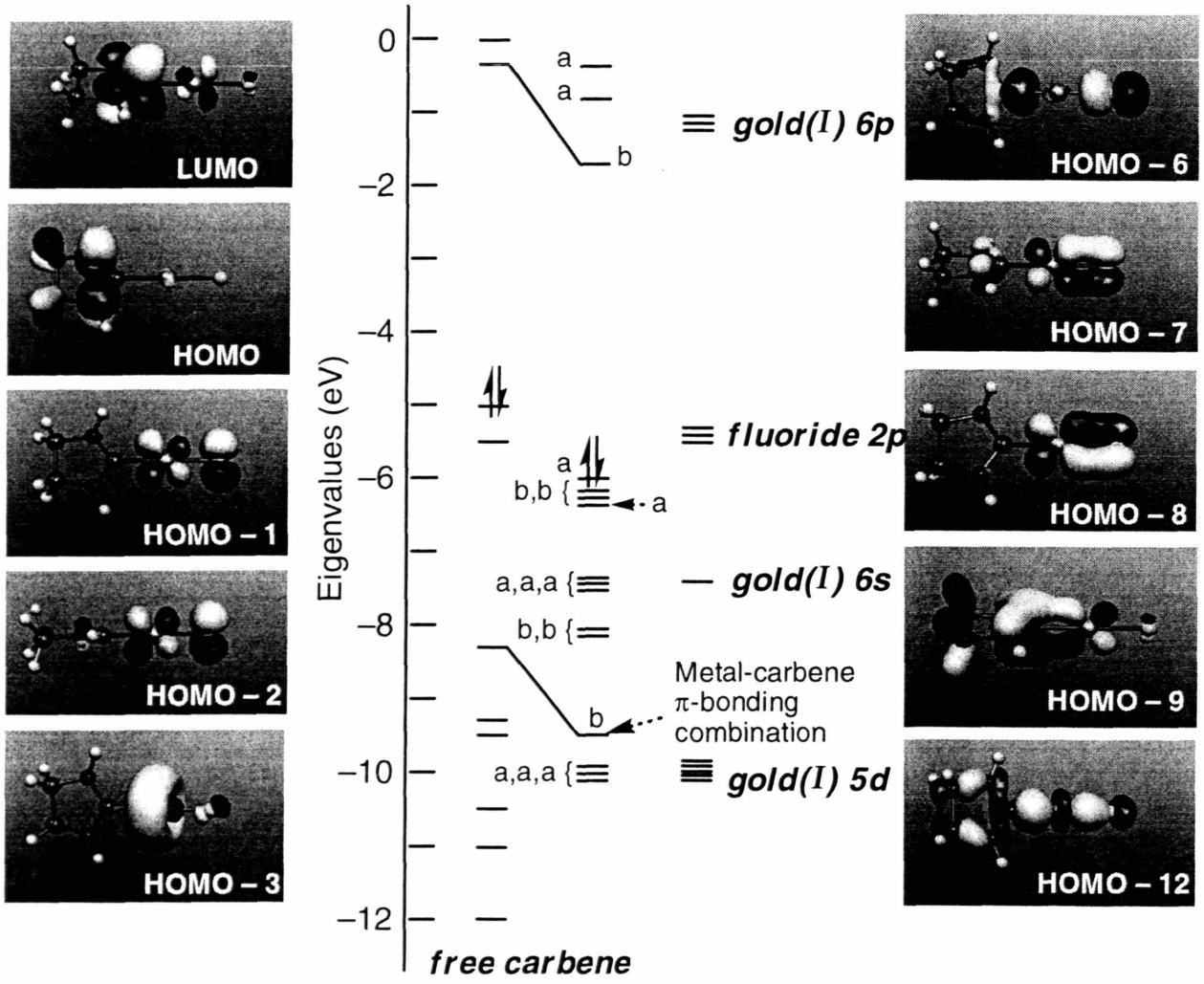


Figure 2. Kohn-Sham orbital energy-level diagram for the gold model complex **A**. Orbital eigenvalues of the carbene are those of the geometry-optimized, free ligand; those of gold are of Au^+, and those of fluorine are of F^-. All values include implicit solvation by CH_2Cl_2 (ε = 8.93) at 298.15 K. Images of selected orbitals are given in the insets.

The highest occupied Kohn-Sham orbital (HOMO) of **A** arises from the NHC π– system, with contributions from the four backbone C–H bonding orbitals. Three orbitals resulting from gold–fluoride interactions are only slightly lower in energy. The two molecular orbitals immediately below the HOMO in energy are dπ–pπ antibonding combinations between gold and fluoride. Mulliken population analysis[32] indicates that the HOMO – 1 and HOMO – 2 consist of 36.5 and 34.8% Au character respectively, with fluoride contributing 60.0 and 59.5%. Their nearest Au–F π-bonding counterparts are the HOMO – 7 (43.4% Au, 37.1% F) and HOMO – 8 (60.7% Au, 36.7% F). In contrast, a computational study of d^8 iridium complexes [*trans*-$(H_3P)_2Ir(CO)X$] found that the Ir d and fluorine p atomic orbitals interact only slightly, and that the higher-energy π^* combinations comprise almost purely metal-based combinations.[33] Apart from the participation of fluoride, the orbitals resulting from metal-carbene π interactions in **A** (LUMO, HOMO – 1, HOMO – 2, HOMO – 7, HOMO – 8, HOMO – 9) resemble those encountered previously.[19] All potential π^* combinations between Au and F are maximally occupied, and the Wiberg Au–F bond order[34] (in the Löwdin basis) is 0.933.

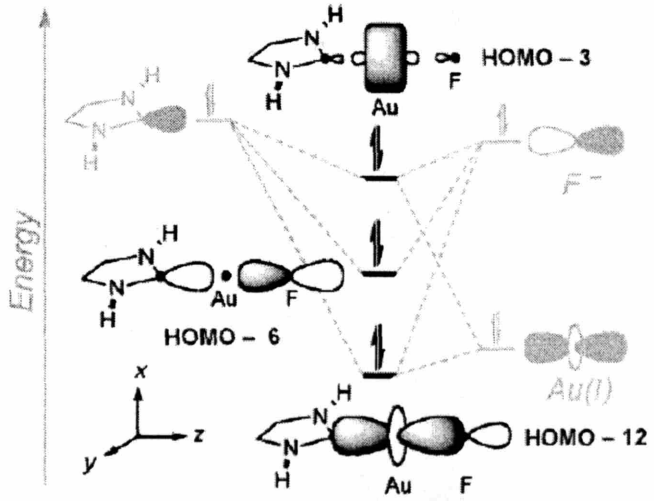


Figure 3. Qualitative energy diagram for the interaction of the Au^+ d_{z^2} orbital with F^- and NHC σ-donor orbitals.

Three filled orbitals arise from the $C_{carbene}$–Au–F σ interactions, as illustrated in Figure 3. The HOMO – 3 has d_{z^2} symmetry along the Au–F axis with σ-antibonding character toward fluoride. The intermediate orbital in this series is the HOMO – 6; it is an antiphase combination of the fluorine p_z orbital and an sp^2 hybrid on the gold-bound carbon and is essentially nonbonding toward gold. The primary C–Au–F σ-bonding orbital is the HOMO – 12, a constructive overlap of the gold $5d_{z^2}$ orbital and lobes of σ-symmetry on fluorine and carbon. A natural population analysis carried out for **A**[35] found electrostatic charges of +0.42 for Au, –0.77 for F, and +0.20 for the carbenic carbon. Further calculations were carried out on **A**•$2CH_2Cl_2$ to examine the nature of the hydrogen-bonding interaction. Explicit solvation of fluoride by CH_2Cl_2 perturbs the electronic structure of **A** only minimally. Geometry optimization indicates a small distension of the interacting C–H bonds, and the gold–fluorine bond lengthens by 0.021 Å. Natural electrostatic charges indicate appreciable polarization of the solvate C–H bonds: the hydrogens near fluorine acquire charges of +0.317 each. For comparison, the charge calculated for hydrogens in isolated CH_2Cl_2 (in a solvent continuum) is +0.295. The electrostatic charge calculated for fluorine is approximately unchanged at –0.77.

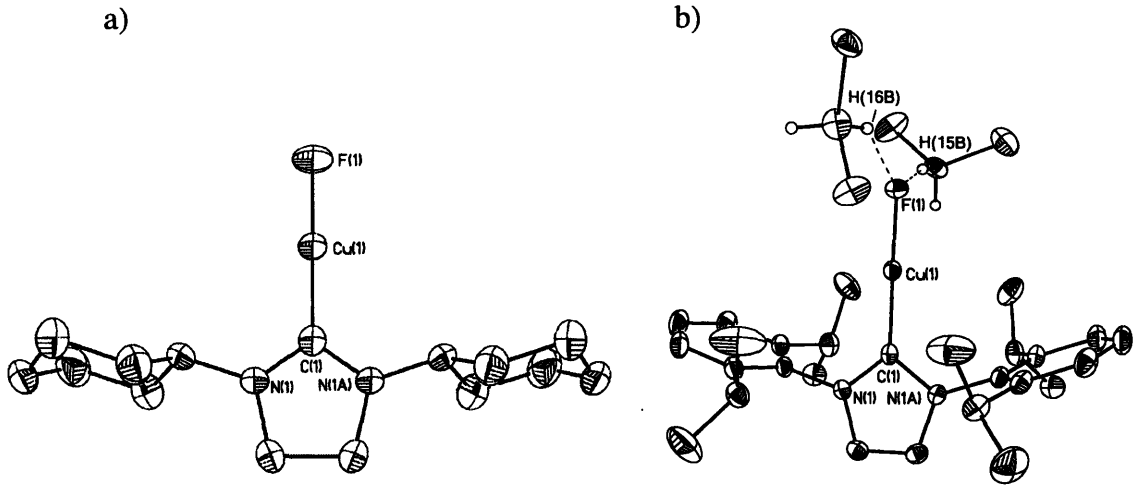


Figure 4. X-ray crystal structure of (SICy)CuF (a) and (IPr)CuF•($2CH_2Cl_2$) (b), shown as 50% ellipsoids. Ligand hydrogen atoms and disorder are omitted for clarity. Selected bond lengths

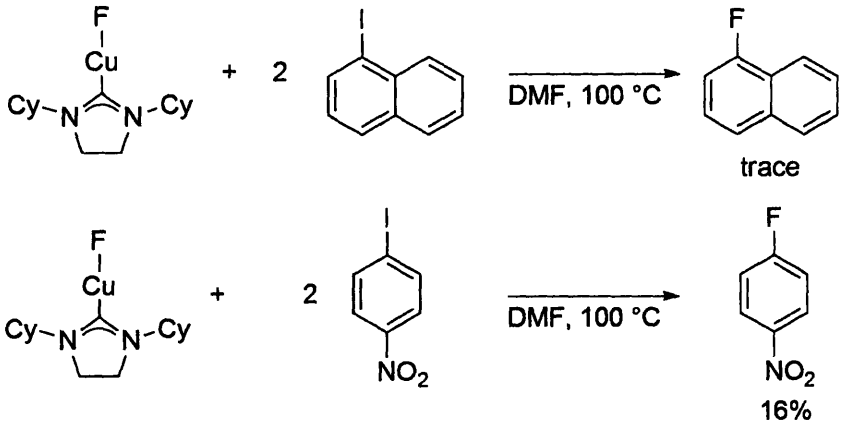
(Å) and angles (deg): (a) Cu(1)–F(1) 1.797(5), Cu(1)–C(1) 1.861(8); C(1)–Cu–F 180.000(6); (b) Cu–F = 1.8202(14), Cu–C(1) = 1.862(2), F–H(15B) = 2.193, F–H(16B) = 2.305; C(1)–Cu–F = 177.20(8).

We were interested in synthesizing other (NHC)metal fluoride complexes, and chose to make a series of copper(I) fluoride complexes because we could synthesize the widest array of *t*ert-butoxide precursors of this metal efficiently. The unsaturated analogue of (SIPr)CuF, (IPr)CuF (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), was synthesized to compare how ligand electronics affect the reactivity of copper(I) fluoride complexes. Also, a sterically smaller copper(I) fluoride complex was synthesized, (SICy)CuF (SICy = 1,3-dicyclohexylimidazolin-2-ylidene). The X-Ray crystal structures for both complexes were determined (Figure 4). The solid-state structure of (IPr)CuF shows C–H interactions between fluoride and dichloromethane molecules (F–H = 2.19 and 2.31 Å) similar to the ones observed for **2b** and **2c**. Unfortunately, (SIPr)CuF and (IPr)CuF crystallize with different fluoride hydrogen-bonding interactions, which makes direct comparison of their Cu–F bond distances less meaningful; however, even with the different interactions, their bond distances are quite similar 1.8202(14) Å and 1.8426(10) Å for (IPr)CuF and (SIPr)CuF respectively. Interestingly, (SICy)CuF does not show any weak C–H hydrogen-bonding interactions with fluoride in the solid state, even though crystals were grown out of dichloromethane.

The facile introduction of fluorine into an aromatic ring remains an ongoing challenge in organic synthesis,[4c] and we hoped that NHC group 11 fluoride complexes would be effective reagents for the conversion of aryl iodides to aryl fluorides. A copper fluoride complex, (SICy)CuF, proved to be the most active reagent. Reaction of (SICy)CuF with an excess of 2-iodonaphthalene in DMF at 100 °C gave rise after 20 hours to a trace of 2-fluoronaphthalene that

was detectable by ^{19}F NMR. Attempts to optimize the reaction conditions did not lead to significant improvements of yield. Reaction of a more activated iodoarene, 4-iodonitrobenzene, with (SICy)CuF gave somewhat higher yields of fluoroarene product (~16%) after 8 hours at 100 °C in DMF solution. The nearest literature precedent for copper-mediated fluoro-dehalogenation was the reaction of 4-bromonitrobenzene with $(Ph_3P)_3CuF$ in the presence of KF in hexamethylphosphoramide solvent at 150 °C; 16% conversion to 4-fluoronitrobenzene was observed after three hours.[6a] The nucleophilic aromatic substitution of 4-chloronitrobenzene using KF and the phase-transfer catalyst, tetraphenylphosphonium bromide has been carried out at higher temperatures (180 °C) in sulfolane (2,3,4,5-tetrahydrothiophene-1,1-dioxide).[36] Although yields are currently low, (SICy)CuF shows encouraging reactivity and copper(I) fluoride complexes supported by other ligands may eventually lead to more general and useful methods for the nucleophilic fluorination of aryl halides.

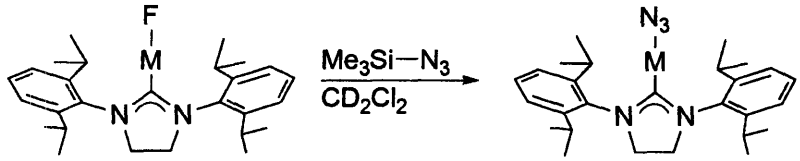
Scheme 3. Fluorination of 4-iodonitrobenzene by (NHC)copper(I) fluoride complexes.[a]



[a]NMR yield relative to an internal standard of C_6H_5F. The reported yield is based on starting copper(I) fluoride complex.

Although complexes **2a–c** show limited activity for the formation of C–F bonds, they are versatile precursors for the synthesis of new metal complexes (Scheme 4). For example, trimethylsilyl azide reacted cleanly with **2a–c** to from metal–azide complexes and fluoro(trimethyl)silane. The products were structurally characterized (Figure 5) and in all cases were found to be two-coordinate monomers. Significant bond lengths and angles are listed in Table 2. Monomeric gold(I) azide complexes[37] are well-precedented: [1,3-di(*tert*-butyl)imidazol-2-ylidene]gold(I) azide[18e] has recently been reported in the literature. Low-coordinate copper(I)[38] and silver(I)[39] azide complexes are much more rare, and only one example, $N_3Cu(PCy_3)_2$ has been structurally characterized. To the best of our knowledge, (SIPr)CuN_3 and (SIPr)AgN_3 are the first two-coordinate copper(I) and silver(I) azide complexes.

Scheme 4. Synthesis of metal–azide complexes via Si–F bond formation.



M = Cu, (**2a**)
Ag, (**2b**)
Au, (**2c**)

M = Cu, (**3a**)
Ag, (**3b**)
Au, (**3c**)

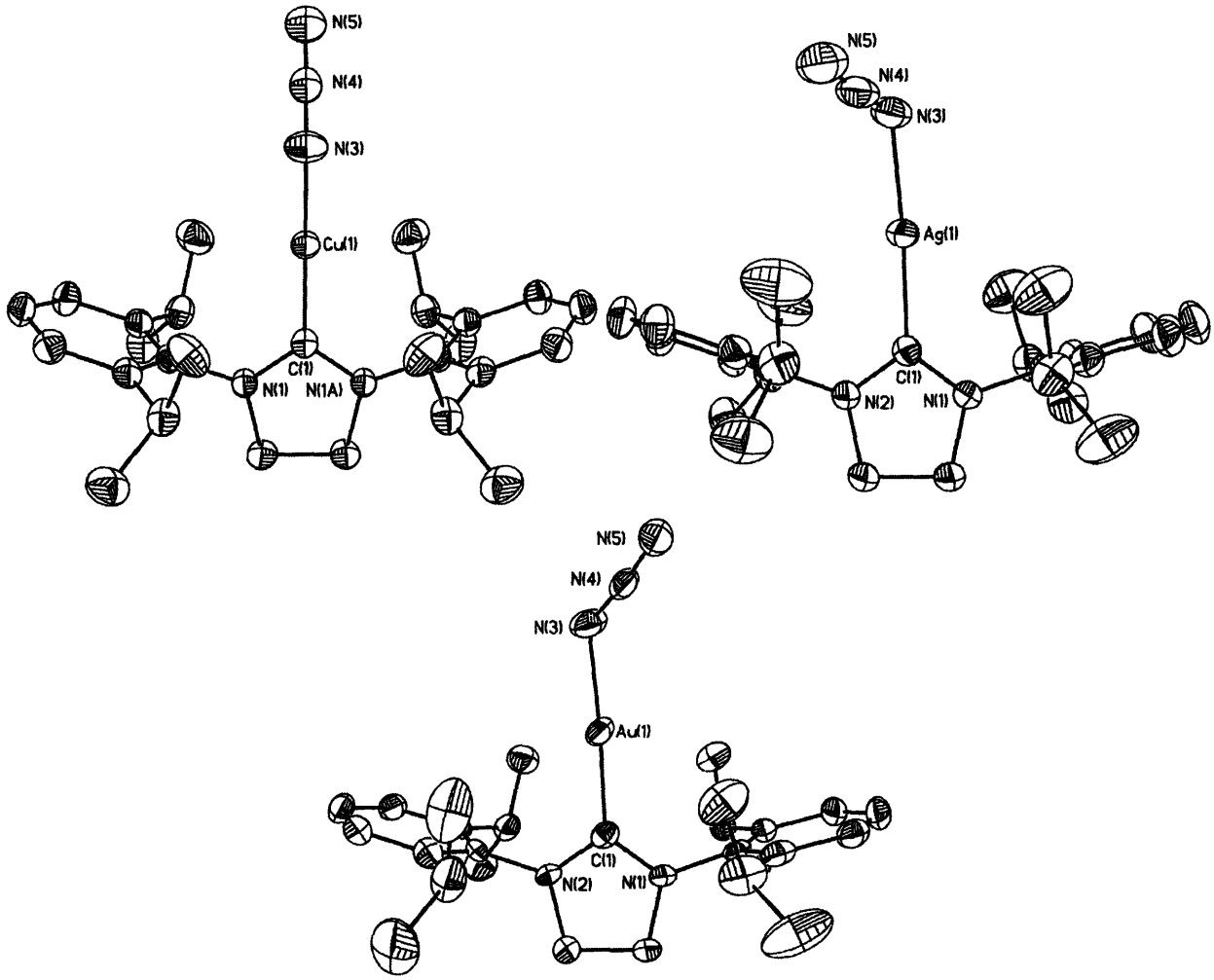


Figure 5. X-ray crystal structure of (SIPr)MN_3 (M = Cu, Ag, Au) complexes shown as 50% ellipsoids. Hydrogen atoms, solvent and disorder are omitted for clarity.

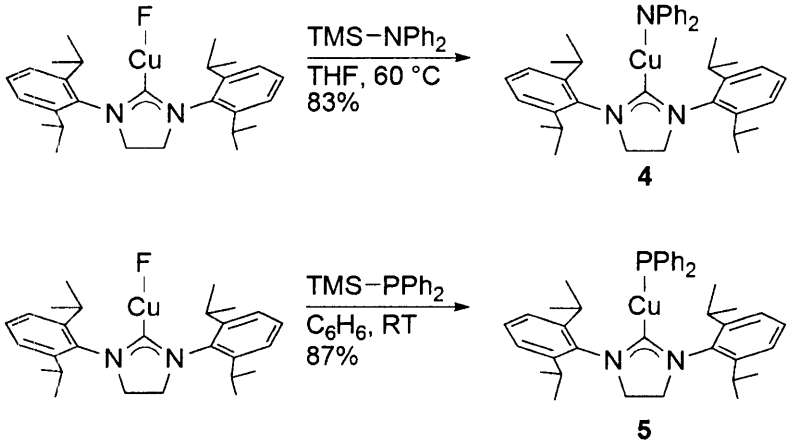
Complex **2a** also reacted cleanly with *N*-(trimethylsilyl)diphenylamine to give the corresponding copper(I) amide complex, **4** (Scheme 5). Single crystals of (SIPr)$CuNPh_2$ were grown from a pentane/diethyl ether solution at room temperature, and the solid-state structure is shown in Figure 6. The copper–nitrogen bond distance in **4**, 1.8606(16) Å, is intermediate between those in (IPr)CuNHPh,[40a] 1.841(2) Å, and [1,2-bis(di-*tert*-butylphosphino)ethane]Cu(NHPh),[40b] 1.890(6) Å, the only other monomeric copper(I) amide complexes found in the literature. The geometry about the amide nitrogen of (SIPr)$CuNPh_2$ is

almost perfectly trigonal planar with the angles about N_{amide} adding to 360° within experimental error.

Table 2. Selected bond distances (Å) and angles (deg) for (SIPr)MN_3 (M = Cu, Ag, Au).

M =	Cu	Ag	Au
M–C(1)	1.892(7)	2.0667(19)	1.972(6)
M–N(3)	1.848(7)	2.1239(19)	2.018(6)
N(3)–N(4)	1.191(10)	1.169(3)	1.184(8)
N(4)–N(5)	1.159(10)	1.179(4)	1.156(8)
C(1)–M–N(3)	175.7(3)	172.88(7)	176.6(2)
M–N(3)–N(4)	134.4(6)	116.16(16)	124.0(5)
N(3)–N(4)–N(5)	175.2(8)	174.2(2)	172.7(8)

Scheme 5. Synthesis of (SIPr)$CuEPh_2$ (E = N, P).



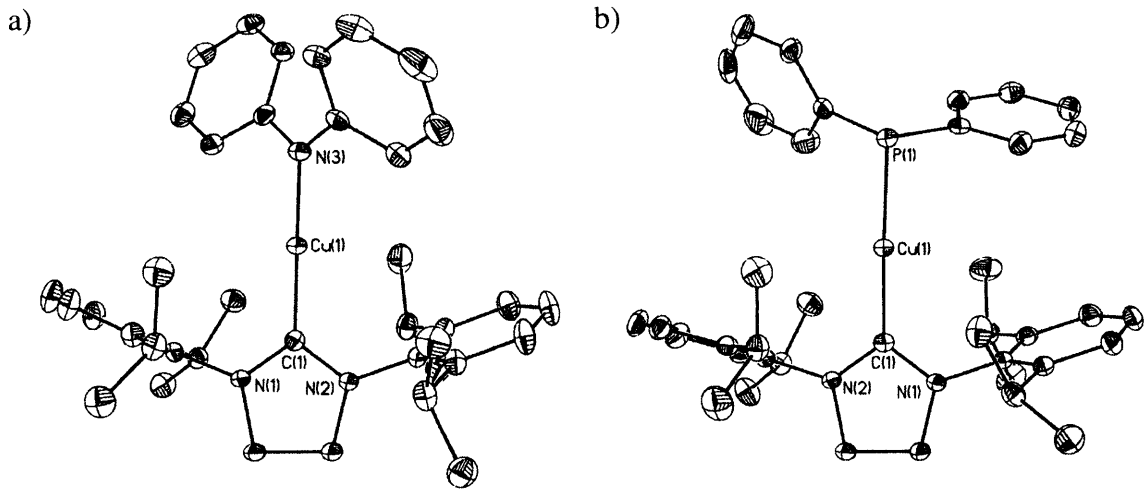


Figure 6. X-ray crystal structures of **4** and **5** shown as 50% ellipsoids. Selected bond lengths (Å) and angles (deg): (a) Cu(1)–N(3) 1.8606(16), Cu(1)–C(1) 1.8667(18); C(1)–Cu(1)–N(3) 178.33(8); (b) Cu(1)–P(1) 2.2183(6), Cu(1)–C(1) 1.9183(17); C(1)–Cu(1)–P(1) 176.65(5).

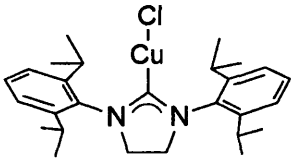
A copper(I) phosphide complex was prepared by reaction of **2a** with *P*-(trimethylsilyl)diphenylphosphine. A single peak at –26.1 ppm was observed in the ^{31}P NMR spectrum of **5**, typical of copper(I) phospide complexes.[41–43] In the ^{13}C NMR spectrum of **5** in C_6D_6, the resonance for the carbene carbon is split into a doublet by dipolar coupling to phosphorus ($^2J_{C-P}$ = 17.9 Hz), consistent with a terminal rather than a bridging phosphido group. Single crystals of complex **5** were grown by vapor diffusion of hexanes into a diethyl ether solution at –40 °C. Analysis by X-ray diffraction revealed a monomeric structure (Figure 6b). The Cu–P bond distance of 2.2183(6) Å is nearly identical to those of a bridging phosphido–copper tetramer [CuP(*t*-Bu)$_2$]$_4$ (2.210 Å, average).[42b] The geometry about phosphorus in **5** is pyrimidal ($\Sigma_{<P}$ = 308°). Although complex **5** is the first neutral monomeric copper–phosphide complex, monomeric lithium phosphidocuprates have been reported; however, lithium–phosphorus interactions observed in solid-state structures likely discourage phosphide-bridging between two copper centers.[43]

In conclusion, a series of group 11 metal(I) fluoride complexes were synthesized and structurally characterized, including the first isolable gold(I) fluoride. DFT calculations find a large partial negative charge on fluorine, and a slight lengthening of the Au–F bond, with polarization of the solvent C–H bonds, through hydrogen bonding with dichloromethane. While the metal–fluoride complexes displayed only modest activity for the conversion of aryl iodides to aryl fluorides, they were shown to be useful reagents for the synthesis of new inorganic complexes.

Experimental Section

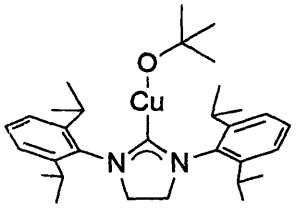
General Considerations. Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA, or Desert Analytics, Tucson, AZ. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for diethyl ether and tetrahydrofuran; the tetrahydrofuran was also passed through a third column packed with activated 4Å molecular sieves) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Benzene, and pentane, anhydrous, were purchased from Aldrich in Sure-Seal™ bottles, and stored in a glovebox over 4Å molecular sieves. All non-dried solvents used were reagent grade or better. IR spectra were recorded on a Nicolet Impact 410 spectrometer as KBr pellets. NMR solvents were dried as follows: C_6D_6 (Cambridge Isotope Laboratories) over sodium/benzophenone, CD_2Cl_2 (Cambridge Isotope

Laboratories) over calcium hydride, and acetone-d_6 over 4 Å molecular sieves. All NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ^{1}H NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. ^{19}F NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm). ^{31}P NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of 85% H_3PO_4 (0 ppm). ^{13}C NMR spectra were recorded on a Varian 300 MHz or a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak. The starting materials copper(I) chloride (Strem), silver(I) oxide (Strem), chloro(dimethylsulfide)gold(I) (Aldrich), sodium *tert*-butoxide (Aldrich), triethylamine tris(hydrofluoride) (Aldrich), trimethylsilyl azide (Aldrich), and *P*-(trimethylsilyl)diphenylphosphine (Aldrich) and were used as received. The starting materials [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) *tert*-butoxide,[16d] 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride,[44] 1,3-dicyclohexylimidazolinium chloride,[45] and *N*-(trimethylsilyl)diphenylamine[46] were synthesized as described previously.

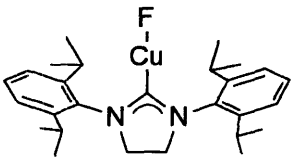


[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) chloride. In a glovebox, a round-bottomed flask equipped with a Teflon-coated stirbar was charged with copper(I) chloride (1.30 g, 13.13 mmol) and sodium *tert*-butoxide (1.20 g, 12.53 mmol). Tetrahydrofuran (100 mL) was added, and the mixture was stirred for 2 hours. 1,3-Bis-(2,6-diisopropylphenyl)imidazolinium chloride (5.00 g, 11.93 mmol) was added, and the mixture was stirred for an additional 12 hours. In the air, the mixture was filtered through Celite, washed with dichloromethane (5 x 30 mL), and concentrated *in vacuo* to give the title complex (5.44 g,

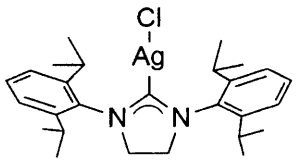
95%). ^{1}H NMR (CD_2Cl_2): δ 7.45 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, *J* = 7.6 Hz, 4 H, *meta*-CH), 4.03 (s, 4 H, NC$\underline{H}_2$), 3.08 (sept, *J* = 6.9 Hz, 4 H, C$\underline{H}$(CH_3)$_2$), 1.35 (d, *J* = 7.0 Hz, 24 H, CH(C$\underline{H}_3$)$_2$). ^{13}C NMR (CD_2Cl_2): δ 203.2 (N$\underline{C}$Cu), 147.4 (*ortho*-C), 135.0 (*ipso*-C), 130.2 (*para*-C), 125.0 (*meta*-C), 54.3 (N$\underline{C}H_2$), 29.4 ($\underline{C}$H(CH_3)$_2$), 25.7 (CH($\underline{C}H_3$)$_2$), 24.1 (CH($\underline{C}H_3$)$_2$). Anal. Calcd. $C_{27}H_{38}N_2CuCl$: C, 66.24; H, 7.82. Found: C, 66.29; H, 8.01.



[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) tert-butoxide (1a). In a glovebox, a round-bottomed flask equipped with a Teflon-coated stirbar was charged with (SIPr)CuCl, (3.04 g, 6.31 mmol) and sodium *tert*-butoxide (0.606 g, 6.31 mmol). Anhydrous tetrahydrofuran (80 mL) was added. The resulting orange suspension was stirred for 2 hours, filtered through Celite, and concentrated *in vacuo* to give **1a** as an off-white solid, (3.12 g, 94%). ^{1}H NMR (C_6D_6): δ 7.20 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.07 (d, *J* = 7.6 Hz, 4 H, *meta*-CH), 3.18 (s, 4 H, NC$\underline{H}_2$), 2.99 (sept, *J* = 6.9 Hz, 4 H, C$\underline{H}$(CH_3)$_2$), 1.50 (d, *J* = 6.7 Hz, 12 H, CH(C$\underline{H}_3$)$_2$), 1.28 (s, 9 H, O(C$\underline{H}_3$)$_3$), 1.19 (d, *J* = 7.0 Hz, 12 H, CH(C$\underline{H}_3$)$_2$). ^{13}C NMR (C_6D_6): δ 206.4 (N$\underline{C}$Cu), 147.2 (*ortho*-C), 136.0 (*ipso*-C), 130.1 (*para*-C), 125.0 (*meta*-C), 53.6 (N$\underline{C}H_2$), 37.5 (O$\underline{C}$(CH_3)$_3$, 29.4 (CH($\underline{C}H_3$)$_2$), 25.9 (CH($\underline{C}H_3$)$_2$), 24.5 ($\underline{C}$H(CH_3)$_2$). Anal. Calcd. $C_{31}H_{47}N_2CuO$: C, 70.62; H, 8.98. Found: C, 70.64; H, 9.04.



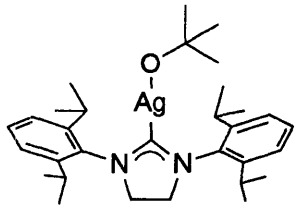
[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) fluoride (2a). In a glovebox, (SIPr)Cu(O*t*-Bu) (2.16 g, 4.10 mmol) and benzene (20 mL) were added to a round-bottomed flask equipped with a Teflon coated stirbar. The flask was sealed with a septum, taken out of the glovebox, and triethylamine tris(hydrofluoride) (0.223 mL, 1.37 mmol) was added via syringe. The resulting white suspension was stirred for 2 hours. In a glovebox, the white solid was collected by filtration, washed with benzene (2 x 3 mL), and dried at 65°C for 12 hours to afford the title compound (1.52 g, 78%). ^{1}H NMR (CD_2Cl_2): δ 7.45 (t, J = 7.8 Hz, 2 H, *para*-CH), 7.30 (d, J = 8.0 Hz, 4 H, *meta*-CH), 4.01 (s, 4 H, NC$\underline{H}_2$), 3.07 (sept, J = 6.9 Hz, 4 H, C$\underline{H}$(CH$_3$)$_2$), 1.36 (d, J = 6.9 Hz, 12 H, CH(C$\underline{H}_3$)$_2$), 1.35 (d, J= 7.0 Hz, 12 H, CH(C$\underline{H}_3$)$_3$). ^{19}F NMR (CD_2Cl_2): δ –238.8. ^{13}C NMR (CD_2Cl_2): δ 203.8 (br., N$\underline{C}$Cu), 147.4 (*ortho*-C), 135.3 (*ipso*-C), 130.2 (*para*-C), 125.0 (*meta*-C), 54.3 (N$\underline{C}$H$_2$), 29.4 ($\underline{C}$H(CH$_3$)$_2$), 25.7 (CH($\underline{C}$H$_3$)$_2$), 24.1 (CH($\underline{C}$H$_3$)$_2$). Anal. Calcd. $C_{27}H_{38}N_2CuF$: C, 68.54; H, 8.10. Found: C, 68.06; H, 8.22.



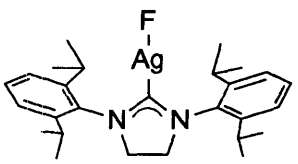
[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]silver(I) chloride

This complex was synthesized by a route analogous to that developed by Wang and Lin.[17a] In a fume hood, an Erlenmeyer flask equipped with a Teflon-coated stirbar was charged with SIPr•HCl (12.95 g, 30.92 mmol), silver(I) oxide (4.30 g, 18.55 mmol). Dichloromethane (200 mL) was added, and the mixture was stirred in the dark for 24 hours. The mixture was filtered and concentrated *in vacuo*. The resulting yellow solid was suspended in diethyl ether (20 mL), then collected by filtration to give the title compound as a white solid (13.37 g, 81%). ^{1}H NMR (CD_2Cl_2): δ 7.46 (t, J = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, J = 7.6 Hz, 4 H, *meta*-CH), 4.08 (s, 4 H, NC$\underline{H}_2$), 3.07 (sept, J = 6.9 Hz, 4 H, C$\underline{H}$(CH$_3$)$_2$), 1.34 (pseudo t, J = 6.8 Hz, 24 H, CH(C$\underline{H}_3$)$_2$).

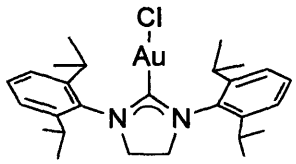
^{13}C NMR (CD_2Cl_2): δ 207.9 (d, $J_{C-^{109}Ag}$ = 253 Hz, $J_{C-^{107}Ag}$ = 237 Hz, $\underline{C}_{ipso}$–Ag)[47], 147.3 (*ortho*-C), 135.2 (*ipso*-C), 130.4 (*para*-C), 125.1 (*meta*-C), 54.5 (d, J_{Ag-C} = 8.6 Hz, N$\underline{C}H_2$), 29.3 ($\underline{C}H(CH_3)_2$), 25.7 ($CH(\underline{C}H_3)_2$), 24.3 ($CH(\underline{C}H_3)_2$). Anal. Calcd. $C_{27}H_{38}N_2AgCl$: C, 60.74; H, 7.17. Found: C, 60.87; H, 7.11.



[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]silver(I) *tert*-butoxide (1b). In a glovebox, an Erlenmeyer flask equipped with a Teflon-coated stirbar was charged with (SIPr)AgCl (3.00 g, 5.62 mmol) and sodium *tert*-butoxide (0.540 g, 5.62 mmol). Tetrahydrofuran (200 mL) was added, the flask was sealed with a septum, and the mixture was stirred for 1.5 hours. The mixture was filtered and the solution was concentrated *in vacuo* to give the title compound (2.75 g, 86%). ^1H NMR (C_6D_6): δ 7.20 (t, J = 7.8 Hz, 2 H, *para*-CH), 7.07 (d, J = 7.6 Hz, 4 H, *meta*-CH), 3.18 (s, 4 H, N$\underline{C}H_2$), 2.99 (sept, J = 6.9 Hz, 4 H, $\underline{C}H(CH_3)_2$), 1.50 (d, J = 6.7 Hz, 12 H, $CH(\underline{C}H_3)_2$), 1.28 (s, 9 H, $O(\underline{C}H_3)_3$), 1.19 (d, J = 7.0 Hz, 12 H, $CH(\underline{C}H_3)_2$). ^{13}C NMR (C_6D_6): δ 209.5 (d, $J_{\underline{C}ipso-^{109}Ag}$ = 221 Hz, $J_{C-^{107}Ag}$ = 192 Hz, $\underline{C}_{ipso}$–Ag)[47], 147.1 (*ortho*-C), 135.8 (*ipso*-C), 130.3 (*para*-C), 125.1 (*meta*-C), 69.1 ($O\underline{C}(CH_3)_3$ 53.8 (d, J_{Ag-C} = 8.1 Hz, N$\underline{C}H_2$), 37.4 ($OC(\underline{C}H_3)_3$), 29.4 ($CH(\underline{C}H_3)_2$), 25.9 ($CH(\underline{C}H_3)_2$), 24.5 ($CH(\underline{C}H_3)_2$). Anal. Calcd. $C_{31}H_{47}N_2AgO$: C, 65.14; H, 8.29. Found: C, 65.16; H, 8.42.

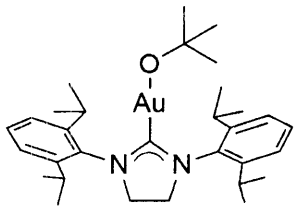


[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]silver(I) fluoride (2b). In a glovebox, a stirbar, (SIPr)AgO*t*-Bu (2.00 g, 3.49 mmol), and benzene (20 mL) were added to a Schlenk flask wrapped in aluminum foil. Outside of the glovebox, triethylamine tris(hydrofluoride) (0.190 mL, 1.17 mmol) was added via syringe. The resulting white suspension was stirred for 30 minutes. In a glovebox, the white solid was collected by filtration, washed with benzene (2 x 10 mL), and dried at 85 °C for 15 hours to afford the title compound (1.60 g, 89%). ^{1}H NMR (CD_2Cl_2): δ 7.45 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, *J* = 7.8 Hz, 4 H, *meta*-CH), 4.07 (s, 4 H, NCH_2), 3.06 (sept, *J* = 6.8 Hz, 4 H, $CH(CH_3)_2$), 1.34 (d, *J* = 6.9 Hz, 24 H, $CH(CH_3)_2$). ^{19}F NMR (CD_2Cl_2): δ –243.4 (d, J_{Ag-F} = 143 Hz). ^{13}C NMR (CD_2Cl_2): δ 206.6 (NCAg), 147.3 (*ortho*-C), 135.3 (*ipso*-C), 130.4 (*para*-C), 125.2 (*meta*-C), 54.4 (d, J_{Ag-C} = 9.2 Hz, NCH_2), 29.3 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$). Anal. Calcd. $C_{27}H_{38}N_2AgF$: C, 62.67; H, 7.40. Found: C, 62.27; H, 7.18.

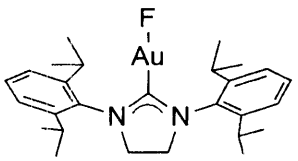


[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) chloride. This complex was synthesized by a route analogous to that of Lin and co-workers[18f]: An Erlenmeyer flask equipped with a Teflon-coated stirbar was charged with (SIPr)AgCl (0.848 g, 1.61 mmol), and chloro(dimethylsulfide)-gold(I) (0.475 g, 1.61 mmol). Dichloromethane (50 mL) was added followed by dimethylsulfide (1 mL, 13.62 mmol). The mixture was stirred in the dark for 60 hours, filtered and concentrated *in vacuo*. The resulting yellow solid was washed with diethyl ether (2 x 5 mL) to afford the title compound as a cream-colored solid (0.902 g, 90%). ^{1}H NMR (CD_2Cl_2): δ 7.48 (t, *J* = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, *J* = 7.6 Hz, 4 H, *meta*-CH), 4.06 (s, 4 H, NCH_2), 3.06 (sept, *J* = 6.9 Hz, 4 H, $CH(CH_3)_2$), 1.40 (d, *J* = 6.7 Hz, 12 H, $CH(CH_3)_2$), 1.34 (d, *J*

= 6.9 Hz, 12 H, $CH(C\underline{H}_3)_2$). ^{13}C NMR (CD_2Cl_2): δ 196.3 ($N\underline{C}Au$), 147.3 (*ortho*-C), 134.6 (*ipso*-C), 130.5 (*para*-C), 125.1 (*meta*-C), 54.1 ($N\underline{C}H_2$), 29.4 ($\underline{C}H(CH_3)_2$), 25.3 ($CH(\underline{C}H_3)_2$), 24.4 ($CH(\underline{C}H_3)_2$). Anal. Calcd. $C_{27}H_{38}N_2AuCl$: C, 52.05; H, 6.15. Found: C, 51.81; H, 5.87.



[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) *tert*-butoxide (1c). In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated stirbar was charged with (SIPr)AuCl (0.210 g, 0.34 mmol) and sodium *tert*-butoxide (0.033 g, 0.34 mmol). Benzene (10 mL) was added, and the mixture was stirred in the dark for 2 hours. The resulting suspension was filtered through Celite, and concentrated *in vacuo* to afford **1c** as an off-white solid (0.210 g, 93%). ^1H NMR (C_6D_6): δ 7.22 (t, J = 7.8 Hz, 2 H, *para*-CH), 7.07 (d, J = 7.6 Hz, 4 H, *meta*-CH), 3.18 (s, 4 H, $NC\underline{H}_2$), 2.99 (sept, J = 6.9 Hz, 4 H, $C\underline{H}(CH_3)_2$), 1.54 (d, J = 6.7 Hz, 12 H, $CH(C\underline{H}_3)_2$), 1.31 (s, 9 H, $O(C\underline{H}_3)_3$), 1.18 (d, J = 7.0 Hz, 12 H, $CH(C\underline{H}_3)_2$). ^{13}C NMR (C_6D_6): δ 196.0 ($N\underline{C}Au$), 147.1 (*ortho*-C), 135.7 (*ipso*-C), 130.2 (*para*-C), 124.9 (*meta*-C), 71.5 ($O\underline{C}(CH_3)_3$), 53.3 ($N\underline{C}H_2$), 37.0 ($O\underline{C}(CH_3)_3$, 29.5 ($CH(\underline{C}H_3)_2$), 25.5 ($CH(\underline{C}H_3)_2$), 24.7 ($\underline{C}H(CH_3)_2$). Anal. Calcd. $C_{31}H_{47}N_2AuO$: C, 56.36; H, 7.17. Found: C, 56.53; H, 7.30.



[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) fluoride (2c). In a glovebox, a round-bottomed flask equipped with a Teflon-coated stirbar was charged with (SIPr)AuO*t*-Bu (0.551 g, 0.83 mmol). Benzene (20 mL) was added, the flask was sealed with a septum, and

taken out of the glovebox. Triethylamine tris(hydrofluoride) (0.045 mL, 0.28 mmol) was added via syringe, and the mixture was stirred in the dark for 2 hours. The resulting suspension was collected by filtration in a glovebox. The white solid was then dissolved in dichloromethane (2 mL) and hexanes were vapor diffused into it at –40 °C. After 24 hours, crystals had grown, and the supernatant was decanted off to give **2c** (0.244 g, 48%). ^{1}H NMR (CD_2Cl_2): δ 7.48 (t, J = 7.8 Hz, 2 H, *para*-CH), 7.29 (d, J = 7.6 Hz, 4 H, *meta*-CH), 4.06 (s, 4 H, $NC\underline{H}_2$), 3.06 (sept, J = 6.9 Hz, 4 H, $C\underline{H}(CH_3)_2$), 1.40 (d, J = 6.7 Hz, 12 H, $CH(C\underline{H}_3)_2$), 1.34 (d, J = 6.9 Hz, 12 H, $CH(C\underline{H}_3)_2$). ^{19}F NMR (CD_2Cl_2): δ –247.0. ^{13}C NMR (CD_2Cl_2): δ 185.9 (d, $J_{C\text{-}F}$ = 60.5 Hz, $N\underline{C}Au$), 147.3 (*ortho*-C), 134.8 (*ipso*-C), 130.4 (*para*-C), 125.2 (*meta*-C), 53.9 (d, $^{2}J_{C\text{-}F}$ = 1.7 Hz, $N\underline{C}H_2$), 29.5 ($\underline{C}H(CH_3)_2$), 25.3 ($CH(\underline{C}H_3)_2$), 24.4 ($CH(\underline{C}H_3)_2$). Anal. Calcd. $C_{27}H_{38}N_2AuF$: C, 53.46; H, 6.31. Found: C, 53.42; H, 6.50. IR (KBr pellet, cm^{-1}): 500.1 (Au–F stretch).

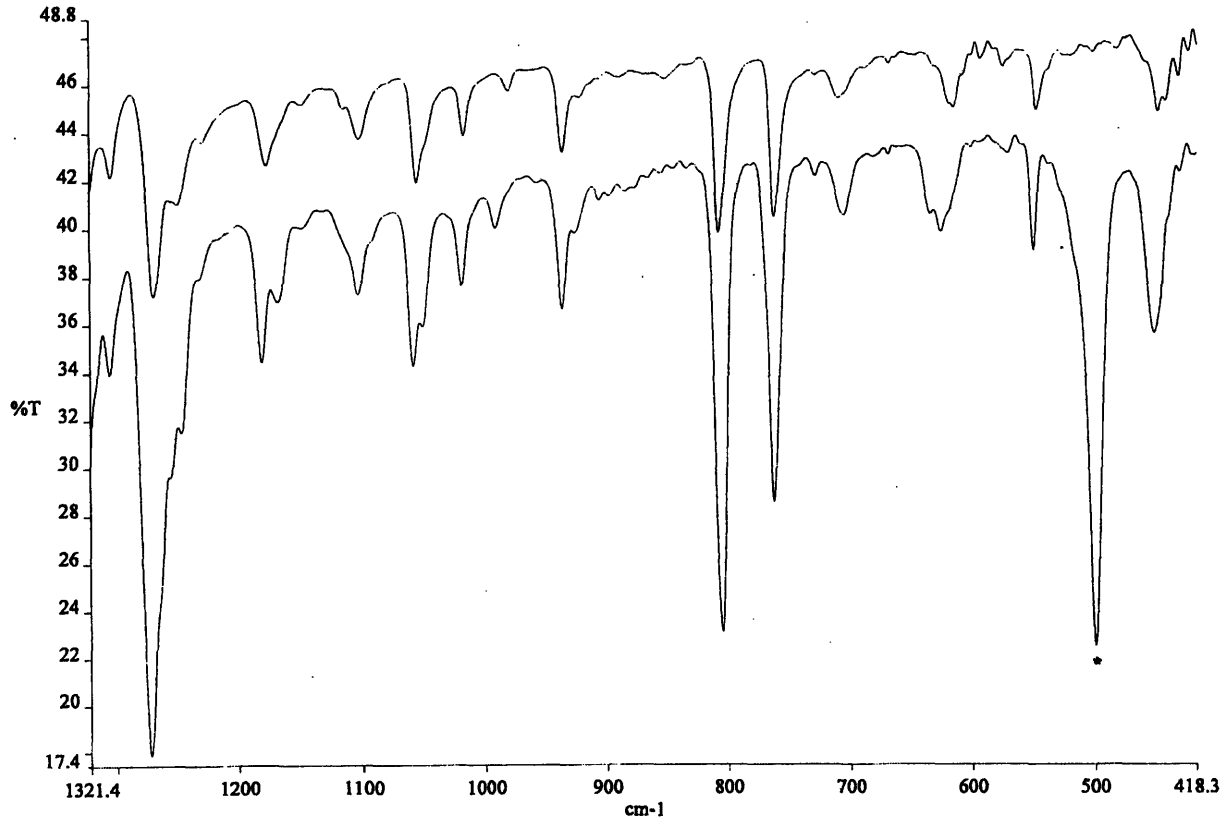
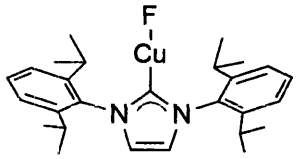
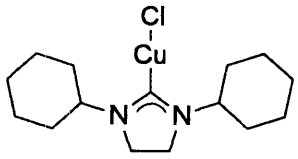


Figure 7. Overlay of (SIPr)AuCl (top) and (SIPr)AuF (bottom) IR spectra. The stretch assigned to Au–F is marked with an asterisk.

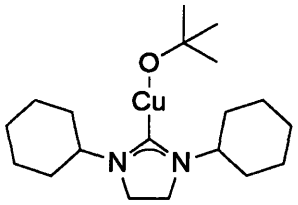


[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) fluoride. In a glovebox, [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) *tert*-butoxide (0.512 g, 0.98 mmol) and benzene (anhydrous, 10 mL) were added to a Schlenk flask equipped with a Teflon-coated stirbar. The flask was taken out of the glovebox, and triethylamine tris(hydrofluoride) (0.05 mL, 0.31 mmol) was added via syringe. The resulting white suspension was stirred for 6 hours, and the solvent was removed on a vacuum line. In a glovebox, the white solid was suspended in pentane (3 mL), filtered, and washed with benzene (2 mL) to afford the title compound (0.407 g, 89%). ^{1}H NMR (CD_2Cl_2): δ 7.54 (t, J = 7.8 Hz, 2 H, *para*-CH), 7.36 (d, J = 7.9 Hz, 4 H, *meta*-CH), 7.19 (s, 2 H, NC<u>H</u>), 2.57 (sept, J = 6.9 Hz, 4 H, C<u>H</u>$(CH_3)_2$), 1.31 (d, J = 7.0 Hz, 12 H, CH(C<u>H</u>$_3)_2$), 1.24 (d, J = 7.0 Hz, 12 H, CH(C<u>H</u>$_3)_2$). ^{19}F NMR (CD_2Cl_2): δ –240.7. ^{13}C NMR (CD_2Cl_2): δ 180.7 (N<u>C</u>Cu), 146.2 (*ortho*-C), 135.2 (*ipso*-C), 130.9 (*para*-C), 124.7 (*meta*-C), 124.0 (N<u>C</u>H), 29.2 (<u>C</u>H$(CH_3)_2$), 25.0 (CH(<u>C</u>H$_3)_2$), 24.1 (CH(<u>C</u>H$_3)_2$). Anal. Calcd. $C_{27}H_{36}N_2CuF$: C, 68.83; H, 7.70. Found: C, 68.52; H, 7.65.

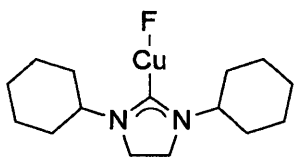


[1,3-dicyclohexylimidazolin-2-ylidene]copper(I) chloride. In a glovebox, a round-bottomed flask equipped with a Teflon-coated stirbar was charged with copper(I) chloride (1.10 g, 12.20 mmol) and sodium *tert*-butoxide (1.06 g, 12.20 mmol). Tetrahydrofuran (100 mL) was added,

and the mixture was stirred for 2 hours. 1,3-dicyclohexylimidazolinium chloride (3.00 g, 11.07 mmol) suspended in tetrahydrofuran (20 mL) was added, and the mixture was stirred for an additional 3 hours. The mixture was filtered through Celite, and concentrated *in vacuo* to give the title complex (3.46 g, 94%). ^{1}H NMR (acetone-d_6): δ 3.78 (m, 2 H, NC<u>H</u>), 3.64 (s, 4 H, NC<u>H</u>$_2$, 1.83 (m, 8 H), 1.64 (m, 6 H), 1.37 (m, 4 H), 1.14 (m, 2 H). ^{13}C NMR (CD_2Cl_2): δ 197.5 (N<u>C</u>Cu), 60.1(N<u>C</u>H$_2$), 44.7, 32.4, 25.8, 25.7. Anal. Calcd. $C_{15}H_{26}N_2CuCl$: C, 54.04; H, 7.86. Found: C, 54.09; H, 7.60.



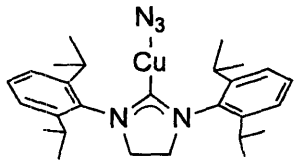
[1,3-dicyclohexylimidazolin-2-ylidene]copper(I) *tert*-butoxide. In a glovebox, a round-bottomed flask equipped with a Teflon-coated stirbar was charged with (SICy)CuCl, (3.00 g, 9.00 mmol) and sodium *tert*-butoxide (0.865 g, 9.00 mmol). Anhydrous tetrahydrofuran (80 mL) was added. The resulting orange suspension was stirred for 2 hours filtered through Celite, and concentrated *in vacuo* to give the title complex as an off-white solid, (3.24 g, 97%). ^{1}H NMR (C_6D_6): δ 4.23 (m, 2 H, NC<u>H</u>), 2.72 (s, 4 H, NC<u>H</u>$_2$, 1.77 (s, 9 H), 1.76 (m, 4 H), 1.59 (m, 4 H), 1.46 (m, 2 H) 1.18 (m, 8H) 0.89 (m, 2 H). ^{13}C NMR (C_6D_6): δ 197.5 (N<u>C</u>Cu), 69.3 (O<u>C</u>), 60.1 (N<u>C</u>H$_2$), 43.8, 37.7, 32.2, 26.2, 26.1, 26.0. Anal. Calcd. $C_{19}H_{35}N_2CuO$: C, 61.50; H, 9.51. Found: C, 61.77; H, 9.54.



[1,3-dicyclohexylimidazolin-2-ylidene]copper(I) fluoride. In a glovebox, (SICy)Cu(O*t*-Bu) (2.52 g, 6.79 mmol) and benzene (25 mL) were added to a Schlenk flask equipped with a Teflon-

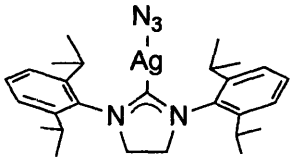
coated stirbar. The flask was sealed with a septum, and taken out of the glovebox. Triethylamine tris(hydrofluoride) (0.369 mL, 2.26 mmol) was added via syringe, and the solution was stirred for 30 minutes. The resulting light tan solution was concentrated *in vacuo*, washed with hexanes (3 x 10 mL), and dried under vacuum at 50 °C for 12 hours to afford the title compound as an off-white solid (1.01 g, 79%). ^{1}H NMR (CD_2Cl_2): δ 3.92 (m, 2 H, NC<u>H</u>), 3.46 (s, 4 H, NC<u>H</u>$_2$, 1.83 (m, 8 H), 1.66 (m, 2 H), 1.49 (m, 4 H), 1.40 (m, 4 H), 1.11 (m, 2 H). ^{13}C NMR (CD_2Cl_2): δ 198.4 (N<u>C</u>Cu), 60.1(N<u>C</u>H$_2$), 44.4, 32.2, 25.9, 25.8. ^{19}F NMR (CD_2Cl_2): δ –239.8. Anal. Calcd. $C_{15}H_{26}N_2CuF$: C, 56.85; H, 8.27. Found: C, 56.47; H, 8.07.

CAUTION: Metal–azide complexes are toxic and potentially explosive. Preparations were only carried out only on NMR scale. The metal–azide products were not handled in the solid state except single-crystal for X-ray diffraction studies. NMR analysis of the reaction between (SIPr)MF (M = Cu, Ag, Au) and trimethylsilyl azide showed the presence of only one metal product in each case, along with trimethylsilyl fluoride byproduct and a trace of trimethylsilyl azide starting material.

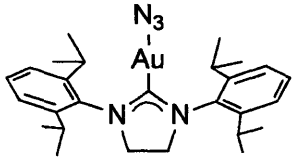


[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) azide. In a glovebox, (SIPr)CuF (0.012 g, 0.026 mmol) and CD_2Cl_2 (0.7 mL) was added to a screw-cap NMR tube. The tube was sealed with a septum cap, and taken out of the glovebox. Trimethylsilyl azide (4 μL, 0.031 mmol) was added, and the reaction mixture was analyzed by NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 7.46 (t, *J* = 7.6 Hz, 2 H, *para*-CH), 7.30 (d, *J* = 7.9 Hz, 4 H, *meta*-CH), 4.02 (s, 4 H, NC<u>H</u>$_2$), 3.06 (sept, *J* = 6.9 Hz, 4 H, C<u>H</u>(CH$_3$)$_2$), 1.34 (pseudo t, *J* = 6.9 Hz, 24 H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (CD_2Cl_2): δ 203.1 (N<u>C</u>Cu), 147.3 (*ortho*-C), 134.9 (*ipso*-C), 130.35

(*para*-C), 125.0 (*meta*-C), 54.4 (N<u>C</u>H$_2$), 29.4 (<u>C</u>H(CH$_3$)$_2$), 25.7 (CH(<u>C</u>H$_3$)$_2$), 24.1 (CH(<u>C</u>H$_3$)$_2$). IR (CH_2Cl_2, cm^{-1}): 2076 ($\nu_{as}N_3^-$), 1485, 1458, 954.

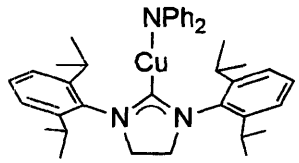


[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]silver(I) azide. In a glovebox, (SIPr)AgF (0.017 g, 0.026 mmol) and CD_2Cl_2 (0.7 mL) was added to a screw-cap NMR tube. The tube was sealed with a septum cap, and taken out of the glovebox. Trimethylsilyl azide (4.5 μL, 0.031 mmol) was added, and the reaction mixture was analyzed by NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 7.46 (t, J = 7.7 Hz, 2 H, *para*-CH), 7.30 (d, J = 7.7 Hz, 4 H, *meta*-CH), 4.07 (s, 4 H, NC<u>H</u>$_2$), 3.06 (sept, J = 6.9 Hz, 4 H, C<u>H</u>(CH$_3$)$_2$), 1.34 (pseudo t, J = 8.8 Hz, 24 H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (CD_2Cl_2): δ 207.1 (d, $J_{C-^{109}Ag}$ = 254 Hz, $J_{C-^{107}Ag}$ = 220 Hz, <u>C$_{ipso}$</u>–Ag)[47], (N<u>C</u>Ag), 147.3 (*ortho*-C), 135.1 (*ipso*-C), 130.5 (*para*-C), 125.2 (*meta*-C), 54.5 (d, J_{Ag-C} = 8.1 Hz, N<u>C</u>H$_2$), 29.4 (<u>C</u>H(CH$_3$)$_2$), 25.6 (CH(<u>C</u>H$_3$)$_2$), 24.3 (CH(<u>C</u>H$_3$)$_2$). IR (CH_2Cl_2, cm^{-1}): 2054 ($\nu_{as}N_3^-$), 1485, 1458, 954.

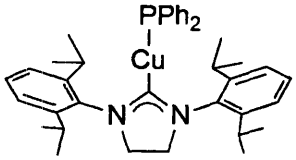


[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) azide. In a glovebox, (SIPr)AuF (0.020 g, 0.033 mmol) and CD_2Cl_2 (0.7 mL) was added to a screw-cap NMR tube. The tube was sealed with a septum cap, and taken out of the glovebox. Trimethylsilyl azide (5.3 μL, 0.040 mmol) was added, and the reaction mixture was analyzed by NMR spectroscopy. ^{1}H NMR (CD_2Cl_2): δ 7.48 (t, J = 7.7 Hz, 2 H, *para*-CH), 7.30 (d, J = 7.8 Hz, 4 H, *meta*-CH), 4.06 (s, 4 H, NC<u>H</u>$_2$), 3.05 (sept, J = 6.9 Hz, 4 H, C<u>H</u>(CH$_3$)$_2$), 1.40 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$), 1.34 (d, J

= 7.0 Hz, 12 H, CH(C$\underline{H}_3$)$_2$). ^{13}C NMR (CD_2Cl_2): δ 194.8 (N$\underline{C}$Au), 147.3 (*ortho*-C), 134.6 (*ipso*-C), 130.5 (*para*-C), 125.0 (*meta*-C), 54.4 (N$\underline{C}H_2$), 29.5 ($\underline{C}$H(CH$_3$)$_2$), 25.3 (CH($\underline{C}$H$_3$)$_2$), 24.4 (CH($\underline{C}$H$_3$)$_2$). IR (CH_2Cl_2, cm^{-1}): 2064 ($\nu_{as}N_3^-$), 1496, 1460, 954.



[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) diphenylamide. In a glovebox, a sealable Schlenk flask equipped with a Teflon-coated stirbar was charged with (SIPr)CuF (0.132 g, 0.279 mmol) and *N*-(trimethylsilyl)diphenylamine (0.081 g, 0.336 mmol). Tetrahydrofuran (5 mL) was added, the flask was sealed and heated at 60 °C for 12 hours. The solvent was removed *in vacuo*. The resulting solid was washed with pentane (3 x 1 mL) to afford the title complex as a light yellow solid (0.144 g, 83%). ^{1}H NMR (C_6D_6): δ 7.32 (t, J = 7.8 Hz, 2 H), 7.12 (d, J = 7.8 Hz, 4 H), 6.95 (t, J = 6.9 Hz, 4 H), 6.71 (t, J= 8.4 Hz, 4 H), 6.68 (t, J = 8.1 Hz, 2 H), 3.16 (s, 4 H, NC$\underline{H}_2$), 2.90 (sept, J = 6.9 Hz, 4 H, C$\underline{H}$(CH$_3$)$_2$), 1.26 (d, J = 6.1 Hz, 12 H, CH(C$\underline{H}_3$)$_2$) 1.15 (d, J = 6.9 Hz, 12 H, CH(C$\underline{H}_3$)$_2$. ^{13}C NMR (C_6D_6): δ 205.7 (N$\underline{C}$Cu), 156.0, 147.5, 135.6, 130.3, 129.4, 125.2, 120.2, 116.3, 53.6 (N$\underline{C}H_2$), 29.5 ($\underline{C}$H(CH$_3$)$_2$), 25.6 (CH($\underline{C}$H$_3$)$_2$), 24.3 (CH($\underline{C}$H$_3$)$_2$). $C_{39}H_{48}N_3Cu$: C, 75.26; H, 7.77. Found: C, 75.10; H, 7.75.



[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) diphenylphosphide. In a glovebox, a sealable Schlenk flask equipped with a Teflon-coated stirbar was charged with (SIPr)CuF (0.205 g, 0.43 mmol). Benzene (5 mL) was added, the flask was sealed with a Teflon stopcock, and removed from the glovebox. Under a positive flow of argon, the Teflon stopcock

was replaced with a septum, and *P*-(trimethylsilyl)diphenylphosphine (0.111 mL, 0.43 mmol) was added via syringe, and the mixture was stirred for 30 minutes. In a glovebox, the resulting suspension was filtered, washed with pentane (2 x 5 mL) to give the title compound (0.240 g, 87%), as a white solid. ^{1}H NMR (C_6D_6): δ 7.26 (m, 6 H), 7.07 (d, J = 7.8 Hz, 4 H, *meta*-CH), 6.97 (m, 6 H), 3.13 (s, 4 H, NC$\underline{H}_2$), 2.91 (sept, J = 6.9 Hz, 4 H, C$\underline{H}$(CH_3)$_2$), 1.29 (br d, J = 6.1 Hz, 12 H, CH(C$\underline{H}_3$)$_2$) 1.16 (d, J = 6.9 Hz, 12 H, CH(C$\underline{H}_3$)$_2$. ^{13}C NMR (d_8-THF): δ 205.1 (d, $^{2}J_{P\text{-}C}$ = 17.9 Hz, N$\underline{C}$Cu), 148.1 (*ipso*-C, P-C_6H_5, $J_{P\text{-}C}$ = 29.3 Hz), 148.0 (*ortho*-C), 136.1 (*ipso*-C), 133.7 (*ortho*-C, P-C_6H_5, $J_{P\text{-}C}$ = 16.7 Hz), 130.4 (*para*-C), 127.7 (*meta*-C, P-C_6H_5, $J_{P\text{-}C}$ = 5.2 Hz), 125.3 (*meta*-C), 123.2 (*para*-C, P-C_6H_5), 54.7 (N$\underline{C}H_2$), 29.8 ($\underline{C}$H(CH_3)$_2$), 25.9 (CH($\underline{C}H_3$)$_2$), 24.3 (CH($\underline{C}H_3$)$_2$). ^{31}P NMR (C_6D_6): δ –26.1. $C_{39}H_{48}N_2PCu$: C, 73.27; H, 7.57. Found: C, 73.26; H, 7.54.

Reaction of (SICy)CuF with 4-Iodonitrobenzene. In a glovebox, a J-Young NMR tube was charged with (SICy)CuF (0.035 g, 0.110 mmol) and 4-iodonitrobenzene (0.055 g, 0.220 mmol). DMF (0.7 mL) was added, and the tube was sealed, taken out of the glovebox, and heated at 100 °C for 8 hours, and 150 °C for 15 hours. The tube was cooled to room temperature, and fluorobenzene (0.0107 mL, 0.110 mmol) was added as an internal standard. Analysis of the solution by ^{19}F NMR spectroscopy indicated that 4-fluoronitrobenzene was formed in 16% yield.

Computational Details. Calculations were performed within the Gaussian 98 program suite,[48] and employed the exchange functional of Becke[49] along with the correlation functional of Perdew.[50] Integrals over one-electron operators were evaluated throughout with a (75,302) grid that was pruned for nonmetal atoms. Nonmetal atoms were described with the 6-31+G(d,p) basis set.[51] The gold orbitals were described with the Stuttgart effective core potential and their associated basis set,[52] which was contracted as follows: Au, (8s,7p,6d) → [6s,5p,3d].

Relativistic effects with the Stuttgart ECP and its associated basis set are introduced with a potential term (i.e., a one-electron operator) that replaces the two-electron exchange and Coulomb operators resulting from interaction between core electrons and between core and valence electrons. In this way, relativistic effects, especially the scalar effects, are included implicitly, rather than as explicit four-component, one-electron functions in the Dirac equation.

All calculations incorporate implicit solvation in dichloromethane through Tomasi's polarizable continuum model (PCM) at 298.15 K, with dielectric constant $\varepsilon = 8.93$. Self-consistent field convergence was achieved with Pulay's direct inversion in the iterative subspace extrapolation.[53] Equilibrium geometries of complexes lacking specific CH_2Cl_2 were optimized in redundant internal coordinates,[54] without imposed symmetry. Harmonic frequency calculations confirm the structures so generated to be energy minima. Geometry optimizations of specifically solvated complexes also proceeded in redundant internal coordinates, with implicit (PCM) dichloromethane solvation, and were unconstrained, except as follows: (i) distances between F and dichloromethane carbons were fixed at their crystallographic values, (ii) One F–C–Cl angle per solvent was constrained to the experimental value, and (iii) one Cl–$C_{(solv)}$–$C_{(carbene)}$–N dihedral angle per solvent molecule was fixed at the crystallographic value. Despite these constraints, net motion of CH_2Cl_2 is still possible. Force-constant matrix diagonalization found imaginary vibrational frequencies for all specifically solvated structures; the imaginary frequencies corresponded to CH_2Cl_2 libration or carbene rotation. Stability tests validated the integrity of all converged densities.

Population analyses were performed with the program AOMix by Gorelsky.[55,56]

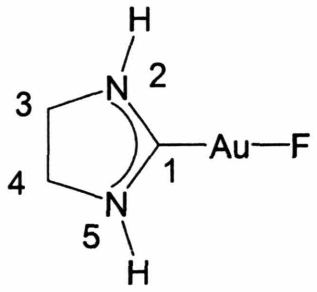


Table 3. Selected interatomic distances for **2c** vs. **A**. Labels in parentheses refer to crystallographic designations.

Interatomic distance	Calculated	Experimental
Au–F	2.029	2.028(2)
Au–C_1	1.974	1.956(3)
C_1–N_2 (C_1–N_2, .cif)	1.349	1.342(3)
N_2–C_3 (N_2–C_3, .cif)	1.480	1.481(3)
C_3–C_4 (C_2–C_3, .cif)	1.551	1.534(4)
C_4–N_5 (C_2–N_1, .cif)	1.480	1.472(4)
C_1–N_5 (C_1–N_1, .cif)	1.349	1.338(3)
rms dev	0.011	
Av. dev	+0.009	

Table 4. Calculated Natural atomic charges (*B3YLP* level)

	A, no specific	A, with specific solvation[a]
Au	0.462	0.468
Carbene C	0.226	0.226
Fluorine	–0.804	–0.796
Solvent carbons		–0.502, –0.503
Chlorines		–0.050, –0.051, –0.052, –0.054
Proximal CH_2Cl_2 hydrogen		0.315, 0.316
Remote CH_2Cl_2 hydrogen		0.279, 0.279

[a]Correspondingly calculated charges on dichloromethane (PCM CH_2Cl_2 solvation): C, –0.530; Cl, –0.030; H, 0.295.

Table 5. Calculated interatomic distances (Å) associated with solvating dichloromethanes in **A.**

	A
F–proximal H	2.177, 2.132
Proximal H–C	1.103, 1.103
Remote H–C	1.097, 1.097
C–Cl	1.802, 1.802, 1.803, 1.803
M–F	2.050
$M–C_{(carbene)}$	1.975

Table 6. Mulliken electrostatic charges calculated for selected atoms of **A** with variations in basis set and functional.

	BP86/ 6-31+G(d,p)	BP86/6-1G(d)	BP86/6-31G	B3LYP/6-31+G(d,p)
Au[a]	–0.714145	–0.176945	–0.162770	–0.560115
$C_{carbene}$	0.433350	0.387030	0.469926	0.408689
F	–0.473835	–0.400855	–0.378936	–0.541312

[a]In all instances, the gold atom is described by the Stuttgart 1997 ECP and basis set.

Table 8. Crystallographic data for **3a–c**, **4**, and **5**.

	3a	**3b**	**3c**	**4**	**5**
empirical formula	$C_{28}H_{40}N_5Cl_2Cu$	$C_{27}H_{38}AgN_5$	$C_{28}H_{40}AuCl_2N_5$	$C_{39}H_{48}N_3Cu$	$C_{39}H_{48}CuN_2P$
FW	581.09	540.49	714.52	622.34	639.30
T, K	100(2)	200(2)	123(2)	100(2)	100(2)
Crystal syst	orthorhombic	triclinic	monoclinic	triclinic	triclinic
Space group	*Pbcm*	*P*1	$P2_1/n$	*P*1	*P*1
a, Å	7.8799(13)	9.8682(7)	10.7478(3)	11.0068(4)	10.2091(16)
b, Å	17.044(3)	11.3745(10)	18.3575(6)	12.6662(6)	10.8946(15)
c, Å	22.823(4)	12.4198(11)	16.6540(4)	13.6282(6)	16.494(2)
α, deg	90	85.608(3)	90	77.233(2)	74.462(5)
β, deg	90	85.199(3)	104.0390(10)	75.877(2)	88.005(5)
γ, deg	90	85.439(3)	90	72.227(2)	83.516(5)
V, Å^3	3065.3(9)	1381.3(2)	3187.73(16)	1732.38(13)	1756.2(4)
ρ_{calc}, g/cm^{-1}	1.259	1.299	1.489	1.193	1.209
Z	4	2	4	2	2
μ, mm^{-1}	0.911	0.752	4.806	0.660	0.696
F(000)	1224	564	1424	664	680
cryst size, mm^3	0.28 x 0.17 x 0.13	0.10 x 0.10 x 0.05	0.17 x 0.17 x 0.17	0.13 x 0.05 x 0.05	0.15 x 0.15 x 0.05
θ range, deg	1.78 to 23.25	2.08 to 28.28	1.68 to 28.28	1.98 to 28.28	1.95 to 27.10
no. of data/restraints/params	2269/0/175	6854/0/306	7919/108/382	8579/0/396	7725/0/396
Total no. of reflns	41535	28712	57714	36161	33624
GOF on F^2	1.163	1.064	1.315	1.048	1.058
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0664 wR2 = 0.1619	R1 = 0.0327 wR2 = 0.0807	R1 = 0.0527 wR2 = 0.1095	R1 = 0.0449 wR2 = 0.1002	R1 = 0.0383 wR2 = 0.0903
R indices (all data)	R1 = 0.0733 wR2 = 0.1660	R1 = 0.0375 wR2 = 0.0841	R1 = 0.0547 wR2 = 0.1104	R1 = 0.0597 wR2 = 0.1075	R1 = 0.0448 wR2 = 0.0944

Table 7. Crystallographic data for **2a–c**, (IPr)CuF, and (SICy)CuF.

	2a	**2b**	**2c**	**(IPr)CuF**	**(SICy)CuF**
empirical formula	$C_{27}H_{38}N_2CuF$	$C_{29}H_{42}N_2AgFCl_2$	$C_{29}H_{42}N_2AuFCl_2$	$C_{29}H_{40}N_2CuFCl_2$	$C_{15}H_{26}N_2CuF$
FW	473.13	687.32	776.41	640.97	316.92
T, K	100(2)	123(2)	100(2)	194(2)	194(2)
Crystal syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/m$	$P2_1/n$	$P2_1/n$	$Cmcm$
a, Å	12.3681(4)	9.4472(4)	12.4390(4)	9.3320(9)	6.7573(10)
b, Å	9.0378(3)	16.3907(7)	16.3588(5)	16.4880(16)	8.6396(13)
c, Å	22.8040(7)	10.7238(5)	15.7664(6)	10.7180(10)	26.056(4)
β, deg	97.9880(10)	103.5140(10)	98.695(1)	102.786(2)	90
V, Å^3	2524.31(14)	1614.56(12)	3171.4(2)	1608.2(3)	1521.1(4)
ρ_{calc}, g/cm^{-1}	1.245	1.414	1.626	1.324	1.384
Z	4	2	4	2	4
μ, mm^{-1}	0.888	0.981	5.003	1.037	1.436
F(000)	1008	708	1544	668	672
cryst size, mm^3	0.10 x 0.10 x 0.10	0.22 x 0.20 x 0.18	0.20 x 0.20 x 0.20	0.35 x 0.26 x 0.20	0.22 x 0.14 x 0.08
θ range, deg	1.66 to 26.37	1.95 to 26.37	2.80 to 26.37	1.95 to 26.37	1.56 to 24.98
no. of data/restraints/params	5168/0/288	3432/55/224	6492/0/342	3420 /46/ 231	746 / 0 / 55
Total no. of reflns	33912	22933	57714	9441	3802
GOF on F^2	1.081	1.10	1.095	1.070	1.396
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0343 wR2 = 0.0885	R1 = 0.0242 wR2 = 0.0630	R1 = 0.0228 wR2 = 0.0570	R1 = 0.0362 wR2 = 0.0986	R1 = 0.0556 wR2 = 0.1425
R indices (all data)	R1 = 0.0374 wR2 = 0.0904	R1 = 0.0259 wR2 = 0.0644	R1 = 0.0308 wR2 = 0.0628	R1 = 0.0413 wR2 = 0.1014	R1 = 0.0560 wR2 = 0.1427

X-ray Diffraction Studies: Experiments were performed on single crystals. Colorless crystals were removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. Crystals were affixed to a glass fiber or a cryoloop using the oil, frozen in a nitrogen stream, and optically centered. The data were collected on a Siemens three-circle platform goniometer equipped with a Bruker Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), using both phi and omega scans. The data were at –173 °C unless otherwise noted. The structures were solved by direct methods (SHELXS)[57] and refined against F^2 on all data by full matrix least squares with SHELXL-97 (Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. CIF files for all unpublished structures are available at http://www.reciprocalnet.org/ {numbers 04170 (**2a**), 04157 (**2b**), 04052 [(IPr)CuF], 04064 [(SICy)CuF], 04174 (**3a**), 04221 (**3b**), 04230 (**3c**), 05013 (**4**), 04218 (**5**)}.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) fluoride: Single crystals were grown by the vapor diffusion of pentanes into a dichloromethane solution of **2a** at –20 °C.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]silver(I) fluoride: Single crystals were grown by the vapor diffusion of diethyl ether into a dichloromethane solution of **2b** at –20 °C. The data were collected at –150 °C. An isopropyl group was disordered (C9, C10 and C11) and refined over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. The relative occupancies for the disordered parts were refined freely, while constraining the overall occupation to unity. One peak of significant residual electron density was found less than one angstrom from silver (1.01 e/Å^3) after convergence.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) fluoride: Single crystals were grown by the vapor diffusion of hexanes into dichloromethane solution of **2c** at –40 °C. Four peaks of significant residual electron density was found less than one angstrom from gold (1.32, 1.27, 1.23, 1.22, 1.02 e/Å^3) and 1 peak was found less than 1 angstrom from Cl(3) (1.05 e/A^3) after convergence.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) fluoride: Single crystals were grown by the vapor diffusion of hexanes into a dichloromethane solution at –40 °C. The data were collected at –79 °C. A dichloromethane molecule located on a special position was found to be disordered. Symmetry contraints were relaxed, and the molecule was refined over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. The relative occupancies for the disordered parts were refined freely, while constraining the overall occupation to unity.

[1,3-dicyclohexylimidazol-2-ylidene]copper(I) fluoride: Single crystals were grown by the vapor diffusion of hexanes into a dichloromethane solution at –40 °C. The data were collected at –80 °C.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) azide: Single crystals were grown by the vapor diffusion of hexanes into a dichloromethane solution at –40 °C.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]silver(I) azide: Single crystals were grown by the vapor diffusion of diethyl ether into a dichloromethane solution at 0 °C. The data were collected at –73 °C due to a phase change.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]gold(I) azide: Single crystals were grown by the vapor diffusion of diethyl ether into a dichloromethane solution at –40 °C. The

data were collected at –150 °C due to a low temperature phase change. An isopropyl group was disordered (C25, C26 and C27) and refined over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. A dichloromethane molecule located on a special position was also found to be disordered. Symmetry contraints were relaxed, and the molecule was refined over two positions with the above restraints. The relative occupancies for the disordered parts were refined freely, while constraining the overall occupation to unity.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) diphenylamide: Single crystals were grown from a pentane/diethyl ether solution at room temperature.

[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]copper(I) diphenylphosphide: Single crystals were grown by the vapor diffusion of hexanes into a diethyl ether solution at –40 °C.

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Chapter 2

Efficient Homogeneous Catalysis in the Reduction of CO_2 to CO

Parts of this chapter have been adapted from:

Laitar, D. S.; Müller, P.; Sadighi, J. P. "Efficient Homogeneous Catalysis in the Reduction of CO_2 to CO." *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197.

Nature uses carbon dioxide, on a massive scale, as a one-carbon building block for the synthesis of organic molecules.[1] An important pathway for the consumption of CO_2 is its reduction to CO, with subsequent carbon-carbon bond formation, by the enzyme acetyl-CoA synthase/CO dehydrogenase (ACS-CODH).[2] Because the efficient use of CO_2 presents an ongoing challenge in synthetic chemistry,[3] the toxic and inflammable CO is far more widely used as a C_1 feedstock. Due to the large energy input required to generate it from CO_2, CO is produced industrially from fossil fuels.[4] Powerful reducing agents are required to overcome the O=CO bond enthalpy of 532 kJ/mol.[5] Even thermodynamically favorable reactions often have high kinetic barriers.[6]

Certain metal complexes abstract oxygen readily from CO_2,[7] but the resulting metal-oxygen bonds are necessarily strong, and catalytic turnover is rare.[8] Moreover, the byproduct metal oxides are generally basic, and many absorb CO_2 to form one equivalent of $[CO_3]^{2-}$ for each molecule of CO produced. Synthetic electrocatalysts have achieved impressive yields and selectivities in the reduction of CO_2 to CO,[9] but their mechanisms remain obscure, and CODH functions efficiently at far smaller overpotentials.[10] Photolytic[11] and photocatalytic[12] approaches, using light and chemical reducing agents to drive the reaction, show promise, but the chemical processes involved are incompletely understood. The development of well-defined deoxygenation reactions of CO_2 in homogeneous solution could lead to a better understanding of how to break these bonds efficiently, pointing the way to more practical synthetic catalysis.

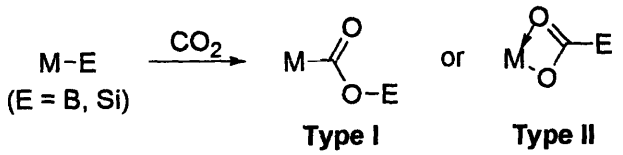
This chapter describes the synthesis of a new carbene-supported copper(I) boryl complex. The boryl complex abstracts oxygen from CO_2, and undergoes subsequent turnover readily. Using an easily handled diboron reagent as the net oxygen acceptor,[13] these key steps permit unprecedented turnover numbers and frequencies for the chemical reduction of CO_2 to CO in a

homogeneous system. A copper(I) silyl complex likewise abstracts oxygen from CO_2, forming CO and a copper(I) siloxide product. One potential intermediate in this reaction, a silanecarboxylate copper(I) complex cleanly decarbonylates to give the same siloxide product. The activation parameters for this decarbonylation were determined.

While exploring the chemistry of organocopper(I) complexes supported by N-heterocyclic carbene (NHC) ligand,[14] we sought to synthesize copper(I) complexes with Cu–E bonds, where E is an oxophilic main group element, and examine their reactivity towards CO_2. Copper(I) boryl and silyl complexes were chosen as initial targets. Metal boryls often display distinctive reactivity,[15] and are key intermediates in a number of remarkable catalytic transformations.[16] Copper boryls have likely been generated *in situ*, in the formation of C–B bonds,[17] but well-defined examples have not been described.

Copper silyl complexes[18,19] were also an appealing target since Si–O bonds are quite strong (128 kcal/mol for Me_3Si–OH),[20] and the insertion of CO_2 into Cu–Si bonds has not been reported. The insertion of CO_2 into M–E (E = B, Si) bonds can potentially form complexes with either M–C and E–O bonds (Type I), or M–O and E–C bonds (Type II) (Scheme 1). The insertion products of either class are unknown for E = B, but both types have been described for E = Si, though they are not always synthesized directly from CO_2 and metal silyls. Metal silanecarboxylates (Type I) have been prepared either by the insertion of CO_2 into M–Si bonds,[21] or by reaction of metal acetates with silyl carboxylic acids.[22] Silyl metallocarboxylates (Type II) have also been prepared by a number of synthetic routes including silylation of metallocarboxylates anions, insertion of CO into the M–O bond of a metal siloxide, or attack on a metal carbonyl by siloxide anion.[22] Certain silyl metallocarboxylates[22b] and silanecarboxylate metal complexes[23] have been shown to extrude CO.

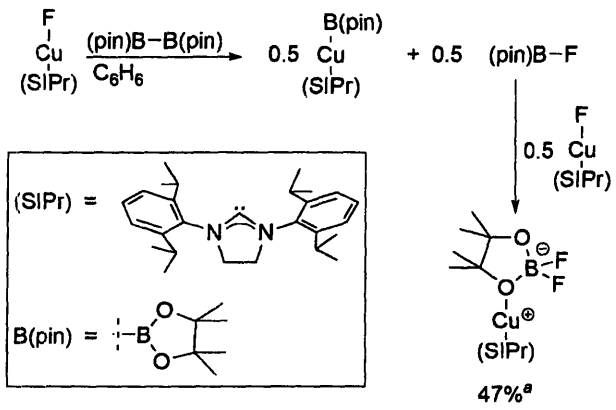
Scheme 1. Two possible products from the insertion of CO_2 into M–E bonds.

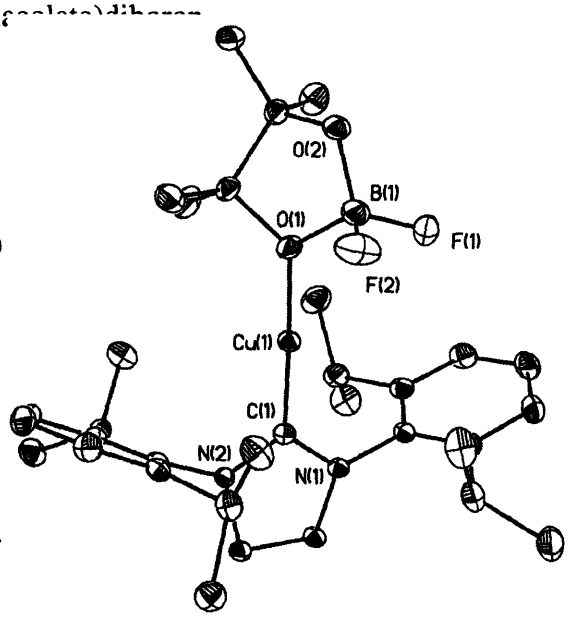


Reduction of carbon dioxide by copper(I) boryl complexes

The synthesis of (SIPr)CuB(pin) [SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, pin = pinacolate: 2,3-dimethyl-2,3-butanediolate] was first attempted by reaction of (SIPr)CuF[24] with bis(pinacolato)diboron [(pin)B–B(pin)] in benzene solution. A rapid reaction occurred, with precipitation of a white solid in ~50% yield. Single crystal X-ray diffraction analysis indicated that the product isolated was not the desired (SIPr)CuB(pin), but rather an O-bound difluoro(pinacol)borate complex, [(SIPr)Cu][F_2B(pin)] (Figure 1). The Cu–O bond length found in the structure, 1.8462(16) Å, is similar to that of (IPr)CuO*t*-Bu is 1.8641(18) Å.[14b] The B–O bond distance for the copper-bound oxygen, 1.506(3) Å, is somewhat longer than the distal B–O bond distance of 1.441(3) Å. Two broad resonances for the pinacol methyl groups are observed in the ^{1}H NMR spectrum of [(SIPr)Cu][F_2B(pin)] in dichloromethane, consistent with slow dissociation of the difluoro(pinacol)borate anion on the NMR timescale at room temperature. In the more coordinating solvent acetonitrile, anion dissociation is more rapid, and the pinacol methyl groups of the difluoroborate anion are equivalent in the ^{1}H NMR spectrum of [(SIPr)Cu][F_2B(pin)] at room temperature.

Scheme 2. Reaction of (SIPr)CuF with bis(pinacolato)diboron





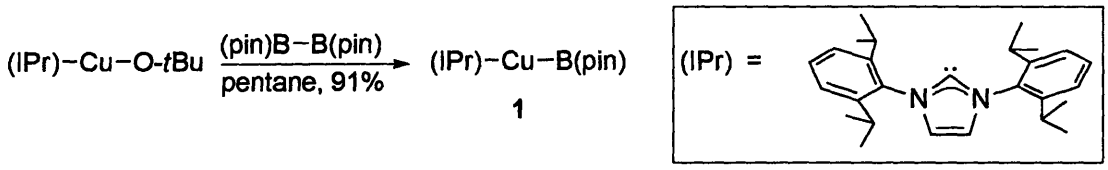
[a]Maximum yield for the reaction as run is 50%.

Figure 1. X-Ray crystal structure of [(SIPr)Cu][F_2B(pin)]•(C_4H_8O) shown as 50% ellipsoids. Solvent, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.8462(16), Cu(1)–C(1) 1.862(2), O(1)–B(1) 1.506(3), O(2)–B(1) 1.441(3), F(1)–B(1) 1.394(3), F(2)–B(1) 1.394(3), C(1)–Cu(1)–O(1) 175.61(9).

The formation of [(SIPr)Cu][F_2B(pin)], believed to proceed through abstraction of fluoride from (SIPr)CuF by (pin)B–F, suggests that the desired product (SIPr)CuB(pin) was indeed formed. The rapid subsequent reaction of the boron-based byproduct with the starting copper complex, which limits the yield of the boryl to 50% at best, was avoided through the use of a copper alkoxide instead of a copper fluoride. The borate ester that results from transmetallation is less Lewis-acidic than a fluoroborane, and is stable under the reaction conditions. Thus (IPr)Cu*Ot*-Bu, {[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]-copper(I) *tert*-butoxide}, reacted cleanly and rapidly with (pin)B–B(pin), forming the desired

(IPr)CuB(pin) in 91% yield (**1**, Scheme 3). Complex **1** was characterized by a combination of ^{1}H and ^{11}B NMR spectroscopy. The boryl complex (IPr)CuB(pin) is more easily isolated than its saturated analogue, (SIPr)CuB(pin), and is used throughout the rest of this study. In the solid state, **1** is stable indefinitely at –40 °C; however, benzene solutions of **1** slowly deposit metallic copper at room temperature. Decomposition of the boryl to a mixture of unidentified byproducts was 25% complete after one day, as judged by ^{11}B NMR spectroscopy.

Scheme 3. Synthesis of (IPr)CuB(pin).



Diffusion of hexane vapor into a concentrated solution of **1** in toluene, carried out at –40 °C to avoid thermal decomposition, produced single crystals suitable for analysis by X-ray diffraction. The resulting crystal structure (Figure 2) shows a monomeric complex with a nearly linear coordination geometry about copper, and a Cu–B distance of 2.002(3) Å. The $Cu–C_{carbene}$ distance of 1.937(2) Å is slightly longer than those found previously for (IPr)CuO*t*-Bu, (IPr)CuCl, and (IPr)$CuCH_3$ (1.864(2), 1.881(7), and 1.913(6) Å, respectively), consistent with the strong *trans*-influence of the boryl group.[15b]

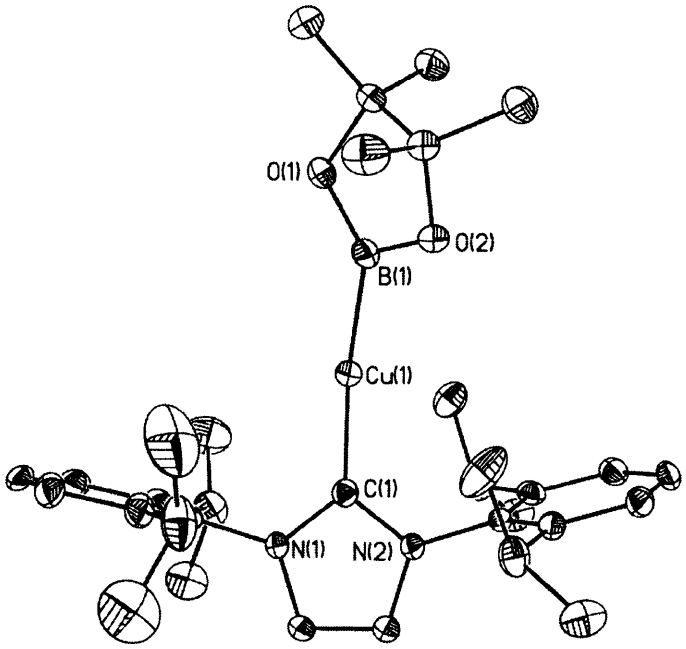
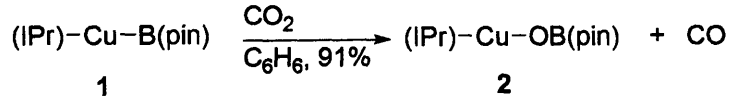


Figure 2. X-ray crystal structure shown as a 50% thermal ellipsoid representation of boryl complex **1**•($0.5C_6H_{12}$). Hydrogen atoms (calculated) and solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–B(1) 2.002(3), Cu(1)–C(1) 1.937(2), C(1)–Cu(1)–B(1) 168.1(1), N(1)–C(1)–N(2) 103.0(2).

Complex **1** reacts with CO_2 under atmospheric pressure in C_6D_6 solution, forming a new complex quantitatively, within minutes, as indicated by its ^{11}B NMR spectrum. The starting resonance, a broad singlet at 41.7 ppm, was replaced by a singlet at 21.8 ppm, indicative of boron bound to three oxygen atoms.[25] Shifts of key ligand-derived resonances in the ^1H NMR spectrum were also observed. Single crystals of this new copper complex were grown by diffusion of hexane vapor into a concentrated toluene solution. The X-ray crystal structure (Figure 3) revealed the product to be (IPr)CuOB(pin) (**2**): The copper boryl complex had abstracted oxygen from CO_2, implying the release of CO as the byproduct (Scheme 4).

Scheme 4. Stoichiometric deoxygenation of CO_2 by (IPr)CuB(pin).



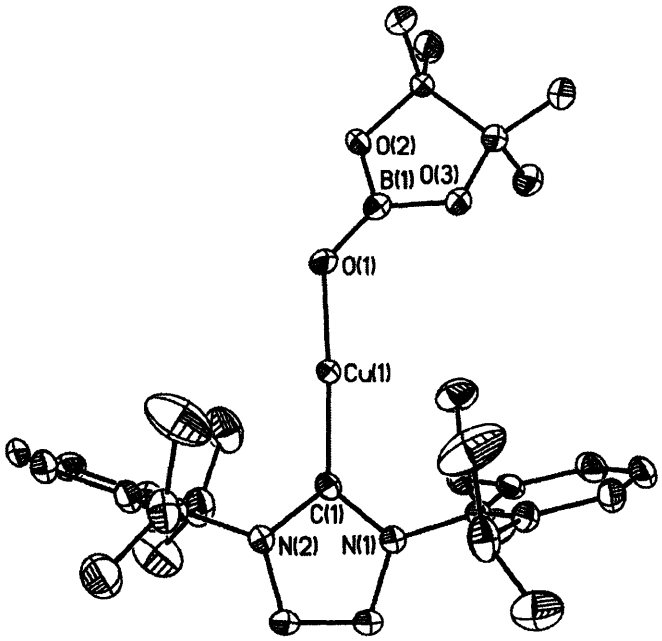


Figure 3. X-ray crystal structure, shown as 50% thermal ellipsoid representation, of borate complex **2**•(C_7H_8). Hydrogen atoms (calculated) and solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.810(2), O(1)–B(1) 1.306(3), Cu(1)–C(1) 1.857(2), C(1)–Cu(1)–O(1) 174.9 (1), B(1)–O(1)–Cu(1) 133.6(2), N(1)–C(1)–N(2) 103.1(2).

To confirm the formation of CO, ^{13}C-labeled CO_2 was introduced to a resealable NMR tube containing a solution of **1** in THF-d_8. A new resonance appeared at 184 ppm in the ^{13}C NMR spectrum, consistent with the generation of ^{13}CO. Analysis by ^{11}B (Figure 4a) and ^{1}H NMR spectroscopy indicated the complete conversion of **1** to **2**. When the reaction of **1** with $^{13}CO_2$ was carried out at –80 °C, the ^{13}C NMR spectrum suggested the formation of several possible intermediates. Efforts to identify these intermediates have been hampered by their instability: liberation of ^{13}CO was significant after minutes at –60 °C, and complete at –40 °C,

after a half-hour of warming from –80 °C. The sole labeled products visible in this spectrum (Figure 4b) were ^{13}CO and its adduct (δ 164 ppm) with borate byproduct **2**, formed reversibly on cooling to low temperatures, which may be generated independently.

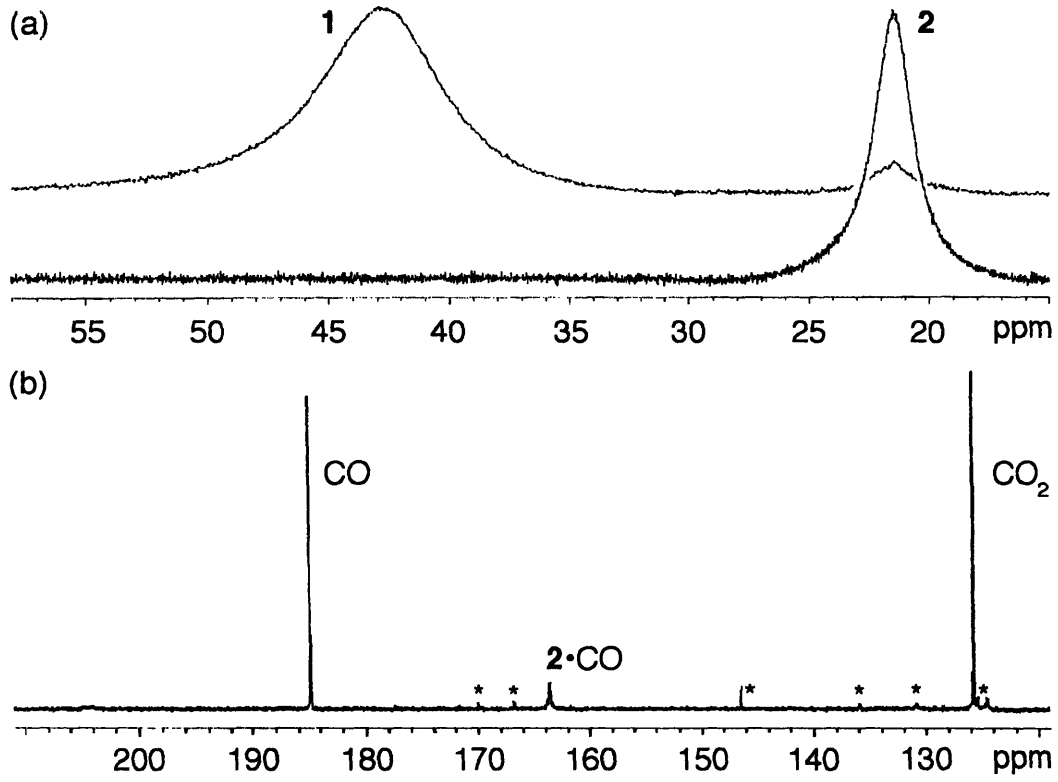
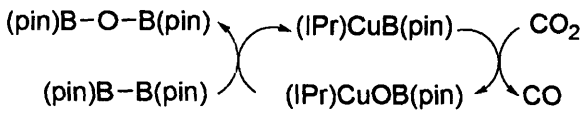


Figure 4. (a) ^{11}B NMR spectra of key boron-containing complexes before and after reaction with CO_2: **1** (containing 5% **2**) and **2**; (b) ^{13}C NMR spectrum after reaction of **1** with excess $^{13}CO_2$ (THF-d_8, –80 to –40 °C, 30 min); * denotes ligand-derived resonances; solvent and aliphatic resonances omitted for clarity.

Scheme 5. Proposed catalytic cycle for the deoxygenation of CO_2.



If the (pinacol)borate group of **2** could be replaced with a new boryl group, this facile reduction of CO_2 to CO might be incorporated into a catalytic cycle (Scheme 5). By analogy to the original synthesis of **1**, activation of the Cu–O bond by transmetallation with a B–B bond appeared promising. Indeed, treatment of **2** in C_6D_6 solution with (pin)B–B(pin) smoothly generated **1** and the very stable byproduct (pin)B–O–B(pin), over a reaction time of about 20 minutes. The catalytic deoxygenation of CO_2 was attempted next. Addition of a THF solution of (IPr)CuO*t*-Bu to a 100-fold excess of (pin)B–B(pin) under an atmosphere of CO_2 resulted in the complete conversion of (pin)B–B(pin) to (pin)B–O–B(pin) within 20 hours at ambient temperature, as judged by ^{11}B NMR analysis of an aliquot from the reaction mixture (Scheme 6, Figure 5a). When labeled CO_2 was used as the limiting reagent, in the presence of *ca.* 2 mol% of precatalyst **1**, the ^{13}C NMR spectrum indicated complete consumption of CO_2, with CO representing the sole significant product (Figure 5b).

Scheme 6. Ambient temperature conversion of CO_2 to CO with (IPr)CuB(pin) catalyst.

$$\text{(pin)B–B(pin)} + CO_2 \xrightarrow[C_6H_6,\ \text{RT 20 hrs}]{\text{1 mol\% (IPr)CuO-}t\text{Bu}} CO + \text{(pin)B–O–B(pin)}$$

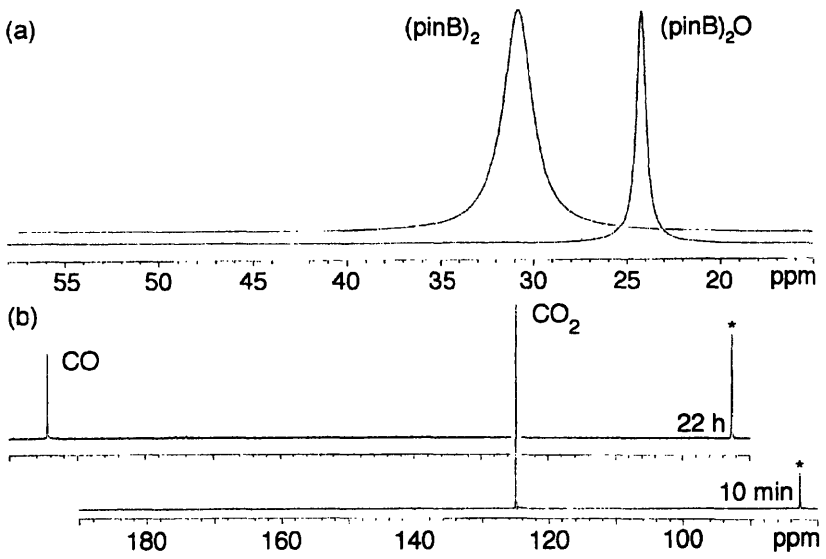


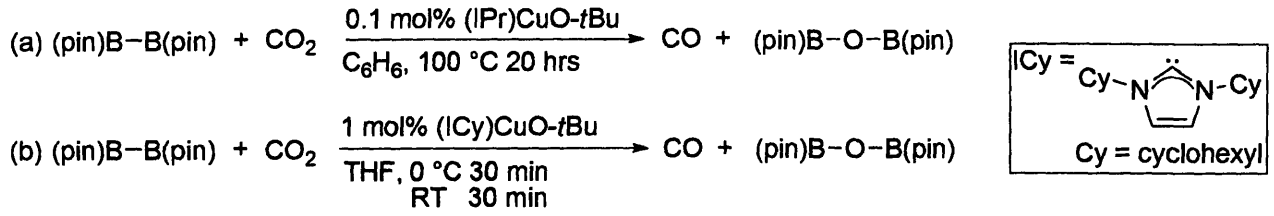
Figure 5 (a) ^{11}B NMR spectra showing conversion of (pin)B–B(pin) to (pin)B–O–B(pin) by catalytic reduction of CO_2 (excess CO_2, 1 mol% **1**, ambient temp, THF-d_8, 20 h); (b) ^{13}C NMR spectra, offset for clarity, before and after catalytic reduction of $^{13}CO_2$ to ^{13}CO (excess (pin)B–B(pin), *ca.* 2 mol% **1**, ambient temp, THF-d_8); * denotes pin (Me_2CO) resonance.

In the absence of copper catalyst, under otherwise identical conditions, no (pin)B–O–B(pin) was observed, demonstrating that the diboron compound by itself is kinetically unable to reduce CO_2 to any observable extent. Control reactions run using copper precatalyst and (pin)B–B(pin) in the absence of CO_2, under an atmosphere of argon or even dry air, showed at most stoichiometric formation of (pin)B–O–B(pin) with respect to copper. Thus, oxidation of (pin)B–B(pin) by adventitious air does not contribute significantly to the formation of (pin)B–O–B(pin) under these conditions, and essentially all conversion observed in the catalytic reactions results from the deoxygenation of CO_2.

Considerably higher turnover numbers were achieved at higher reaction temperatures. The turnover of pinacolborate **2** by (pin)B–B(pin), known from stoichiometric studies to be the

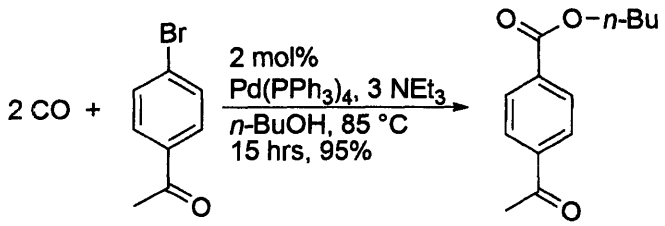
slow step, presumably occurs much more rapidly; the boryl complex **1**, generated *in situ*, is sufficiently stable toward decomposition to react productively with CO_2. The reaction of CO_2 with (pin)B–B(pin) at 100 °C, using 0.1 mol% (IPr)CuO*t*-Bu precatalyst, gave rise to (pin)B–O–B(pin) as the sole boron-containing product, corresponding to 1000 catalytic turnovers per copper (Scheme 7a).

Scheme 7. Deoxygenation of CO_2 with high turnover numbers (a) and frequencies (b).



To achieve more rapid catalytic turnover under mild conditions, the bulky IPr was replaced by the less sterically demanding ICy (1,3-dicyclohexylimidazol-2-ylidene) as a supporting ligand for copper. The complex (ICy)CuB(pin), generated *in situ*, is notably more prone to thermal decomposition than **1**, and catalytic reactions of CO_2 with (pin)B–B(pin) using 1 mol% (ICy)CuO*t*-Bu displayed only 81% conversion at ambient temperature, with visible precipitation of copper metal after less than one hour. However, when the reaction was run at 0 °C for 30 minutes, then at ambient temperature for 30 minutes, complete conversion of (pin)B–B(pin) to (pin)B–O–B(pin) was observed. This turnover frequency, corresponding to 100 turnovers within one hour, is dramatically higher than that achieved using the IPr supporting ligand (Scheme 7b).

Scheme 8. Alkoxycarbonylation of an aryl halide with CO generated from CO_2.



Admission of the CO generated from CO_2 to a flask containing 4-bromoacetophenone, *n*-butanol, triethylamine base and $Pd(PPh_3)_4$ (2 mol%) lead to the formation of 4-(*n*-butoxycarbonyl)acetophenone in 90% isolated yield based on aryl halide (Scheme 8).[26] This carbonylation provides chemical proof of the catalytic reduction of CO_2, while demonstrating the use of the *in-situ*-generated CO in the formation of C–C bonds.

Synthesis of a copper(I) silyl complex and its reactivity towards CO_2

Reaction of $KSiPh_3$ with the previously reported (IPr)CuCl[14a] gave (IPr)$CuSiPh_3$ as a white solid in good yield (**3**, Scheme 9). Complex **3** is stable for days in C_6D_6 solution when protected from oxygen and water. A single peak was observed in the ^{29}Si NMR spectrum of **3** at –0.86 ppm relative to tetramethylsilane and is significantly downfield compared to that of $(Me_3P)_3CuSiPh_3$ (–21.5 ppm).[18a] Complex **3** crystallizes out of a THF/hexanes mixture at –40 °C with two molecules in the asymmetric unit. Similar bond distances and angles are found in the structures, one of which is shown in Figure 6. Both complexes are two-coordinate monomers with Cu–Si bond distances of 2.2693(5) Å and 2.2753(5) Å; nearly identical to that found in another neutral 2-coordinate copper silyl complex, $(Me_3Si)_3Si$–CuSn[$Si(SiMe_3)_3$]Ar* (Ar* = 2,6-$C_6H_3Mes_2$, Mes = 2,4,6-trimethylphenyl) 2.2727(11) Å,[18b] and somewhat shorter than that in the 4-coordinate copper silyl complex, $(Me_3P)_3CuSiPh_3$ (2.340(2) Å).[18a]

Scheme 9. Synthesis of (IPr)CuSiPh$_3$.[a]

$$(IPr)Cu-Cl \xrightarrow[THF,\ 67\%]{KSiPh_3} (IPr)Cu-SiPh_3$$

3

[a] $KSiPh_3$ was generated *in situ* from $(SiPh_3)_2$ and 2 K°.

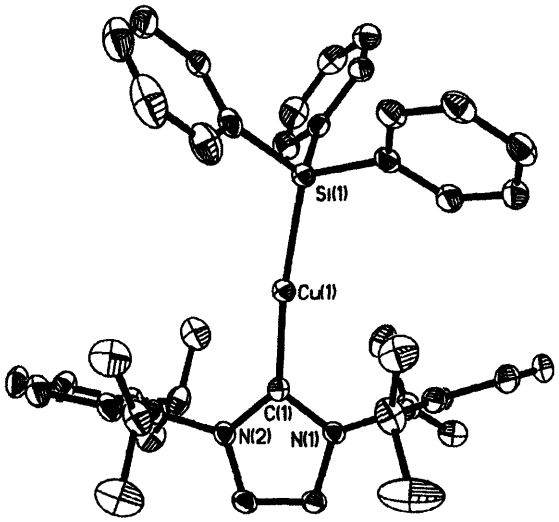


Figure 6. X-ray crystal structure of (IPr)CuSiPh$_3$ shown as 50% ellipsoids. For clarity, hydrogen atoms (calculated) and disorder have been omitted, and only one of two molecules in the asymmetric unit is shown. Bond distances (Å) and angles (°) [corresponding values for the second molecule]: Cu(1)–Si(1) 2.2693(5) [2.2753(5)], Cu(1)–C(1) 1.9252(14) [1.9308(14)], C(1)–Cu(1)–Si(1) 171.34(4) [171.28(4)].

(IPr)CuSiPh$_3$ reacted slowly with CO_2 (1 atm) in C_6D_6 at ambient temperature to give a new complex (10% conversion after 20 hours). Complete consumption of **3** was observed when the reaction was run for 20 hours at 80 °C, and the same product was formed (**4**, Scheme 10). When $^{13}CO_2$ was used, ^{13}CO was detected by ^{13}C NMR spectroscopy, strongly suggesting that complex **4** is (IPr)CuOSiPh$_3$. An X-ray diffraction study on single crystals of the new complex

confirmed that (IPr)CuOSiPh$_3$ had in fact been formed (Figure 7). The bond lengths and angles in the solid-state structure of **4** are not unusual, though it should be noted that the *para*-hydrogen atom of an adjacent IPr ligand is within Van der Waals contact (2.52 Å) with the siloxide oxygen atom of **4**, indicating a weak interaction. Similar interactions have been observed for (IPr)CuO*t*-Bu.[14b] We had hoped to identify the complex derived from (IPr)CuSiPh$_3$ and CO_2 prior to decarbonylation; however, no intermediates were observed by ^{1}H NMR spectroscopy, suggesting that insertion of CO_2 into the Cu–Si bond of **3**, rather than extrusion of CO from the resulting complex, is the rate-limiting step.

Scheme 10. Reaction of (IPr)CuSiPh$_3$ with CO_2.

$$\underset{\mathbf{3}}{(\text{IPr})\text{Cu}-\text{SiPh}_3} \xrightarrow[\text{20 hrs, 91\%}^a]{CO_2,\ C_6H_6\ 80\ ^\circ\text{C}} \underset{\mathbf{4}}{(\text{IPr})\text{Cu}-\text{OSiPh}_3} + \text{CO}$$

[a]Isolated yield.

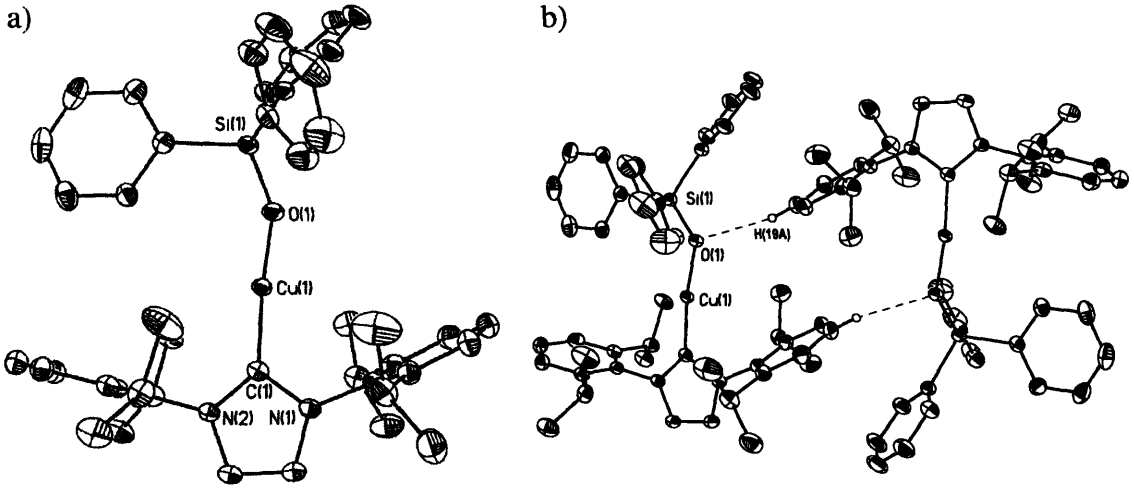
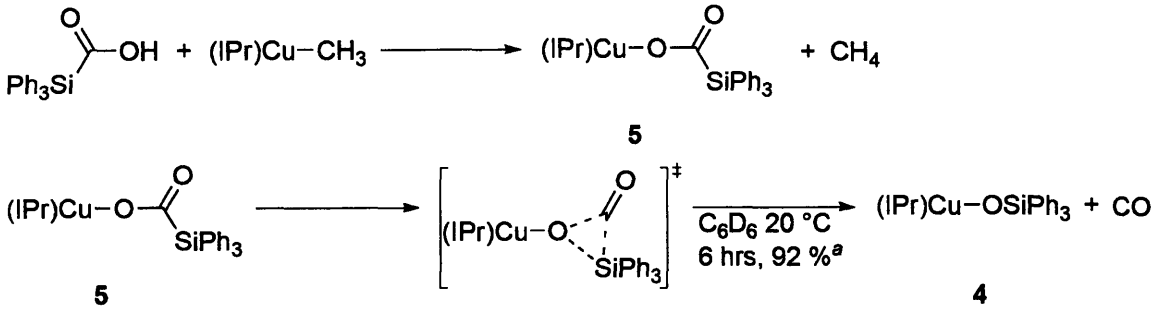


Figure 7. (a) X-ray crystal structure of (IPr)CuOSiPh$_3$ shown as 50% ellipsoids. (b) Extend structure showing O–H$_{meta}$ interaction. For clarity, hydrogen atoms (calculated), except H(19A)

in Figure 7b, have been omitted. Bond distances (Å) and angles (°): Cu(1)–O(1) 1.7997(10), Cu(1)–C(1) 1.8566(13), C(1)–Cu(1)–O(1) 171.57(5).

Since triphenylsilanecarboxylic acid is a relatively stable compound,[27] the synthesis of a potential intermediate in the reaction of CO_2 with (IPr)$CuSiPh_3$ was undertaken (Scheme 11). A C_6D_6 solution of (IPr)$CuCH_3$[14a] reacts with triphenylsilanecarboxylic acid to form (IPr)CuO_2CSiPh_3 (**5**) and methane. Complex **5** is thermally sensitive, decomposing to (IPr)$CuOSiPh_3$ and CO at room temperature in C_6D_6 ($t_{1/2} \approx 40$ min). Despite its thermal instability, single crystals were grown at –40 °C by the vapor diffusion of hexanes into a concentrated ether solution of **5**, generated *in situ* from (IPr)$CuCH_3$ and the acid. X-ray diffraction analysis revealed that in the solid state, **5** is monomeric with a linear, 2-coordinate geometry about copper (Figure 8a). Although relatively rare, copper κ^1-carboxylates have been characterized previously,[28] and the bond distances and angles in **5** are similar to those in (IPr)CuOAc.[14a] The distal oxygen atom in **5** is within Van der Waals contact with a *meta*-hydrogen of an adjacent IPr ligand (H_{meta}–O = 2.36 Å). Similar interactions have been observed in the solid state structure of (IPr)CuOAc.[14a]

Scheme 11. *In situ* generation of (IPr)CuO_2CSiPh_3, and its subsequent decarbonylation via a proposed cyclic intermediate.



[a]Isolated yield from (IPr)$CuCH_3$.

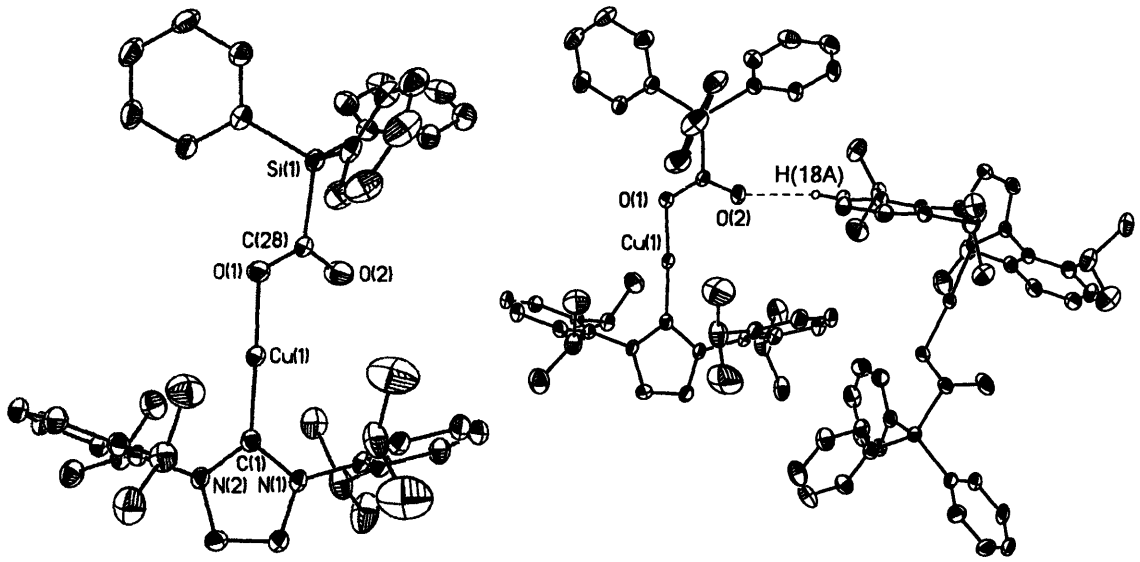


Figure 8. X-ray crystal structure of **5** shown as 50% ellipsoids. For clarity, hydrogen atoms (calculated) have been omitted. Bond distances (Å) and angles (°): Cu(1)–O(1) 1.8554(17), Cu(1)–C(1) 1.862(2), Si(1)–C(28) 1.917(2), O(1)–C(28) 1.282(3), O(2)–C(28) 1.219(3), C(1)–Cu(1)–O(1) 174.78(9), Cu(1)–O(1)–C(28) 117.08(16), Si(1)–C(28)–O(1) 115.45(17).

The rate of CO extrusion from **5** in C_6D_6 was measured using ^1H NMR spectroscopy. Resonances specific to **5** were integrated over time relative to an internal standard (Figure 9). The reaction is unimolecular with a first-order rate constant of 3.01(±14) x 10^{-4} s^{-1} at 20 °C. Statistically identical rate constants were measured for different concentrations of **5**. Measurement of the rate dependence on temperature over a range of 10–50 °C (Table 1) gave activation parameters of $\Delta H^{\ddagger}$ = 21.0(±0.8) kcal/mol and $\Delta S^{\ddagger}$ = –4(±3) cal/(mol•K). The significant enthalpic barrier and small change in entropy are consistent with a unimolecular reaction involving a relatively unstrained cyclic transition state.

Attempts to synthesize another potential CO_2 insertion product, (IPr)CuC(O)$OSiPh_3$, by reaction of CO with (IPr)$CuOSiPh_3$ were unsuccessful: Addition of ^{13}CO to a THF solution of

(IPr)CuOSiPh$_3$ did not produce any new ^{13}C-labeled peaks in the ^{13}C NMR spectrum after days at room temperature, or hours at –80 °C. The absence of a reaction may be due to unfavorable thermodynamics, or to a large kinetic barrier to insertion.

In summary, we have achieved the catalytic reduction of CO_2 to CO in homogeneous solution using copper(I) boryl catalysts, with high turnover numbers and frequencies depending on the reaction conditions and supporting ligand. Both the oxygen abstraction and the catalyst turnover involve well-defined reactants and products, facilitating further study and pointing the way to future advances in catalytic reactions of CO_2. Carbon dioxide also inserts into the Cu–Si bond of a copper silyl complex. The resulting complex evolves CO to give the structurally-characterized copper siloxide complex. One potential intermediate, a copper(I) silanecarboxylate, was synthesized and shown to extrude CO. The decarbonylation is unimolecular with a significant enthalpic barrier and a small negative entropy of activation.

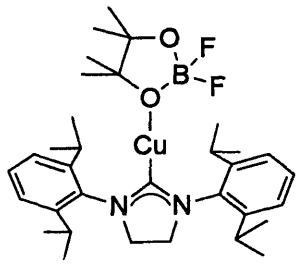
Experimental Section

General Considerations. All synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Anhydrous toluene, hexanes, and tetrahydrofuran were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina and a third column packed with activated 4 Å molecular sieves (for tetrahydrofuran) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Benzene and pentane, anhydrous, were purchased from Aldrich in Sure-Seal™ bottles, and

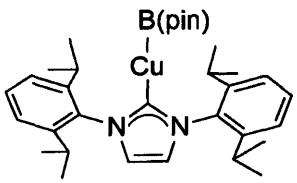
stored in a glovebox over 4Å molecular sieves. All non-dried solvents used were reagent grade or better.

IR spectra were recorded on a Nicolet Impact 410 spectrometer as KBr pellets. NMR solvents C_6D_6 (Cambridge Isotope Laboratories) and C_4D_8O (Cambridge Isotope Laboratories) were dried over sodium/benzophenone. All NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ^1H NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. ^{11}B NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced to an external standard of 0.5 M BF_3 in diethyl ether (0 ppm). ^{13}C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak. ^{29}Si NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced to an external standard of neat $SiMe_4$ (0 ppm). NMR temperatures were calibrated using the separation between the ^1H NMR peaks of neat methanol (10 °C) or neat ethylene glycol (20–50 °C).

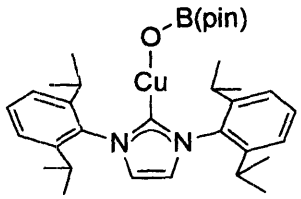
The starting materials copper(I) chloride (Strem), sodium *tert*-butoxide (Aldrich), hexamethyldisilane (Aldrich), and potassium (Strem) were used as received. Bis(pinacolato)diboron (Frontier) was recrystallized from toluene/pentane at –40 °C. Triphenylsilane carboxylic acid (Aldrich) was washed with dichloromethane and dried. [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) *tert*-butoxide[14b] and 1,3-dicyclohexylimidazolium chloride[29] were synthesized as described previously. [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) chloride[14a] and [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) methyl[14a] were synthesized as described previously. [1,3-Dicyclohexylimidazol-2-ylidene]copper(I) *tert*-butoxide was synthesized analogously to [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) *tert*-butoxide.[14b]



[1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] copper(I) (pinacolato)difluoroborate. In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated stirbar was charged with [1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] copper(I) fluoride (0.200 g, 0.423 mmol) and bis(pinacolato)diboron (0.107 g, 0.423 mmol). Benzene (5 mL) was added, and the mixture was stirred vigorously for 20 minutes. The resulting white suspension was filtered and dried *in vacuo* to afford the title complex (0.124 g, 47%, maximum yield for the reaction is 50%). ^{1}H NMR (CD_2Cl_2): δ 7.45 (t, J = 7.8 Hz, 2 H, *para*-CH), 7.30 (d, J = 7.8 Hz, 4 H, *meta*-CH), 4.09 (s, 2 H, NC<u>H</u>), 3.07 (sept., J = 6.9 Hz, 4 H, C<u>H</u>$(CH_3)_2$), 1.37 (d, J = 6.7 Hz, 12 H, CH(C<u>H</u>$_3)_2$), 1.35 (d, J = 6.7 Hz, 12 H, CH(C<u>H</u>$_3)_2$), 0.80 (s, 6 H, pinacol-C<u>H</u>$_3$), 0.68 (br s, 6 H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 202.5 (N<u>C</u>Cu), 147.4 (*ortho*-C), 134.8 (*ipso*-C), 130.3 (*para*-C), 125.0 (*meta*-C), 54.3 (N<u>C</u>H_2), 29.4 (<u>C</u>H$(CH_3)_2$), 24.4 (CH(<u>C</u>$H_3)_2$), 25.3 (br s, OC(<u>C</u>$H_3)_2$), 24.5 (CH(<u>C</u>$H_3)_2$) The resonances for $F_2B(O\underline{C}(CH_3)_2)_2$ were too broad to be definitively assigned. ^{19}F NMR (CD_2Cl_2): δ −149.2. Anal. Calcd. $C_{33}H_{48}N_2O_2F_2BCu$: C, 64.23; H, 7.84. Found: C, 64.27; H, 8.13.



[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacolato)boryl (1). In a glovebox, a Teflon-coated stirbar, [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) *tert*-butoxide (0.204 g, 0.388 mmol) and bis(pinacolato)diboron (0.099 g, 0.390 mmol) were added to a 20-mL scintillation vial, which had been wrapped in black electrical tape to protect its contents from light. Pentane (anhydrous, 5 mL) was added, and the mixture was stirred vigorously for 20 minutes. The resulting white suspension was filtered and dried *in vacuo* to afford the title compound (0.205 g, 91%) (samples typically contained ~5% (IPr)CuOB(pin) presumably due to reaction with adventitious moisture or oxygen). This impurity is less soluble than **1**, and further manipulations to attempt its removal resulted in loss of yield without allowing a purer sample of **1** to be isolated. ^{1}H NMR (C_6D_6): δ 7.15 (t, J = 7.6 Hz, 2 H, *para*-CH), 7.05 (d, J = 7.8 Hz, 4 H, *meta*-CH), 6.21 (s, 2 H, NC<u>H</u>), 2.65 (sept., J = 6.9 Hz, 4 H, C<u>H</u>$(CH_3)_2$), 1.48 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3)_2$), 1.09 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3)_2$) 1.06 (s, 12 H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 187.2 (N<u>C</u>Cu), 146.1 (*ortho*-C), 135.5 (*ipso*-C), 130.7 (*para*-C), 124.4 (*meta*-C), 122.4 (N<u>C</u>H), 79.2 (O<u>C</u>$(CH_3)_2$), 29.4 (<u>C</u>H$(CH_3)_2$), 26.5 (OC(<u>C</u>H$_3)_2$), 25.7 (CH(<u>C</u>H$_3)_2$), 24.1 (CH(<u>C</u>H$_3)_2$). ^{11}B NMR (C_6D_6): δ 41.7. Anal. Calcd. $C_{33}H_{48}N_2O_2BCu$: C, 68.44; H, 8.35. Found: C, 68.53; H, 8.27.



[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacolato)borate (2). In a glovebox, a 100-mL round-bottomed flask equipped with a Teflon-coated stirbar was charged with **1** (0.100 g, 0.173 mmol) and benzene (5 mL) and sealed with a vacuum adaptor. The flask was taken out of the glovebox, the solution was degassed on a vacuum line by one freeze-pump-

thaw cycle and CO_2 (1.1 atm) was added. After stirring for 10 minutes, the reaction mixture was concentrated *in vacuo* to give the title complex as a bright white solid (0.094 g, 91%). ^{1}H NMR (C_6D_6): δ 7.21 (t, J = 7.7 Hz, 2 H, *para*-CH), 7.07 (d, J = 7.7 Hz, 4 H, *meta*-CH), 6.27 (s, 2 H, NC<u>H</u>), 2.56 (sept., J = 6.9 Hz, 4 H, C<u>H</u>(CH_3)$_2$), 1.39 (d, J = 6.6 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$), 1.10 (s, 12 H, pinacol-C<u>H</u>$_3$), 1.08 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 183.2 (N<u>C</u>Cu), 146.1 (*ortho*-C), 135.5 (*ipso*-C), 130.9 (*para*-C), 124.6 (*meta*-C), 123.0 (N<u>C</u>H), 79.2 (O<u>C</u>(CH_3)$_2$), 29.3 (<u>C</u>H(CH_3)$_2$), 25.7 (OC(<u>C</u>H$_3$)$_2$), 25.4 (CH(<u>C</u>H$_3$)$_2$), 24.2 (CH(<u>C</u>H$_3$)$_2$). ^{11}B NMR (C_6D_6): δ 21.8. Anal. Calcd. $C_{33}H_{48}N_2O_3BCu$: C, 66.60; H, 8.13. Found: C, 66.71; H, 8.25.

General Procedure for Room Temperature Deoxygenation of Carbon Dioxide:

In a glovebox, a 25-mL resealable Schlenk flask equipped with a Teflon-coated stirbar, was charged with bis(pinacolato)diboron (0.317 g, 1.25 mmol). The flask was sealed with a Teflon stopcock, taken out of the glovebox, and connected to a Schlenk line. The flask was evacuated and back-filled with CO_2 (1.1 atm). Under a positive pressure of CO_2 the stopcock was replaced with a rubber septum, and a solution of (IPr)CuO*t*-Bu (12.5 μmol; 2 mL of a 6.24 mM stock solution in benzene) was added via syringe. The rubber septum was quickly replaced with a stopcock, and the flask was stirred at room temperature for 20 hours. The reaction mixture was concentrated *in vacuo,* taken into a glovebox and dissolved in benzene (0.7 mL). ^{11}B NMR analysis of the crude reaction mixture showed complete consumption of bis(pinacolato)diboron.

Room Temperature Deoxygenation of $^{13}CO_2$:

In a glovebox, (pin)B–B(pin) (0.080 g, 0.32 mmol) and (IPr)CuO*t*-Bu (1.5 mg, 0.0028 mmol, dissolved in 0.7 mL THF) was added to a J-Young NMR tube. The tube was sealed, taken out of the glovebox, and connected to a Schlenk line. The solution was degassed by one freeze-pump-thaw cycle, and back-filled with $^{13}CO_2$. An initial ^{13}C NMR spectrum was recorded at –80 °C,

and the solution was allowed to stand for 22 hours at room temperature (during that time, the tube was occasionally inverted to ensure mixing). The tube was then inserted into an NMR probe cooled to –80 °C and another spectrum was recorded. ^{13}C NMR showed complete consumption of $^{13}CO_2$, and ^{11}B NMR showed 50 % consumption of (pin)B–B(pin).

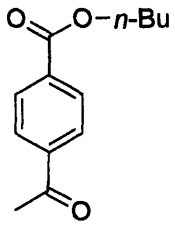
General Procedure for High Temperature Deoxygenation of Carbon Dioxide:

In a glovebox, a 25-mL resealable Schlenk flask equipped with a Teflon-coated stirbar was charged with bis(pinacolato)diboron (0.317 g, 1.25 mmol) and THF (1 mL). The flask was sealed with a Teflon stopcock, taken out of the glovebox, and connected to a Schlenk line. The solution was degassed by one freeze-pump-thaw cycle and back-filled with CO_2 (1.1 atm). Under a positive pressure of CO_2, the stopcock was replaced with a rubber septum, and a solution of (IPr)CuO*t*-Bu (1.25 μmol; 0.5 mL of a 2.5 mM stock solution in THF) was added via syringe. The rubber septum was quickly replaced with a stopcock, and the flask was heated at 100 °C for 20 hours. The flask was then cooled to room temperature, and the solution was concentrated *in vacuo*. In a glovebox, the crude reaction mixture was dissolved in benzene (0.7 mL). Analysis by ^{11}B NMR spectroscopy indicated complete consumption of bis(pinacolato)diboron.

General Procedure for Low Temperature Deoxygenation of Carbon Dioxide:

In a glovebox, a 25-mL resealable Schlenk flask equipped with a Teflon-coated stirbar was charged with bis(pinacolato)diboron (0.317 g, 1.25 mmol) and THF (4 mL). The flask was sealed with a Teflon stopcock, taken out of the glovebox, and connected to a Schlenk line. The solution was degassed by one freeze-pump-thaw cycle and back-filled with CO_2 (1.5 atm). Under a positive pressure of CO_2 the stopcock was replaced with a rubber septum, and the flask was cooled to 0 °C. A solution of (ICy)CuO*t*-Bu (0.0125 mmol; 1 mL of a 12.5 mM stock

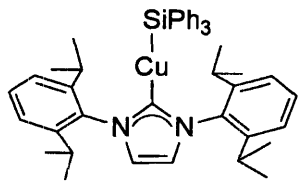
solution in THF) was added via syringe. The rubber septum was quickly replaced with a stopcock, and the flask was stirred at 0 °C for 30 minutes. The flask was taken out of the ice bath stirred for 30 minutes, and the solution was concentrated *in vacuo*. In a glovebox, the crude reaction mixture was dissolved in benzene (0.7 mL). Analysis by ^{11}B NMR spectroscopy indicated complete consumption of bis(pinacolato)diboron.



***n*-Butyl 4-acetylbenzoate:** The synthesis of *n*-butyl 4-acetylbenzoate was based upon a known procedure.[26] In a glovebox, a 25-mL resealable Schlenk tube equipped with a Teflon-coated stirbar was charged with bis(pinacolato)diboron (0.317 g, 1.25 mmol), and THF (4 mL) was added. The tube was sealed, taken out of the glovebox and connected to a Schlenk line. The solution was then degassed by two freeze-pump-thaw cycles and back-filled with CO_2 (1.5 atm). The Teflon stopcock was replaced with a rubber stopper, the flask was cooled to 0 °C, and (ICy)CuO*t*-Bu (0.0125 mmol; 1 mL of a 12.5 mM stock solution in THF) was added via syringe. The Teflon stopcock was quickly replaced and the solution was stirred for 2 hours at 0 °C. A 15-mL resealable Schlenk tube equipped with a Teflon-coated stirbar was charged with 4-bromoacetophenone (0.124 g, 0.625 mmol) and $Pd(PPh_3)_4$ (0.015 g, 0.013 mmol), sealed with a rubber stopper and evacuated on a Schlenk line. This tube was back-filled with argon, and *n*-butanol (3 mL) was added via syringe, followed by triethylamine (0.261 mL, 1.88 mmol). The stopper was replaced with a Teflon stopcock, and the reaction mixture was degassed by one freeze-pump-thaw cycle. Both Schlenk flasks were connected by means of a vacuum bridge; which was evacuated, then sealed under static vacuum. The stopcocks on both Schlenk flasks

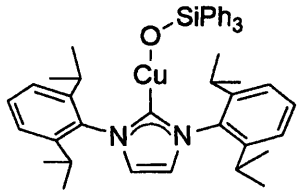
were opened, and the vessels were placed in an 85 °C oil bath for 15 hours. The contents of the 15-mL Schlenk flask were transferred to a round-bottomed flask and the volatiles were removed *in vacuo*. The crude product was purified by column chromatography on silica gel, using 3:1 CH_2Cl_2:EtOAc as eluant, to afford the title compound as a pale yellow oil (0.123 g, 95 %, average of two runs). ^{1}H NMR (C_6D_6): δ 8.06 (d, J = 7.9 Hz, 2 H), 7.69 (d, J = 7.9 Hz, 2 H), 4.15 (t, J = 6.6 Hz, 2 H), 2.05 (s, 3 H), 1.46 (m, 2 H), 1.23 (m, 2 H) 0.79 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (C_6D_6): δ 196.4, 165.8, 140.8, 134.8, 130.3, 128.7, 65.5, 31.3, 26.7, 19.8, 14.2. Anal. Calcd. $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.79; H, 7.59.

Low Temperature NMR experiments: In a glovebox, **1** (0.030 g) was added to J-Young NMR tube, and the tube was sealed with a Teflon stopcock. Outside of the glovebox, the tube was evacuated on a Schlenk line, and THF-d_8 (0.7 mL) was added via vacuum transfer from of a purple Na/benzophenone kettle pot. The tube was cooled to –78 °C, and $^*CO_2$ (1.5 atm) was added. The tube was sealed, and rapidly inserted into a pre-cooled (–80 °C) NMR spectrometer.



[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) triphenylsilyl (3): In a glovebox, a 20-mL scintillation vial was charged with hexaphenyldisilane (0.300 g, 0.578 mmol) and THF (10 mL). Potassium metal (0.112 g, 3.36 mmol) was added, and the reaction mixture was stirred for 15 hours. The solution was then filtered through Celite into a Schlenk flask containing (IPr)CuCl (0.564 g, 1.15 mmol) suspended in THF (10 mL). The reaction mixture was stirred for one hour, filtered through Celite into a Schlenk flask, and concentrated *in vacuo*. The resulting tan solid was suspended in pentane (5 mL) and collected by filtration to afford the title complex (0.550 g, 67%) as an off-white solid. ^{1}H NMR (C_6D_6): δ 7.50 (m, 6 H, Si-Ph), 7.25

(t, J = 7.8 Hz, 2 H, *para*-CH, IPr), 7.20–7.14 (9 H, Si-Ph), 7.07 (d, J = 7.7 Hz, 4H, *meta*-CH, IPr), 6.20 (s, 2 H, NC<u>H</u>), 2.55 (sept, J = 6.9 Hz, 4 H, C<u>H</u>(CH_3)$_2$)), 1.27 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$), 1.07 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 184.9 (N_2<u>C</u>Cu), 147.7 (Si-Ph), 146.2 (*ortho*-<u>C</u>, IPr), 137.6 (Si-Ph), 135.2 (*ipso*-C, IPr), 130.9 (*para*-CH, IPr), 127.6 (Si-Ph), 126.8 (Si-Ph), 124.6 (*meta*-CH, IPr), 122.5 (NC<u>H</u>), 29.4 (<u>C</u>H(CH_3)$_2$), 25.7 (CH(<u>C</u>H$_3$)$_2$), 24.0 (CH(<u>C</u>H$_3$)$_2$). ^{29}Si NMR (C_6D_6): δ –0.84. Anal. Calcd. $C_{45}H_{51}N_2CuSi$: C, 75.96; H, 7.22. Found: C, 74.92; H, 7.02.

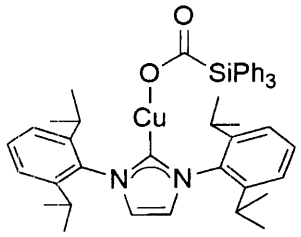


[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) triphenylsiloxide (4):

Method A: In a glovebox, a 15-mL resealable Schlenk flask was charged with **3** (0.226 g, 0.318 mmol) and benzene (3 mL). The Schlenk flask was sealed with a Teflon stopcock, taken out of the glovebox and the solution was degassed on a Schlenk line. Carbon dioxide (1 atm) was added, the flask was sealed, and the solution was stirred vigorously at 80 °C. After 20 hours, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The flask was then taken into a glovebox. The crude product was dissolved in benzene (10 mL) and filtered through Celite. The colorless solution was concentrated *in vacuo* and the resulting solid was washed with pentane to afford the title complex (0.210 g, 91%) as a white solid.

Method B: In a glovebox, a round-bottomed flask was charged with (IPr)$CuCH_3$ (0.046 g, 0.098 mmol) and Ph_3SiCO_2H (0.030 g, 0.098 mmol). Benzene (2 mL) was added, the flask was sealed with a septum, and the reaction mixture was stirred for 20 hours. The reaction mixture was then concentrated *in vacuo* to afford the title complex (0.071 g, 99%) as a white solid.

^{1}H NMR (C_6D_6): δ 7.72 (m, 6 H, Si-Ph), 7.25 (t, J = 7.8 Hz, 2 H, *para*-CH, IPr), 7.22–7.14 (9 H, Si-Ph), 7.05 (d, J = 7.8 Hz, 4H, *meta*-CH, IPr), 6.20 (s, 2 H, NC<u>H</u>), 2.53 (sept, J = 6.9 Hz, 4 H, C<u>H</u>(CH_3)$_2$)), 1.24 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$), 1.04 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 182.9 (N_2<u>C</u>Cu), 146.1 (*ortho*-<u>C</u>, IPr), 143.7 (Si-Ph), 136.1 (Si-Ph), 135.5 (*ipso*-C, IPr), 131.1 (*para*-CH, IPr), 128.9 (Si-Ph), 127.6 (Si-Ph), 124.7 (*meta*-CH, IPr), 123.0 (N<u>C</u>H), 29.3 (<u>C</u>H(CH_3)$_2$), 25.3 (CH(<u>C</u>H$_3$)$_2$), 24.1 (CH(<u>C</u>H$_3$)$_2$). Anal. Calcd. $C_{45}H_{51}N_2CuSiO$: C, 74.29; H, 7.07. Found: C,74.33; H, 7.08.



[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) triphenylsilylcarboxylate (5):

In a glovebox, a 20-mL scintillation vial was charged with (IPr)$CuCH_3$ (0.0153 g, 0.033 mmol) and Ph_3SiCO_2H (0.010 g, 0.033 mmol) and C_6D_6 was added. Once gas evolution ceased, the solution was transferred to an NMR tube, taken out of the glovebox, and rapidly inserted into an NMR spectrometer. Samples typically contained ~15% decarbonylation product **4,** as judged by ^{1}H NMR spectroscopy due to the high thermal instability of **5** ($t_{1/2}$ = 40 minutes at 20 °C). ^{1}H NMR (C_6D_6): δ 7.85 (d, J = 7.0 Hz, 6 H, Si-Ph), 7.19 (d, J = 7.8 Hz, 2 H, *meta*-CH, IPr), 7.12 (t, J = 7.3 Hz, 3 H, Si-Ph), 7.04 (d, J = 7.8 Hz, 4H, *meta*-CH, IPr), 6.21 (s, 2 H, NC<u>H</u>), 2.56 (sept, J = 6.9 Hz, 4 H, C<u>H</u>(CH_3)$_2$)), 1.36 (d, J = 6.4 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$), 1.04 (d, J = 6.9 Hz, 12 H, CH(C<u>H</u>$_3$)$_2$). ^{13}C NMR (C_6D_6, 6 °C): δ 188.4 (O_2<u>C</u>Si), 182.0 (N_2<u>C</u>Cu), 146.0 (*ortho*-<u>C</u>, IPr), 137.2 (Si-Ph), 135.8 (Si-Ph), 135.2 (*ipso*-C, IPr), 131.0 (*para*-CH, IPr), 129.5 (Si-Ph), 128.0 (Si-Ph), 124.6 (*meta*-CH, IPr), 123.1 (N<u>C</u>H), 29.3 (<u>C</u>H(CH_3)$_2$), 25.3 (CH(<u>C</u>H$_3$)$_2$), 24.2 (CH(<u>C</u>H$_3$)$_2$).

Attempts to isolate **5** cleanly on preparative scale were unsuccessful due to its high thermal instability.

Kinetic studies on the decarbonylation of 5:

In a glovebox, a 20-mL scintillation vial was charged with (IPr)$CuCH_3$ (0.015 g, 0.033 mmol), Ph_3SiCO_2H (0.010 g, 0.033 mmol), and a few crystals of 1,4-dimethoxybenzene (~ 2 mg). C_6D_6 (0.7 mL) was added via syringe. After all solids had dissolved, the solution (0.7 mL) was transferred to an NMR tube, taken out of the glovebox, and quickly inserted into an NMR spectrometer whose temperature was regulated at 20 °C. Spectra were taken at regular time intervals, and a peak unique to complex **5** (7.85 ppm) was integrated relative to the internal standard for each spectrum. The experiment was repeated at different temperatures (10, 30, 40 and 50 °C), and the rate constants reported are the average of at least two runs at each temperature. Rate constants were obtained by least-squares fits to the equation $\ln|A_f - A| = -kt + |A_f - A_0|$, which were linear for at least four half-lives. Activation parameters were determined from plots of $\ln(k/T)$ vs $(1/T)$.[30]

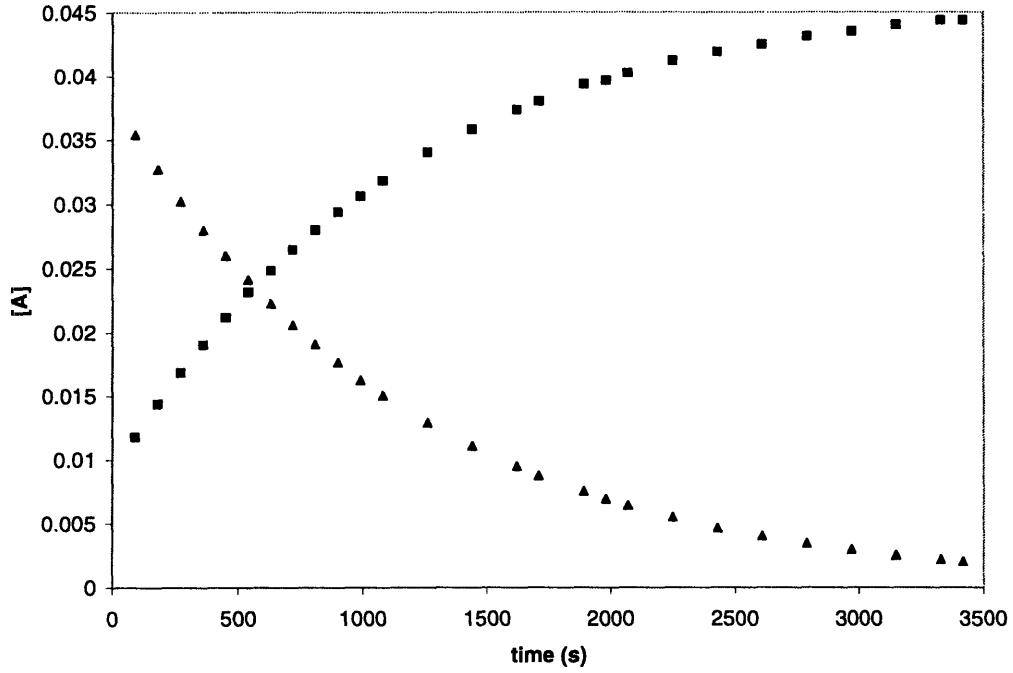


Figure 9. Typical kinetic run showing disappearance of **5** (triangles) and formation of **4** (squares) at 30 °C.

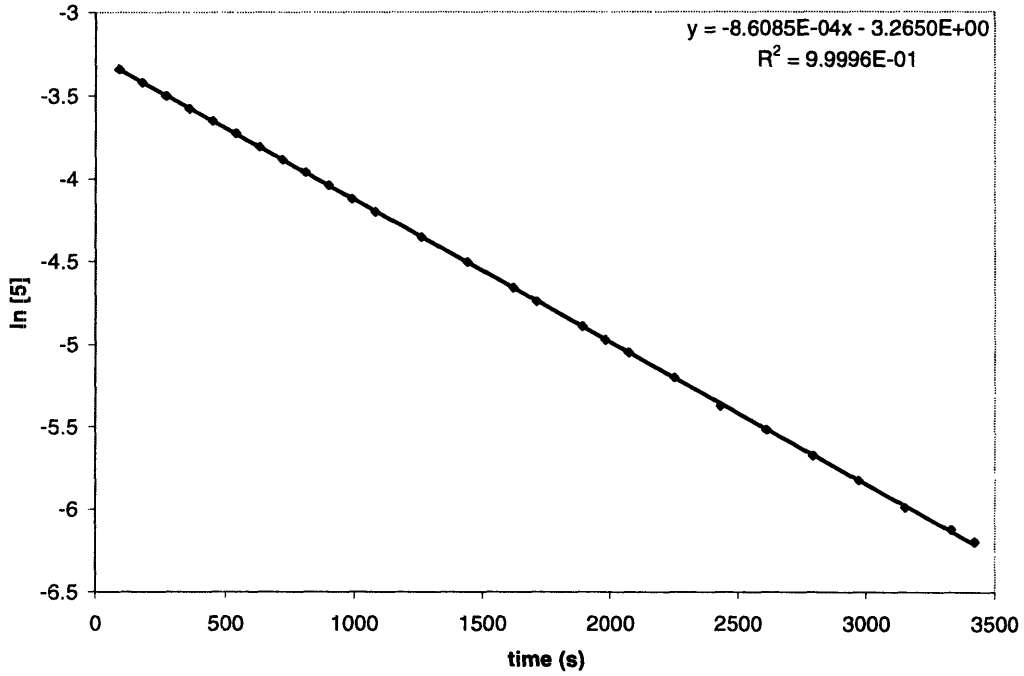


Figure 10. Plot showing the ln [**5**] vs t at 30 °C in C_6D_6.

Table 1. Temperature dependence on the rate of decarbonylation of **5** in C_6D_6.

T	k x 10^{-3}
283	0.05970(14)
293	0.301(14)
303	0.83(4)
313	2.43(14)
323	7.9(5)

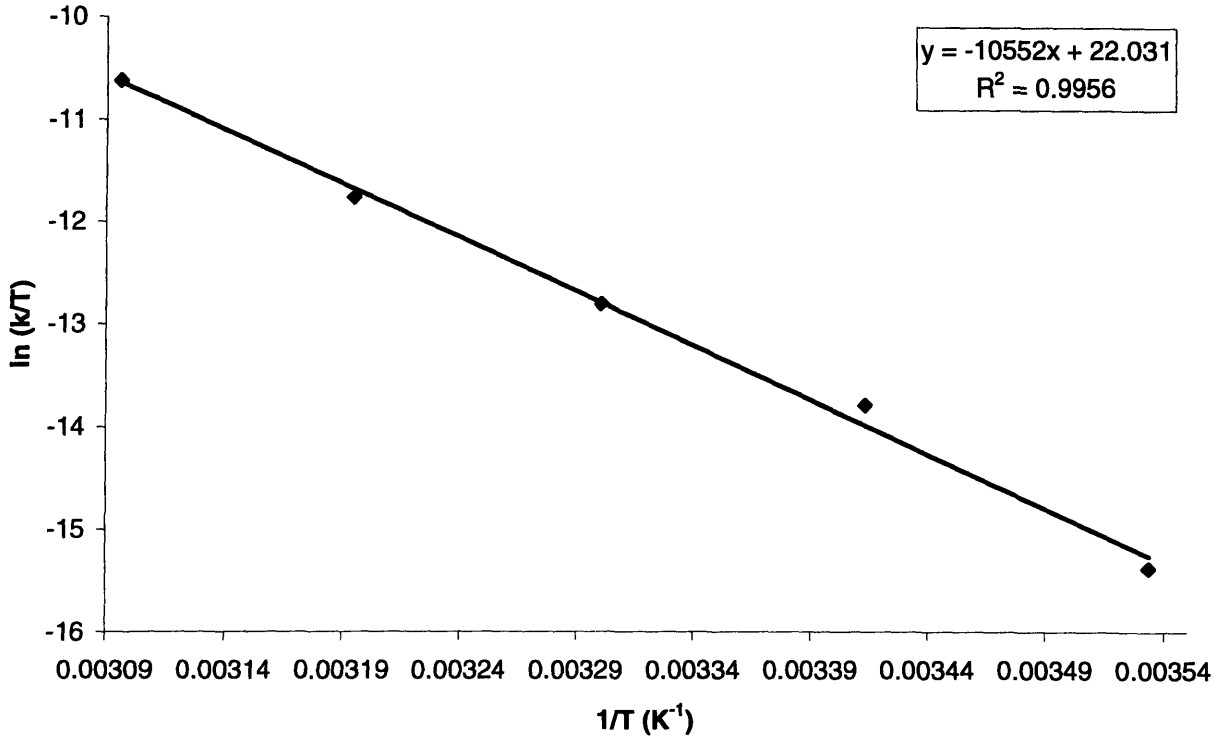


Figure 11. Eyring plot for the decarbonylation of **5** in C_6D_6

Table 2. Crystallographic data for [(SIPr)Cu][(pin)BF_2], **1**, and **2**.

	[(SIPr)Cu][(pin)BF_2]	**1**	**2**
empirical formula	$C_{37}H_{58}N_2O_3BF_2Cu$	$C_{36}H_{55}BCuN_2O_2$	$C_{40}H_{56}BCuN_2O_3$
fw	691.20	622.17	729.29
T, K	100(2)	100(2)	100(2)
Crystal syst, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a, Å	12.2853(9)	10.9221(14)	10.5264(19)
b, Å	15.9341(11)	24.520(3)	14.999(3)
c, Å	19.3085(11)	14.4271(18)	25.090(4)
β, deg	96.231(2)	107.785(4)	90.035(5)
V, Å^3	3757.4(4)	3679.0(8)	3961.3(12)
ρ_{calc}, g/cm^{-1}	1.222	1.123	1.152
Z	4	4	4
μ, mm^{-1}	0.627	0.624	0.588
F(000)	1480	1340	1472
cryst size, mm^3	0.10 x 0.10 x 0.10	0.20 x 0.12 x 0.07	0.20 x 0.10 x 0.10
θ range, deg	1.66 to 28.28	2.06 to 26.37	0.81 to 28.70
no. of data/restraints/params	9302/40/427	7514/12/413	10237/0/438
Total no. of reflns	76140	58701	64235
GOF on F^2	1.026	1.054	1.024
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0509	$R1$ = 0.0488	$R1$ = 0.0454
	$wR2$ = 0.1054	$wR2$ = 0.1288	$wR2$ = 0.1015
R indices (all data)[a]	$R1$ = 0.0827	$R1$ = 0.0582	$R1$ = 0.0552
	$wR2$ = 0.1193	$wR2$ = 0.1344	$wR2$ = 0.1063

[a] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

Table 3. Crystallographic data for **3**, **4**, and **5**.

	3	**4**	**5**
empirical formula	$C_{45}H_{51}N_2SiCu$	$C_{45}H_{51}N_2OSiCu$	$C_{46}H_{51}N_2O_2SiCu$
fw	711.51	727.51	755.52
T, K	100(2)	100(2)	100(2)
Crystal syst, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
a, Å	10.9480(9)	17.321(3)	8.9066(6)
b, Å	19.2577(19)	14.811(3)	17.5394(15)
c, Å	20.3032(17)	15.767(3)	25.641(2)
α, deg	86.284(2)	90	90
β, deg	77.3780(10)	98.803(6)	93.404(2)
γ, deg	73.555(2)	90	90
V, Å^3	4006.2(6)	3997.0(13)	3998.4(5)
ρ_{calc}, g/cm^{-1}	1.180	1.209	1.255
Z	4	4	4
μ, mm^{-1}	0.607	0.612	0.616
F(000)	1512	1544	1600
cryst size, mm^3	0.30 x 0.30 x 0.10	0.30 x 0.20 x 0.15	0.15 x 0.08 x 0.05
θ range, deg	1.98 to 28.70	1.82 to 29.57	1.41 to 27.10
no. of data/restraints/params	20646/55/920	11208/0/459	10237/0/438
Total no. of reflns	85232	87734	74271
GOF on F^2	1.030	1.042	1.054
Final R indices [$I > 2\sigma(I)$][a]	$R1 = 0.0377$	$R1 = 0.0362$	$R1 = 0.0460$
	$wR2 = 0.0941$	$wR2 = 0.0924$	$wR2 = 0.1123$
R indices (all data)[a]	$R1 = 0.0500$	$R1 = 0.0447$	$R1 = 0.0694$
	$wR2 = 0.1006$	$wR2 = 0.0984$	$wR2 = 0.1280$

[a] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

X-ray Diffraction Studies: Experiments were performed on single crystals of [(SIPr)Cu][(pin)BF_2], **1**, **2**, **3**, **4**, and **5**. Colorless crystals were removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. Crystals were affixed to a glass fiber or a cryoloop using the oil, frozen in a nitrogen stream, and optically centered. The data were collected on a Siemens three-circle platform goniometer equipped with a Bruker Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), using both phi and omega scans at –173 °C. The structures were solved by direct methods (SHELXS)[31] and refined against F^2 on all data by full matrix least squares with SHELXL-97 (Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. CIF files for all unpublished structures are available at http://www.reciprocalnet.org/ (numbers 04224 ([(SIPr)Cu][(pin)BF_2]), 06009 (**3**), 06015 (**4**), 06054 (**5**)).

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacolato)difluoroborate: Single crystals were grown by the vapor diffusion of hexanes into a THF solution at –40 °C.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacolato)boryl (1). An isopropyl group was found to be disordered (C10, C11 and C12) and was refined with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. The occupancies for the disordered parts were refined freely and converged at a ratio of 42:58. One peak of significant residual electron density remained upon convergence, and was found less than one angstrom from copper (1.62 e/Å^3).

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacolato)borate (2)

The structure was refined as a pseudo-merohedral twin, obeying the twin law 1 0 0 0 –1 0 0 0 –1. This corresponds to a 180° rotation about the crystallographic *a*-axis. In the monoclinic system this operation is not allowed, unless the monoclinic angle is very close to 90°, which is the case here. The twin-ratio was refined freely and converged at a value of 0.5134(9), making the structure of **2** an almost perfect twin.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) triphenylsilyl (3). Two (IPr)$CuSiPh_3$ complexes were found in the asymmetric unit. An isopropyl group of one of the complexes was disordered (C22, C23 and C24) and was refined over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. The occupancies for the disordered parts were refined freely and converged at a ratio of 60:40.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) triphenylsilylcarboxylate (5). An isopropyl group of one of the complexes was disordered (C13, C14 and C15) and was refined over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. The occupancies for the disordered parts were refined freely and converged at a ratio of 62:38.

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Chapter 3

The Insertion of Aldehydes into Cu–B Bonds: a Stoichiometric and Catalytic Study

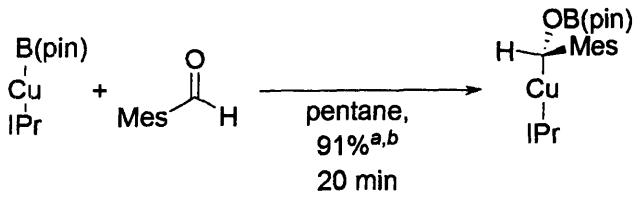
Organoboron compounds are valuable reagents in organic synthesis due to the synthetic versatility of the carbon–boron bond.[1] The insertion of unsaturated substrates into M–B bonds has been studied stoichiometrically,[2] and is a key step in the addition of diboron reagents to organic molecules, an important class of carbon-boron bond forming reactions.[3] Although the diboration of alkenes,[4] alkynes,[5] allenes,[6] and α,β-unsaturated ketones[7] is well-established, the addition of diboron reagents across C=X (X = S, NR) bonds has proven more difficult and current methodologies have a very limited substrate scope with only one thioketone,[8] and three aldimine[9] diboration products reported in the literature. Prior to this work, aldehyde diboration products had not been isolated; however, such compounds have been detected spectroscopically in the reaction mixtures formed from the rhodium-catalyzed reaction of aldehydes with diboron reagents.[10]

The first well-characterized copper boryl complex, (IPr)CuB(pin) [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, pin = pinacolate: 2,3-dimethyl-2,3-butanediolate] is a highly active catalyst for the deoxygenation of carbon dioxide using bis(pinacolato)diboron [(pin)B–B(pin)] as the stoichiometric reductant.[11,12] We hypothesized that CO_2 insertion into the copper–boron bond of (IPr)CuB(pin) would produce a copper–carbon and boron–oxygen bond, based on the high oxophilicity of boron. We have detected the CO_2 insertion product by NMR spectroscopy; however, this complex is unstable at temperatures above –60 °C in THF solution, which has hampered identification of the regiochemistry for the insertion. We hoped that other C=O electrophiles might react with (IPr)CuB(pin) to give products with greater stability, and make identification of the regiochemistry for those insertions possible. In this chapter, the insertion of aldehydes into metal–boron bonds to give isolable products is described. This insertion reaction is a key step for the first efficient diboration of aldehydes.

The insertion of an aldehyde into a Cu–B bond

Mesitaldehyde reacts rapidly with (IPr)CuB(pin) in C_6D_6 solution, and only a single product (**1**; Scheme 1) was formed as judged by NMR spectroscopy. The ^{11}B NMR shift of **1** (21.8 ppm) is consistent with the presence of neutral boron center bound to three oxygen atoms.[13] An X-ray diffraction study on **1** confirmed that Cu–C and B–O bonds had been formed (Figure 1a).[14] The $Cu–C_{alkyl}$ bond distance of 1.9473(19) Å in the solid-state structure of **1** is similar to those in the previously reported (IPr)$CuCH_3$ [1.913(6) Å][15] and (IPr)CuCH(Ph)CH_2B(pin) [1.948(3) Å].[2c]

Scheme 1. Insertion of mesitaldehyde into (IPr)CuB(pin).



[a]Reaction conditions: (IPr)CuB(pin) was generated in situ from (IPr)CuO*t*-Bu and bis(pinacolato)diboron. [b]Isolated yield. Mes = 2,4,6-trimethylphenyl.

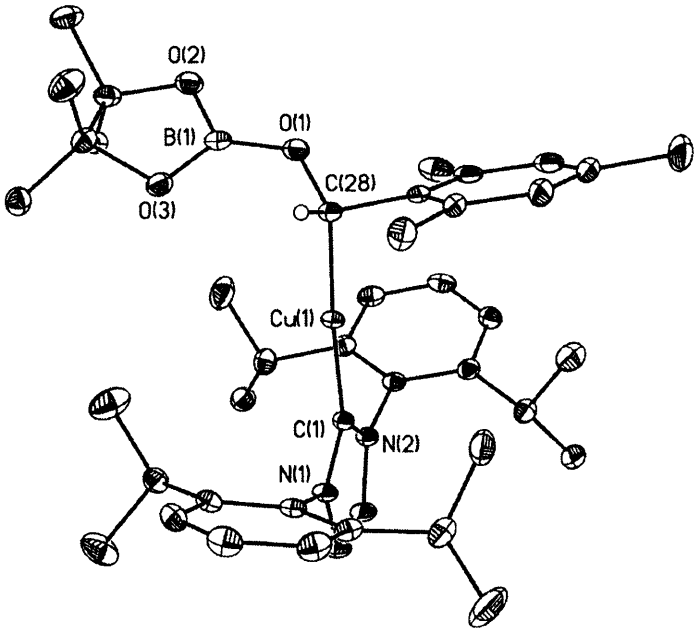


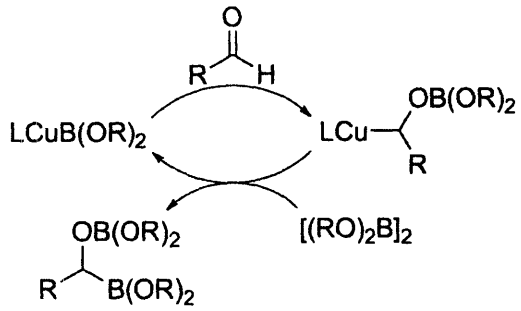
Figure 1. X-ray crystal structure of **1** shown as 30% ellipsoids. Select bond distances (Å) and angles (deg): Cu(1)–C(28) 1.9473(19), Cu(1)–C(1) 1.8975(18), C(28)–O(1) 1.464(2), O(1)–B(1) 1.352(3); C(1)–Cu(1)–C(28) 175.46(8), Cu(1)–C(28)–O(1) 118.74(14), Cu(1)–C(28)–C(29) 101.94(12).

Since copper-alkyl complexes are generally reactive species that have found widespread use in organic synthesis,[16] aldehyde insertion products such as **1** have potential as intermediates in catalytic reactions. For example, complex **1** might react with diboron reagents to form α-[(pinacol)boroxy]-2,4,6-trimethylbenzyl(pinacol)boronate, **2**, and regenerate a copper boryl complex, closing a catalytic cycle for the addition of a diboron reagent across the C=O bond of an aldehyde (Figure 2a). Complex **1** is catalytically competent for the diboration of mesitaldehyde with bis(pinacolato)diboron; however, the regeneration (IPr)CuB(pin) from **1** and (pin)B–B(pin) is slow, presumably due to steric congestion.

Diboration of aldehydes using copper catalysts

A copper catalyst supported by a smaller ligand, [(ICy)CuB(pin)] (ICy = 1,3-dicyclohexylimidazol-2-ylidene), proved more effective, and reaction between mesitaldehyde and bis(pinacolato)diboron was complete after 22 hours at room temperature using 2.3 mol% (ICy)CuO*t*-Bu pre-catalyst (Table 1, entry 8) in benzene solution. The mesitaldehyde diboration product **2** is isolated in 73% yield and characterized by X-ray crystallography (Figure 2b).[17] Two peaks are observed in the ^{11}B NMR spectrum of **2** at 22.6 and 32.7 ppm, characteristic of a borate and a boronate ester respectively.[13]

(a) (b)



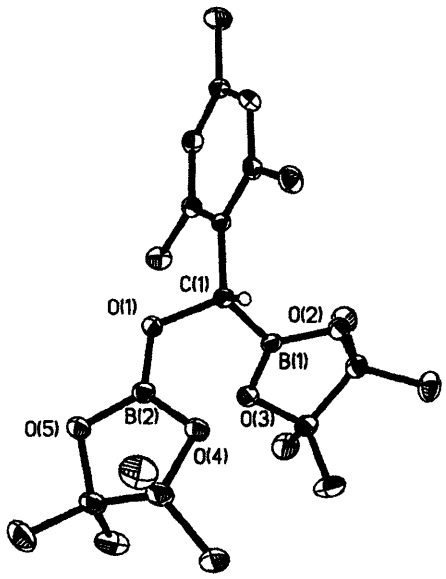
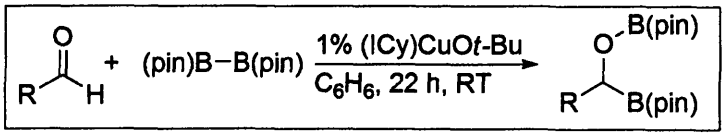


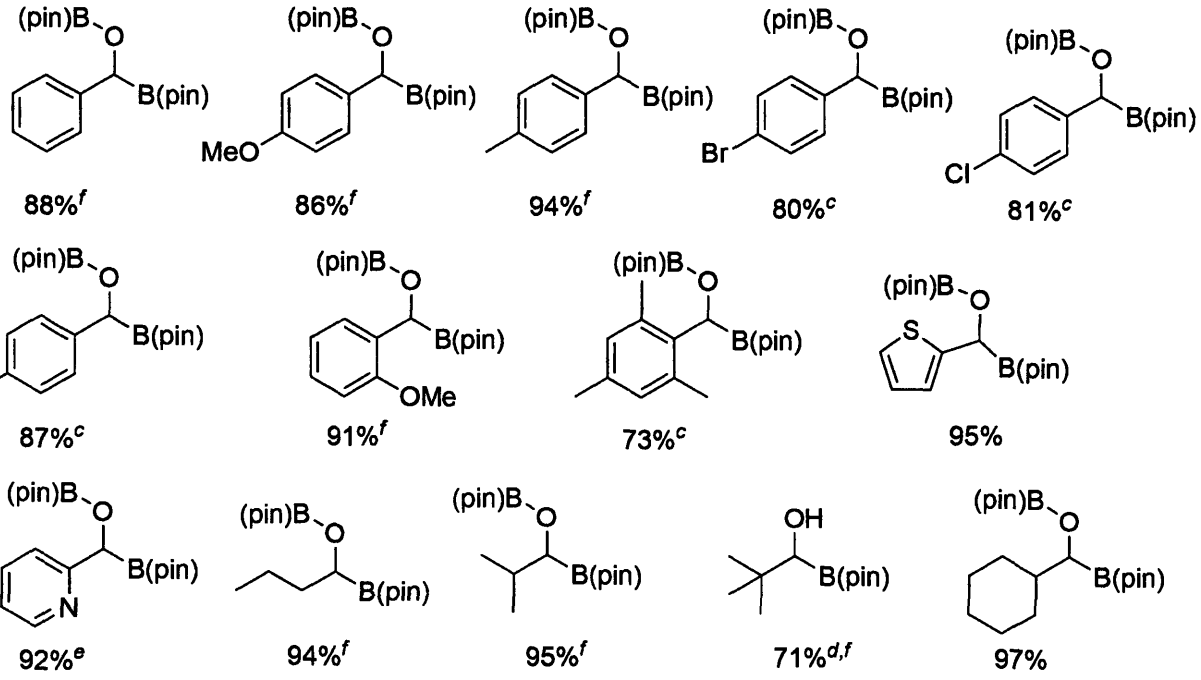
Figure 2 (a) Proposed catalytic cycle for the diboration of aldehydes. (b) X-ray crystal structure of **2** shown as 50% ellipsoids.

The boryl complex supported by the ICy ligand also proved to be an effective diboration catalyst for a wide range of other aldehydes (Table 1). A variety of aryl-substituted aldehydes including those bearing electron-donating and electron-withdrawing groups, and those with

ortho-substituents react cleanly with (pin)B–B(pin). A variety of alkyl-substituted aldehydes also react with (pin)B–B(pin) to give diboration products in excellent yield. It is worth noting that the B–O bond of the pivaldehyde diboration product can be selectively cleaved on silica gel to give 1-hydroxyneopentyl(pinacol)boronate.

Table 1. Copper-catalyzed diboration of aldehydes.[a,b]

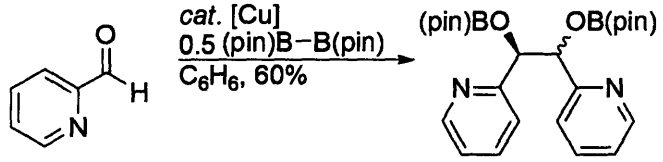




[a]Conditions: unless otherwise noted, 1 mol% (ICy)CuO*t*-Bu, 1 equivalent aldehyde, 1 equivalent bis(pinacolato)diboron, 22 hours. [b]Isolated yield, average of two runs. [c]2.3 mol% (ICy)CuO*t*-Bu was used. [d]Product was isolated as 1-hydroxyneopentyl(pinacol)boronate after column chromatography. [e]10 mol% (ICy)CuO*t*-Bu was used. [f]Compound synthesized by Ms. Emily Y. Tsui.

A number of heteroaryl-substituted aldehydes also react to give diboration products in good to excellent yield. Pyridinecarboxaldehydes have shown interesting reactivity. Although 3-pyridinecarboxaldehyde reacts productively with (pin)B–B(pin), 2-pyridinecarboxaldehyde does not, forming instead 1,2-di(2'-pyridyl)-1,2-bis[(pinacol)boroxy]ethane as the major product (60% yield; Scheme 2).[18] The formation of this product likely results from a faster reaction between the α-boroxyalkylcopper intermediate with 2-pyridinecarboxaldehyde than with (pin)B–B(pin). The reason for this change in selectivity is currently unclear. A similar product, 1,2-di(4'-pyridyl)-1,2-bis[(pinacol)boroxy]ethane, is formed from the reaction of 4-pyridine carboxaldehyde with (pin)B–B(pin), even in the absence of a copper catalyst.

Scheme 2. Diboration of 2-carboxaldehyde.[a]



meso : *rac*
3 : 1

[a]Conditions: 10 mol% (ICy)CuO*t*-Bu, 1 equivalent aldehyde, 0.5 equivalents bis(pinacolato)diboron, 22 hours.

When protected from air and light, the aldehyde diboration products are stable indefinitely in the solid state. Benzene solutions of the diboration products are also stable for prolonged periods at ambient temperature, even those saturated with water. However, upon exposure to oxygen the diboration products slowly oxidize back to aldehydes, concomitant with formation of $[(pin)B]_2O$. The diboration products of aromatic aldehydes react more rapidly than those of aliphatic aldehydes.

In conclusion, an aldehyde inserts cleanly and selectively into a copper–boron bond forming a copper–carbon bond and a boron–oxygen bond. This well-characterized product was shown to react with a diboron reagent to afford an aldehyde diboration product and regenerate the starting copper boryl complex. This regeneration is the turnover step that makes the catalytic diboration of aldehydes possible. A modified precatalyst was shown to be effective for the diboration of a range of aldehydes substrates. We anticipate that these aldehyde diboration products will be useful α-hydroxyalkyl anion equivalents in C–C bond-forming reactions, particularly in cases where the corresponding aldehyde would be incompatible with a Grignard or related reaction.

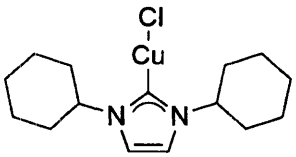
Experimental Section

General Considerations. All synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in oven- or flame-dried glassware cooled under vacuum. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Anhydrous tetrahydrofuran and dichloromethane were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina and for tetrahydrofuran, a third column packed with activated 4Å molecular sieves. Benzene and pentane, anhydrous, were purchased from Aldrich in Sure-Seal™ bottles, and stored in a glovebox over 4Å molecular sieves. All non-dried solvents used were reagent grade or better.

NMR solvent C_6D_6 (Cambridge Isotope Laboratories) was dried over sodium/benzophenone, CD_2Cl_2 was dried over CaH_2. Both solvents were degassed by three

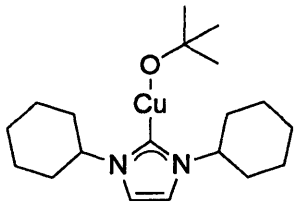
freeze-pump-thaw cycles, and vacuum-transferred prior to use. ^{1}H NMR spectra were recorded on a Varian 300 MHz or 500 MHz instrument, with shifts reported relative to the residual solvent peak. ^{19}F NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of $CFCl_3$. ^{11}B NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced to an external standard of 0.5 M BF_3 in diethyl ether (0 ppm). ^{13}C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak.

The starting compounds [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) *tert*-butoxide,[15] [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacol)boryl,[11] and 1,3-dicyclohexylimidazolium chloride[19] were synthesized as described previously. Benzaldehyde (Aldrich), *n*-butyraldehyde (Alfa Aesar), *p*-anisaldehyde (Aldrich), mesitaldehyde (Aldrich), *p*-tolualdehyde (Aldrich), isobutyraldehyde (Aldrich) , 2-thiophenecarboxaldehyde (Alfa Aesar), 2-furaldehyde (Aldrich), cyclohexanecarboxaldehyde (Aldrich), 2-pyridinecarboxaldehyde (TCI America), 3-pyridinecarboxaldehyde (Aldrich), and 4-pyridinecarboxaldehyde (TCI America) were degassed and stored over 4 Å molecular sieves prior to use. Bis(pinacolato)diboron (Frontier Scientific), 4-chlorobenzaldehyde (Aldrich), 4-bromobenzaldehyde (Aldrich), *o*-anisaldehyde (Aldrich), sodium *tert*-butoxide (Aldrich), and copper(I) chloride were used as received.

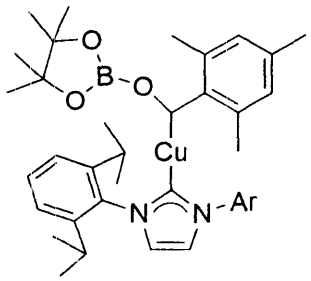


[1,3-Dicyclohexylimidazol-2-ylidene]copper(I) chloride.[20] In a glovebox, a round-bottomed flask equipped with a Teflon-coated magnetic stirbar was charged with CuCl (1.62 g, 16.4 mmol), NaO*t*-Bu (1.50 g, 15.6 mmol), and ICy•HCl (4.03 g, 14.6 mmol). THF (40 mL) was

added, and the reaction mixture was stirred for 1.5 hours. The resulting cloudy solution was filtered through Celite, and concentrated *in vacuo*. The resulting yellow foam was taken up in CH_2Cl_2 (30 mL) and filtered through celite. Upon concentration, the title compound was isolated as a white foam (4.07 g, 82%). ^{1}H NMR (CD_2Cl_2): δ 6.95 (s, 2H, NC<u>H</u>), 4.28 (tt, J = 12.1 Hz, J = 3.9 Hz, 2H), 2.06 (m, 4H), 1.89 (m, 4H), 1.77–1.61 (6H) 1.46 (m, 4H), 1.25 (m, 2H). ^{13}C NMR (CD_2Cl_2): 173.8 (N_2<u>C</u>Cu), 118.0, 61.7, 35.2, 26.0, 25.6. Anal. Calcd. $C_{15}H_{24}N_2CuCl$: C, 54.37; H, 7.30. Found: C, 54.44; H, 7.30.



[1,3-Dicyclohexylimidazol-2-ylidene]copper(I) *tert*-butoxide. In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stirbar was charged with (ICy)CuCl (1.25 g, 3.76 mmol) and NaO*t*-Bu (0.363 g, 3.78 mmol). Tetrahydrofuran (10 mL) was added, and the resulting solution was stirred for 1 hour. After filtering through Celite, the pale yellow solution is concentrated *in vacuo* to give a cream colored foam (1.05 g, 76%). ^{1}H NMR (C_6D_6): δ 6.38 (s, 2H, NC<u>H</u>), 4.32 (m, 2H), 1.88 (s, 9H), 1.81 (m, 4H), 1.48 (4H), 1.41–1.26 (6H) 1.07 (m, 4H), 0.91 (m, 2H). ^{13}C NMR (C_6D_6): 177.5 (N_2<u>C</u>Cu), 117.4, 69.7 (br), 61.0, 37.7 (br), 34.9, 26.0, 25.7. Small amounts of tetrahydrofuran were typically present upon isolation of this complex which were not easily removed. The presence of this THF did not affect this compound's activity as a diboration catalyst. ^{1}H and ^{13}C NMR spectra of this complex are included to attest to its purity.



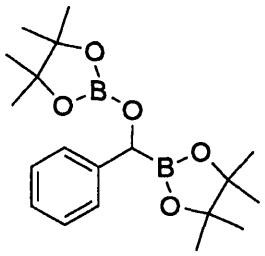
[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) α-[(pinacol)boroxy]-2,4,6-trimethylbenzyl. In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stirbar was charged with (IPr)CuO*t*-Bu (0.300 g, 0.571 mmol), and bis(pinacolato)diboron (0.145 g, 0.571 mmol). Pentane was added (5 mL) followed by mesitaldehyde (0.091 mL, 0.628 mmol). The mixture was stirred for 1 hour, and the resulting white precipitate was collected by filtration to afford **1** (0.368 g, 89%). ^{1}H NMR (C_6D_6): δ 7.23 (t, *J* = 7.8 Hz, 2H, *para*-CH), 7.07 (d, *J* = 7.9 Hz, 2H, *meta*-CH), 7.06 (d, *J* = 7.6 Hz, 2H, *meta*-CH), 6.73 (s, 2H, *meta*-CH (mes)), 6.22 (s, 2H, NC<u>H</u>), 5.54 (s, 1H, CuC<u>H</u>(OB(pin))mes), 2.49 (m, 4H, C<u>H</u>(CH_3)$_2$), 2.28 (s, 3H, *para*-C<u>H</u>$_3$ (mes)), 2.18 (s, 6H, *ortho*-CH_3 (mes)), 1.29 (d, *J* = 7.0 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.23 (d, *J* = 7.0 Hz, 6H, CH(C<u>H</u>$_3$)$_2$), 1.06 (d, *J* = 6.7 Hz, 12H, CH(C<u>H</u>$_3$)$_2$), 1.00 (s, 6H, pinacol-C<u>H</u>$_3$), 0.99 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 185.5 (N_2<u>C</u>Cu), 146.2 (*ortho*-<u>C</u>, mes), 146.1 (*ortho*-<u>C</u>, IPr), 146.1 (*ortho*-<u>C</u>, IPr), 135.6 (*ipso*-C, IPr), 132.2 (*ipso*-C, mes), 130.8 (*para*-CH, IPr), 129.1 (*para*-CH, mes), 129.0 (*meta*-<u>C</u>H, mes), 124.5 (*meta*-CH, IPr), 124.5 (*meta*-CH, IPr), 122.6 (NC<u>H</u>), 80.9 (B(O<u>C</u>(CH_3)$_2$)$_2$), 77.9 (Cu<u>C</u>H), 29.3 (<u>C</u>H(CH_3)$_2$), 29.3 (<u>C</u>H(CH_3)$_2$), 25.5 (CH(<u>C</u>H_3)$_2$), 25.4 (pinacol-<u>C</u>H_3), 25.3 (pinacol-<u>C</u>H_3), 25.1 (CH(<u>C</u>H_3)$_2$), 24.1 (CH(<u>C</u>H_3)$_2$), 22.6 (*ortho*-<u>C</u>H_3 (mes)), 21.5 (*para*-<u>C</u>H_3 (mes)). ^{11}B NMR (C_6D_6): δ 21.8. Anal. Calcd. $C_{43}H_{60}N_2O_3BCu$: C, 71.01; H, 8.32. Found: C, 71.03; H, 8.05.

General procedure for the diboration of aldehydes:

In a glovebox, a flame-dried Schlenk flask equipped with a Teflon-coated magnetic stirbar was charged with bis(pinacolato)diboron (0.127 g, 0.5 mmol). Benzene was added, followed by aldehyde (0.5 mmol). A solution of (ICy)CuO*t*-Bu in benzene was added via syringe. The reaction mixture was stirred at room temperature for 22 hours, and then concentrated *in vacuo*. In a glovebox the product was extracted from the crude solid into pentane (4 x 5 mL). The extracts were combined, filtered through Celite, and concentrated *in vacuo* to give the title compounds.

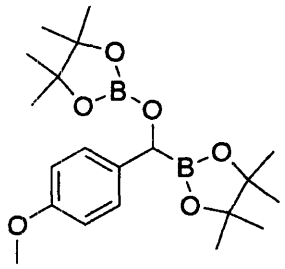
For reactions run at 1% (ICy)CuO*t*-Bu: A solution of (ICy)CuO*t*-Bu (5 μmol; 1.8 mL of a 2.7 mM stock solution in benzene) was added to the Schlenk flask containing a solution bis(pinacolato)diboron and aldehyde in benzene (4 mL).

For reactions run at 2.3% (ICy)CuO*t*-Bu: A solution of (ICy)CuO*t*-Bu (11.5 μmol; 4.6 mL of a 2.4 mM stock solution in benzene) was added to the Schlenk flask containing a solution of bis(pinacolato)diboron and aldehyde in benzene (1.4 mL).

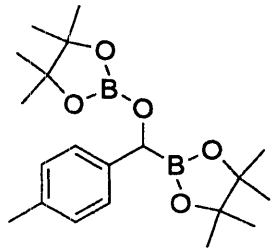


α-[(Pinacol)boroxy]benzyl(pinacol)boronate. The general procedure was followed using 1% (ICy)CuO*t*-Bu to give a white solid (0.158 g, 88%, mp 94–97 °C). ^{1}H NMR (C_6D_6): δ 7.66 (d, J = 7.2 Hz, 2H, *ortho*-CH), 7.16 (t, J = 7.3 Hz, 2H, *meta*-CH), 7.01 (t, J = 7.3 Hz, 1H, *para*-CH), 5.40 (s, 1H, C<u>H</u>B(pin)), 1.08 (s, 6H, pinacol-C<u>H</u>$_3$), 1.07 (s, 6H, pinacol-C<u>H</u>$_3$), 0.97 (s, 6H, pinacol-C<u>H</u>$_3$), 0.96 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 141.7 (*ipso*-<u>C</u>), 128.9 (*meta*-<u>C</u>H), 127.1 (*para*-<u>C</u>H), 126.7 (*ortho*-<u>C</u>H), 84.4 (B(O<u>C</u>(CH$_3$)$_2$)$_2$), 83.0 (B(O<u>C</u>(CH$_3$)$_2$)$_2$), 67.6 (BCH), 25.2 (pinacol-<u>C</u>H$_3$), 25.0 (pinacol-<u>C</u>H$_3$), 24.9 (pinacol-<u>C</u>H$_3$). ^{11}B NMR (C_6D_6): δ 31.8 (C–<u>B</u>),

22.6 (O–B). IR (KBr pellet, cm^{-1}): 2977, 1456, 1327, 1140, 973, 849, 706. Anal. Calcd. $C_{19}H_{30}O_5B_2$: C, 63.38; H, 8.40. Found: C, 63.29; H, 8.55.

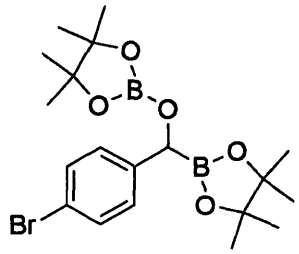


α-[(Pinacol)boroxy]-4-methoxybenzyl(pinacol)boronate. The general procedure was followed using 1% (ICy)CuO*t*-Bu, except that during the work-up, the extraction was carried out using pentane (4 x 5 mL) and benzene (2 mL). The product was isolated as a tan solid (0.169 g, 86%, mp 74–76 °C). ^{1}H NMR (C_6D_6): δ 7.59 (d, J = 8.7 Hz, 2H), 6.79 (d, 8.7 Hz, 2H), 5.38 (s, 1H, C<u>H</u>B(pin)), 3.23 (s, 3H, ArOC<u>H</u>$_3$), 1.10 (s, 6H, pinacol-C<u>H</u>$_3$), 1.06 (s, 6H, pinacol-C<u>H</u>$_3$), 1.02 (s, 6H, pinacol-C<u>H</u>$_3$), 1.00 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 159.4, 133.6, 128.4, 114.5, 84.3 (O<u>C</u>(CH$_3$)$_2$), 83.0 (O<u>C</u>(CH$_3$)$_2$), 67.4 (<u>C</u>B(pin)), 55.0 (ArO<u>C</u>H$_3$), 25.3 (pinacol-<u>C</u>H$_3$), 25.0 (pinacol-<u>C</u>H$_3$), 25.0 (pinacol-<u>C</u>H$_3$), 25.0 (pinacol-<u>C</u>H$_3$). ^{11}B NMR (C_6D_6): δ 31.7 (C–<u>B</u>), 22.4 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 2978, 1437, 1331, 1449, 964, 849. Anal. Calcd. $C_{20}H_{32}O_6B_2$: C, 61.58; H, 8.27. Found: C, 61.43; H, 7.99.

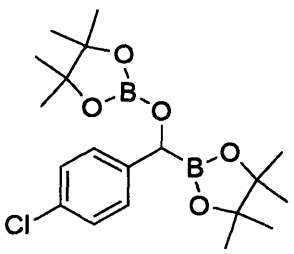


α-[(Pinacol)boroxy]-4-methylbenzyl(pinacol)boronate. The general procedure using 1% (ICy)CuO*t*-Bu was followed to afford the title compound as a white solid (0.176 g, 94%, mp 84–86 °C). ^{1}H NMR (C_6D_6): δ 7.60 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 5.40 (s, 1H,

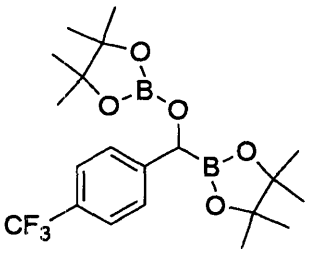
C<u>H</u>B(pin)), 2.05 (s, 3H), 1.09 (s, 6H), 1.08 (s, 6H), 1.00 (s, 6H), 0.98 (s, 6H). ^{13}C NMR (C_6D_6): δ 138.7, 136.3, 129.6, 126.9, 84.3, 83.0, 67.6 (<u>C</u>B(pin)), 25.2, 25.0, 25.0, 25.0, 21.4. ^{11}B NMR (C_6D_6): δ 31.7 (C–<u>B</u>), 22.5 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 2979, 1499, 1368, 1322, 1142, 971, 848. Anal. Calcd. $C_{20}H_{32}O_5B_2$: C, 64.21; H, 8.62. Found: C, 64.12; H, 8.62.



α-[(Pinacol)boroxy]-4-bromobenzyl(pinacol)boronate. The general procedure using 2.3% (ICy)CuO*t*-Bu was followed except that the extraction was carried out with pentane (4 x 5 mL) and benzene (2 mL). After concentration of the combined extracts, the product was further purified by recrystallization from pentane at –40 °C to give colorless crystals (0.177 g, 80%, mp 108–109 °C). ^{1}H NMR (C_6D_6): δ 7.34 (d, J = 8.7 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 5.22 (s, 1H, C<u>H</u>B(pin)), 1.08 (s, 6H, pinacol-C<u>H</u>$_3$), 1.07 (s, 6H, pinacol-C<u>H</u>$_3$), 0.96 (s, 6H, pinacol-C<u>H</u>$_3$), 0.94 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 140.7, 131.9, 128.3, 120.9, 84.5 (O<u>C</u>(CH$_3$)$_2$), 83.2 (O<u>C</u>(CH$_3$)$_2$), 66.9 (<u>C</u>B(pin)), 25.2 (pinacol-<u>C</u>H$_3$), 24.95 (pinacol-<u>C</u>H$_3$), 24.93 (pinacol-<u>C</u>H$_3$), 24.92 (pinacol-<u>C</u>H$_3$). ^{11}B NMR (C_6D_6): δ 31.7 (C–<u>B</u>), 22.5 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 3449, 2966, 1263, 1009, 805. Repeated attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.

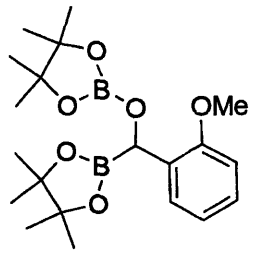


α-[(Pinacol)boroxy]-4-chlorobenzyl(pinacol)boronate. The general procedure was followed using 2.3% (ICy)CuO*t*-Bu except that the extraction was carried out with pentane (4 x 5 mL) and benzene (2 mL). After concentration of the combined extracts, the product was recrystallized from pentane at –40 °C to give colorless crystals (0.161 g, 81%, mp 94–96 °C). ^{1}H NMR (C_6D_6): δ 7.40 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.25 (s, 1H, C<u>H</u>B(pin)), 1.08 (s, 6H, pinacol-C<u>H</u>$_3$), 1.07 (s, 6H, pinacol-C<u>H</u>$_3$), 0.96 (s, 6H, pinacol-C<u>H</u>$_3$), 0.89 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 140.2, 132.8, 129.0, 128.0, 84.5 (O<u>C</u>(CH$_3$)$_2$), 83.2 (O<u>C</u>(CH$_3$)$_2$), 66.9 (<u>C</u>B(pin)), 25.7 (pinacol-<u>C</u>H$_3$), 25.2 (pinacol-<u>C</u>H$_3$), 24.9 (pinacol-<u>C</u>H$_3$), 24.9 (pinacol-<u>C</u>H$_3$). ^{11}B NMR (C_6D_6): δ 31.6 (C–<u>B</u>), 22.5 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 3449, 2978, 1339, 1147, 966, 850. Repeated attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.

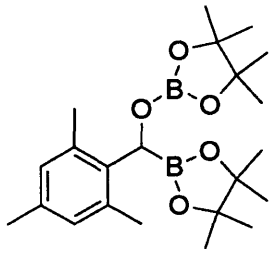


α-[(Pinacol)boroxy]-4-trifluoromethylbenzyl(pinacol)boronate. The general procedure using 2.3% (ICy)CuO*t*-Bu was followed to give a white solid (0.186 g, 87%, mp = 99–100 °C). ^{1}H NMR (C_6D_6): δ 7.52 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 5.29 (s, 1H, C<u>H</u>B(pin)), 1.09 (s, 6H, pinacol-C<u>H</u>$_3$), 1.08 (s, 6H, pinacol-C<u>H</u>$_3$), 0.96 (s, 6H, pinacol-C<u>H</u>$_3$), 0.94 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 145.9, 128.8 (q, J_{C-F} = 31.7 Hz, <u>C</u>CF$_3$), 126.6, 125.7 (q, J_{C-F} = 4.0 Hz), 125.5 (q, J_{C-F} = 271.8 Hz, <u>C</u>F$_3$), 84.7 (O<u>C</u>(CH$_3$)$_2$), 83.3 (O<u>C</u>(CH$_3$)$_2$), 67.1 (<u>C</u>B(pin)), 25.2 (pinacol-<u>C</u>H$_3$), 24.94 (pinacol-<u>C</u>H$_3$), 24.9 (pinacol-<u>C</u>H$_3$), 24.9 (pinacol-<u>C</u>H$_3$). ^{19}F NMR (C_6D_6): δ –62.3. ^{11}B NMR (C_6D_6): δ 31.6 (C–<u>B</u>), 22.5 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 2982, 1933, 1619,

1326, 1121, 851. Repeated attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.

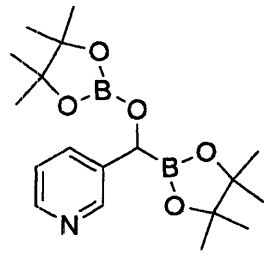


α-[(Pinacol)boroxy]-2-methoxybenzyl(pinacol)boronate. The general procedure using 1% (ICy)CuO*t*-Bu was followed to give a colorless oil which solidified after several days (0.177 g, 91%, mp = 58–60 °C). ^{1}H NMR (C_6D_6): δ 7.80 (m, 1H), 7.04 (m, 1H), 6.91 (m, 1H), 6.51 (m, 1H), 5.81 (s, 1H, C<u>H</u>B(pin)), 3.30 (s, 3H, ArOC<u>H</u>$_3$), 1.08 (s, 6H, pinacol-C<u>H</u>$_3$), 1.06 (s, 6H, pinacol-C<u>H</u>$_3$), 1.05 (s, 6H, pinacol-C<u>H</u>$_3$), 1.02 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 157.0, 131.0, 128.8, 128.2, 121.3, 110.9, 83.9, 82.8, 62.9 (<u>C</u>B(pin)), 55.4 (ArO<u>C</u>H$_3$), 25.2, 25.1, 25.0, 25.0. ^{11}B NMR (C_6D_6): δ 31.9 (C–<u>B</u>), 22.8 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 2980, 1493, 1371, 1143, 968, 849, 752, 668, 533. Anal. Calcd. $C_{19}H_{30}O_6B_2$: C, 60.68; H, 8.04. Found: C, 60.33; H, 7.93.

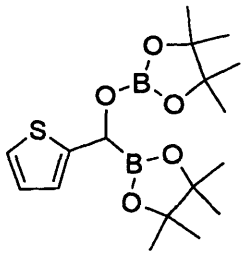


α-[(Pinacol)boroxy]-2,4,6-trimethylbenzyl(pinacol)boronate. The general procedure using 2.3% (ICy)CuO*t*-Bu was followed except that the product was further purified by recrystallization from pentane at –40 °C to give colorless crystals (0.146 g, 73%, mp = 103–105 °C). ^{1}H NMR (C_6D_6): δ 6.77 (s, 2H), 5.85 (s, 1H, C<u>H</u>B(pin)), 2.63 (s, 6H), 2.09 (s, 3H), 1.05 (s,

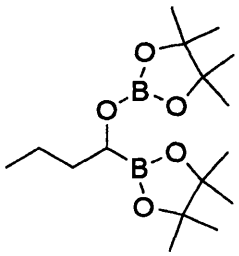
6H, pinacol-C$\underline{H}_3$), 1.03 (s, 6H, pinacol-C$\underline{H}_3$), 1.03 (s, 6H, pinacol-C$\underline{H}_3$), 0.98 (s, 6H, pinacol-C$\underline{H}_3$). ^{13}C NMR (C_6D_6): δ 137.6, 136.6, 135.5, 130.1, 84.4 (O$\underline{C}$(CH$_3$)$_2$), 82.8 (O$\underline{C}$(CH$_3$)$_2$), 63.7 ($\underline{C}$B(pin)), 25.20 (pinacol-$\underline{C}$H$_3$), 25.19 (pinacol-$\underline{C}$H$_3$), 25.1 (pinacol-$\underline{C}$H$_3$), 25.0 (pinacol-$\underline{C}$H$_3$), 21.4, 21.3. ^{11}B NMR (C_6D_6): δ 32.7 (C–$\underline{B}$), 22.6 (O–$\underline{B}$). IR (KBr pellet, cm^{-1}): 2989, 1497, 1429, 1371, 1141, 851. Repeated attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.



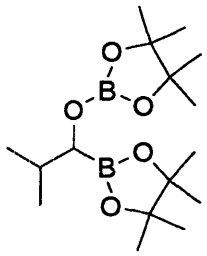
α-[(Pinacol)boroxy]-3-pyridylmethyl(pinacol)boronate. A Schlenk flask equipped with a Teflon-coated magnetic stirbar was charged with bis(pinacolato)diboron (0.127 g, 0.500 mmol) and (ICy)CuO*t*-Bu (0.0184 g, 0.050 mmol). A solution of 3-pyridinecarboxaldehyde (0.047 mL, 0.500 mmol) in benzene (6 mL) was added, and the reaction mixture was stirred for 22 hours. The resulting orange suspension was filtered, and the solid was extracted with dichloromethane (3 x 2 mL). The extracts were combined and concentrated *in vacuo* to afford the title compound as a white solid (0.163 g, 92%, mp = 120 °C dec). ^{1}H NMR (CD_2Cl_2): δ 8.41 (m, 2H), 7.69 (m, 1H), 7.24 (m, 1H), 4.90 (s, 1H, C$\underline{H}$B(pin)), 1.22 (s, 6H, pinacol-C$\underline{H}_3$), 1.21 (s, 6H, pinacol-C$\underline{H}_3$), 1.19 (s, 6H, pinacol-C$\underline{H}_3$), 1.17 (s, 6H, pinacol-C$\underline{H}_3$). ^{13}C NMR (C_6D_6): δ 147.6, 147.5, 137.4, 134.4, 123.7, 84.6, 83.5, 66.0, 25.1, 25.0, 24.9. ^{11}B NMR (C_6D_6): δ 29.6 (C–$\underline{B}$), 22.1 (O–$\underline{B}$). IR (KBr pellet, cm^{-1}): 2980, 1482, 1422, 1309, 1153, 1062, 964, 850, 564. Anal. Calcd. $C_{18}H_{29}O_5B_2N$: C, 59.88; H, 8.10. Found: C, 60.23; H, 7.49.



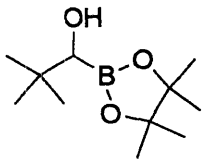
α-[(Pinacol)boroxy]-2-thienylmethyl(pinacol)borate. The general procedure using 1% (ICy)CuO*t*-Bu was followed to afford the title compound as a pale yellow oil (0.174 g, 95%). ^{1}H NMR (C_6D_6): δ 7.15 (m, 1H), 6.84 (m, 1H), 6.73 (m, 1H), 5.61 (s, 1H, C<u>H</u>B(pin)), 1.06 (s, 12H, pinacol-C<u>H</u>$_3$), 1.02 (s, 6H, pinacol-C<u>H</u>$_3$), 1.01 (s, 6H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 144.6, 127.2, 125.3, 125.1, 84.7 (O<u>C</u>(CH$_3$)$_2$), 83.2 (O<u>C</u>(CH$_3$)$_2$), 63.1 (<u>C</u>B(pin)), 25.2 (pinacol-<u>C</u>H$_3$), 25.04 (pinacol-<u>C</u>H$_3$), 24.98 (pinacol-<u>C</u>H$_3$), 24.94 (pinacol-<u>C</u>H$_3$). ^{11}B NMR (C_6D_6): δ 31.4 (C–<u>B</u>), 22.5 (O–<u>B</u>). IR (KBr plate, neat, cm^{-1}): 2981, 1439, 1270, 1143, 1033, 967. Anal. Calcd. $C_{17}H_{28}O_5B_2S$: C, 55.77; H, 7.71. Found: C, 55.87; H, 7.40.



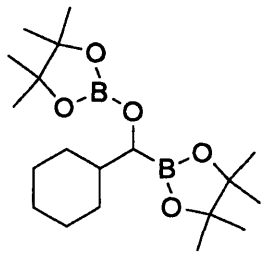
α-[(Pinacol)boroxy]-*n*-butyl(pinacol)boronate. The general procedure using 1% (ICy)CuO*t*-Bu was followed to afford the title compound as a yellow oil (0.153 g, 94%). ^{1}H NMR (C_6D_6): δ 4.33 (dd, J = 5.0, 8.5 Hz, 1H, C<u>H</u>B(pin)), 1.93 (m, 1H), 1.84 (m, 1H), 1.64 (sextet, J = 7.5 Hz, 2H), 0.92 (t, 7.5 Hz, 3H). ^{13}C NMR (C_6D_6): δ 84.1, 82.7, 64.3 (<u>C</u>B(pin)), 36.0, 25.2, 25.2, 25.1, 25.0, 25.0, 20.4, 14.6. ^{11}B NMR (C_6D_6): δ 32.7 (C–<u>B</u>), 22.6 (O–<u>B</u>). IR (KBr plate, neat, cm^{-1}): 2978, 1507, 1390, 1268, 1146, 970, 850. Anal. Calcd. $C_{16}H_{32}O_5B_2$: C, 58.94; H, 9.89. Found: C, 58.75; H, 9.51.



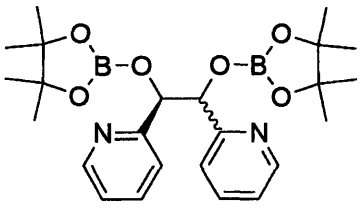
α-[(Pinacol)boroxy]-isobutyl(pinacol)boronate. The general procedure using 1% (ICy)CuO*t*-Bu was followed afford the title compound as a colorless oil (0.154 g, 95%). ^{1}H NMR (C_6D_6): δ 4.14 (d, J = 5.0 Hz, 1H, C<u>H</u>B(pin)), 2.20 (septet, J = 6.8 Hz, 1H, $(CH_3)_2C\underline{H}$), 1.16 (dd, J = 1.8 Hz, 6.8 Hz), 6H, $(C\underline{H}_3)_2CH$), 1.11 (s, 12H, pinacol-C<u>H</u>$_3$), 1.06 (s, 12H, pinacol-C<u>H</u>$_3$). ^{13}C NMR (C_6D_6): δ 84.0 (B(O<u>C</u>$(CH_3)_2)_2$), 82.6 (B(O<u>C</u>$(CH_3)_2)_2$), 70.5 (<u>C</u>B(pin)), 32.5 ($(CH_3)_2\underline{C}$), 25.3 (pinacol-<u>C</u>H$_3$), 25.3 (pinacol-<u>C</u>H$_3$), 25.2 (pinacol-<u>C</u>H$_3$), 25.0 (pinacol-<u>C</u>H$_3$), 20.3 ($(\underline{C}H_3)_2C$), 19.6 ($(\underline{C}H_3)_2C$). ^{11}B NMR (C_6D_6): δ 32.4 (C–<u>B</u>), 22.3 (O–<u>B</u>). IR (KBr plate, neat, cm^{-1}): 2933, 1507, 1272, 1114, 970, 850. Anal. Calcd. $C_{16}H_{32}O_5B_2$: C, 58.94; H, 9.89. Found: C, 58.86; H, 10.28.



1-Hydroxyneopentyl(pinacol)boronate. The general procedure was followed using 1% (ICy)CuO*t*-Bu, except that the crude reaction mixture was concentrated and purified by column chromatography (7 : 3 dichloromethane : diethyl ether, R_f = 0.5), without protection from oxygen or water, to afford the title compound as a colorless oil (0.076 g, 71%). ^{1}H NMR (C_6D_6): δ 3.30 (s, 1H, C<u>H</u>B(pin), 2.04 (s, 1H, O<u>H</u>), 1.13 (s, 9H, C(C<u>H</u>$_3)_3$), 0.99 (s, 12H, pinacol-<u>C</u>H$_3$). ^{13}C NMR (C_6D_6): δ 84.4 (O<u>C</u>$(CH_3)_2$), 70.3 (<u>C</u>B(pin)), 35.4 (<u>C</u>$(CH_3)_3$), 27.6 (C(<u>C</u>H$_3)_3$), 25.2 (pinacol-<u>C</u>H$_3$), 25.1 (pinacol-<u>C</u>H$_3$). ^{11}B NMR: δ 32.8 (C–<u>B</u>). IR (KBr film, cm^{-1}): 3613, 2979, 2952, 1324, 1143, 1047, 845. Repeated attempts at elemental analysis failed to give satisfactory results; ^{1}H and ^{13}C NMR spectra for this compound are included to attest to its purity.



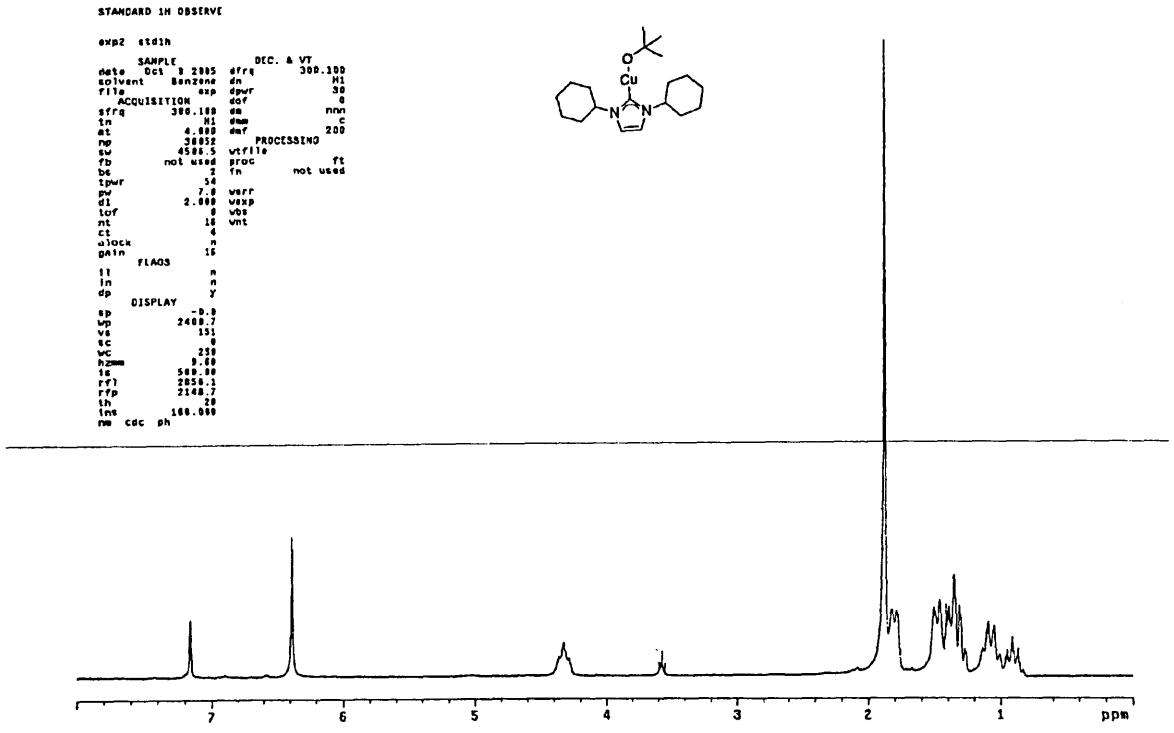
α-[(Pinacol)boroxy]-cyclohexyl(pinacol)boronate. The general procedure using 1% (ICy)CuO*t*-Bu was followed to afford the title compound as a white solid (0.177 g, 97%, mp = 85–86 °C). ^{1}H NMR (C_6D_6): δ 4.14 (d, J = 5.0 Hz, 1H, C<u>H</u>B(pin)), 1.97 (m, 1H), 1.90 (m, 2H), 1.71 (m, 2H), 1.55 (m, 2H), 1.40 (m, 1H), 1.21 (m, 3H), 1.11 (s, 12H), 1.09 (s, 12H). ^{13}C NMR (C_6D_6): δ 84.0 (O<u>C</u>(CH$_3$)$_2$), 82.6 (O<u>C</u>(CH$_3$)$_2$), 69.9 (<u>C</u>B(pin)), 42.3, 31.0, 30.0, 27.24, 27.20, 27.18, 25.32 (pinacol-<u>C</u>H$_3$), 25.27 (pinacol-<u>C</u>H$_3$), 25.1 (pinacol-<u>C</u>H$_3$). ^{11}B NMR (C_6D_6): δ 32.5 (C–<u>B</u>), 22.4 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 3000, 2928, 1450, 1142, 972, 673. Anal. Calcd. $C_{19}H_{35}O_5B_2$: C, 62.33; H, 9.91. Found: C, 62.10; H, 9.75.



Di(2'-pyridyl)-1,2-bis[(pinacol)boroxy]ethane. The reaction was set up according to the general procedure except that 0.25 mmol of bis(pinacolato)diboron and a catalyst loading of 10% (ICy)CuO*t*-Bu catalyst loading were used. After 22 hours, the precipitated product was collected by filtration and dried *in vacuo*. The resulting white solid (0.070 g, 60%, mp = 240 °C dec) comprised a 12:1 mixture of the *meso* and *rac* isomers as judged by ^{1}H NMR. (For comparison, an ^{1}H NMR spectrum obtained from the concentrated crude reaction mixture showed a 3:1 ratio of *meso* and *rac* isomers. ^{1}H NMR (CD_2Cl_2) for the *meso* isomer: δ 8.61 (m, 2H), 8.17 (m, 2H), 8.09 (m, 2H), 7.63 (m, 2H), 4.73 (s, 2H), 1.34 (s, 12H), 1.26 (s, 12H). ^{13}C NMR (CD_2Cl_2): δ

160.9, 141.6, 140.7, 125.3, 124.3, 80.2 (O<u>C</u>(CH_3)$_2$), 78.3 (O<u>C</u>H), 26.7 (pinacol-<u>C</u>H_3), 25.9 (pinacol-<u>C</u>H_3). ^{11}B NMR (CD_2Cl_2): δ 11.0 (O–<u>B</u>). IR (KBr pellet, cm^{-1}): 2976, 1621, 1479, 1027, 900, 811, 767, 543. Anal. Calcd. $C_{24}H_{34}N_2B_2O_6$: C, 61.57; H, 7.32. Found: C, 61.29; H, 7.14.

Control Reactions: No reaction was observed between bis(pinacolato)diboron and benzaldehyde, 2-pyridinecarboxaldehyde, or 3-pyridinecarboxaldehyde using the general procedure in the absence of (ICy)CuO*t*-Bu.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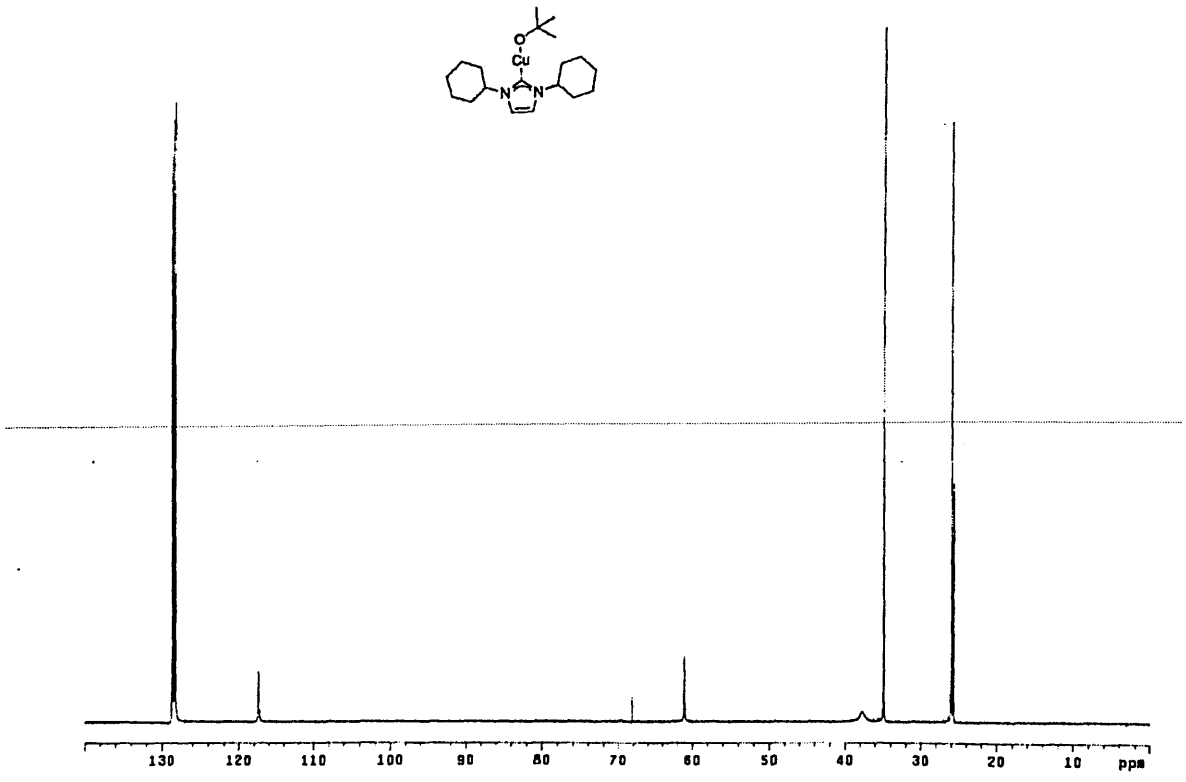
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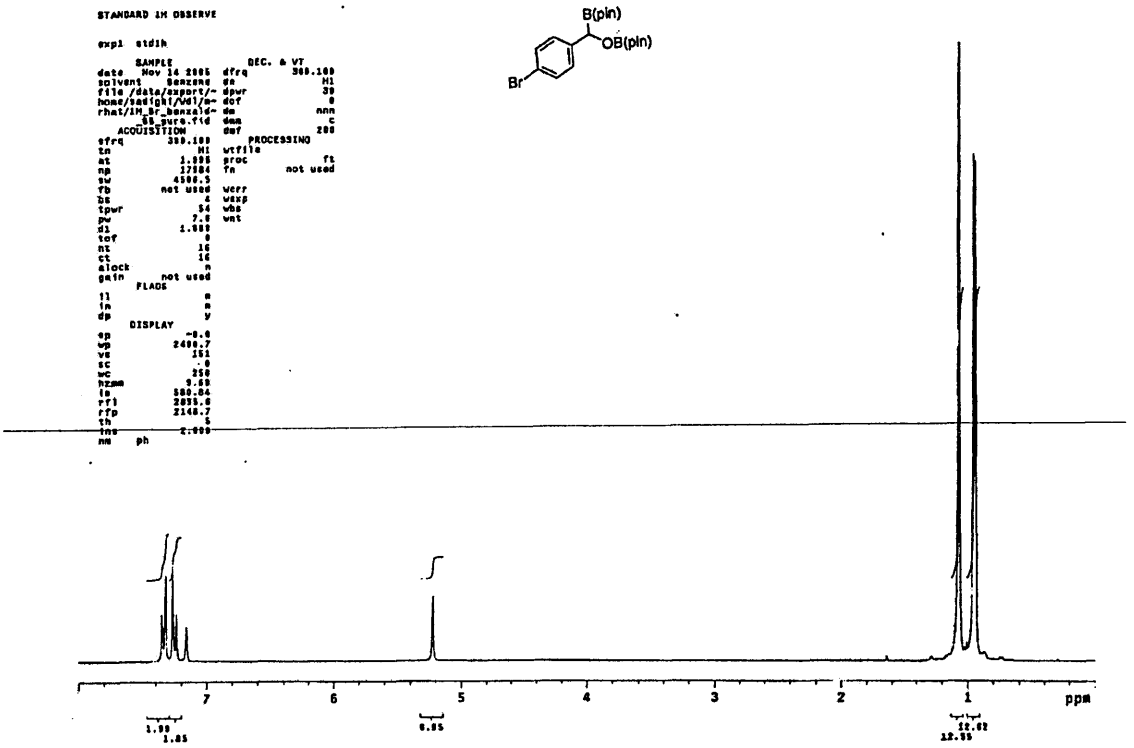
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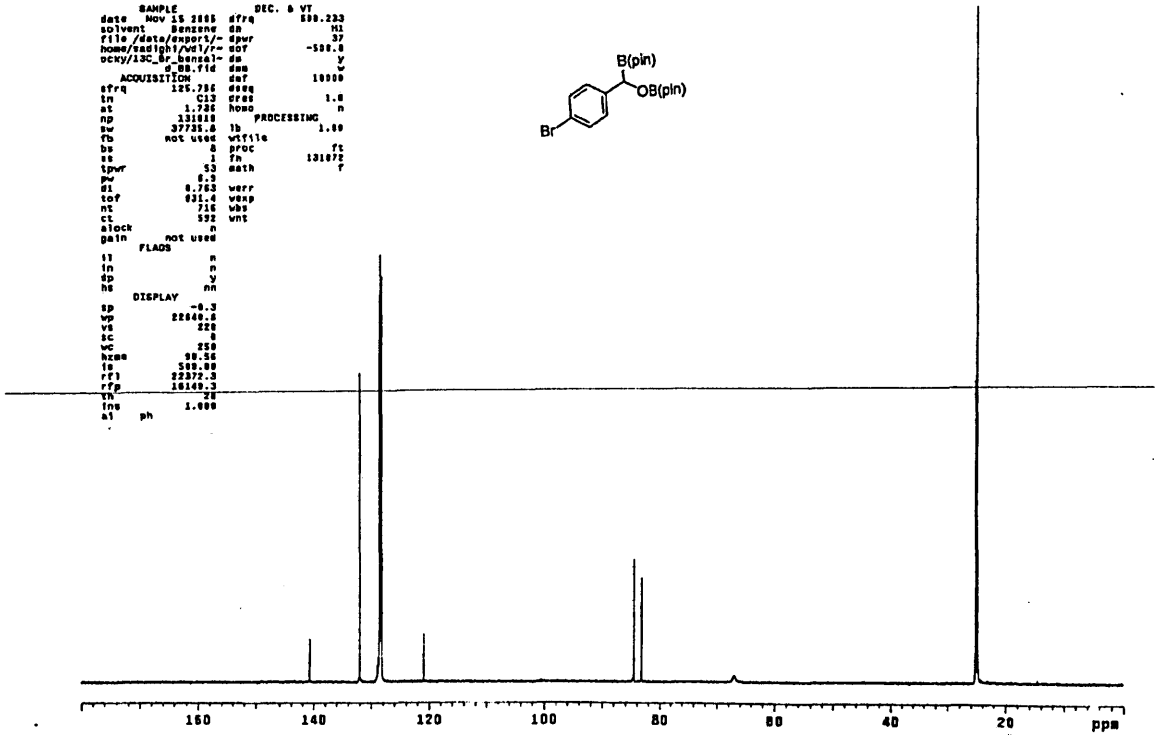
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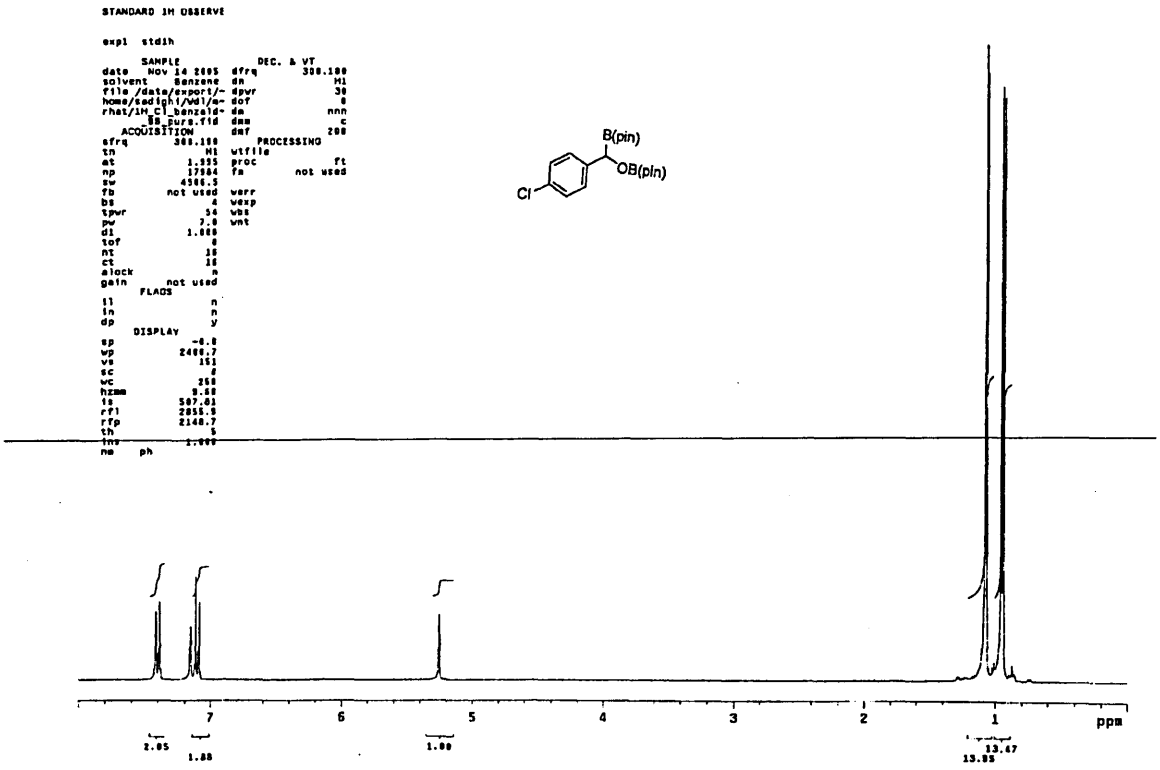
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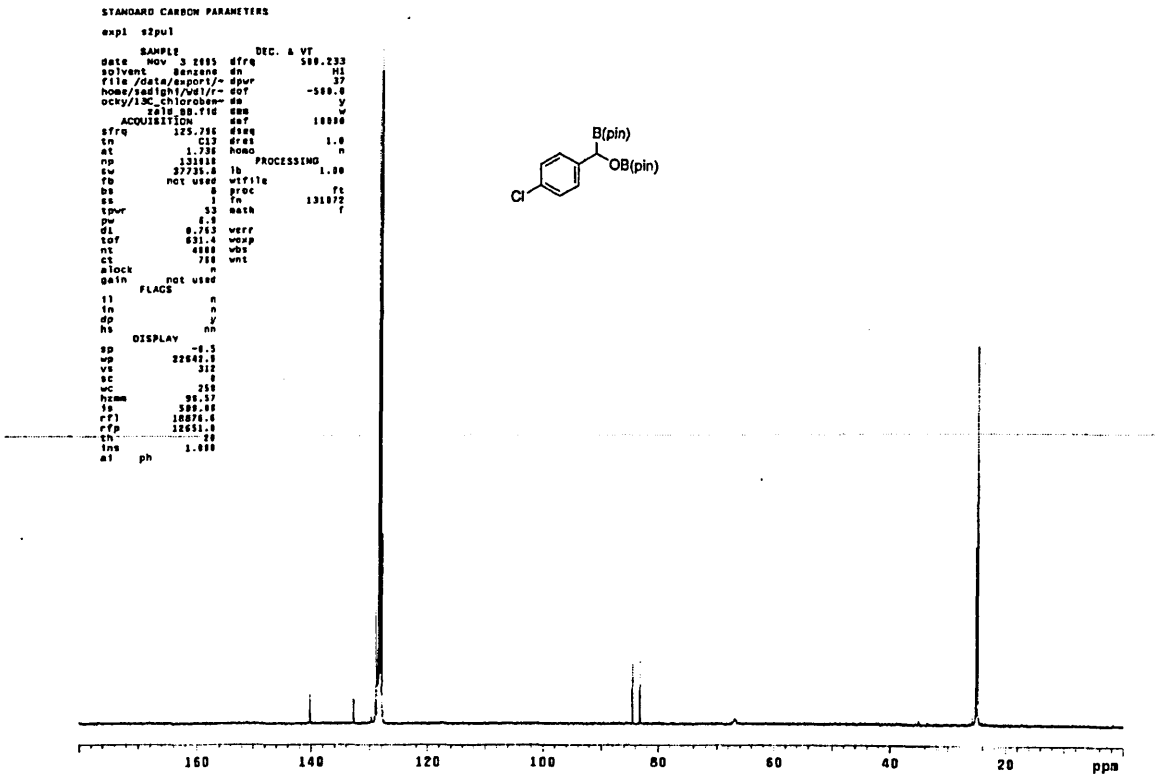
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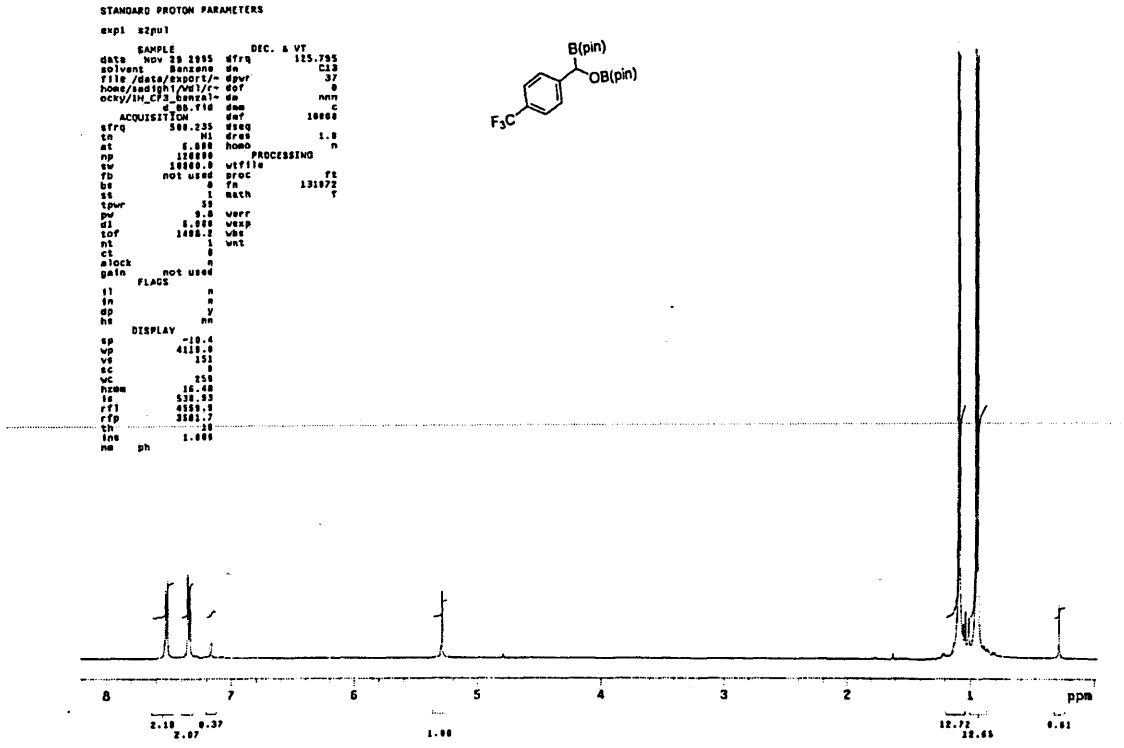
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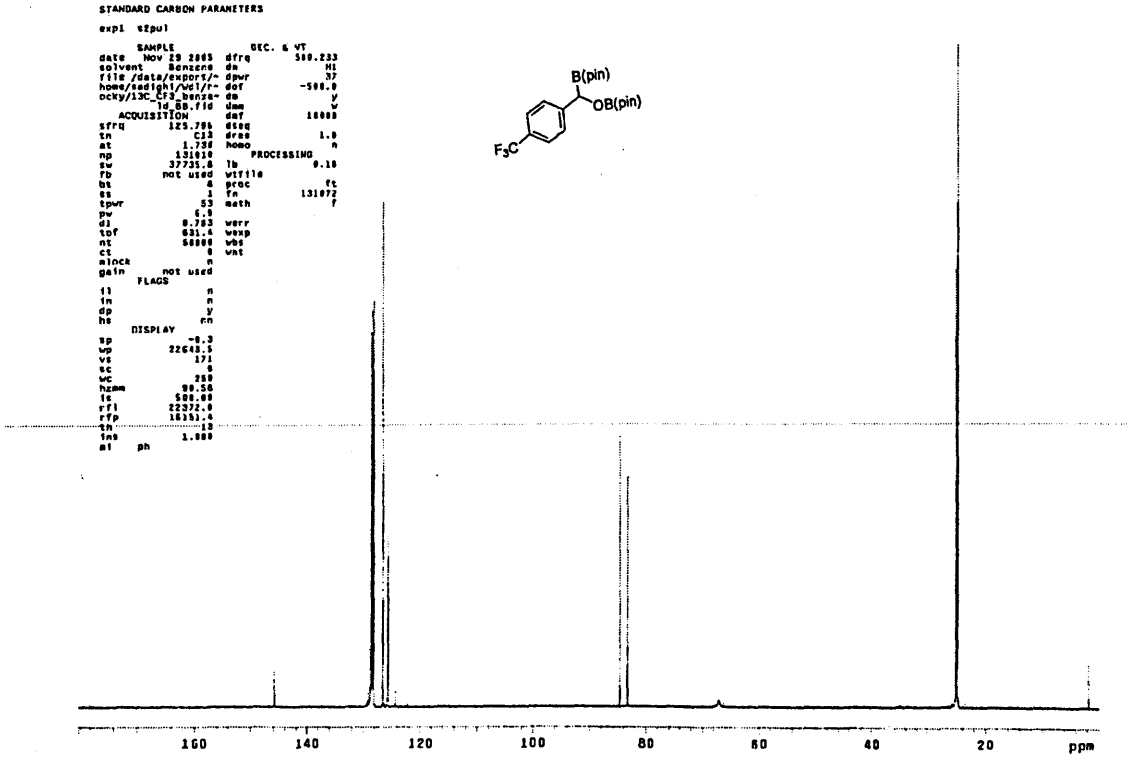
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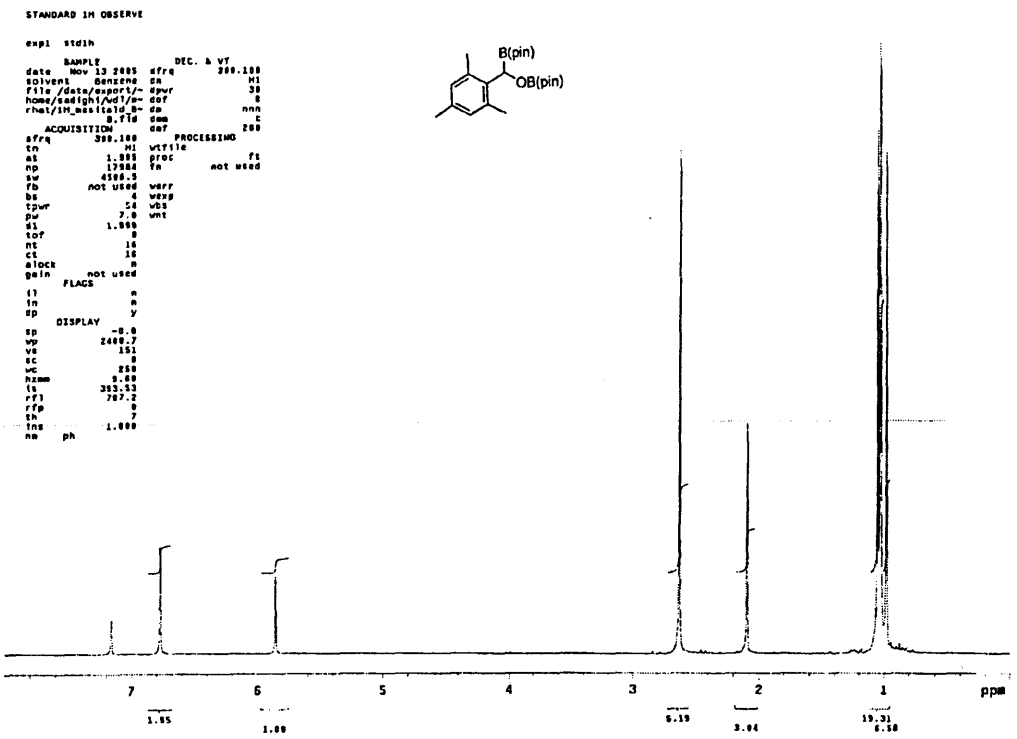
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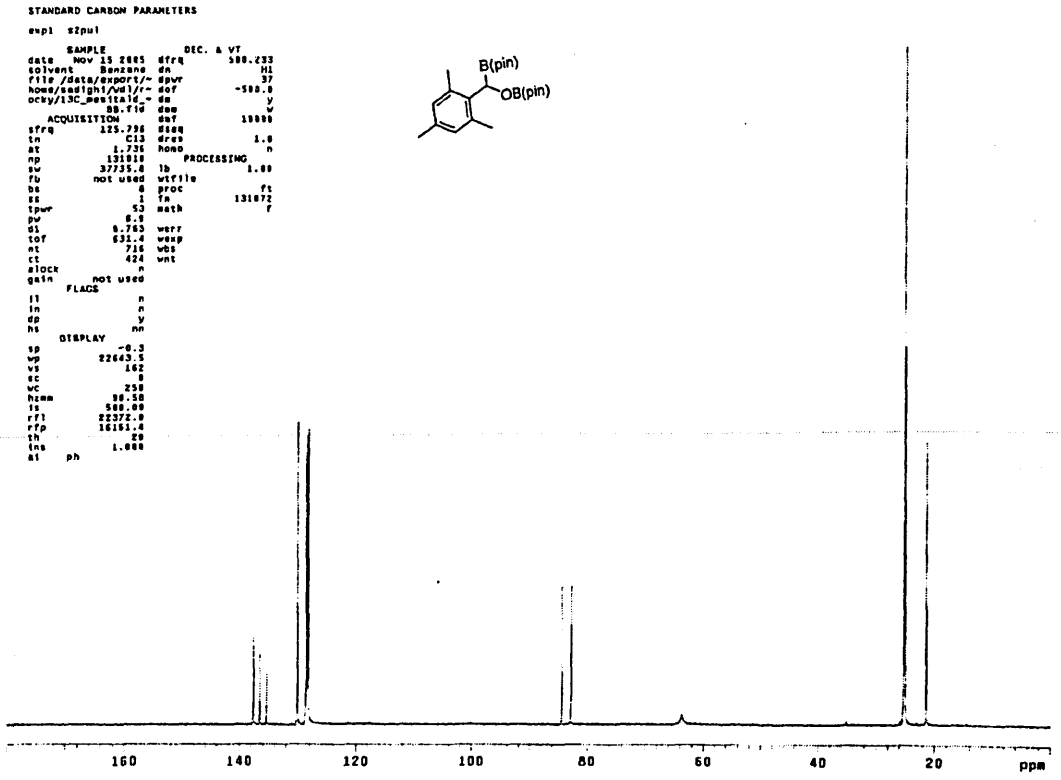
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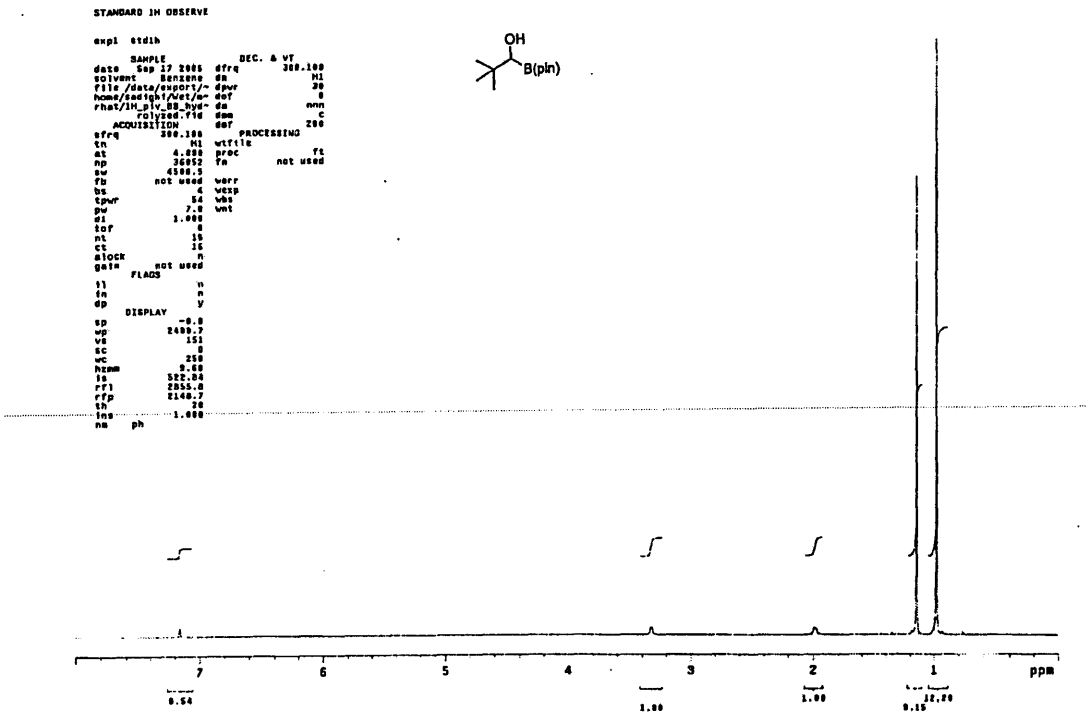
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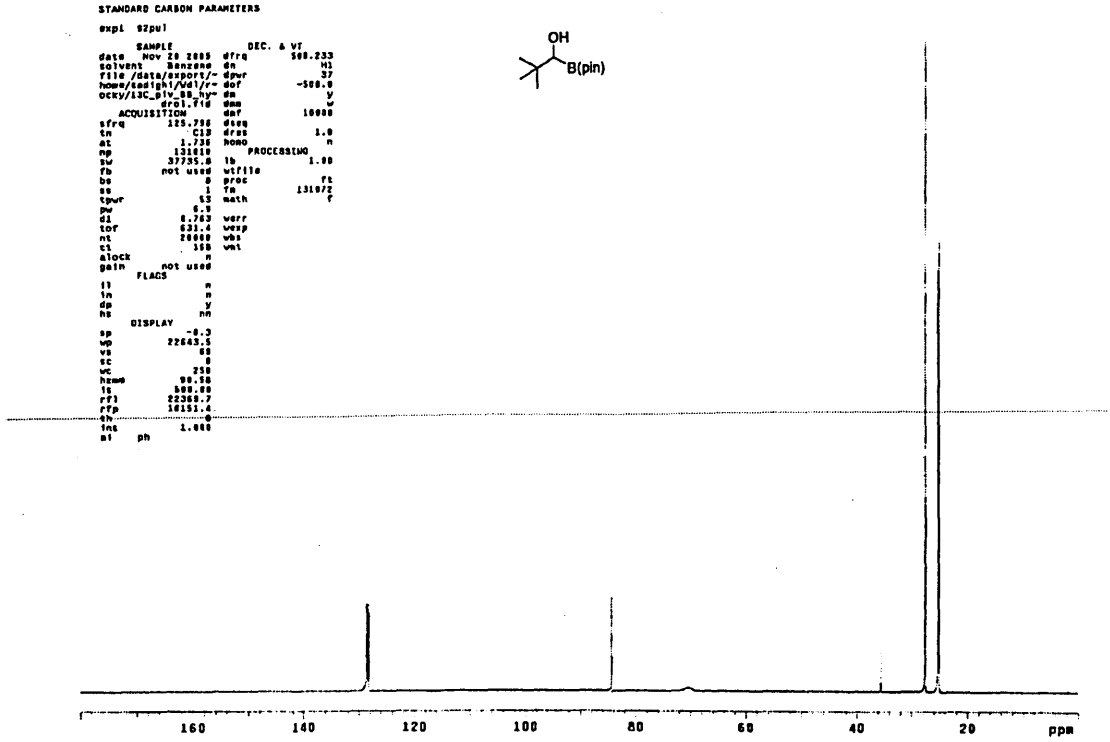
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20
ppm

X-ray Diffraction Studies: Experiments were performed on single crystals of **1** (grown by the vapor diffusion of pentane into a concentrated diethyl ether solution at –40 °C) and **2** (grown from a saturated hexamethyldisiloxane/toluene solution at –40 °C). Colorless crystals were removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. A crystal was affixed to a glass fiber or a cryoloop using the oil, frozen in a nitrogen stream, and optically centered. The data were collected on a Siemens three-circle platform goniometer equipped with a Bruker Smart Apex CCD detector with graphite-monochromated MoKα radiation (λ = 0.71073 Å), using both phi and omega scans at –173 °C. The structures were solved by direct methods (SHELXS)[20] and refined against F^2 on all data by full matrix least squares with SHELXL-97 (Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. CIF files these structures are available at http://www.reciprocalnet.org/ [numbers 05091 (**1**), 05179 (**2**)].

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) α-[(pinacol)boroxy]-2,4,6-trimethylbenzyl (1). The (pinacol)borate group in this complex was found to be disordered over two positions; however, attempts to model the minor component (~9% of the total occupancy) led to unstable refinements even with strong restraints; For this reason, the minor component was not included in the final model. One peak of significant electron density (1.12 e/Å^3) remained after convergence which corresponds to O(1) of the minor component of the disordered (pinacol)borate group.

	1	2
empirical formula	$C_{43}H_{60}N_2O_3BCu$	$C_{22}H_{36}B_2O_5$
fw	727.28	402.13
T, K	100(2)	100(2)
Crystal syst, space group	monoclinic, $P2_1/n$	orthorhombic, *Pbca*
a, Å	11.8285(13)	16.6596(5)
b, Å	20.610(2)	13.4080(6)
c, Å	17.6358(18)	20.9886(9)
α, deg	90	90
β, deg	101.158(4)	90
γ, deg	90	90
V, Å^3	4218.1(8)	4688.3(3)
ρ_{calc}, g/cm^{-1}	1.145	1.139
Z	4	8
μ, mm^{-1}	0.555	0.077
F(000)	1560	1744
cryst size, mm^3	0.15 x 0.15 x 0.15	0.10 x 0.10 x 0.10
θ range, deg	1.91 to 28.70	1.94 to 29.57
no. of data/restraints/params	10890/0/466	6578/0/273
Total no. of reflns	88667	100005
GOF on F^2	1.092	1.070
Final *R* indices [$I > 2\sigma(I)$][a]	*R*1 = 0.0499, *wR*2 = 0.1231	*R*1 = 0.0603, *wR*2 = 0.1571
R indices (all data)[a]	*R*1 = 0.0625, *wR*2 = 0.1303	*R*1 = 0.0696, *wR*2 = 0.1655

[a] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

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Chapter 4

Copper(I) β-Boroalkyls from Alkene Insertion: Isolation and Rearrangement

Parts of this chapter have been adapted from:

Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. "Copper(I) β-Boroalkyls from Alkene Insertion: Isolation and Rearrangement" *Organometallics* **2006**, *25*, 2405–2408.

The formation of alkylboron reagents from alkenes has generated notable interest due to the synthetic versatility of the carbon–boron bond.[1] In the catalytic addition of diboron reagents to alkenes, which forms two carbon–boron bonds and permits a wide range of subsequent elaboration, a key step is the insertion of a C=C bond into a metal–boron bond.[2–6] This insertion has been implicated as competitive with metal–hydride insertion in some metal-catalyzed hydroboration reactions.[7] The β-boroalkyl intermediates formed through this insertion are typically prone to β-hydride elimination,[8] and the discrete borometallation of alkenes, in contrast to that of alkynes,[9] has not been reported to date.

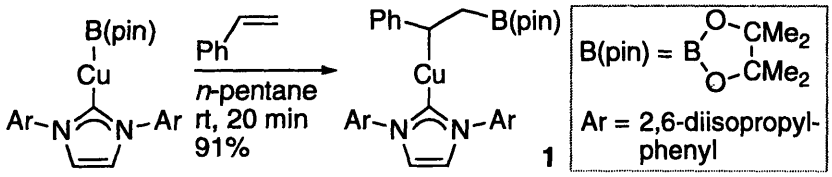
The first well-characterized copper boryl complex[10,11] is highly reactive toward carbon dioxide, and we were interested in examining its reactions with other unsaturated substrates such as alkenes. Although alkyl complexes of d^{10} metal centers undergo β-hydride elimination less readily than those of metals with partially filled d-orbitals, copper(I) alkyls have been shown to decompose by this route as well as by net Cu–C bond homolysis.[12,13] Because N-heterocyclic carbene (NHC) ligands impart considerable stability to σ-organocopper(I) complexes, we hoped that alkene insertion into the (NHC)copper boryl complex would lead to isolable products. Herein we describe the regioselective insertion of alkenes into the copper–boron bond, with a Hammett study of substituent electronic effects on the reactivity of vinylarenes. The structurally characterized styrene insertion product does undergo β-hydrogen elimination, resulting in rearrangement to an α-boroalkyl complex, but only at elevated temperatures.

Insertion of olefins into Cu–B bonds

The structurally characterized copper(I) boryl complex (IPr)CuB(pin)[10] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), pin = pinacolate: 2,3-dimethyl-2,3-butanediolate) reacts

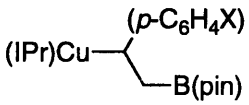
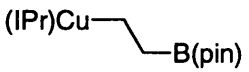
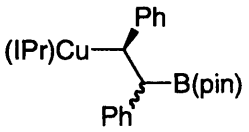
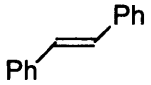
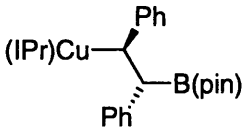
rapidly and cleanly with styrene (Scheme 1) to form a single product as judged by ^{1}H NMR spectroscopy. Protonolysis of the styrene insertion product **1** with ethanol produces 2-phenethyl(pinacol)boronate as the only boron-containing product, corroborating its assignment as an α-phenyl-β-boroethyl complex.

Scheme 1.



The results of insertion reactions using styrenes and other alkene substrates are given in Table 1. A number of *para*-substituted styrenes (entry 1) react efficiently, forming a single regioisomer in each case. Although alkyl-substituted alkenes such as 1-hexene and cyclopentene react very slowly with (IPr)CuB(pin), ethylene itself undergoes insertion in high yield (entry 2). Both *trans*- and *cis*-stilbene (entries 3, 4) show high selectivity for *syn* addition, although the insertion of *cis*-stilbene leads to a detectable degree of isomerization (~5% as judged by ^{1}H NMR spectroscopy) to form the *anti* product, suggesting that a radical pathway may be involved to some extent. It is worth noting that an internal alkyne, 2-butyne, also inserts readily, affording the corresponding *cis*-2-borovinylcopper complex in an isolated yield of 90%.

Table 1. Insertion of alkenes into (IPr)CuB(pin).[a]

Entry	Substrate	Product	Yield (%)
1			
		X = H	91
		F	70
		Me	88
		OMe	92
		NMe_2	89
2			86[b]
3			76[c,d]
		syn : *anti* = 25 :1	
4			81[c,e]

(a) (IPr)CuB(pin) was generated in situ from (IPr)CuO*t*-Bu and (pin)B–B(pin) (1 equivalent). Unless noted otherwise, insertions were carried out in *n*-pentane solvent at room temperature for 20 minutes, using 1.1 equivalents of alkene. (b) Carried out under 1 atm C_2H_4. (c) Reaction time was 15 h. (d) 2 equiv *cis*-stilbene used; yield refers to both isomers. (e) Indicated stereochemistry is relative.

Single crystals of **1** were grown by the diffusion of pentane vapor into an ether solution at –40 °C. Analysis by X-ray diffraction revealed a nearly linear two-coordinate structure, and confirmed the regiochemistry of the styrene insertion (Figure 1). Although the complex (IPr)CuEt was recently isolated and characterized spectroscopically,[12e] structurally characterized copper alkyl complexes possessing β-hydrogens are rare.[12d,13c,13d] The Cu(1)–C_{alkyl} bond distance in **1** (1.948(3) Å) is similar to that of (IPr)$CuCH_3$ (1.913(6) Å).[14]

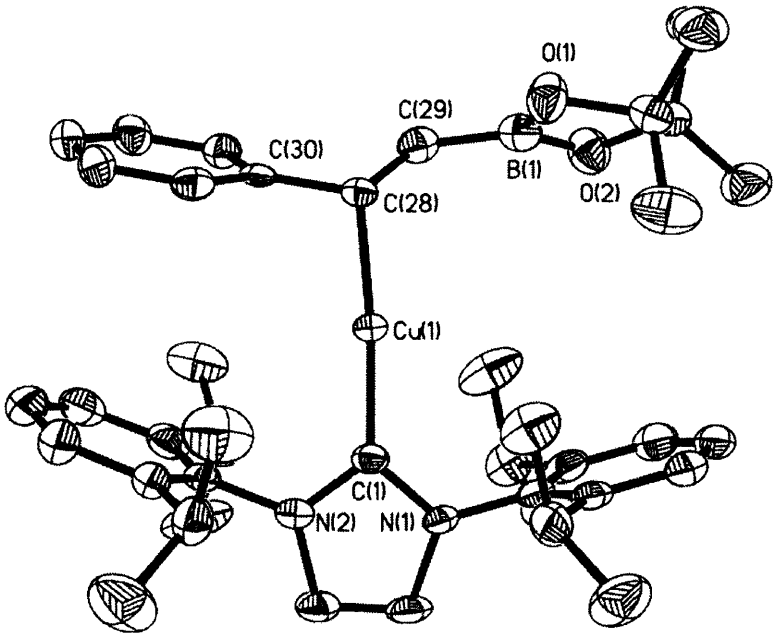
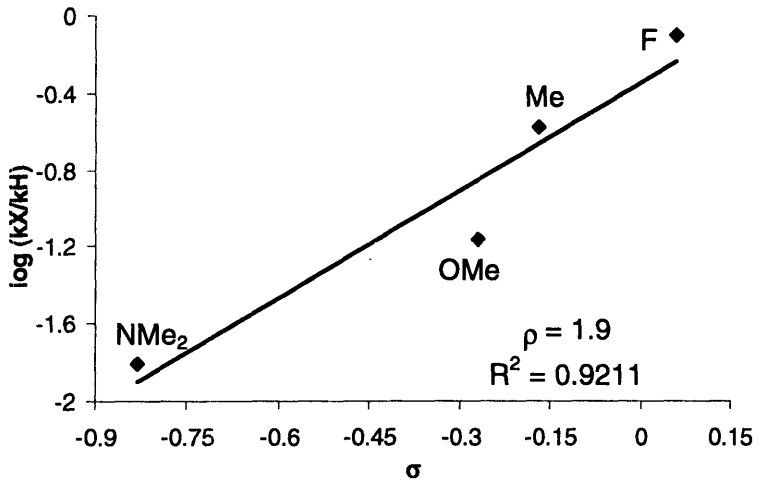


Figure 1. Solid state structure of **1**•($0.5C_5H_{12}$) shown as 50% ellipsoids. For clarity, hydrogen atoms, disorder, and solvent have been omitted. Select bond lengths (Å) and angles (°): Cu(1)–C(28) 1.948(3), Cu(1)–C(1) 1.898(4), C(28)–C(29) 1.526(5), C(29)–B(1) 1.579(6), B(1)–O(1) 1.353(6), B(1)–O(2) 1.359(5); C(1)–Cu(1)–28) 175.07(16), Cu(1)–C(28)–C(29) 114.9(3), Cu(1)–C(28)–C(30) 104.5(2).

To examine the role of electronic effects, competitive insertion experiments were carried out using *para*-substituted styrenes.[15] A benzene solution containing styrene (2.0 equivalents) and 4-$XC_6H_4CH{=}CH_2$ (X = NMe_2, OMe, Me, F; 2.0 equivalents) was rapidly added to a solution of (IPr)CuB(pin). The relative product ratios, assessed by ^{1}H NMR spectroscopy, indicated that electron-donating substituents slow the reaction: styrene reacts *ca.* 60 times more rapidly than 4-(dimethylamino)styrene. The reactions were complete within minutes after mixing, and the product ratios did not change over several hours. Competition experiments using more electron-poor styrenes (*p*-Cl, *p*-CF_3) gave qualitatively similar results; however, these substrates undergo observable side-reactions[16] and are not included in the study.



X	σ_p	k_X/k_H
F	0.06	0.79(1)
Me	–0.17	0.27(1)
OMe	–0.27	0.068(15)
NMe_2	–0.83	0.016(2)

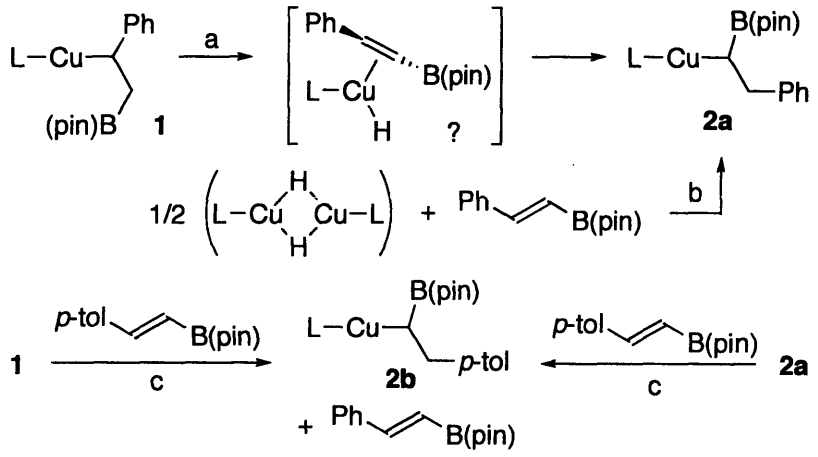
Figure 2: Hammett plot of the relative rates of insertion of 4-substituted styrenes into (IPr)CuB(pin) at room temperature in C_6H_6.

A plot of the relative ratios of the insertion products against σ_p gave a moderate fit (R^2 = 0.92) with ρ = +1.9±0.4 (Figure 2).[17] If alkene insertion into the copper–boron bond is rate-determining, the ρ value is consistent with the buildup of negative charge on the incipiently copper-bound carbon. The carbocupration of enones and alkynes by dialkylcuprate(I) reagents has been described in terms of significant electron-donation from the electron-rich copper center to the substrate,[18] followed by rate-determining insertion; both substrate binding and insertion are facilitated by the π-acidity of the substrate.[19] Here, the relative rates for the borocupration of styrenes suggest that the substrate likewise behaves essentially as an electrophile. In contrast, the small and negative ρ values determined for hydroboration reactions suggest the buildup of some positive charge in the substrate during insertion.[20,21] More detailed mechanistic discussion must await further investigation.

Thermal rearrangement of 1

Although **1** is stable for prolonged periods at ambient temperature, heating in benzene solution at 70 °C for 20 hours resulted in the formation of a new complex, along with some deposition of elemental copper (Scheme 2). Analysis by ^{1}H NMR spectroscopy indicated the formation of the rearranged alkyl complex (IPr)CuCH[B(pin)]CH_2Ph (**2a**). This rearrangement presumably occurs via β-hydride elimination followed by reinsertion of the resulting olefin into a Cu–H bond. In a separate experiment, *trans*-2-phenylvinyl(pinacol)boronate, which should be formed by β-hydride elimination from **1**, reacted cleanly and rapidly with the previously characterized[22] copper hydride $[(IPr)CuH]_2$ to form **2a**. The rapidity of this hydrometallation suggests that β-hydride elimination is the slow step in the rearrangement of **1** to **2a**. The thermal rearrangement of **1** was also conducted in the presence of *trans*-2-(*p*-tolyl)vinyl(pinacol)boronate (1.5 equivalents). The resulting ^{1}H NMR spectrum indicated the formation of both **2a** and (IPr)CuCH[B(pin)]CH_2(*p*-tolyl) (**2b**), and the presence of free *trans*-2-phenylvinyl-(pinacol)boronate. This observation is consistent with the generation of a copper-alkene complex, in which the alkene is substitutionally labile, as an intermediate in the rearrangement. Heating a benzene solution of **2a** in the presence of 2-(*p*-tolyl)vinyl(pinacol)boronate (1.5 equivalents) for 20 hours, likewise leads to a mixture of **2a** and **2b**,[23] indicating that the α-boroalkyl complexes can also undergo β-hydride elimination and hinting at the participation of a similar intermediate.

Scheme 2.



(a) C_6H_6, 70 °C, 24h; 54%. (b) $[(IPr)CuH]_2$ generated in situ from (IPr)CuO*t*-Bu and $(EtO)_3SiH$; *n*-pentane, room temp, 1 h; 91%. (c) C_6D_6, 70 °C, 24h; mixture of **2b** and **2a** observed.

An X-ray diffraction study was performed on single crystals grown by vapor diffusion of pentanes into a toluene solution of **2a** (Figure 3). Other metal α-boroalkyls show varying degrees of metal-boron orbital interaction.[24] The somewhat acute Cu(1)–C(28)–B(1) angle of 96.3(2)° might indicate an attractive copper-boron interaction; however, the long Cu(1)–B(1) bond distance of 2.608(3) Å (the only measured Cu–B σ bond is 2.002(3) Å) and the trigonal planar geometry about boron imply that any such interaction is weak in this case. In solution, no boron-copper interaction is observed for **2a** based on its ^{11}B NMR spectrum: The chemical shift observed for **2a** (33.4 ppm) is typical of neutral, three-coordinate boron,[25] and differs only slightly from that of **1** (34.7 ppm).

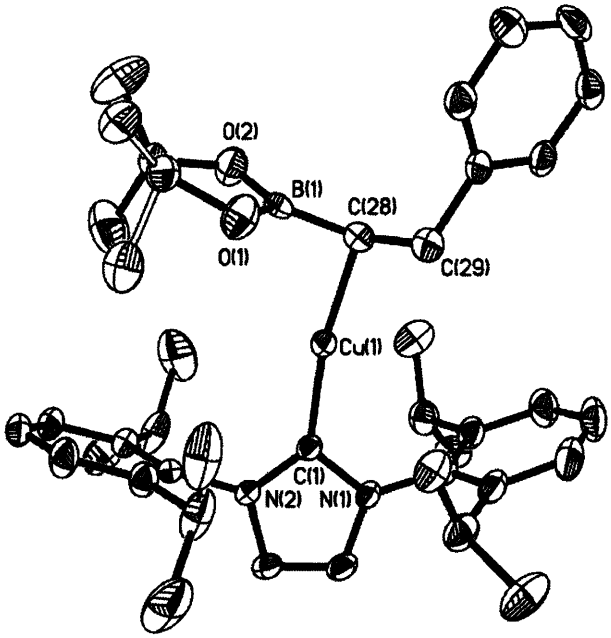


Figure 3. Solid state structure of **2a**•($0.5C_7H_8$) shown as 50% ellipsoids. For clarity, hydrogen atoms, disorder, and solvent have been omitted. Select bond lengths (Å) and angles (°): Cu(1)–C(28) 1.959(3), Cu(1)–C(1) 1.895(3), Cu(1)–B(1) 2.608(3), C(28)–C(29) 1.536(5), C(28)–B(1) 1.520(5), B(1)–O(1) 1.393(5), B(1)–O(2) 1.371(4), C(1)–Cu(1)–C(28) 169.51(13), Cu(1)–C(28)–C(29) 106.9(2), Cu(1)–C(28)–B(1) 96.3(2).

In conclusion, alkenes insert cleanly and regioselectively into (IPr)CuB(pin) to give isolable β-boroalkyl complexes. A Hammett study using 4-substituted styrenes showed that electron-releasing substituents slow the reaction markedly. At elevated temperatures, the styrene insertion product rearranges via β-hydrogen elimination and reinsertion to give an (α-boroalkyl)copper(I) complex.

Experimental Section.

General Considerations. All synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an

atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Anhydrous toluene, hexanes, and tetrahydrofuran were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina and a third column packed with activated 4Å molecular sieves (for tetrahydrofuran) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Benzene and pentane, anhydrous, were purchased from Aldrich in Sure-Seal™ bottles, and stored in a glovebox over 4Å molecular sieves. All non-dried solvents used were reagent grade or better.

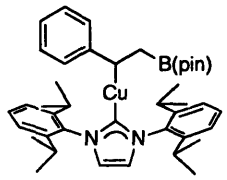
NMR solvent C_6D_6 (Cambridge Isotope Laboratories) was dried over sodium/benzophenone, degassed by three freeze-pump-thaw cycles, and vacuum-transferred prior to use. ^{1}H NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak. ^{19}F NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of $CFCl_3$. ^{11}B NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced to an external standard of 0.5 M BF_3 in diethyl ether (0 ppm). ^{13}C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak.

The starting compounds [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (pinacol)boryl[10] and 4-dimethylaminostyrene[26] were synthesized as described previously. Styrene (Lancaster), 4-fluorostyrene (Alfa Aesar), 4-methylstyrene (Alfa Aesar), 4-methoxystyrene (Alfa Aesar), 2-butyne (Aldrich), and *cis*-stilbene (Lancaster) were degassed prior to use. Ethylene (Airgas), *trans*-stilbene, *trans*-2-phenylvinyl(pinacol)boronate (Lancaster

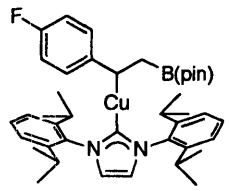
Synthesis) and *trans*-2-(*p*-tolyl)vinyl(pinacol)boronate (Lancaster Synthesis) were used as received.

General procedure for reaction of olefins and alkynes with (IPr)CuB(pin):

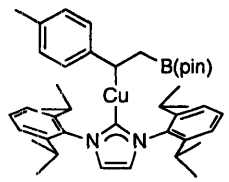
In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stirbar was charged with (IPr)CuO*t*-Bu (0.300 g, 0.571 mmol) and bis(pinacolato)diboron (0.146 g, 0.574 mmol). *n*-Pentane (5 mL) was added, and the reaction mixture was stirred for 10 minutes. The appropriate olefin or alkyne (0.628 mmol) was added via syringe and the reaction mixture was stirred for 20 minutes. The resulting white precipitate was collected by filtration.



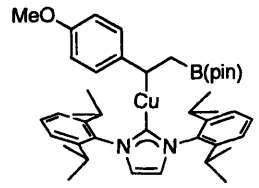
[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 1-phenyl-2-[(pinacol)boro]ethyl (1): The general procedure was followed to give the title compound (0.354 g, 91%). ^{1}H NMR (C_6D_6): δ 7.23 (t, *J* = 7.8 Hz, 2 H), 7.05 (m, 6 H), 7.01 (d, *J* = 7.6 Hz, 2 H), 6.82 (d, *J* = 7.6 Hz, 2 H), 6.74 (t, *J* = 7.1 Hz, 1 H), 6.20 (s, 2 H), 2.57 (t, *J* = 7.8 Hz, 1 H), 2.49 (m, 4 H), 1.64 (d, *J* = 7.8 Hz, 2 H), 1.30 (d, *J* = 6.9 Hz, 6 H), 1.28 (d, *J* = 6.9 Hz, 6 H), 1.068 (d, *J* = 6.9 Hz, 6 H), 1.066 (d, *J* = 6.9 Hz, 6 H), 0.984 (s, 6 H), 0.979 (s, 6 H). ^{13}C NMR (C_6D_6): δ 186.0 ($N_2\underline{C}Cu$), 159.5 (ipso-C_6H_5), 146.0 (*o*-Ar), 145.9 (*o*-Ar), 135.7 (*ipso*-Ar), 130.7 (*p*-Ar), 128.0 (*m*-C_6H_5), 125.1 (*o*-C_6H_5), 124.4 (*m*-Ar), 122.3 ($N\underline{C}H$), 117.4 (*p*-C_6H_5), 82.1 ($B(O\underline{C}(CH_3)_2)_2$, 30.7 ($Cu\underline{C}_\alpha$), 29.3 ($\underline{C}H(CH_3)_2$), 25.5 ($B(OC(\underline{C}H_3)_2)_2$, 25.2 ($CH(\underline{C}H_3)_2$), 24.1 ($CH(\underline{C}H_3)_2$), 16.0 (br., $\underline{C}H_2B(pin)$). ^{11}B NMR (C_6D_6): δ 34.7.



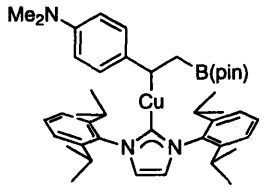
[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 1-(4-fluorophenyl)-2-[(pinacol)boro]ethyl: The general procedure was followed to give the title compound (0.280 g, 70%). ^{1}H NMR (C_6D_6): δ 7.22 (t, J = 7.8 Hz, 2 H), 7.03 (d, J = 7.6 Hz, 2 H), 7.01 (d, J = 7.6 Hz, 2 H), 6.75 (m, 2 H), 6.63 (m, 2 H), 6.17 (s, 2 H), 2.47 (m, 5 H), 1.58 (m, 2 H), 1.28 (d, J = 7.0 Hz, 6 H), 1.25 (d, J = 7.0 Hz, 6 H), 1.06 (d, J = 7.0 Hz, 6 H), 1.05 (d, J = 7.0 Hz, 6 H), 0.98 (s, 12 H). ^{13}C NMR (C_6D_6): δ 186.0 ($N_2\underline{C}Cu$), 157.5 (d, J J_{C-F} = 232 Hz, $\underline{C}$–F), 155.1 (ipso-C_6H_4F), 145.9 (*o*-Ar), 135.7 (*ipso*-Ar), 130.7 (*p*-Ar), 125.3 (d, J_{C-F} = 6.3 Hz), 124.4 (*m*-Ar), 122.4 (N$\underline{C}$H), 114.3 (d, J_{C-F} = 20 Hz)), 82.1 (B(O$\underline{C}(CH_3)_2)_2$, 29.4 (Cu$\underline{C}_\alpha$), 29.2 ($\underline{C}H(CH_3)_2$), 25.5, 25.4, 24.0 (CH($\underline{C}H_3)_2$), 16.5 (br., $\underline{C}H_2$B(pin)). ^{19}F NMR (C_6D_6): δ –130.2. ^{11}B NMR (C_6D_6): δ 34.7.



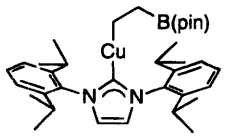
[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 1-(4-methylphenyl)-2-[(pinacol)boro]ethyl: The general procedure was followed to give the title compound (0.350 g, 88%). ^{1}H NMR (C_6D_6): δ 7.23 (t, J = 7.7 Hz, 2 H), 7.05 (m, 4 H), 6.84 (d, J = 8.0 Hz, 2 H), 6.75 (d, J = 8.2 Hz, 2 H), 6.20 (s, 2 H), 2.50 (m, 5 H), 2.35 (s, 3 H), 1.65 (d, J = 8.2 Hz, 2 H), 1.30 (m, 12 H), 1.07 (d, J = 6.9 Hz, 12 H), 0.99 (s, 12 H). ^{13}C NMR (C_6D_6): δ 186.1 ($N_2\underline{C}Cu$), 156.2, 145.9, 135.8, 130.6, 128.7, 125.1, 124.9, 124.4, 122.4, 82.0, 29.9 ($\underline{C}_\alpha$Cu), 29.3, 25.6, 25.4, 25.2, 24.1, 21.6 (*p*-CH_3), 16.3 (br., $\underline{C}H_2$B(pin)). ^{11}B NMR (C_6D_6): δ 35.5.



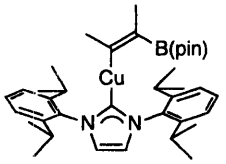
[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 1-(4-methoxyphenyl)-2-[(pinacol)boro]ethyl: The general procedure was followed to give the title compound (0.374 g, 92%). ^{1}H NMR (C_6D_6): δ 7.25 (t, J = 7.8 Hz, 2 H), 7.06 (m, 4 H), 6.71 (m, 4H), 6.19 (s, 2 H), 3.58 (s, 3 H), 2.50 (m, 5 H), 1.65 (m, 2 H), 1.32 (d, J = 6.9 Hz, 6 H), 1.30 (d, J = 6.9 Hz, 6 H), 1.07 (d, J = 6.9 Hz, 12 H), 0.99 (s, 12 H). ^{13}C NMR (C_6D_6): δ 186.1 ($N_2\underline{C}Cu$), 153.1, 152.0, 145.9, 135.7, 130.6, 125.5, 124.4, 122.3, 114.2, 82.0, 55.7 ($O\underline{C}H_3$), 29.3, 28.9 ($\underline{C}_{\alpha}Cu$), 25.6, 25.4, 25.2, 24.1, 16.8 (br., $\underline{C}H_2B(pin)$). ^{11}B NMR (C_6D_6): δ 34.8.



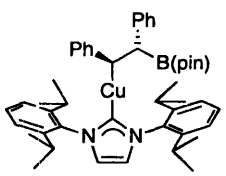
[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 1-(4-dimethylaminophenyl)-2-[(pinacol)boro]ethyl: The general procedure was followed to give the title compound (0.368 g, 89%). ^{1}H NMR (C_6D_6): δ 7.23 (t, J = 7.7 Hz, 2 H), 7.08 (m, 4 H), 6.76 (d, J = 8.5 Hz, 2 H), 6.62 (d, J = 8.5 Hz, 2 H), 6.20 (s, 2 H), 2.76 (s, 6 H), 2.52 (m, 5 H), 1.68 (m, 2 H), 1.33 (d, J = 6.9 Hz, 6 H), 1.32 (d, J = 6.9 Hz, 6 H), 1.08 (d, J = 6.9 Hz, 12 H), 1.00 (s, 12 H). ^{13}C NMR (C_6D_6): δ 186.4 ($N_2\underline{C}Cu$), 150.4, 146.0, 144.5, 135.8, 130.6, 125.5, 124.4, 122.3, 116.2, 82.0, 43.4 ($N(\underline{C}H_3)_2$), 29.3, 28.8 ($\underline{C}_{\alpha}Cu$), 25.6, 25.4, 25.3, 24.1, 16.8 (br., $\underline{C}H_2B(pin)$). ^{11}B NMR (C_6D_6): δ 35.5.



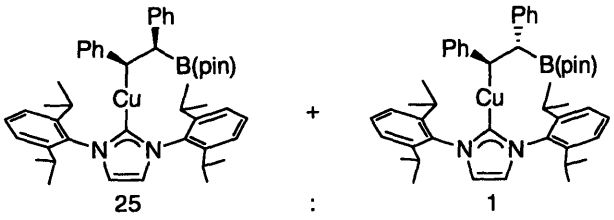
[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 2-[(pinacol)boro]ethyl: The general procedure was followed except that the pentane suspension of (IPr)CuB(pin) was degassed on a Schlenk line, and ethylene (1atm) was added to give the title compound (0.297 g, 86%). ^{1}H NMR (C_6D_6): δ 7.21 (t, J = 7.7 Hz, 2 H), 7.07 (m, J = 7.4 Hz, 4 H), 6.23 (s, 2 H), 2.64 (sept., J = 6.9 Hz, 4 H), 1.43 (d, J = 6.9 Hz, 12 H), 1.21 (m, 2 H), 1.10 (d, J = 6.9 Hz, 12 H), 1.05 (s, 12 H), 0.44 (m, 2 H). ^{13}C NMR (C_6D_6): δ 186.7 ($N_2\underline{C}Cu$), 146.2, 135.8, 130.6, 124.4, 122.1, 81.7, 29.3, 25.4, 24.1, 10.3 (CH_2B(pin), 2.4 ($Cu\underline{C}H_2$). ^{11}B NMR (C_6D_6): δ 34.5.



[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (*Z*)-3-[(pinacol)boro]-2-butenyl: The general procedure was followed, except that a large excess of 3-butyne (~0.25 mL) was used due to its high volatility, to give the title compound (0.326 g, 90%). ^{1}H NMR (C_6D_6): δ 7.27 (t, J = 7.8 Hz, 2 H), 7.14 (d, J = 7.6 Hz, 2 H), 6.26 (s, 2 H), 2.68 (sept, J = 6.9 Hz, 4 H), 2.22 (s, 3 H), 1.74 (s, 3 H), 1.45 (d, J = 6.9 Hz, 12 H), 1.13 (d, J = 6.9 Hz, 12 H), 0.96 (s, 12 H). ^{13}C NMR (C_6D_6): δ 192.8 (C_α), 187.2 ($N_2\underline{C}Cu$), 146.3, 136.6, 132.9 (br., $\underline{C}$B(pin))130.6, 124.6, 122.7, 81.5, 29.4, 25.6, 25.4, 25.2, 24.0, 15.5. ^{11}B NMR (C_6D_6): δ 30.4.

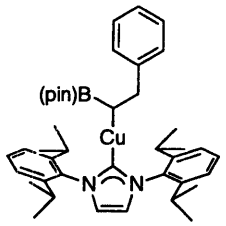


***trans*-Stilbene insertion:** The general procedure was followed, except the reaction mixture was stirred for 15 hrs, to give the title compound (0.351 g, 81%). ^{1}H NMR (C_6D_6): δ 7.51 (d, J = 6.9 Hz, 2 H), 7.21 (t, J = 7.7 Hz, 2 H), 7.06–7.01 (6 H), 6.85 (t, J = 7.4 Hz, 1 H), 6.81 (t, J = 7.2 Hz, 2 H), 6.71 (d, J = 7.2 Hz, 2 H), 6.55 (t, J = 7.2 Hz, 1 H), 6.19 (s, 2 H), 3.54 (d, J = 11.6 Hz, 1 H), 3.12 (d, J = 11.6 Hz, 1 H), 2.57 (m, 4 H), 1.36 (d, J = 6.9 Hz, 6 H), 1.33 (d, J = 6.9 Hz, 6 H), 1.07 (d, J = 6.9 Hz, 12 H), 0.91 (s, 6 H), 0.86 (s, 6 H). ^{13}C NMR (C_6D_6): δ 185.8, 155.2, 147.5, 145.70, 145.68, 135.9, 130.7, 129.8, 128.0, 127.9, 126.4, 124.6, 124.5, 124.1, 122.7, 117.7, 82.3, 37.3, 36.2, 29.31, 29.27, 25.6, 25.3, 25.2, 25.0, 24.2, 24.15. ^{11}B NMR (C_6D_6): δ 34.0.



25 : 1

***cis*-Stilbene insertion:** The general procedure was followed, except 2 equivalents of *cis*-stilbene (0.203 mL, 1.14 mmol) was used and the mixture was stirred for 15 hours, to give a mixture of *syn* and *anti* insertion products (0.330 g, 76%). ^{1}H NMR (C_6D_6): δ 7.36 (d, J = 6.9 Hz, 2 H), 7.24 (t, J = 7.8 Hz, 2 H), 7.07–7.00 (9 H), 6.89 (d, J = 7.2 Hz, 2 H), 6.77 (t, J = 7.1 Hz, 1 H), 6.71 (d, J = 7.2 Hz, 2 H), 6.55 (t, J = 7.2 Hz, 1 H), 6.13 (s, 2 H), 3.30 (d, J = 12.5 Hz, 1 H), 2.82 (d, J = 12.5 Hz, 1 H), 2.40 (sept., J = 6.9 Hz, 2 H), 2.34 (sept., J = 6.9 Hz, 2 H), 1.16 (d, J = 6.9 Hz, 6 H), 1.00–1.05 (18 H), 0.87 (s, 6 H), 0.82 (s, 6 H). ^{13}C NMR (C_6D_6): δ 185.6, 156.8, 148.6, 145.90, 145.8, 135.6, 130.5, 129.2, 128.3, 128.1, 125.7, 124.5, 124.4, 123.9, 122.2, 117.9, 82.5, 43.2, 36.8, 29.2, 29.17, 25.2, 25.1, 25.0, 24.9, 24.2, 23.9. ^{11}B NMR (C_6D_6): δ 34.7.



[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 1-[(pinacol)boro]-2-phenylethyl (2a):

Method A: In a glovebox, a resealable Schlenk flask equipped with a Teflon-coated magnetic stirbar was charged with **1** (0.250 g, 0.356 mmol) and benzene (10 mL). The flask was sealed with a Teflon stopcock, taken out of the glovebox and heated at 70 °C for 24 hours. The flask was allowed to cool and taken into the glovebox, and the reaction mixture was filtered through celite. The solution was then concentrated *in vacuo* and the resulting solid was washed with pentane to afford the title compound as an off-white solid (0.136 g, 54%).

Method B: In a glovebox, a 20-mL scintillation vial equipped with a Teflon-coated magnetic stirbar was charged with (IPr)CuO*t*-Bu (0.300 g, 0.571 mmol) and pentane (5 mL). Triethoxysilane was added (0.116 mL, 0.628 mmol) and the mixture was stirred for 5 minutes. A solution of *trans*-2-phenylvinyl(pinacol)boronate (0.144 g, 0.628 mmol) in *n*-pentane (3 mL) was then added and the mixture was stirred for 1 hour. The resulting white precipitate was collected by filtration to yield the title complex (0.354 g, 91%). ^{1}H NMR (C_6D_6): δ 7.45 (d, J = 6.9 Hz, 2 H), 7.24–7.18 (4 H), 7.08 (4 H), 7.04 (t, J = 6.1 Hz, 1 H), 6.23 (s, 2 H), 3.38 (dd, J = 14.5 Hz, J = 11.3 Hz, 1 H), 2.80 (dd, J = 14.5 Hz, J = 4.1 Hz, 1 H), 2.59 (sept, J = 6.9 Hz, 4 H), 1.43 (d, J = 6.9 Hz, 6 H), 1.42 (d, J = 6.9 Hz, 6 H), 1.09 (d, J = 6.9 Hz, 12 H), 1.03 (s, 6 H), 0.98 (7 H). The proton on C_α was located by 2D NMR spectroscopy (HSQC) and determined to be accidentally degenerate with a pinacol-CH_3 resonance at 0.98 ppm. ^{13}C NMR (C_6D_6): δ 184.9, 152.2, 146.2,

135.7, 130.8, 128.7, 128.2, 124.6, 124.5, 124.4, 122.5, 80.2, 34.9, 29.3, 29.2, 25.7, 25.5, 25.4, 24.2, 24.1, 18.1. ^{11}B NMR (C_6D_6): δ 33.4.

Thermal Rearrangement of 1 in the presence of *trans*-2-(*p*-tolyl)vinyl(pinacol)boronate: In a glovebox, **1** (0.040 g, 0.0585 mmol) and *trans*-2-(*p*-tolyl)vinyl(pinacol)boronate (0.021 g, 0.0878 mmol) were dissolved in C_6D_6 (0.7 mL) and the solution was added to an NMR tube. The NMR tube was sealed with a Teflon stopcock and heated at 70 °C for 24 hours. The tube was then cooled to room temperature and inserted into the NMR probe. The ^{1}H NMR spectrum indicated that a mixture of **2a** and **2b** had formed.

Reversible β-Hydride Elimination Experiment:

In a glovebox, **2a** (0.040 g, 0.0585 mmol) and *trans*-2-(*p*-tolyl)vinyl(pinacol)boronate (0.020 g, 0.0878 mmol) were dissolved in C_6D_6 (0.7 mL) and the resulting solution was added to an NMR tube. The NMR tube was sealed with a Teflon stopcock and heated at 70 °C for 24 hours. The tube was then cooled to room temperature and inserted into the NMR probe. The ^{1}H NMR spectrum indicated a mixture of **2b** and starting complex **2a**.

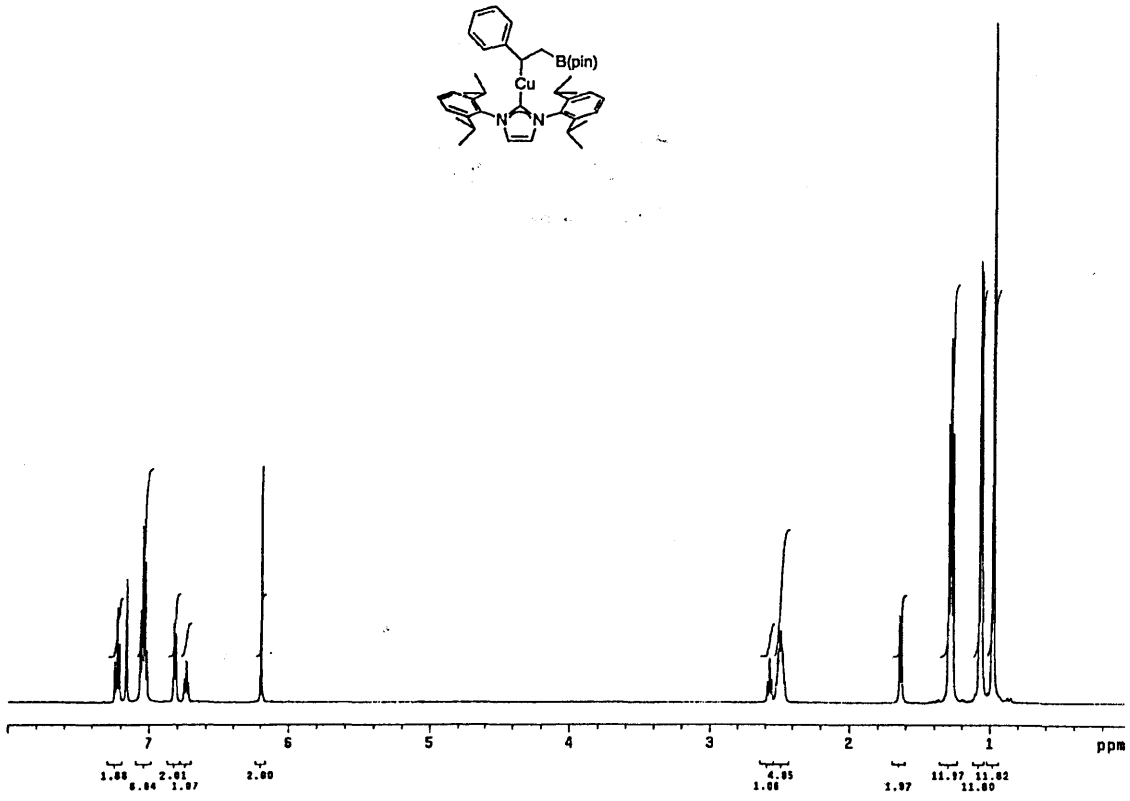
Hammett Substituent Effect Study:

In a glovebox, styrene (0.200 mL, 1.73 mmol) and a 4-substituted styrene (1.73 mmol) were added to a 10 mL volumetric flask. Benzene was added such that the total volume of solution was 10 mL. After homogenization, the solution (0.500 mL, 0.0863 mmol of each olefin) was rapidly added to a benzene solution of (IPr)CuB(pin) (0.025 g, 0.0431 mmol dissolved in 2 mL). After stirring for 10 minutes, the solvent was removed *in vacuo* and the resulting solid was dissolved in C_6D_6 (0.7 mL). The ratios of the insertion products were measured by integration of ^{1}H NMR spectra as follows: For styrene vs 4-fluorostyrene, the β-protons

[(IPr)CuCH(Ar)C$\underline{H}_2$B(pin)] of each complex were compared directly. For the other styrenes, the β-protons of the insertion products overlapped, and the ratios were measured indirectly by integration of the β-protons of both complexes compared with a distinct resonance of the 4-substituted styrene insertion product after simple arithmetic. Specifically, the C$\underline{H}_3$, OC$\underline{H}_3$, N(C$\underline{H}_3$)$_2$ peaks of the 4-substituted styrene insertion products were compared with the β-protons of both complexes.

Note on characterization of alkene insertion products

Attempted elemental analyses of the insertion products did not give satisfactory results, even for samples in which no impurities were evident by ^{1}H or ^{13}C NMR spectroscopy. We attribute this to the very high air-sensitivity of these complexes, and to their perhaps imperfect thermal stability over the timeframe required to send analytical samples. Attempts at melting point determination for the insertion products of styrene, *p*-fluorostyrene, *p*-dimethylaminostyrene, and *trans*-stilbene, as well as for the α-boroalkyl complex **2a**, were unsuccessful: all these complexes rapidly turned orange, then black, in color on heating to temperatures much over 100 °C (the temperatures varied according to sample and heating rate). The following pages display the ^{1}H and ^{13}C NMR spectra of all isolated complexes as a measure of their purity. Based on these spectra, we judge the reported complexes to be over 90% pure. Reasonably extensive efforts to purify them further have proven self-defeating due to the sensitive nature of these products.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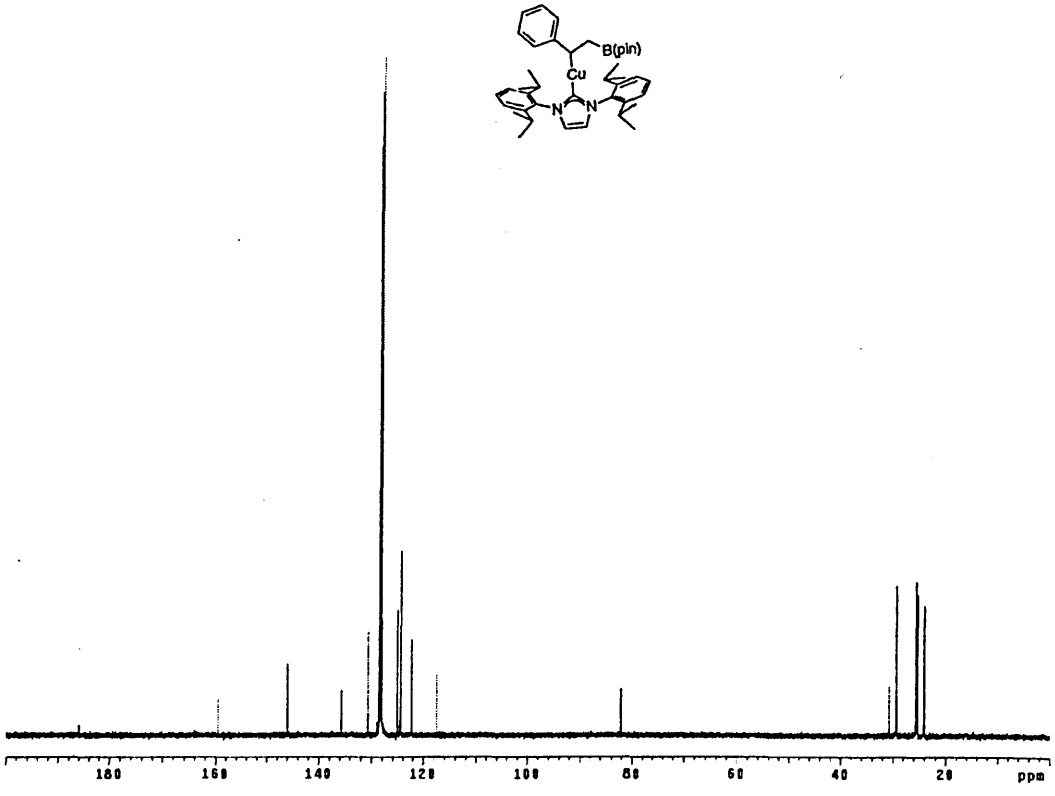
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N
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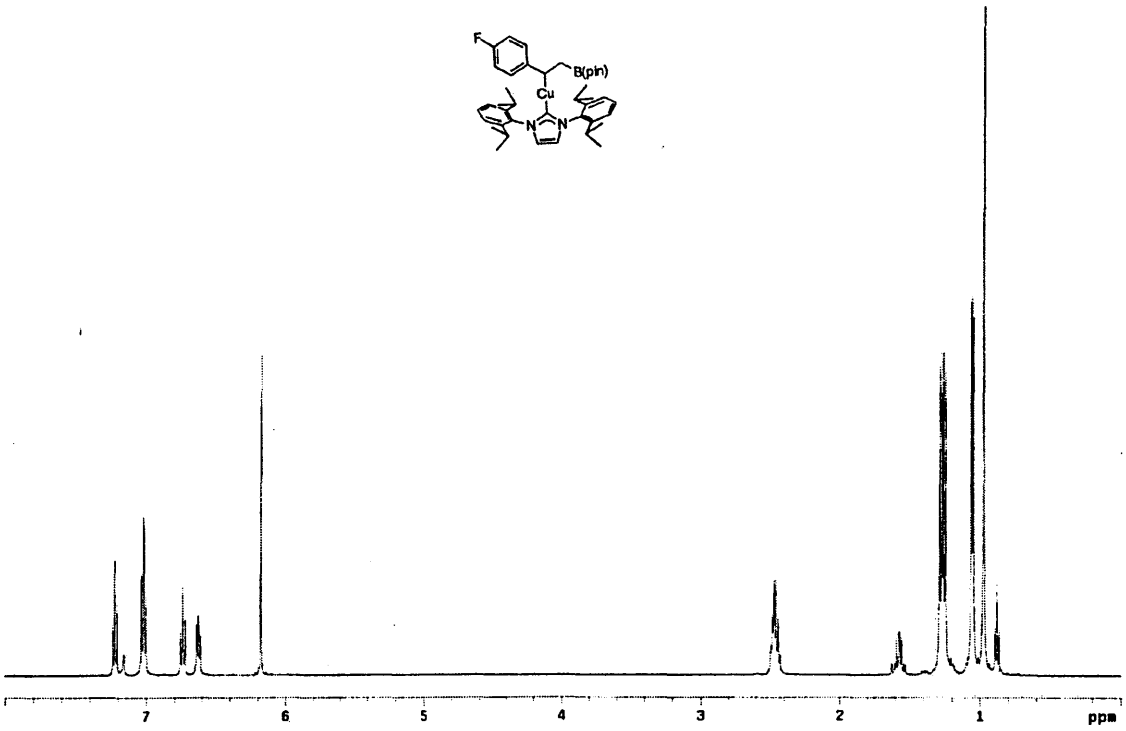
ppm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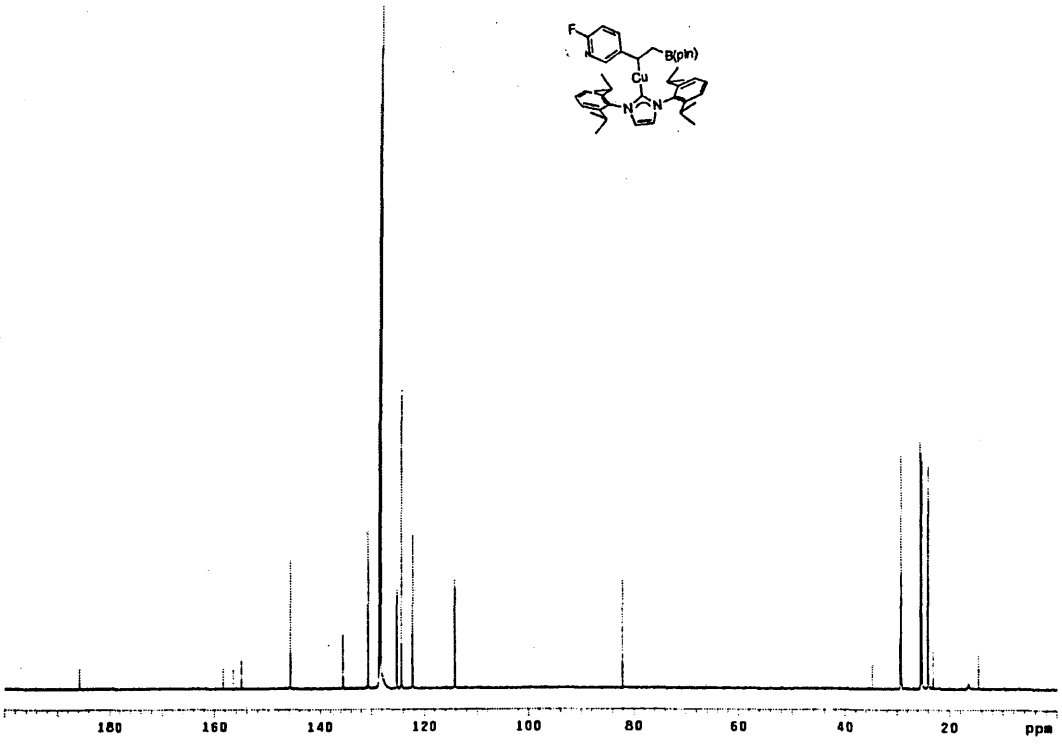
ppm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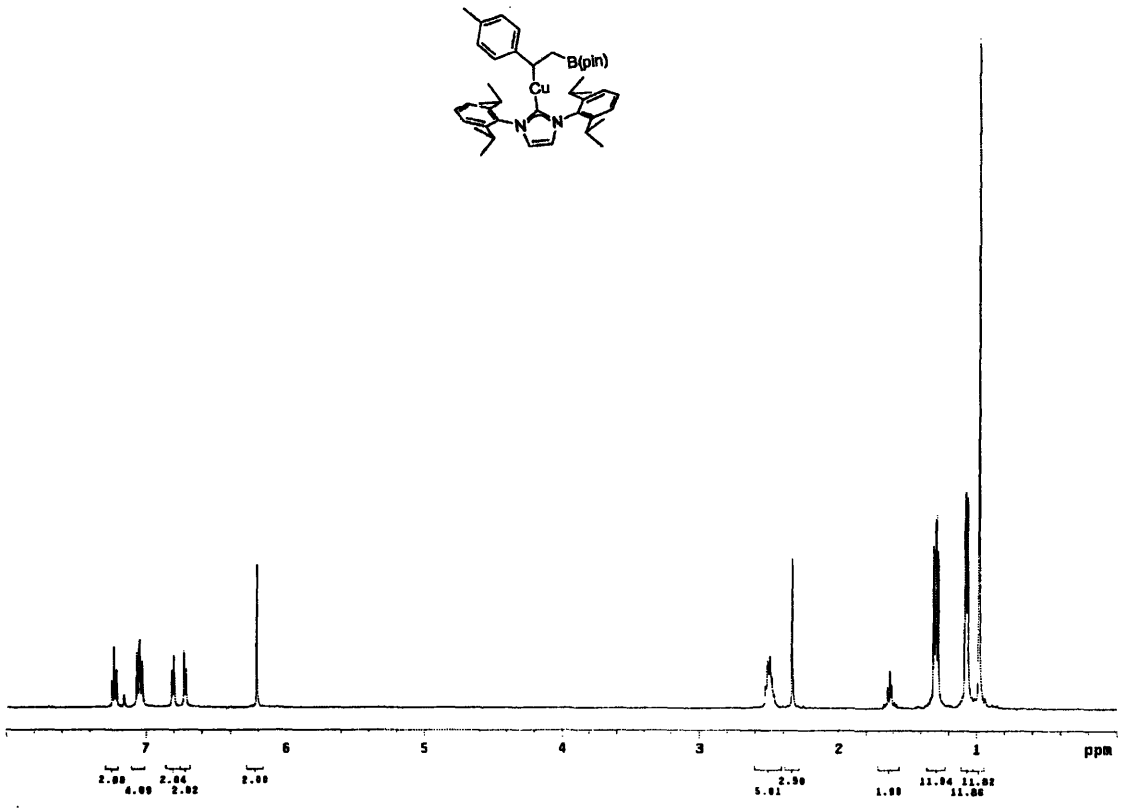
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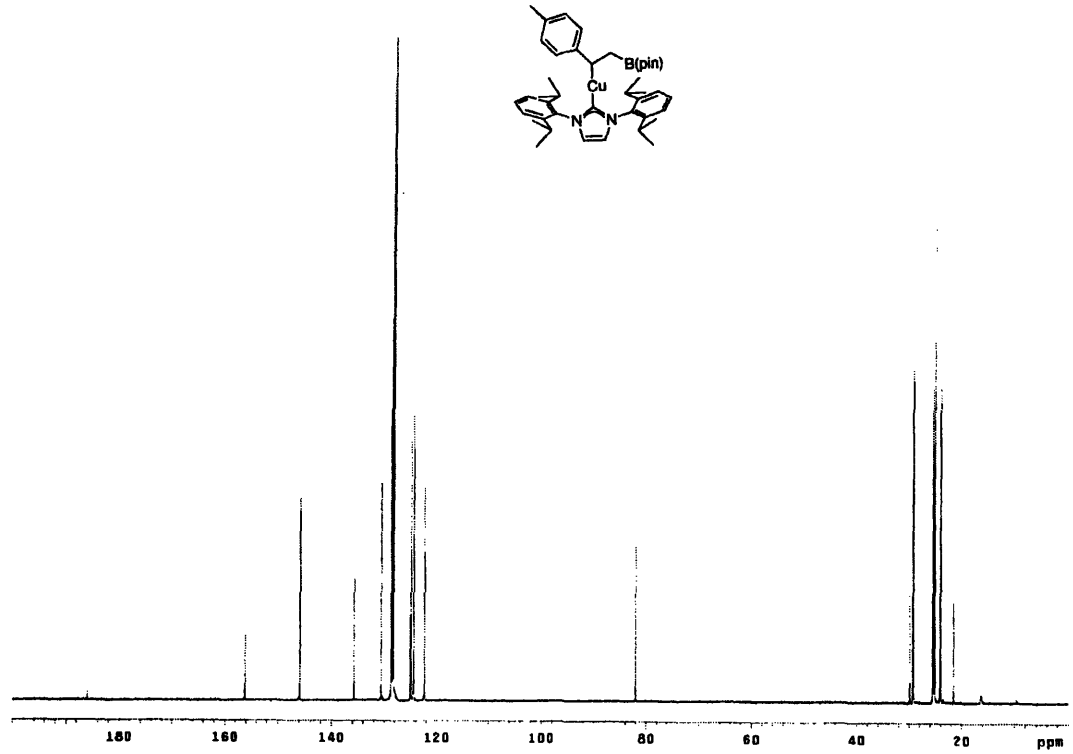
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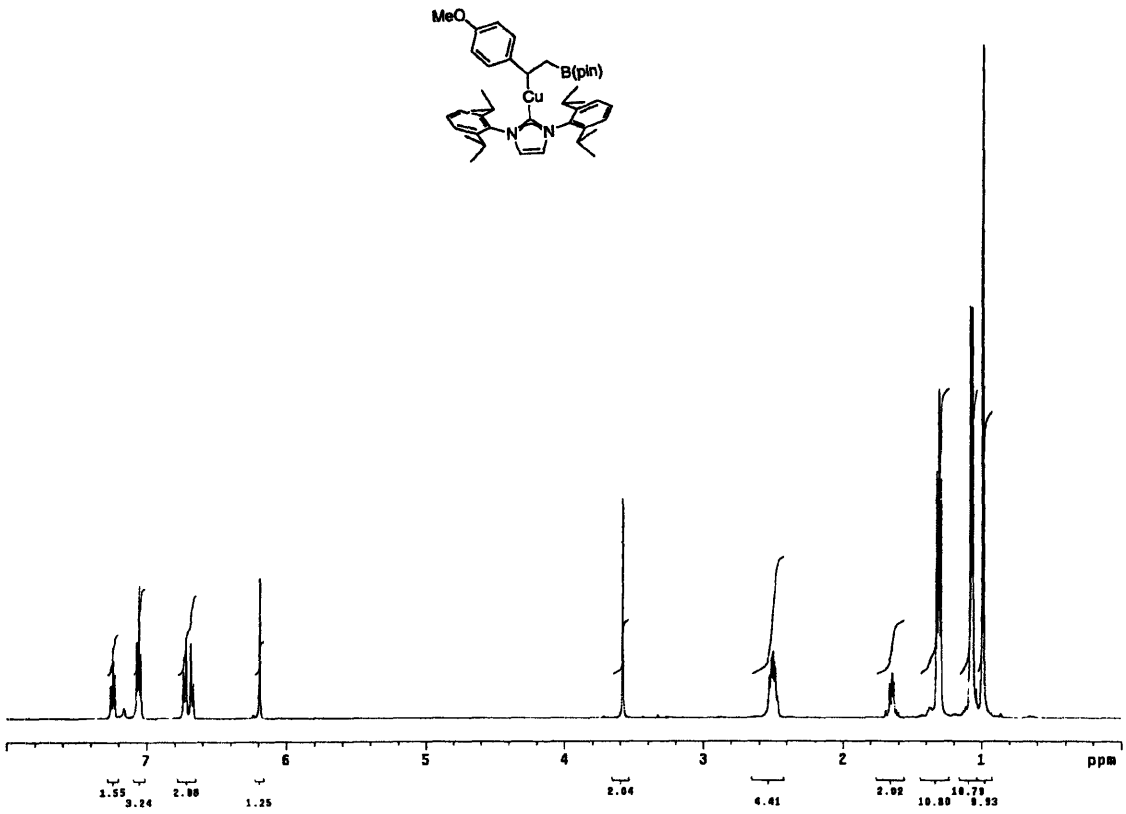
20
ppm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ppm
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6.41
2.02
10.80
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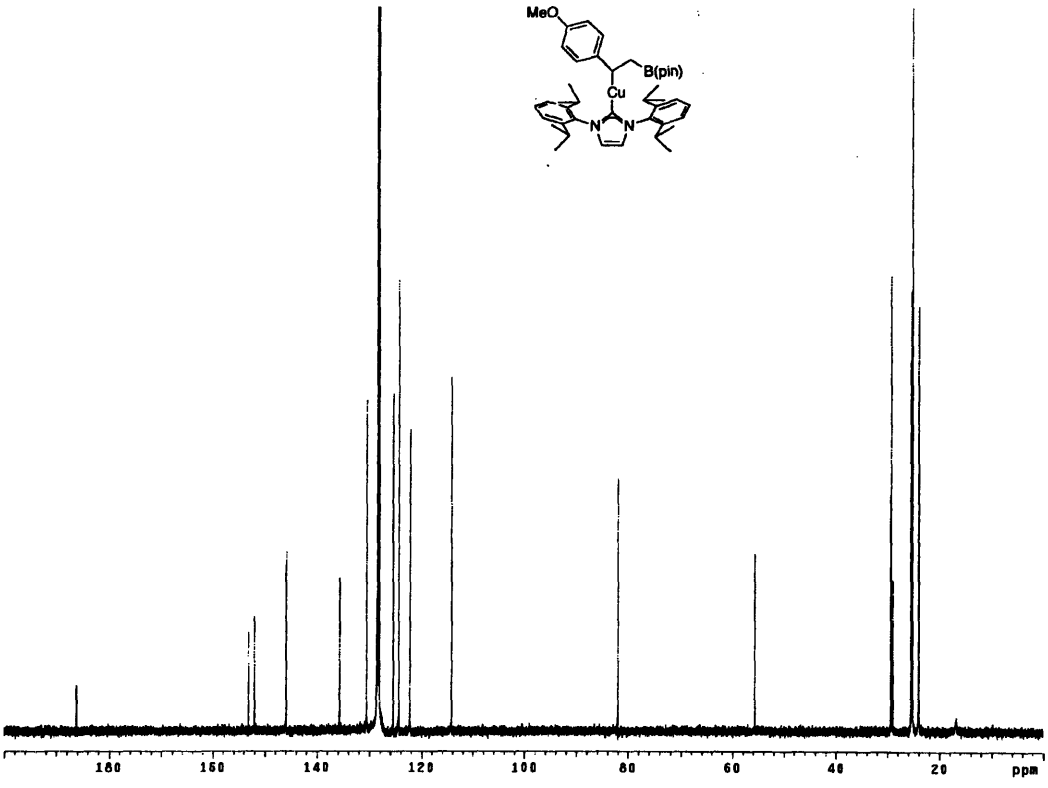
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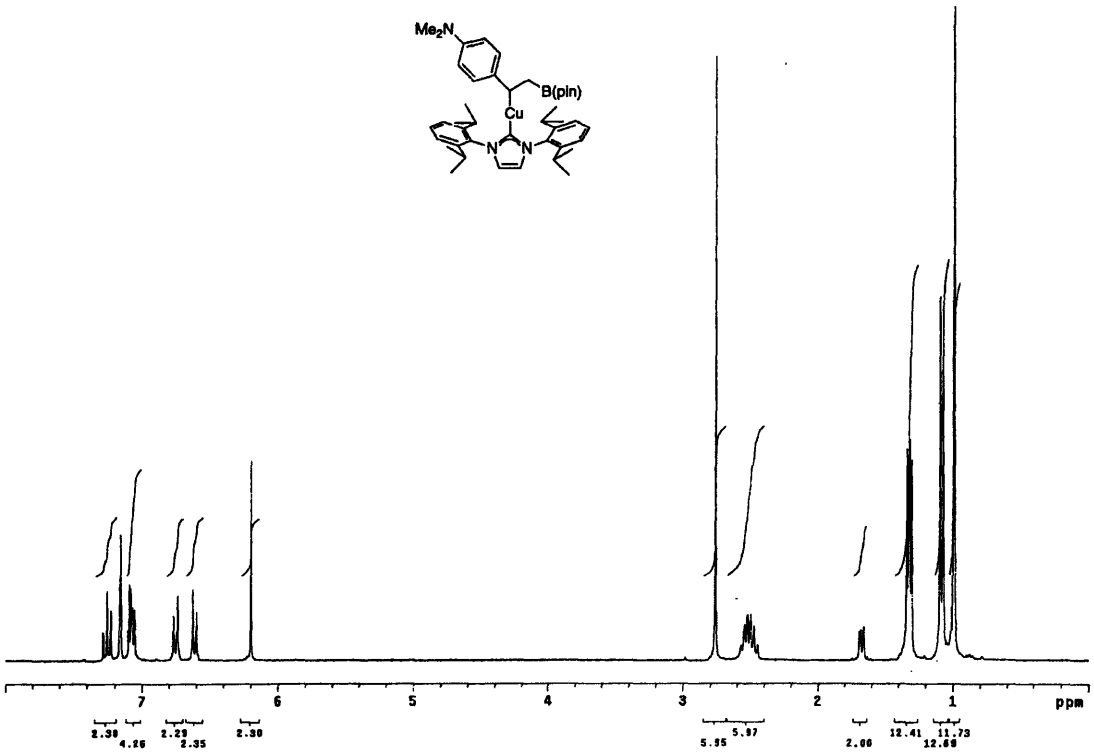
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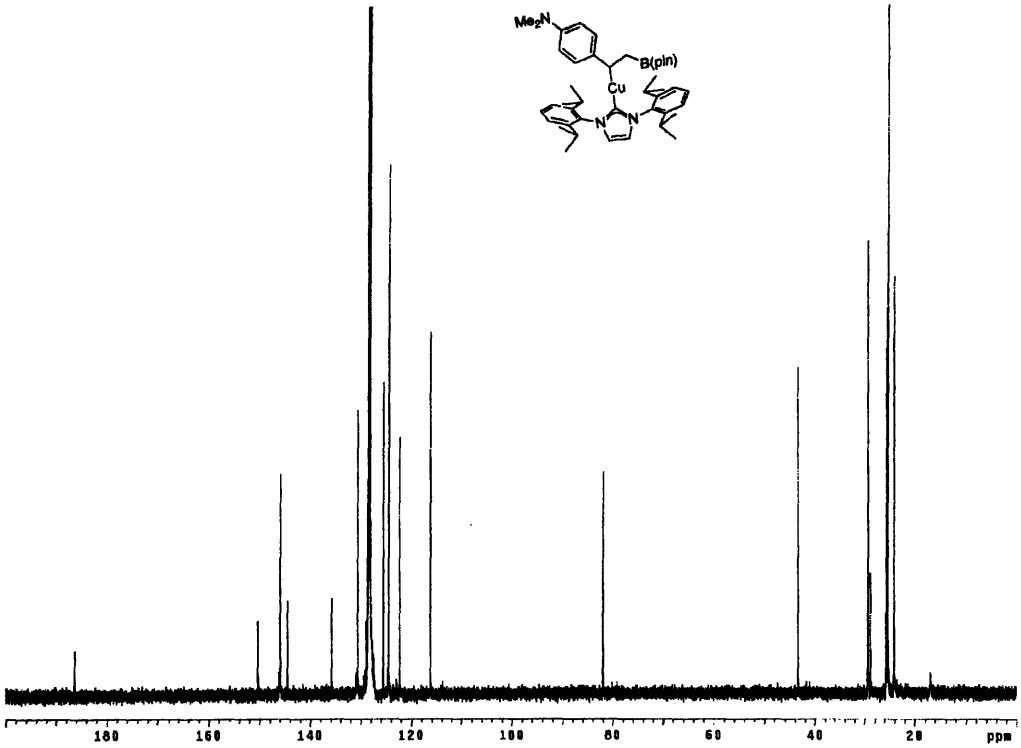
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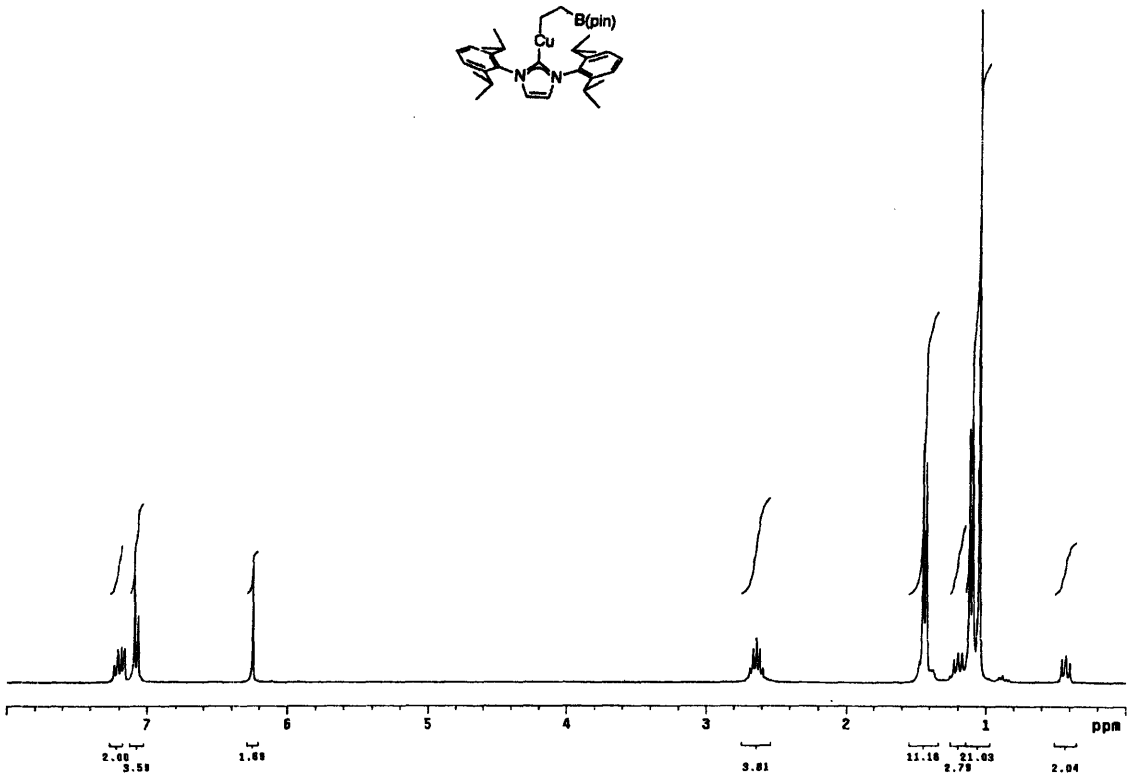
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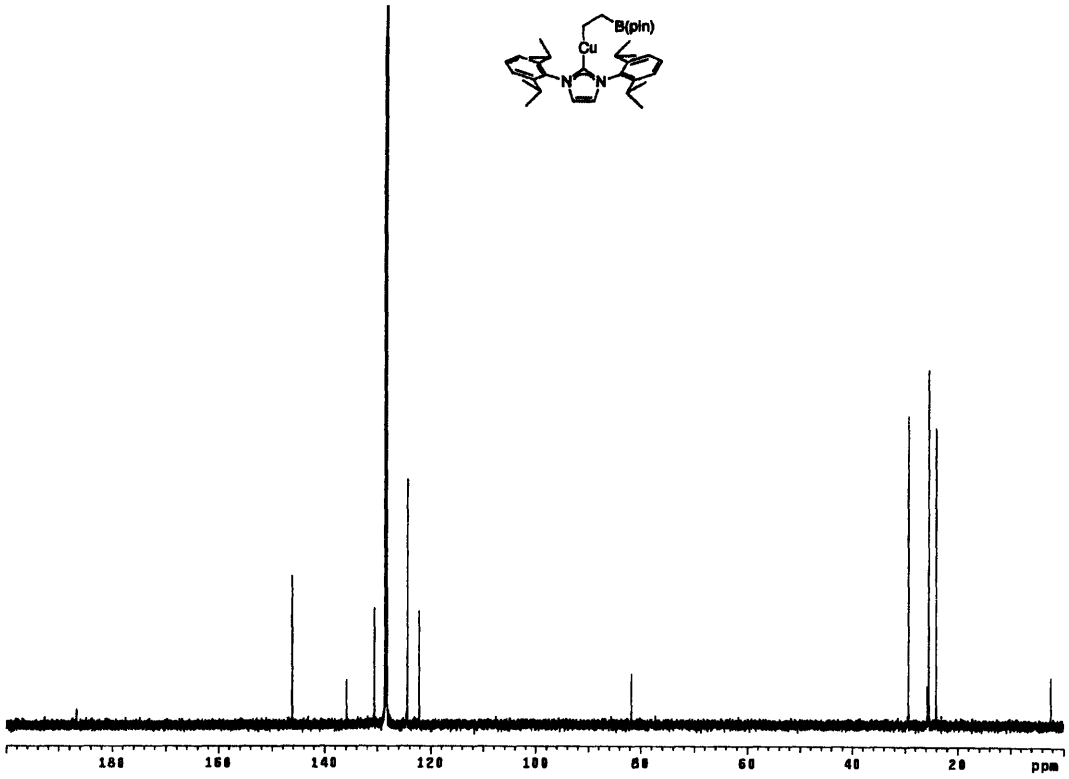
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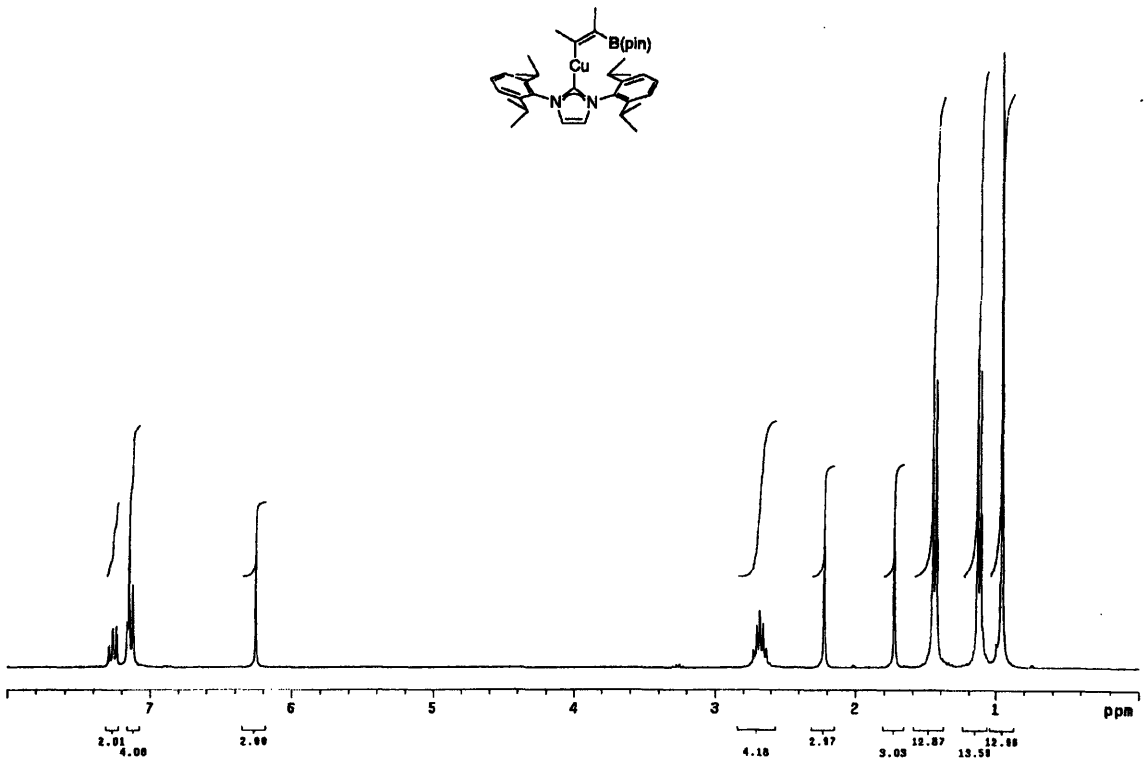
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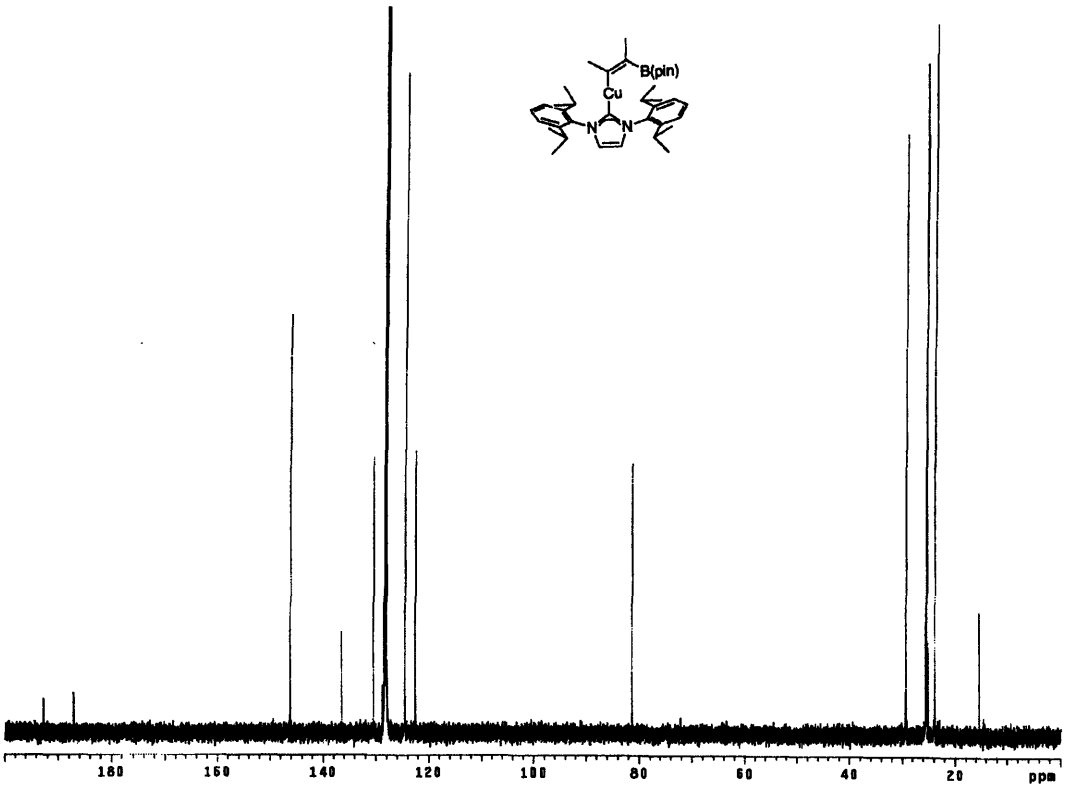
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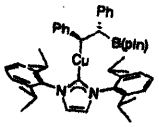

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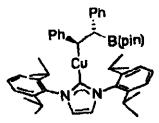

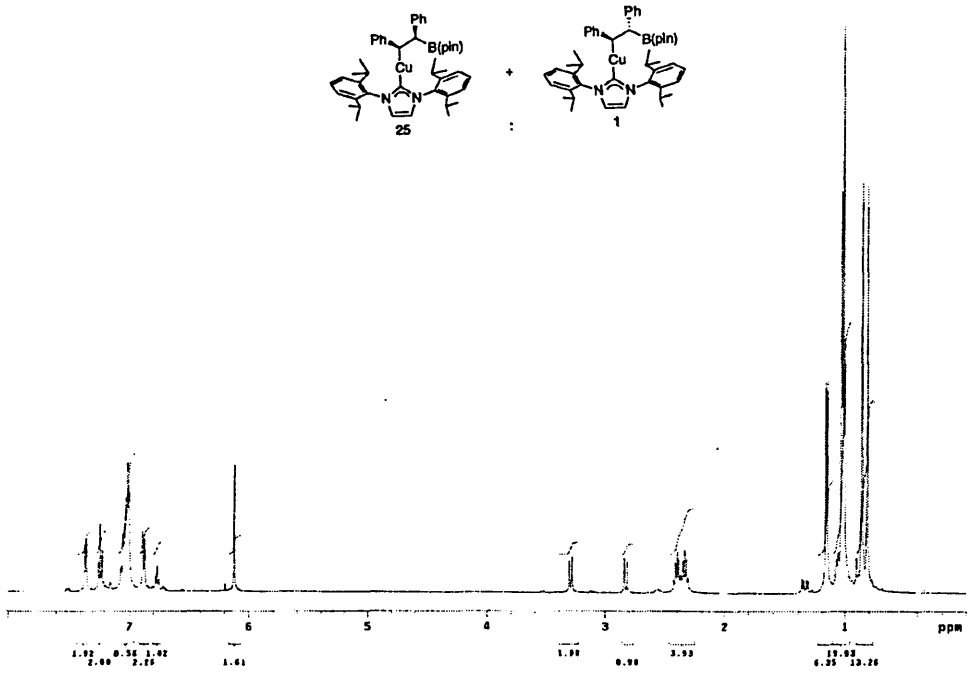
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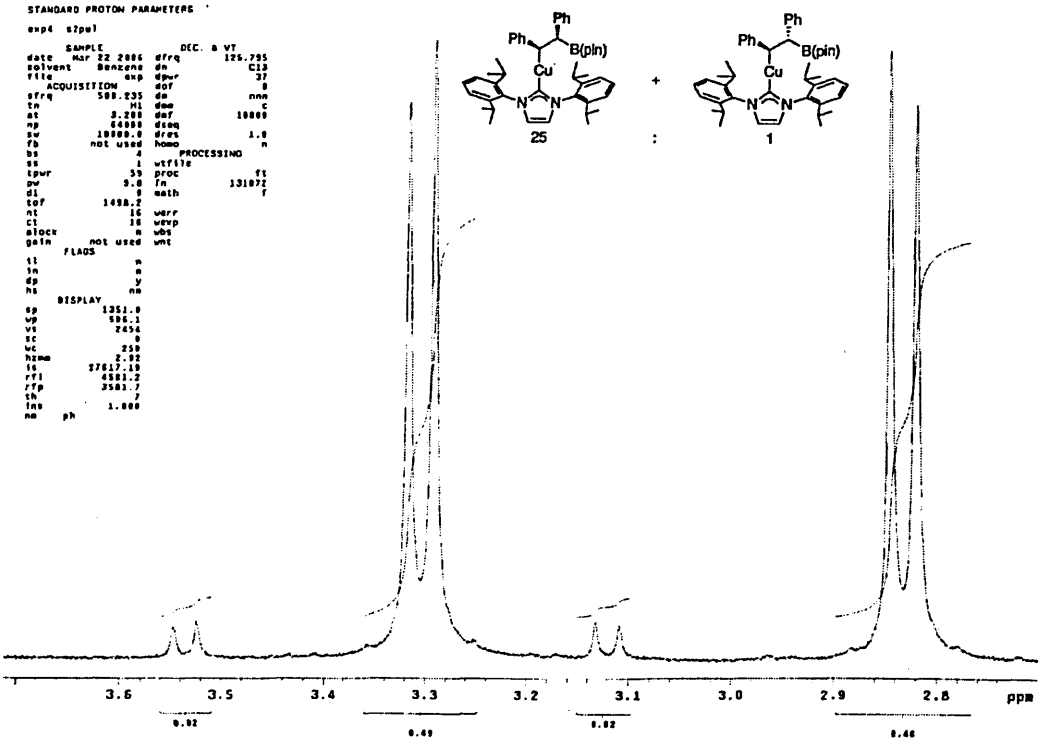
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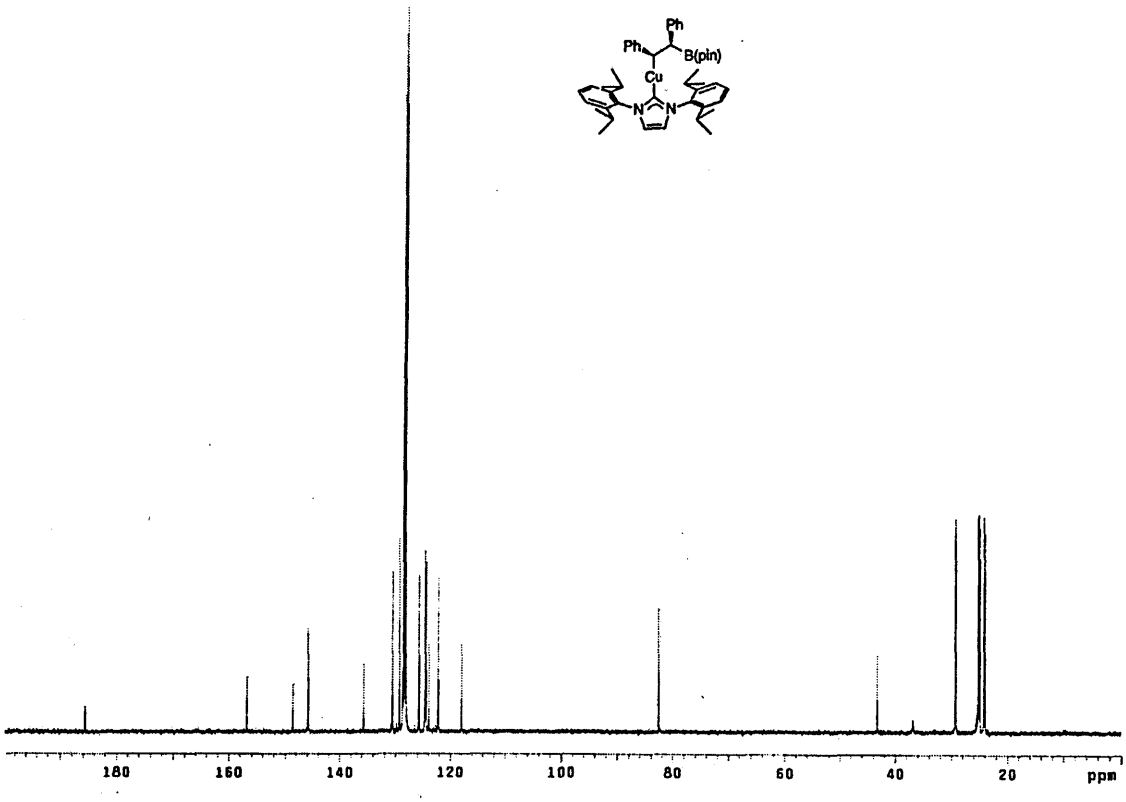
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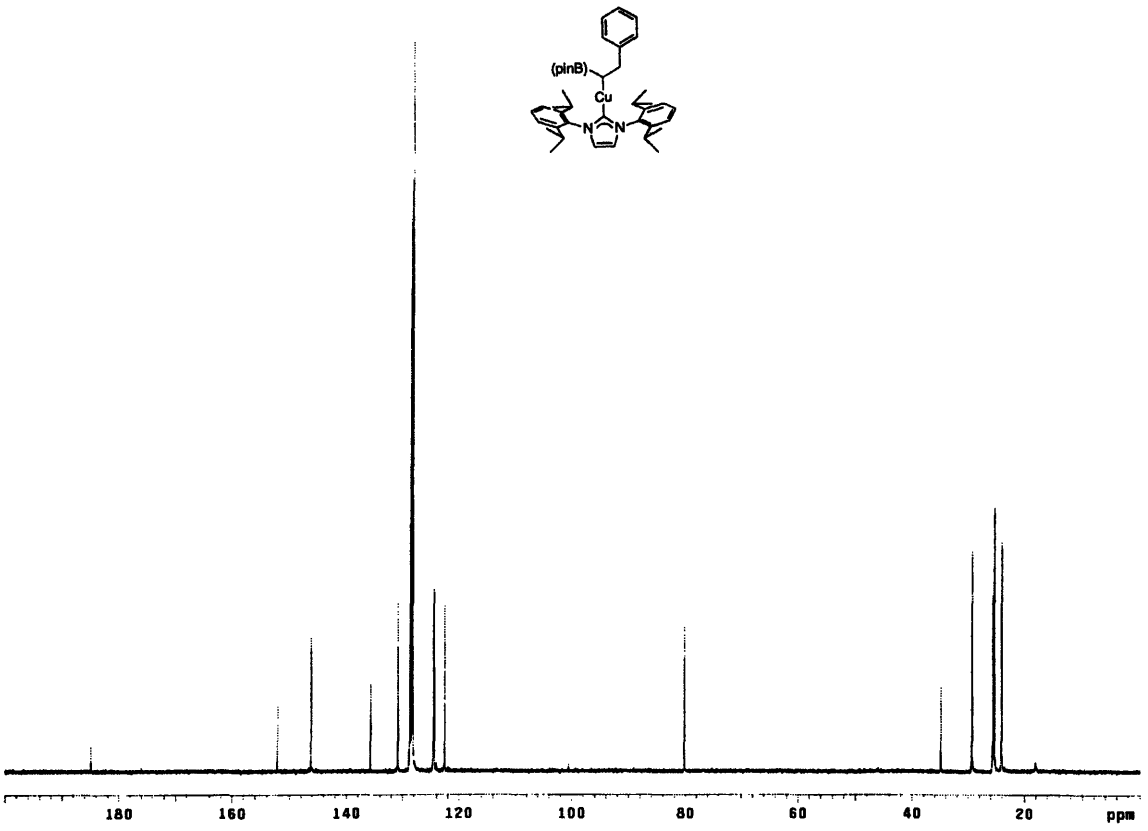
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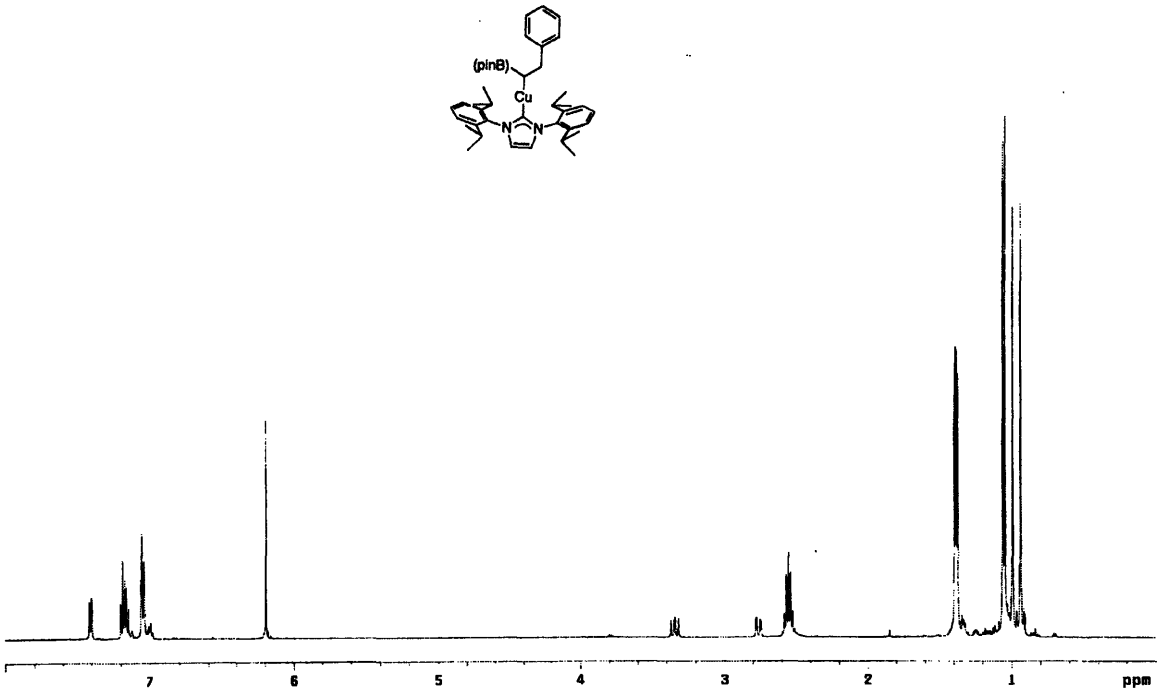
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ppm

Table 2. Crystallographic details for **1** and **2**.

	1	**2**
empirical formula	$C_{43.50}H_{62}BCuN_2O$	$C_{44.50}H_{60}BCuN_2O$
fw	719.30	729.29
T, K	100(2)	100(2)
Crystal syst, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a, Å	11.8285(13)	12.5994(8)
b, Å	9.6981(4)	19.7548(15)
c, Å	21.9595(8)	17.9349(14)
β, deg	106.996(2)	110.025(2)
V, Å^3	4139.8(3)	4688.3(3)
ρ_{calc}, g/cm^{-1}	1.154	1.155
Z	4	4
μ, mm^{-1}	0.563	0.557
F(000)	1548	1564
cryst size, mm^3	0.20 x 0.05 x 0.05	0.21 x 0.10 x 0.10
θ range, deg	1.94 to 25.02	1.94 to 29.57
no. of data/restraints/params	7312/285/544	8592/251/586
Total no. of reflns	46339	75308
GOF on F^2	1.133	1.029
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0657, $wR2$ = 0.1349	$R1$ = 0.0671, $wR2$ = 0.1578
R indices (all data)[a]	$R1$ = 0.0929, $wR2$ = 0.1449	$R1$ = 0.0789, $wR2$ = 0.1672

[a] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

X-ray Diffraction Studies: Experiments were performed on single crystals of **1** and **2** grown by the vapor diffusion of pentanes into a concentrated ether solution (**1**) or pentanes into a toluene solution (**2**) at –40 °C. Colorless crystals were removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. Crystals were affixed to a glass fiber or a cryoloop using the oil, frozen in a nitrogen stream, and optically centered. The data were collected on a Siemens three-circle platform goniometer equipped with a Bruker Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), using both phi and omega scans at –173 °C. The structures were solved by direct methods (SHELXS)[27] and refined against F^2 on all data by full matrix least squares with SHELXL-97 (Sheldrick, G. M.

SHELXL 97; Universität Göttingen: Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) (1-phenyl)-2-(pinacolato)boroethyl (1). An isopropyl group was disordered [C(25), C(27) and C(28)] and refined over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. A pentane molecule located on a special position was also found to be disordered. Symmetry contraints were relaxed, and the molecule was refined over two positions with the restraints mentioned above. The relative occupancies for the disordered parts were refined freely, while constraining the overall occupation to unity.

[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) 1-[(pinacol)boro]-2-phenylethyl (2). Two methyl groups of the (pinacol)boronate were disordered [C(37), and C(38)] and were refined over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. A toluene molecule located on a special position was also disordered. Symmetry constraints were relaxed, and the molecule was refined over two positions with the restraints mentioned above. The relative occupancies for the disordered parts were refined freely, while constraining the overall occupation to unity. One peak of significant residual electron density (3.20 e/Å^3) remained upon final refinement which was less than 1 Å away from copper. This peak corresponds to a disorder involving Cu(1) and a different orientation of the boroalkyl group. The disorder represents less than 10% of the occupancy for those atoms, and attempts to

include it in the model were unsuccessful yielding mathematically unstable refinements even with strong restraints.

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(1) See for example: (a) *Organoboranes for Synthesis*; Ramachandran, P. V., Brown, H. C., Eds.; ACS Symposium Series 783; American Chemical Society: Washington, DC 2001. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

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(15) For related studies on migratory insertion reactions of *p*-substituted styrenes, see for example: (a) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53–L54; (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670–2682; (c) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134–3146; (d) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436–2448.

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(18) The dominant importance of metal-to-alkene electron-donation has been demonstrated both for the binding of substituted styrenes by a d^{10} Pd(0) center, and for the associative substitution of Pd(0)-bound styrenes: Popp, B. V.; Thorman, J. L.; Morales, C. M.; Landis, C. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 14832–14842.

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Appendix

Copper(I) Complexes of Heavily Fluorinated β-Diketiminate Ligands: Synthesis, Electronic Properties, and Reactivity

Parts of this appendix have been adapted from:

Laitar, D. S.; Mathison, C. J. N.; Davis, W. M.; Sadighi, J. P. "Copper(I) Complexes of a Heavily Fluorinated β-Diketiminate Ligand: Synthesis, Electronic Properties and Intramolecular Aerobic Hydroxylation." *Inorg. Chem.* **2003**, *42*, 7354–7356.

The aerobic oxidation of organic substrates represents an ongoing goal in synthetic catalysis.[1] Copper(I) complexes have been shown to react with dioxygen to form strong oxidants, typically dimeric copper(II)-copper(II) peroxide or copper(III)-copper(III)-bis-μ-oxo complexes.[2,3] These high-valent products, some of them capable of C–H bond hydroxylation,[3] are interesting reagents for the oxidation of organic substrates and have potential as intermediates in catalytic cycles. Recently, the reactivity of copper(I) β-diketiminate complexes with dioxygen has been studied in detail.[4]

Copper catalysts have also been used for a variety C–N bond forming reactions including olefin aziridination[5] and C–H bond amination.[6] Copper(III) imido complexes have been proposed as intermediates in these reactions; however definitive spectroscopic detection is lacking.[5a,7] Since the isolation of a d^8 terminal imido complex by Hillhouse and Mindiola,[8c] the synthesis of other late transition metal imido complexes has been intensively pursued,[8] and sterically bulky β-diketiminate ligands have been used to stabilize such complexes.[8h,i] Although discrete complexes resulting directly from the reaction of (β-diketiminate)copper(I) complexes with nitrene sources have not been characterized, Warren and coworkers have shown that (β-diketiminate)copper complexes are competent aziridination catalysts using the imidoiodinane PhI=NTs (Ts = *p*-toluenesulfonyl) as the nitrene source.[5d] We felt that a β-diketimine ligand with sufficient steric bulk and protection against oxidative degredation degradation might permit the observation or even isolation of a copper(III) terminal imido complex.

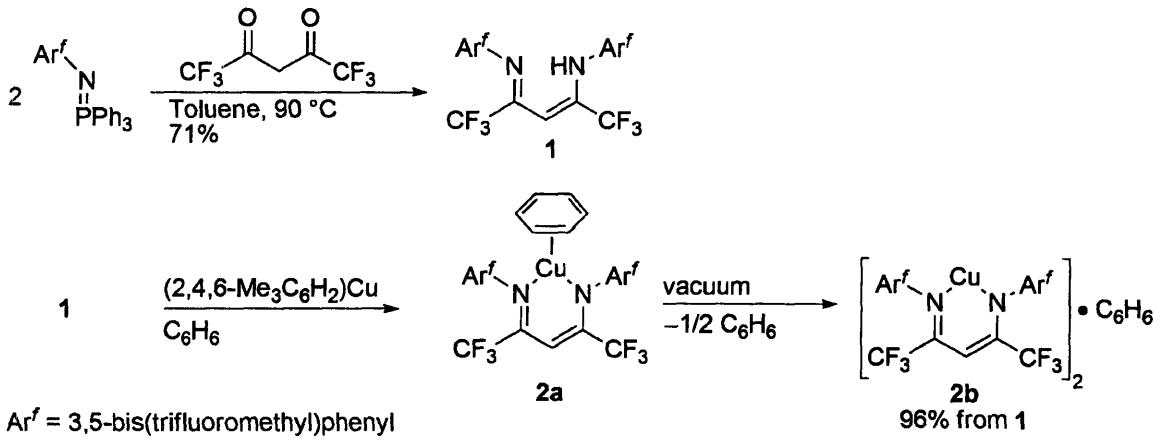
This Appendix describes the preparation of a series of fluorinated β-diketiminate ligands,[9] by a convenient aza-Wittig reaction,[10] and the synthesis of several copper(I) complexes from them is described. These ligands are quite electron-poor, as judged by an infrared study of several related (β-diketiminate)copper(I) carbonyl complexes. Nonetheless, the copper(I) β-

diketiminate complexes reacted readily with dioxygen, resulting either in formation of dinuclear bis-μ-hydroxide complexes or in clean *ortho*-hydroxylation of a ligand *N*-aryl group depending on the *N*-substituent.[11] The reactivity of copper(I) β-diketiminate complexes toward aryl azides was also explored and an imido-bridged dicopper(II) complex was isolated and structurally characterized.

Synthesis and aerobic oxidation of copper(I) β-diketiminate complexes

Ligand **1** was synthesized in good yield by the aza-Wittig reaction of 2 equivalents of [3,5-bis(trifluoromethyl)phenylimino]triphenylphosphorane with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione in toluene at 90 °C. We have been unable to prepare this ligand by traditional routes.[12] Reaction of **1** with mesitylcopper(I) in benzene solution produced benzene adduct **2a** in high yield. The coordinated benzene is labile, and concentration *in vacuo* converts **2a** to the dinuclear benzene adduct **2b** (Scheme 1). Crystals suitable for X-ray crystallography were grown by slow cooling of a hot hexane/benzene solution of **2a** (Figure 1). The X-ray structure shows **2a** to be a monomeric η^2-benzene adduct. The benzene ring remains essentially planar, and the C(22)–C(23) bond length [1.385(6) Å] is equivalent within error to that of free benzene (1.39 Å),[13] indicating little π-back-bonding from copper.[14] Other benzene complexes of copper(I) with poorly donating anions have been structurally characterized;[15] to our knowledge, this is the first such adduct supported by a β-diketiminate ligand. We have found analogs without the backbone CF_3 groups to be unstable and have been unable to isolate them.

Scheme 1. Synthesis of **1** and its copper(I) complexes.



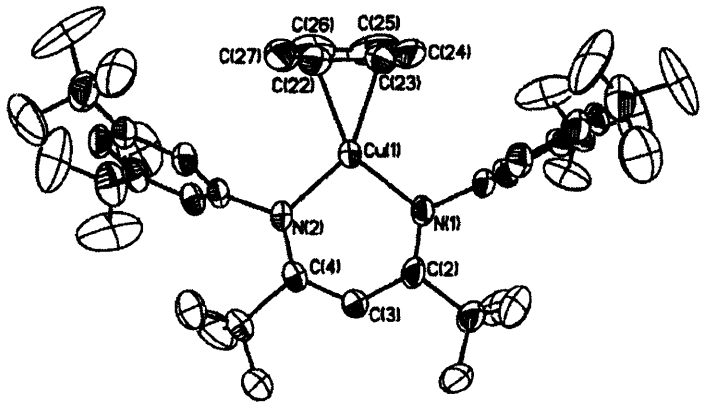


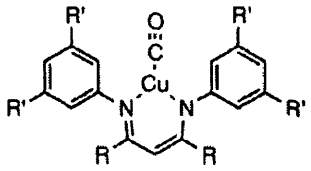
Figure 1. Representation of **2a**, shown as 50% ellipsoids. For clarity, all hydrogen atoms, and disorder were omitted. Selected bond distances (Å) and angles (deg): Cu(1)–C(22) 2.117(4), Cu(1)–C(23) 2.102(4), C(22)–C(23) 1.385(6); N(1)–Cu(1)–N(2) 99.62(12), C(22)–Cu(1)–C(23) 38.35(17), Cu(1)–C(22)–C(27) 108.1(3), Cu(1)–C(23)–C(24) 106.1(3).

To assess the electron-withdrawing nature of ligand **1**, less fluorinated analogs **4**–**6** were synthesized, and the carbonyl stretching frequency, ν_{CO}, of the copper carbonyl complexes derived from them were measured (Table 1).[16] The all-methyl analog of **1** gives rise to the

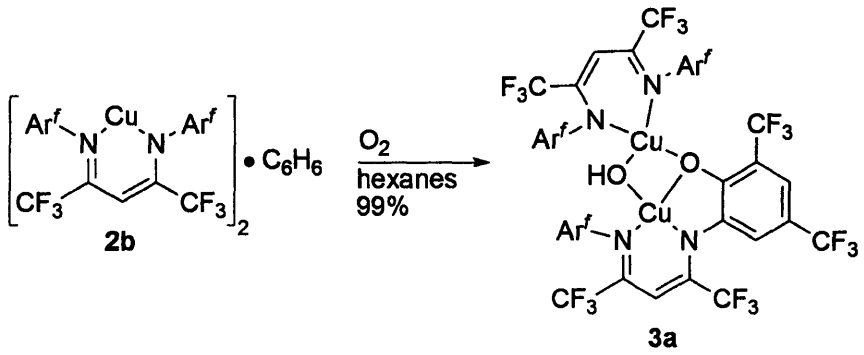
lowest carbonyl stretching frequency, resulting from the most electron-rich metal center, as expected. Two CF_3 groups at the ligand backbone exert a larger electron-withdrawing effect than four at the *meta* positions of the *N*-aryl groups: ν_{CO} increases by 24 versus 17 cm^{-1}. Replacement of all methyl groups with CF_3 groups results in an increase in ν_{CO} of 37 cm^{-1}, a substantial effect given the modest metal-to-ligand backbonding from Cu(I).[17]

Table 1. ν_{CO} for Inter-Related (β-Diketiminate)Cu(CO) Complexes.

Ligand	R	R'	ν_{CO} (cm^{-1})
1	CF_3	CF_3	2110
4	CF_3	CH_3	2097
5	CH_3	CF_3	2090
6	CH_3	CH_3	2073



Scheme 2. Aerobic oxidation of **2b**.



Despite the electron-poor nature of ligand **1**, the copper(I) complex **2b** reacts readily with dioxygen (Scheme 2). Exposure of a hexane solution of **2b** to dry air led to the rapid formation of a brown precipitate; the oxidation proceeded in near-quantitative yield after 30 minutes at room temperature. The ^1H and ^{19}F NMR spectra of the product indicated the formation of an asymmetric, paramagnetic species, **3a**. Single crystals of the oxidation product, were grown by slow diffusion of hexane into a saturated solution of **3a** in C_6F_6. The ^1H and ^{19}F NMR, IR, and UV-vis spectra obtained from the crystals match those of the bulk material. Analysis of a single crystal by X-ray diffraction revealed a dinuclear structure for **3a**, in which one of the ligand *N*-

aryl groups had been hydroxylated to give a bridging phenolate (Figure 2). The hydroxyl hydrogen atom was detected on the Fourier difference map in the X-ray study, and its presence was further corroborated by the stretch at 3671 cm^{-1} in the IR spectrum of **3a**, consistent with other known μ-hydroxocopper complexes.[4a] The structure displays considerable tetragonal distortion at the copper centers; the dihedral angle between the two (β-diketiminate)copper planes is 53.68°.

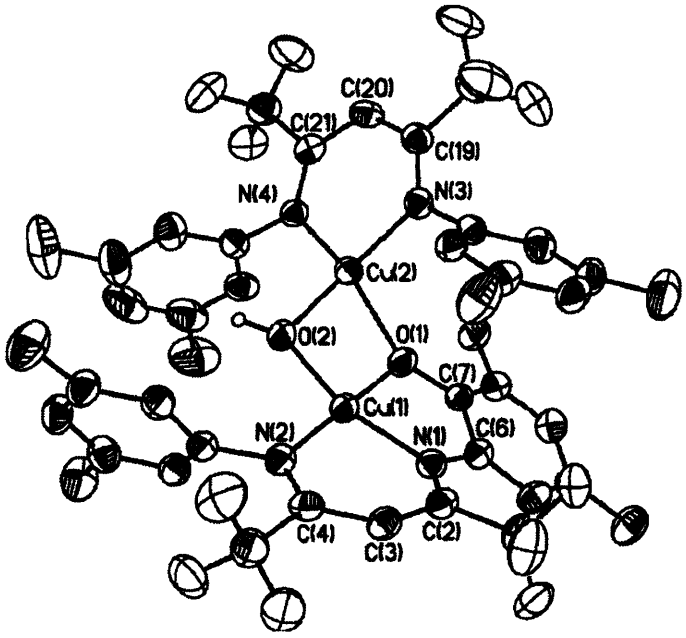
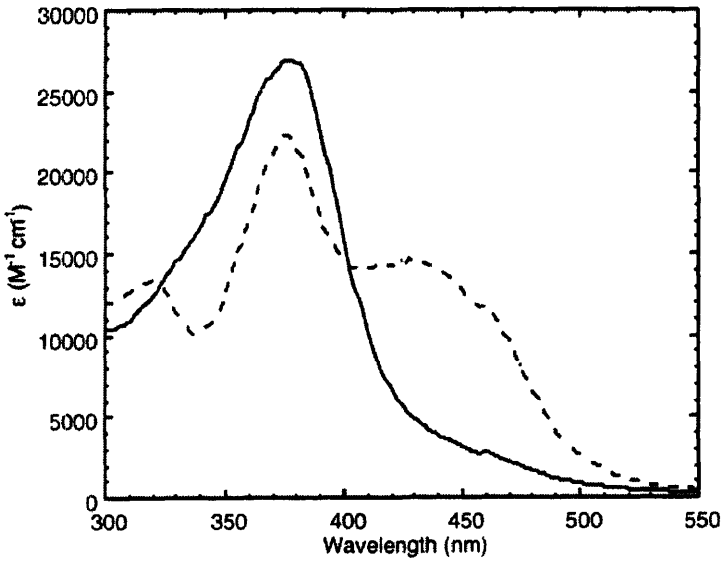


Figure 2. Representation of **3a•(0.5C_6F_6)**, shown as 50% ellipsoids. For clarity, the following were omitted: the fluorine atoms of all aryl CF_3 groups, all hydrogen atoms except for the hydroxyl proton, and solvent. Selected interatomic distances (Å) and angles (deg): Cu(1)–Cu(2) 2.9345(12), Cu(1)–O(1) 1.935(3), Cu(2)–O(1) 2.028(3), Cu(1)–O(2) 1.908(3), Cu(2)–O(2) 1.911(3), O(1)–C(7) 1.325(4); N(1)–Cu(1)–N(2) 97.05(12), N(3)–Cu(2)–N(4) 97.31(13), O(1)–Cu(1)–O(2) 78.92(11), O(1)–Cu(2)–O(2) 76.57(10), Cu(1)–O(1)–Cu(2) 95.51(11), Cu(1)–O(2)–Cu(2) 100.41(12).

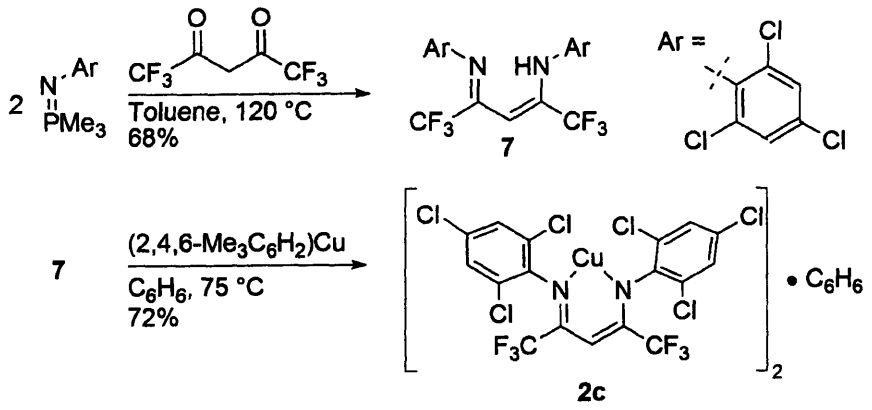
The UV-Vis spectra of starting material **2b** and oxidation product **3a** in dichloromethane solution are shown in Figure 3. The starting material spectrum shows a single absorption at 379 nm (ε = 26900 M^{-1} cm^{-1}). The spectrum of dinuclear Cu(II,II) complex **3a** displays an absorption maximum at 376 nm (ε = 22300 M^{-1} cm^{-1}), with new bands at 320 nm (ε = 13300 M^{-1} cm^{-1}) and at 430 nm (ε = 14700 M^{-1} cm^{-1}). This pattern is reminiscent of that observed upon oxygenation of other copper(I) β-diketiminates,[4c] even though the oxidation state obtained in this case is different. The magnetic susceptibility of **3a** was measured for a powder sample using a SQUID magnetometer. The effective magnetic moment, μ_{eff}, at ambient temperature and a field strength of 0.5 T, is 1.93 μ_B; the magnetic behavior is consistent with weak antiferromagnetic coupling between the two copper(II) centers. For comparison, the square planar bis[(β-diketiminate)copper(II) μ-hydroxide] reported by Dai and Warren has a smaller effective magnetic moment, 1.39μ_B.[4a] Intramolecular aerobic hydroxylation of an aryl group is well-precedented;[2b,3a,b] in this case, the aryl group was cleanly and rapidly oxidized despite the presence of two electronically deactivating CF_3 groups. Reaction of other (β-diketiminate)copper(I) species with O_2 generally gives rise to dimeric Cu(III) μ-oxo complexes, or to monomeric Cu(III) η^2-peroxo complexes, depending on the ligand;[4] the oxidizing intermediate in the formation of **3a** has not yet been identified. Aerobic oxidation of the β-diketiminate ligand backbone, which has been reported for Cu(II) and Zn(II) complexes,[20] was not observed in the oxidation of **2b**.

Figure 3. UV-vis spectra of **2b** (s) and **3a** (- - -) in CH_2Cl_2.



In the hope of suppressing the ligand hydroxylation observed in the aerobic oxidation of **2a**, we modified the ligand to incorporate *N*-aryl groups with oxidation-resistant *ortho*-substituents (Scheme 3). An *N*-(2,4,6-trichlorophenyl)-substituted *β*-diketimine ligand, **7**, was synthesized analogously to **1**. The reaction between *N*-(2,4,6-trichlorophenyl)iminotriphenylphosphorane and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was very slow, and the smaller *N*-(2,4,6-trichlorophenyl)iminotrimethylphosphorane was used instead to give **7** in 68% yield. Ligand **7** was cleanly metallated with mesitylcopper(I) in benzene solution to form the corresponding (*β*-diketiminate)copper (I) benzene adduct **2c**. The υ_{CO} measured for [**7**•Cu(CO)] was very similar to that of [**1**•Cu(CO)] (2111 cm^{-1} versus 2110 cm^{-1}), reflecting the electron-withdrawing ability of the trichlorophenyl group.

Scheme 3. Synthesis and metallation of β-diketimine ligand **7**.



Complex **2c** rapidly reacts rapidly with dioxygen in a variety of solvents at room temperature and always formed a mixture of products. From the reaction mixture, the bis-(β-diketiminate)dicopper(II) complex **3b** was isolated and the solid-state structure is shown in Figure 5. The Cu–Cu and Cu–O bond distances, 3.0367(12) and 1.930(2) Å, of **3b** are similar to those of other bis[(β-diketiminate)copper(II) μ-hydroxide] complexes.[4a,c] The hydroxyl hydrogen atoms were detected on the Fourier difference map, which strongly supports assignment of **3b** as a Cu(II)-Cu(II) bis-μ-hydroxide dimer rather than a Cu(III)-Cu(III) bis-μ-oxo complex. The source of the hydrogen atoms is currently unknown. Organic oxidation products were not detected by either ^{1}H NMR spectroscopy or gas chromatography, even when the aerobic oxidation of **2c** was run in the presence of substrates such as benzene, diphenylmethane, toluene, anisole or styrene.

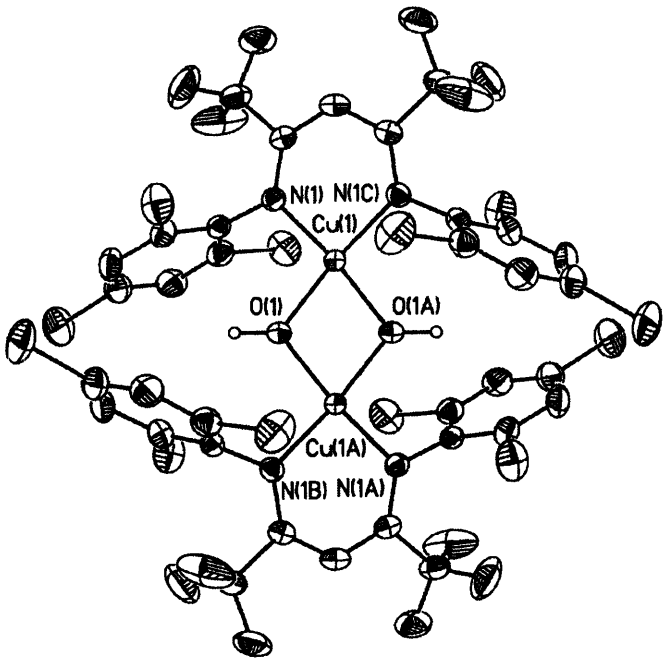
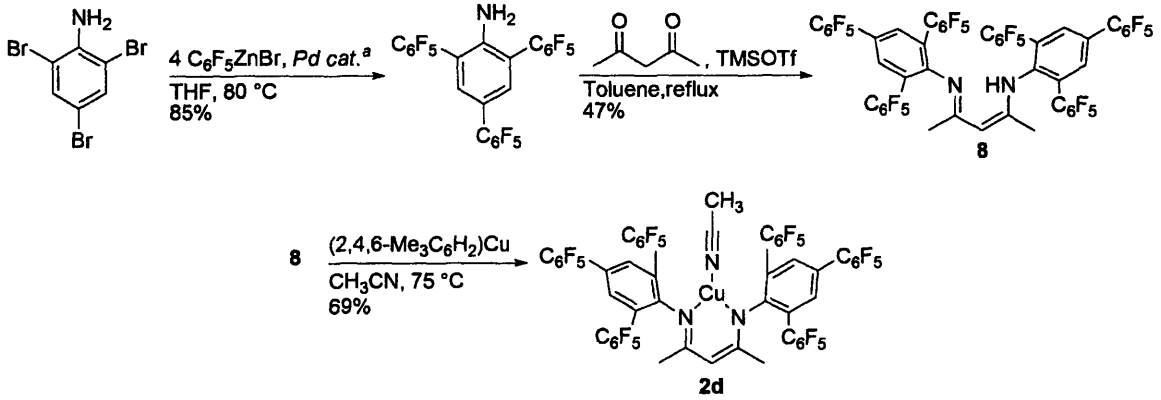


Figure 5. Representation of **3b**•(C_7H_8), shown as 50% ellipsoids. For clarity, all hydrogen atoms except for the hydroxyl proton and solvent have been omitted. Selected interatomic distances (Å) and angles (deg): Cu(1)–Cu(1A) 3.0367(12), Cu(1)–O(1) 1.930(2), N(1)–Cu(1)–N(1C) 94.30(17), O(1)–Cu(1)–O(1A) 76.25(18), Cu(1)–O(1)–Cu(1A) 103.74(18).

In search of more sterically demanding ligands, we undertook the preparation of the previously unknown 2,4,6-tris(pentafluorophenyl)aniline through Pd-catalyzed cross-coupling. Using a catalyst system developed by Buchwald and coworkers,[19] we found that 2,4,6-tribromoaniline reacts with excess pentafluorophenylzinc bromide[20] in high yield, with no protection of the amino group necessary (Scheme 4). Unfortunately, the iminophosphorane derived from this aniline did not react productively with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione under conditions similar to those used for the synthesis of ligand **7** and ligands derived from this dione remain elusive. However, condensation of this aniline with 2,4-pentanedione afforded *β*-diketimine ligand **8** in 47% yield. Reaction of *β*-diketimine ligand **8** with mesitylcopper(I) gave an as-yet unidentified copper(I) complex, the ^{1}H NMR spectrum of which was inconsistent with

its assignment as an *N,N'*-chelated copper(I) β-diketiminate. In contrast, when the reaction was run in acetonitrile, the (β-diketiminate)copper (I) acetonitrile adduct **2d** was cleanly formed. The solid-state structure of complex **2d** is shown in Figure 4. The most notable features of this structure are a bending the β-diketiminate backbone π-system out of planarity by 8° and a significantly twisting one of the *N*-aryl groups which we believe reduces the steric repulsion between the *ortho*-pentafluorophenyl groups.

Scheme 4. Synthesis and metallation of ligand **8**.



[a]*Pd cat.* = 0.3% $Pd(OAc)_2$, 0.6% 2-(dicyclohexylphosphino)biphenyl per 2,4,6-tribromoaniline.

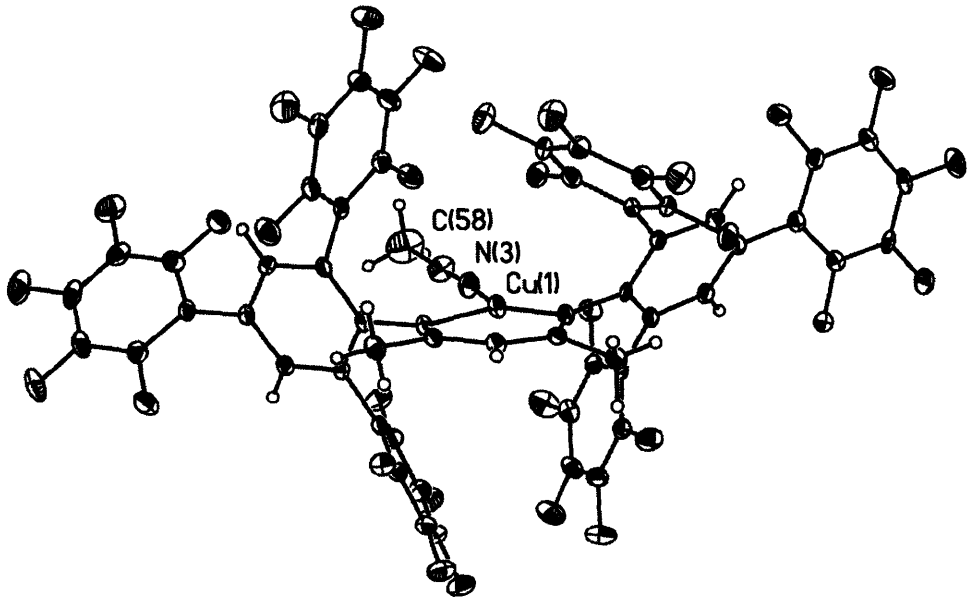


Figure 4. Representation of **2d**•(CH_3CN), shown as 30% ellipsoids. For clarity, solvent was omitted. Selected interatomic distances (Å) and angles (deg): Cu(1)–N(3) 1.875(3), N(3)–C(58) 1.126(4), Cu(1)–N(3)–C(58) 164.0(3).

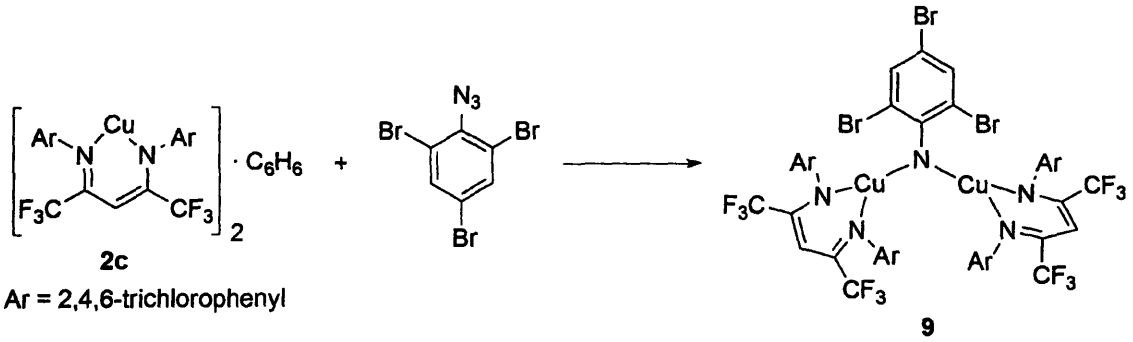
Unlike complex **2c**, **2d** was stable for days under an atmosphere of dioxygen. This lack of reactivity is probably due to the significant steric congestion around the copper center and also to the stronger coordination of the ancillary ligand acetonitrile compared with the benzene ligand of complex **2c**. Other (*β*-diketiminate)copper(I) acetonitrile adducts have, however, been shown to react readily with dioxygen.[4c,d] Other oxidants such as hypervalent iodine reagents were very slow to react, and eventually formed complex mixtures of products.

Reactivity of (*β*-diketiminate)copper(I) complexes toward aryl azides

When complex **2c** was treated with equimolar 2,4,6-tribromophenyl azide in acetone solution, a rapid reaction ensued, with visible effervescence. The ^{1}H NMR spectrum of the reaction mixture indicated that only half of the aryl azide had reacted. Single crystals of the reaction product were grown from an acetone solution at –40 °C, and analysis by X-ray diffraction revealed the structure to be that of the imido-bridged, nominally C_2-symmetric dicopper(II) complex **9** (Figure 6; Scheme 5). The Cu–Cu distance is relatively short at 2.9358(11) Å, and the geometry about each copper center is nearly T-shaped. A π-stacking interaction between the 2,4,6-tribromophenyl ring and two flanking aryl rings of the *β*-diketiminate ligands was observed in the solid-state structure. The ^{1}H NMR spectrum of complex **9** in acetone-d_6 displays sharp resonances typical of a diamagnetic complex indicating that the copper centers are strongly anitferromagnetically coupled. Four resonances arising from the *β*-diketiminate aryl hydrogens were observed at room temperature, consistent with slow

rotation about the N–C_{ipso} bonds on the NMR time scale, confirming that the C_2-symmetric geometry also occurs in solution. Complex **9** does not react further with additional aryl azide, nor does it transfer nitrene to olefins such as *trans*-stilbene and stryrene. In contrast to the aerobic oxidation of **2b**, which leads to ligand hydroxylation, reaction of **2b** with pentafluorophenyl azide formed an imido-bridged dicopper(II) complex similar to **9**, with no ligand activation observed.

Scheme 5. Synthesis of an imido-bridged dicopper(II) complex.



2c

Ar = 2,4,6-trichlorophenyl

9

The somewhat more sterically encumbered 2,4,6-tris(trifluoromethyl)phenyl azide does not react with **2c** in benzene solution at room temperature. At elevated temperatures, **2c** catalyzes the conversion of 2,4,6-tris(trifluoromethyl)phenyl azide to 2,2',4,4',6'6'-hexakis(trifluoromethyl)azobenzene, with no intermediates observed spectroscopically during the course of the reaction. The much larger 2,4,6-tris(pentafluorophenyl)phenyl azide does not react with **2c** even at elevated temperature. The sterically demanding (β-diketiminate)copper complex **2d** reacts with pentafluorophenyl azide to give a multitude of paramagnetic products. No reaction was observed between **2d** and other larger aryl azides such as 2,4,6-trichlorophenylazide even at elevated temperatures.

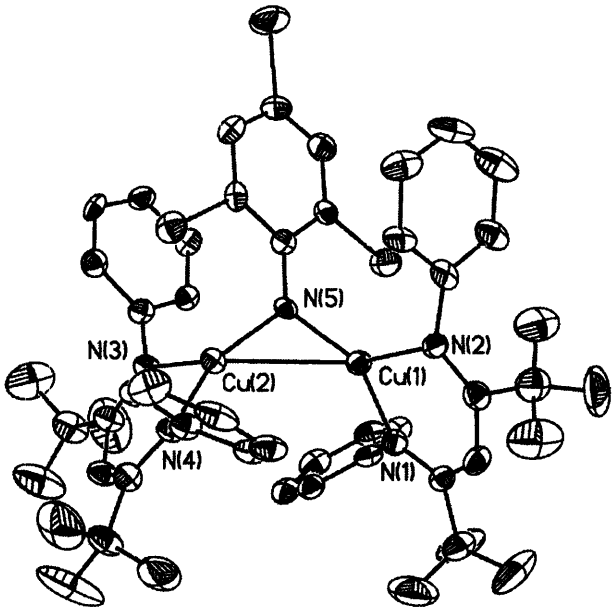


Figure 6. Representation of **9**•[0.5$(CH_3)_2CO$], shown as 50% ellipsoids. For clarity, all hydrogen and chlorine atoms, solvent and disorder have been omitted. Selected interatomic distances (Å) and angles (deg): Cu(1)–Cu(2) 2.9358(11), Cu(1)–N(5) 1.821(5), Cu(2)–N(5) 1.823(5), Cu(1)–N(5)–Cu(2) 107.4(3), N(1)–Cu(1)–N(5) 146.5(2), N(2)–Cu(1)–N(5) 117.6(2), N(3)–Cu(2)–N(5) 115.2(2), N(4)–Cu(2)–N(5) 148.5(2).

In conclusion, an aza-Wittig reaction using 1,1,1,5,5,5-hexafluoro-2,4-pentanedione afforded new, heavily fluorinated β-diketimine ligands in good yield. Ligand **1** is quite electron-poor, as reflected by the infrared stretching frequencies for four inter-related copper(I) carbonyl complexes. Nonetheless, a benzene adduct of its copper(I) complex reacts rapidly with dry air under ambient conditions, generating an oxidizing intermediate sufficiently powerful to hydroxylate a ligand-based 3,5-bis(trifluoromethyl)phenyl group, while leaving the diketiminate backbone unchanged. Several copper complexes supported by β-diketiminate ligands incorporating *ortho*-substituted *N*-aryl groups were synthesized. A bis[(β-diketiminate)copper(II) μ-hydroxide] complex was isolated from the aerobic oxidation of one of

these complexes Also, an imido-bridged dicopper(II) complex was isolated and structurally characterized from the reaction of a (β-diketiminate)copper(I) complex with an aryl azide.

Experimental Section

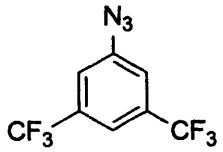
General Considerations. Unless stated otherwise, all synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in flame-dried glassware cooled under vacuum. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA, or Desert Analytics, Tucson, AZ. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for diethyl ether and tetrahydrofuran; the tetrahydrofuran was also passed through a third column packed with activated 4Å molecular sieves) or through neutral alumina and copper(II) oxide (for toluene and hexanes). Benzene, anhydrous, was purchased from Aldrich in Sure-Seal™ bottles, and was further dried over sodium/benzophenone, and vacuum-transferred before use. Acetone was dried over activated molecular sieves, degassed by at least three freeze-pump-thaw cycles and vacuum-transferred before use. All non-dried solvents used were reagent grade or better. IR spectra were recorded on a Nicolet Impact 410 spectrometer as KBr pellets or in a KBr solution IR cell (0.1 mm path length). UV–Vis spectra were recorded on a Spectral Instruments 440 Series spectrophotometer.

NMR solvents were dried as follows: C_6D_6 (Cambridge Isotope Laboratories) over sodium/benzophenone, C_6F_6 (Aldrich) and acetone-d_6 (Cambridge Isotope Laboratories) over activated molecular sieves, CD_2Cl_2 (Cambridge Isotope Laboratories) over calcium hydride. All

NMR solvents were degassed by three freeze-pump-thaw cycles and vacuum-transferred prior to use. ^{1}H NMR spectra were recorded on a Varian 300 MHz instrument, with shifts reported relative to the residual solvent peak or, for C_6F_6, to an external standard of C_6D_6 referenced to the residual solvent peak. ^{19}F NMR spectra were recorded on a Varian 300 MHz instrument, with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm) or internally to C_6F_6 (–163 ppm). ^{13}C NMR spectra were recorded on a Varian 300 MHz or a Varian 500 MHz instrument, with shifts referenced relative to the solvent peak.

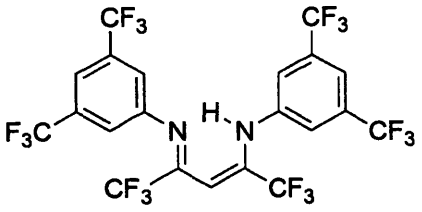
The starting materials trifluoroacetic acid (Oakwood Products), sodium nitrite (Alfa Aesar), sodium azide (Alfa Aesar), triphenylphosphine (Lancaster), trimethylphosphine (Aldrich), 3,5-bis(trifluoromethyl)aniline (Oakwood Products), 3,5-dimethylaniline (Aldrich), 2,4,6-trichloroaniline (Aldrich), 2,4,6-tribromoaniline (Aldrich), (trimethylsilyl)trifluoromethylsulfonate, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Oakwood Products), 2,4-pentanedione (Aldrich), magnesium (Strem), 2-bromomesitylene (Acros), bromopentafluorobenzene (Oakwood Products), copper(I) chloride (Strem), palladium acetate (Aldrich), dicyclohexylphosphinobiphenyl (Strem), carbon monoxide (BOC gases) and anhydrous 2-methyl-2-propanol (Aldrich) were used as received. Zinc dust (Aldrich) was activated by washing with 1 M aq. HCl, water, acetone, and diethyl ether and dried at 150 °C under vacuum for 15 hours. Mesitylcopper(I),[21] copper(I) *tert*-butoxide,[22] 2,4,6-trichlorophenyl azide,[23] and 2,4,6-tribromophenyl azide[23] were prepared according to literature methods.

CAUTION: While we have encountered no problems after multiple preparations of 3,5-bis(trifluoromethyl)phenyl azide, the addition of sodium azide to an acidic solution produces hydrazoic acid, which is highly toxic and potentially explosive. Further, some organic azides are known to explode. All due caution should be used.



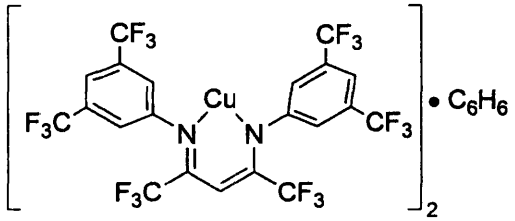
3,5-Bis(trifluoromethyl)phenyl azide.[24]

Trifluoroacetic acid (100 mL) and 3,5-bis(trifluoromethyl)aniline (6 mL, 38.4 mmol) were added to a 500-mL Erlenmeyer flask equipped with a Teflon-coated stirbar. The flask was cooled to –10 °C using a salt-ice bath, and solid sodium nitrite (5.04 g, 73.0 mmol) was added in small portions over 15 minutes. The reaction mixture was stirred for 30 minutes. Solid sodium azide (5.24 g, 80.7 mmol) was then added in portions over 5 minutes, and the reaction mixture was stirred for 1 hour and 45 minutes. Water (200 mL) was then carefully added and the solution was warmed to room temperature. The reaction mixture was extracted with pentane (3 x 50 mL) and the pentane extracts were combined and washed with water (150 mL), saturated aqueous sodium bicarbonate solution (100 mL) and brine (100 mL). The pentane solution was then dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified by vacuum distillation (40 °C, 6 x 10^{-3} torr) to afford the title compound as a straw yellow oil (9.38 g, 96 %). ^{1}H NMR (C_6D_6, 300.1 MHz): δ 7.33 (s, 2H), 6.79 (s, 1H). ^{19}F NMR (C_6D_6, 282.346 MHz): δ –63.40 (s, 6F). ^{13}C NMR (C_6D_6, 75.467 MHz): δ 142.9 (s), 133.6 (q, J = 33.6 Hz, $\underline{C}CF_3$), 123.7 (q, J = 272.3 Hz, $\underline{C}F_3$), 119.6 (m), 118.6 (m). Anal. Calcd. for $C_8H_3N_3F_6$: C, 37.66; H, 1.19. Found: C, 37.54; H, 1.17.



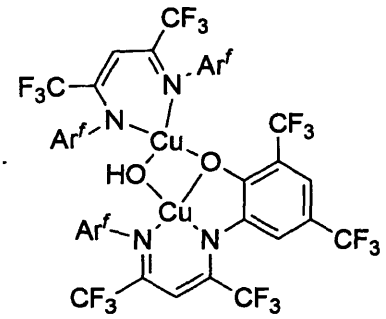
Preparation of β-Diketimine 1.

A flame-dried resealable Schlenk tube equipped with a Teflon-coated stirbar was charged with triphenylphosphine (8.36 g, 31.8 mmol), evacuated, and backfilled with argon. The Teflon stopcock was replaced with a rubber septum, and diethyl ether (anhydrous, 40 mL) was added via syringe. A solution of 3,5-bis(trifluoromethyl)phenyl azide (7.90 g, 30.9 mmol) in diethyl ether (anhydrous, 10 mL) was added via cannula such that gas was evolved in a controlled manner. The resulting solution was stirred for 15 hours, then concentrated *in vacuo*. Toluene (anhydrous, 100 mL) was added via syringe, followed by 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (2.0 mL, 14.0 mmol). The tube was sealed and the reaction mixture was heated at 90 °C for 15 hours, yielding an orange solution. The solvent was removed *in vacuo*, and the resulting oil was pushed through a plug of silica gel using hexanes and ethyl acetate (19:1) as eluant. The resulting solid was recrystallized from hot hexanes, affording **1** as yellow crystals (3.50 g, 40%). The mother liquor was concentrated and the residue was purified by column chromatography on silica gel, using hexanes and ethyl acetate (19:1) as the eluant, yielding an additional crop of **1** (2.70 g, 31%). ^{1}H NMR (C_6D_6, 300 MHz): δ 11.11 (s, 1H), 7.50 (s, 2H), 7.16 (overlapping s, 4H), 5.86 (s, 1H). ^{19}F NMR (C_6D_6, 282.7 MHz): δ –63.26 (s. 6F), –63.37 (s, 12F). ^{13}C NMR (CD_2Cl_2, 125.8 MHz): δ 150.9 (q, J = 30.5 Hz), 144.2, 132.9 (q, J = 34.0 Hz), 123.9 (s), 123.5 (q, J = 272.7 Hz), 120.4 (m), 119.3 (q, J =283.1 Hz), 91.4 (m). Anal. Calcd for $C_{21}H_8N_2F_{18}$: C, 40.02; H, 1.28; F, 54.26. Found: C, 39.89; H, 1.13; F, 54.52.



Preparation of (β-Diketiminate)copper(I) Benzene Adduct 2b.

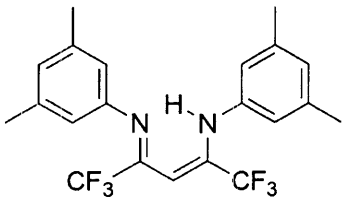
In a glovebox, mesitylcopper(I) (0.434 g, 2.36 mmol) and **1** (1.40 g, 2.22 mmol) were added to a Schlenk flask equipped with a Teflon-coated stirbar. On a vacuum line, benzene (anhydrous, 15 mL) was added. After 4 hours, the solvent was removed under reduced pressure and the solid was washed with cold hexanes (2 x 5 mL) to give **2b** as a yellow powder (1.64 g, 96%). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.56 (s, 2H), 7.08 (s, 4H), 5.89 (s, 1H). ^{19}F NMR (C_6D_6, 282.7 MHz): δ –60.32 (6F), –62.26 (12F). ^{13}C NMR (C_6D_6, 125.8 MHz) δ 152.8 (q, J = 25.9 Hz), 150.9 (s), 128.9 (s), 128.7 (s), 124.5 (s), 124.1 (q, J = 273.1 Hz), 120.9 (q, J = 286.2 Hz), 118.4 (m), 85.25 (m). UV–Vis (CH_2Cl_2) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 379 (26,900). Anal. Calcd for $C_{48}H_{20}Cu_2F_{36}N_4$: C, 39.39; H, 1.38. Found: C, 39.13; H, 1.18.



Aerobic Oxidation of 2b.

In a glovebox, **2b** (0.047 g, 0.032 mmol) was added to a Schlenk flask equipped with a Teflon-coated stirbar. The flask was capped with a rubber septum, brought out of the glovebox and attached to a vacuum line. Hexanes (anhydrous, 2 mL) were added via syringe. The flask was then purged with dry air. The yellow solution immediately turned brown and a precipitate formed. After 30 minutes, the solvent was decanted and the brown solid was isolated, yielding **3a** (0.045 g, 99%). ^{1}H NMR (C_6F_6, 300.099 MHz): δ 21.70 (s, 1H), 16.14 (s, 1H), –9.37 (s, 2H), –10.50 (s, 1H), –12.33 (s, 1H), –17.31 (s, 2H), –21.67 (s, 2H), –23.02 (s, 2H), –25.93 (s, 1H). ^{19}F NMR (C_6F_6, 282.346 MHz): δ –17.15 (s, 6F), –20.30 (s, 3F), –22.47 (s, 3F), –54.38 (s, 3F), –

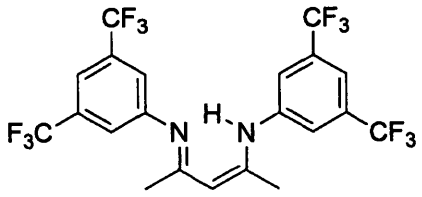
56.25 (s, 3F), –68.74 (s, 6F), –73.51 (s, 12F). Note: Due to the paramagnetic nature of **3a**, definitive peak assignments in the ^{1}H and ^{19}F NMR spectra have not been made. UV–Vis (CH_2Cl_2) λ_{max}, nm (ε, M^{-1} cm^{-1})]: 320 (13,300), 376 (22,300), 460 (11,900). Anal. Calcd. for $C_{42}H_{19}Cu_2F_{36}N_2O_2$: C, 35.55; H. 1.00; F, 48.25. Found: C, 35.51; H, 1.07; F, 47.99.



Preparation of *β*-Diketimine 4.

In an Erlenmeyer flask equipped with a Teflon-coated stirbar, 3,5-dimethylaniline (4.37 mL, 35 mmol) was dissolved in hydrochloric acid (4*N*, 50 mL). The flask was cooled to 0 °C, and a solution of sodium nitrite (2.90g, 42 mmol) in water (20 mL) was added drop wise over 20 minutes. The resulting solution was stirred for 10 minutes. A solution of sodium azide (2.86 g, 44 mmol) in water (20 mL), was then added drop wise over 20 minutes, and the resulting solution was stirred for one hour at 0 °C. The flask was warmed to room temperature, and stirring was continued for an additional hour. Water (100 mL) was then added and the reaction mixture was extracted with hexanes (2 x 50 mL). The extracts were combined and washed with water (100 mL), saturated aqueous sodium bicarbonate solution (100 mL) and brine (100 mL). The hexanes solution was dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The crude product was taken up in pentane (10 mL) and pushed through a plug of alumina. The solution was then concentrated *in vacuo* to afford 3,5-dimethylphenyl azide as a yellow oil (4.20g, 82%).[25] ^{1}H NMR (C_6D_6, 300.100 MHz): δ 6.51 (s, 2H), 6.48 (s, 1H) 1.99 (s, 6H). ^{13}C NMR (C_6D_6, 75.467 MHz): δ 140.4, 139.9, 127.3, 117.5, 21.6.

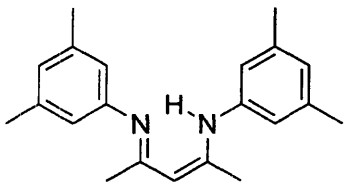
A flame-dried resealable Schlenk tube equipped with a Teflon-coated stirbar was charged with triphenylphosphine (5.10 g, 19.44 mmol), evacuated, and backfilled with argon. The Teflon stopcock was replaced with a rubber septum, and diethyl ether (anhydrous, 30 mL) was added via syringe. The Schlenk tube was placed in a room temperature water bath, and 3,5-dimethylphenyl azide (3.00 g, 20.38 mmol) was added via syringe such that gas was evolved in a controlled manner. The resulting solution was stirred for one hour, and then concentrated *in vacuo*. Toluene (anhydrous, 20 mL) was added via syringe, followed by 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (1.34 mL, 9.48 mmol). The tube was sealed and the reaction mixture was heated at 120 °C for 48 hours, yielding an orange solution. The solvent was removed *in vacuo* and the resulting oil was pushed through a plug of silica using hexanes and ethyl acetate (19:1). The resulting solid was recrystallized from hot hexane affording **4** as yellow flakes (1.91 g, 49%). Concentration of the mother liquor to *ca.* half its original volume at reduced pressure afforded further crystals (0.86 g, 22%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 12.01 (s, 1H), 6.88 (s, 2H), 6.72 (s, 4H), 5.90 (s, 1H) 2.33 (s, 12H). ^{19}F NMR (CD_2Cl_2, 282.7 MHz): δ –62.75. ^{13}C NMR (CD_2Cl_2, 125.796 MHz): δ 149.2 (q, J = 29.6 Hz, N<u>C</u>), 143.3 (s), 139.1, 127.9 (s), 120.9 (s), 119.9 (q, J = 283.5 Hz, <u>C</u>F_3), 89.2 (m, NC<u>C</u>H), 21.5 (s). Anal. Calcd. for $C_{21}H_{20}N_2F_6$: C, 60.87; H, 4.86. Found: C, 60.79; H, 4.77.



Preparation of β-Diketimine 5.

In an oven-dried round-bottomed flask equipped with a Teflon-coated stirbar, 3,5-bis(trifluoromethyl)aniline (3.00 g, 13.09 mmol), 2,4-pentanedione (0.538 mL, 5.24 mmol) and

trimethylsilyl trifluoromethanesulfonate (1.04 mL, 5.76 mmol) were dissolved in toluene (anhydrous, 30 mL). The flask was then fitted with a Soxhlet extractor containing activated 3Å molecular sieves, and heated at vigorous reflux for 24 hours. Upon cooling, a yellow solution containing a white precipitate was obtained. The mixture was filtered, and the precipitate was washed with hexanes (3 x 5 mL). The precipitate was then transferred to an Erlenmeyer flask equipped with a Teflon-coated stirbar. Dichloromethane (50 mL), and a saturated sodium bicarbonate solution (50 mL) were added. The mixture was stirred for 20 minutes, and the dichloromethane layer was separated, and washed with water (50 mL), then brine (50 mL). The organic phase was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The resulting solid was recrystallized from hot hexanes, yielding the title compound as golden yellow flakes (2.00 g, 73%). ^{1}H NMR (CD_2Cl_2, 500.236 MHz): δ 12.68 (s, 1H), 7.60 (s, 2H), 7.43 (s, 4H), 5.12 (s, 1H) 2.08 (s, 6H). ^{19}F NMR (CD_2Cl_2, 282.346 MHz): δ –63.2. ^{13}C NMR (CD_2Cl_2, 125.796 MHz): δ 161.1(s), 147.7 (s), 132.7 (q, J = 33.2 Hz, $\underline{C}CF_3$), 124.5 (q, J = 272.6 Hz, CF_3), 123.0 (m), 117.4 (m), 100.6 (s), 21.5 (s). Anal. Calcd. for $C_{21}H_{14}N_2F_{12}$: C, 48.29; H, 2.70. Found: C, 48.25; H, 2.57.



Preparation of β-Diketimine 6.

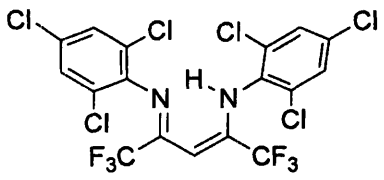
Activated 5Å molecular sieves (20 g), toluene (anhydrous, 20 mL), 3,5-dimethylaniline (4.12 mL, 33 mmol), and 2,4-pentanedione (1.51 mL, 14.7 mmol) were added to a Schlenk flask equipped with a Teflon-coated stirbar. The flask was heated at 90 °C for 24 hours; analysis of an aliquot by ^{1}H NMR indicated approximately 50% conversion to the desired product; starting

aniline and the mono-condensed intermediate were also visible. The reaction mixture was then heated to 120 °C for 24 hours, but no further conversion was indicated by ^{1}H NMR spectroscopy. The reaction mixture was filtered to remove the molecular sieves, which were then washed with dichloromethane (2 x 20 mL). The solution was concentrated *in vacuo*. Crystallization of the crude product from hexanes (10 mL) at –30 °C, over 24 hours, afforded **6** as pale yellow crystals (0.462 g, 10%). ^{1}H NMR (CD_2Cl_2, 300.101 MHz): δ 12.58 (s, 1H), 6.71 (s, 2H), 6.58 (s, 4H), 4.87 (s, 1H) 2.30 (s, 12H), 2.01 (s, 6H). ^{13}C NMR (CD_2Cl_2, 125.796 MHz): δ 159.7, 146.3, 138.9, 125.2, 120.6, 97.7, 21.6, 21.2. Anal. Calcd. for $C_{21}H_{26}N_2$: C, 82.31; H, 8.55. Found: C, 82.04; H, 8.61.

***In situ* preparation of (β-Diketiminate)copper(I) carbonyl complexes from 1, 4, 5, 6.**

Attempts to prepare (β-diketiminate)copper(I) benzene adducts from ligands **5** and **6** were unsuccessful, apparently due to disproportionation. The carbonyl complexes, however, could be generated *in situ* from the respective ligand, a substoichiometric amount of mesitylcopper(I) and an excess of carbon monoxide in C_6D_6. A copper(I) carbonyl complex of **1** was prepared independently, by exposure of the corresponding benzene adduct **2b** to carbon monoxide, followed by removal of excess carbon monoxide. The carbonyl stretch of the complex prepared in this fashion, in C_6D_6, was identical to that obtained through the *in situ* generation described above, suggesting that the presence of excess ligand and byproduct mesitylene do not affect the relevant stretching frequencies. In a typical experiment, complex **5** (0.062 g, 0.15 mmol), mesitylcopper(I) (0.025 g), and 0.7 mL of C_6D_6 were added to a J. Young NMR tube in the glovebox. The tube was sealed, brought out to a Schlenk line, and cooled to –78 °C. An atmosphere of carbon monoxide was established with a single evacuation/back-fill cycle, the tube was resealed, and the contents thawed. Once the mesitylcopper(I) was consumed, as judged

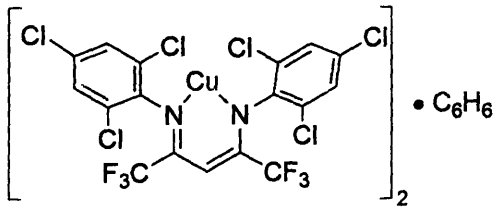
by ^{1}H NMR spectroscopy, the tube was re-cooled to –78 °C and evacuated. In a glovebox, the solution was transferred to a solution IR cell, removed from the glovebox, and an IR spectrum was promptly recorded. For the corresponding copper carbonyl complex derived from **6**, metallation by mesitylcopper(I) was prohibitively slow, and decomposition set in before the reaction was complete. We have found that copper(I) *tert*-butoxide is a much more rapid metallating agent for **6**, giving a clean reaction as judged by ^{1}H NMR, and allowing the carbonyl complex to be generated cleanly for IR studies. Metallation of **5** by copper(I) *tert*-butoxide under CO gave the same results as metallation by mesitylcopper(I).



Preparation of β-Diketimine 7.

On a Schlenk line, a flame-dried resealable Schlenk tube equipped with a Teflon-coated stirbar was charged with 2,4,6-trichlorophenyl azide (2.10 g, 9.44 mmol), evacuated and backfilled with argon. The Teflon stopcock was replaced with a rubber septum, and diethyl ether (anhydrous, 20 mL) was added via syringe. Trimethylphosphine (1.32 mL, 15.1 mmol) was added drop-wise via syringe such that gas was evolved in a controlled manner. The resulting solution was stirred for 4 hours, and then concentrated *in vacuo*. Toluene (anhydrous, 20 mL) was added via syringe, followed by 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (0.534 mL, 3.78 mmol). The tube was sealed and the reaction mixture was heated at 100 °C for 15 hours, and 120 °C for 30 hours. The solvent was removed *in vacuo*, and the resulting oil was pushed through a plug of silica gel using hexanes and ethyl acetate (19:1) as eluant. The resulting solid was recrystallized from hot hexanes, affording **1** as yellow crystals (1.45 g, 68%). ^{1}H NMR (C_6D_6, 300.100 MHz): δ 11.25 (s, 1H, NH), 6.83 (s, 4H, *meta*-H), 6.04 (s, 1H, NCCH). ^{13}C NMR (CD_2Cl_2, 125.796 MHz): δ

152.8 (q, J = 31 Hz, N<u>C</u>), 137.2, 132.9, 131.5, 128.7, 119.1 (q, J = 283 Hz, <u>C</u>F_3), 90.2 (sept, J = 4.5 Hz, NC<u>C</u>H). ^{19}F (C_6D_6, 282.346): δ –67.28 (6 F, C<u>F</u>$_3$).



Preparation of (β-Diketiminate)copper(I) Benzene Adduct 2c.

In a glovebox, mesitylcopper(I) (0.226 g, 1.239 mmol) and **7** (0.500 g, 0.885 mmol) were added to a Schlenk flask equipped with a Teflon-coated stirbar. On a vacuum line, benzene (anhydrous, 5 mL) was added. The reaction mixture was then heated at 75 °C for 15 hours, cooled to room temperature and concentrated *in vacuo*. In a glovebox, the red solid was taken up in pentane (30 mL), filtered through Celite, and concentrated *in vacuo* to afford the title complex as an orange solid (0.450, 72%). ^{1}H NMR (C_6D_6, 300.100 MHz): δ 7.05 (s, 4H), 6.03 (s, 1H). ^{13}C NMR (C_6D_6, 125.796 MHz): δ 154.2 (q, J = 27.6 Hz, N<u>C</u>), 143.2, 130.6, 130.3, 228.9, 128.4, 120.7 (q, J = 286 Hz, <u>C</u>F_3), 85.6 (sept, J = 5.2 Hz, NC<u>C</u>H). ^{19}F NMR (C_6D_6, 282.346 MHz): δ –65.15 (6F).

Aerobic oxidation of 2c.

In a glovebox, a J-Young NMR tube was charged with **2c** (0.030 g, 0.023 mmol) and solvent (toluene, benzene or hexanes) was added (0.7 mL). The tube was sealed, taken out of the glovebox, and degassed by one freeze-pump-thaw cycle on a Schlenk line. Dioxygen was added, and the yellow solution turned immediately brown. The ^{19}F NMR spectra of the resulting solution indicated that several species had formed, though product ratios varied depending on solvent. Over time, a brown solid typically precipitated which was recrystallized in toluene to

give single crystals. Analysis by X-Ray diffraction showed that a Cu(II)-Cu(II)-μ-hydroxide complex had been isolated.

Synthesis of 9.

In a glovebox, a 20-mL scintillation vial was charged with **2c** (0.200 g, 0.150 mmol) and 2,4,6-tribromophenylazide (0.056 g, 0.156 mmol). Acetone (4 mL) was added and the vial was capped and stored at –40 °C for 4 days. The supernatant was then decanted and the dark blue crystals were dried *in vacuo* to afford the title complex (0.120 g, 51%). ^{1}H NMR (acetone-d_6, 300.100 MHz): δ 7.71 (d, J = 2.2 Hz, 2H), 7.63 (d, J = 2.2 Hz, 2H), 7.40 (s, 2H), 7.33 (d, J = 2.2 Hz, 2H), 6.77 (d, J = 2.2 Hz, 2H), 6.01 (s, 2H). ^{19}F NMR (acetone-d_6, 282.347 MHz): δ –64.61 (6F), –65.11 (6F).

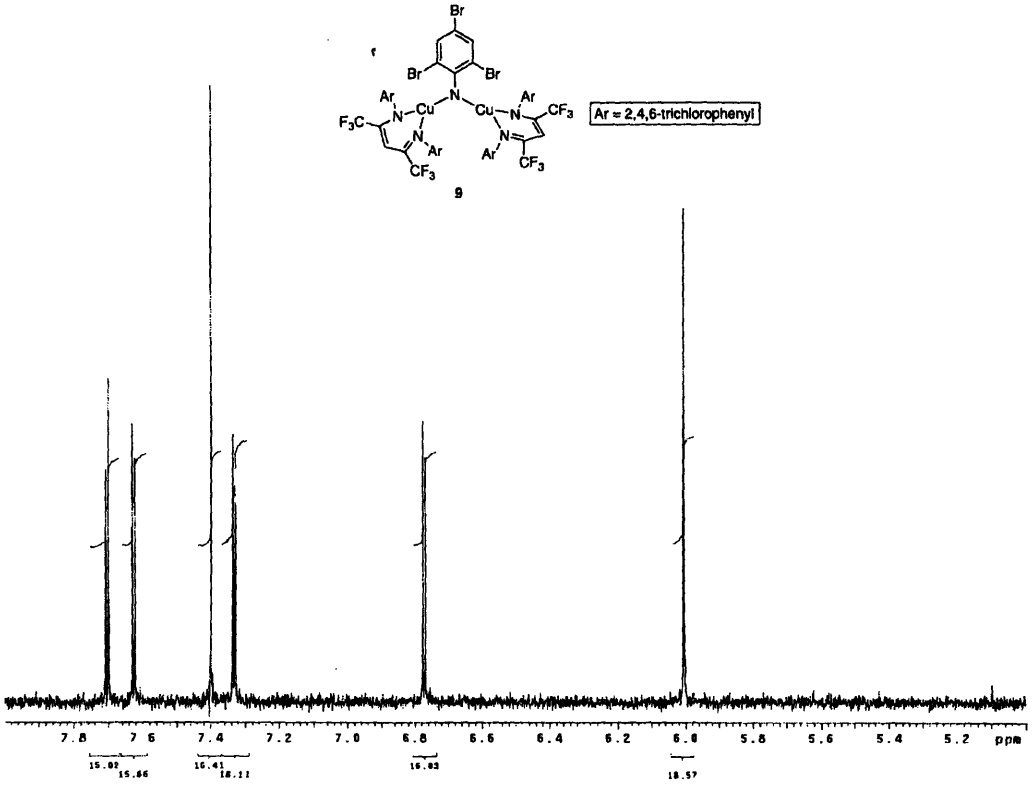
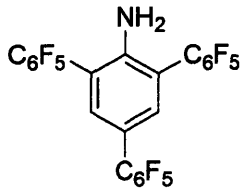
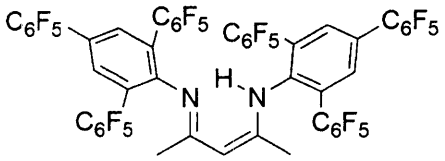


Figure 7. ^{1}H NMR spectrum of **9**.



Preparation of 2,4,6-tris(pentafluorophenyl)aniline[23]: In a glovebox, Zn dust (3.6 g, 55 mmol) and THF (20 mL) were added to a sealable Schlenk flask equipped with a Teflon-coated stirbar, and the flask was sealed and taken out of the glovebox. On a Schlenk line, bromopentafluorobenzene (6.2 mL, 50 mmol) was added to the zinc suspension dropwise over 1 hour. **CAUTION:** This reaction is exothermic and run similarly to Grignard generation. After the addition was complete, the reaction vessel was sealed, and sonicated for 15 hours. The next day, a separate sealable Schlenk tube equipped with a Teflon coated stirbar was charged with $Pd(OAc)_2$ (0.034 g, 0.15 mmol), 2-(dicyclohexylphosphino)biphenyl (0.105 g, 0.300 mmol) and THF (1mL). The Schlenk flask was sealed and the reaction mixture was heated at 80 °C for 1 minute. In a glovebox, 2,4,6-tribromoaniline (4.12 g, 12.5 mmol) and the pre-mixed catalyst were added to the flask containing pentafluorophenyl zinc bromide. The flask was sealed, taken out of the glovebox and heated at 80 °C. After 48 hours, the reaction was judged complete by GC-MS. The reaction mixture was then concentrated *in vacuo*, taken up in dichloromethane (300 mL), and the organic layer was washed with water (3 x 100 mL), and brine (1 x 100 mL). The organic layer was then dried with magnesium sulfate, filtered, and concentrated *in vacuo*. Finally, the product was triturated with hot hexanes (100 mL), cooled to room temperature, filtered, and washed with dichloromethane (10 mL) to give an off-white solid (5.50 g, 85%). Smaller-scale preparations were usually run at 3 mol% Pd (per 2,4,6-tribromoaniline). ^{1}H NMR (C_6D_6, 300.100 MHz): δ 7.17 (s, 2H, *meta*-H), 3.25 (br s, 2H, NH_2). ^{13}C NMR (C_6D_6, 125.796 MHz): δ 145.0 (m, $^1J_{C-F}$ = 248.7 Hz), 144.8 (m, $^1J_{C-F}$ = 246.4 Hz), 144.7 (s), 141.9 (m,

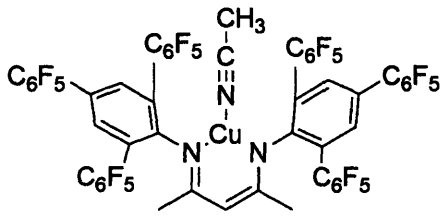
$^{1}J_{C-F}$ = 254.5 Hz), 140.8 (m, $^{1}J_{C-F}$ = 258.8 Hz), 138.6 (m, $^{1}J_{C-F}$ = 252.8 Hz), 135.3 (s), 116.7 (s), 114.7 (td, $^{2}J_{C-F}$ = 16.1 Hz, $^{3}J_{C-F}$ = 3.5 Hz), 113.5 (s), 112.0 (td, $^{2}J_{C-F}$ = 19.0 Hz, $^{3}J_{C-F}$ = 3.5 Hz). ^{19}F NMR (C_6D_6, 282.346 MHz): δ –139.6 (m, 4F, *ortho*-F), –144.6 (m, 2F, *ortho*-F), –153.4 (m, 2F, *para*-F), –156.4 (m, 1F, *para*-F), –160.9 (m, 4F, *meta*-F), –162.7 (m, 2F, *meta*-F). Note: Due to the complexity of the ^{13}C NMR spectrum of 2,4,6-tris(pentafluorophenyl)aniline, definitive peak assignments have not been made. Also, the number of carbon resonances is one less than the expected number due to an accidental degeneracy, which most likely occurs at 138.6 ppm. Anal. Calcd. for $C_{24}H_4NF_{15}$: C, 48.75; H, 0.68. Found: C, 48.51; H, 0.70.



Preparation of β-Diketimine 8.

In an oven-dried round-bottomed flask equipped with a Teflon-coated stirbar, 3,5-bis(trifluoromethyl)aniline (2.165 g, 3.66 mmol), 2,4-pentanedione (0.179 mL, 1.743 mmol) and trimethylsilyl trifluoromethanesulfonate (0.316 mL, 5.76 mmol) were dissolved in toluene (anhydrous, 30 mL). The flask was then fitted with a Soxhlet extractor containing activated 3Å molecular sieves, and heated at vigorous reflux for 5 days. Upon cooling, a yellow suspension was obtained. The mixture was filtered, and the precipitate was washed with hexanes (3 x 5 mL). The precipitate was then transferred to an Erlenmeyer flask equipped with a Teflon-coated stirbar. Dichloromethane (250 mL) and a saturated aqueous sodium bicarbonate solution (100 mL) were added. The mixture was stirred for 20 minutes, and the dichloromethane layer was separated, and washed with water (50 mL), then brine (50 mL). The organic phase was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The resulting solid was recrystallized from hot hexanes/chloroform, yielding the title compound (1.03 g, 47%). ^{1}H NMR

(C_6D_6, 300.100 MHz): δ 11.23 (s, 1H, NH), 7.39 (s, 4H, *meta*-H), 3.92 (s, 1H, NCCH), 1.09 (s, 6H, CH_3). ^{19}F (C_6D_6, 282.346): δ –140.1 (4 F, *ortho*-CF), –141.5 (br s, 4 F, *ortho*-CF), –142.8 (m, 4 F, *ortho*-CF), –152.7 (br s, 4 F, *para*-CF), –153.0 (m, 2 F, *para*-CF), –160.2 (m, 8 F, *meta*-CF), –161.4 (m, 4 F, *meta*-CF).



Preparation of (β-Diketiminate)copper(I) Acetonitrile Adduct (2d).

In a glovebox, mesitylcopper(I) (0.433 g, 2.38 mmol) and **8** (2.12 g, 1.70 mmol) were added to a resealable Schlenk flask equipped with a Teflon-coated stirbar. Acetonitrile (5 mL) was added, the flask was sealed and taken out of the glovebox. The reaction mixture was heated at 85 °C for 8 hours, cooled to room temperature, and concentrated *in vacuo*. In a glovebox, the solid was taken up in toluene, filtered through Celite, and the solution was concentrated *in vacuo*. The resulting solid was washed with hexanes (5 mL) to give the title complex as an orange solid (1.58 g, 69%). ^1H NMR (C_6D_6, 499.578 MHz): δ 7.37 (s, 4H), 4.06 (s, 1H), 1.42 (s, 6H), 0.81 (s, 3H). ^{13}C NMR (C_6D_6, 475.758 Hz): δ 164.6, 152.6, 145.6 (m, $^1J_{C-F}$ = 249.1 Hz), 144.8 (m, $^1J_{C-F}$ = 248.1 Hz), 144.5 (m, $^1J_{C-F}$ = 250.2 Hz), 141.5 (m, $^1J_{C-F}$ = 253.3 Hz), 141.0 (m, $^1J_{C-F}$ = 253.3 Hz), 138.6 (m, $^1J_{C-F}$ = 251.2 Hz), 135.8 (s), 123.3 (s), 120.5 (s), 117.5 (s), 115.0 (td, $^2J_{C-F}$ = 17.1 Hz, $^3J_{C-F}$ = 3.1 Hz), 114.5 (td, $^2J_{C-F}$ = 15.6 Hz, $^3J_{C-F}$ = 3.2 Hz), 97.3 (s), 22.8 (s), 0.68 (s).

Magnetic Measurements.

The magnetic susceptibility of **3a** was determined on a powdered sample, with 0.0277 g contained inside a plastic straw sealed below the sample, using a SQUID susceptometer (Quantum Design MPMSR2), over a temperature range of 5–300 K and at a field strength of 0.5

T. The method of scanning used by the instrument results in automatic correction for the diamagnetic contribution from the sample holder. The values of χ_m were adjusted for diamagnetic contributions (-545×10^{-6} cm^{-3} mol^{-1}) using the constitutive corrections of Pascal's constants.[26] The plot of X_M versus T shows a rise in magnetic susceptibility at low temperatures due to the presence of a small amount of an unidentified paramagnetic impurity. We corrected for this impurity by plotting the measured susceptibility values at temperatures below the minima against 1/T.[27] The intercept of the resulting line corresponds to the temperature independent paramagnetism (568×10^{-6} cm^3 g-atom^{-1}) for **3a**. The slope of the line corresponds to the Curie susceptibility of the paramagnetic impurity ($X_{impurity} = 1.10 \times 10^{-2} / T$ cm^3 g-atom^{-1}). The corrected susceptibilities were found by subtracting $X_{impurity}$ from the experimentally measured X value. The corrected values were converted to effective magnetic moments using Equation 1:

$$\mu_{eff} = \sqrt{7.997\, \chi_m\, T} \qquad (1)$$

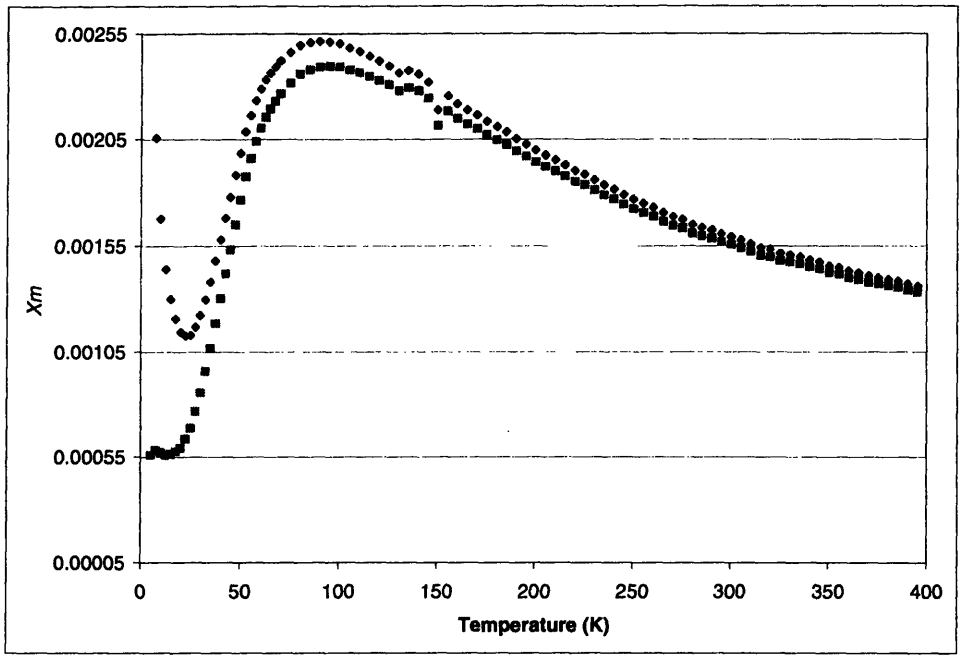


Figure 8. Plot X_M versus T(K). Experimental values corrected for a paramagnetic impurity are shown as squares, and uncorrected values are shown as diamonds.

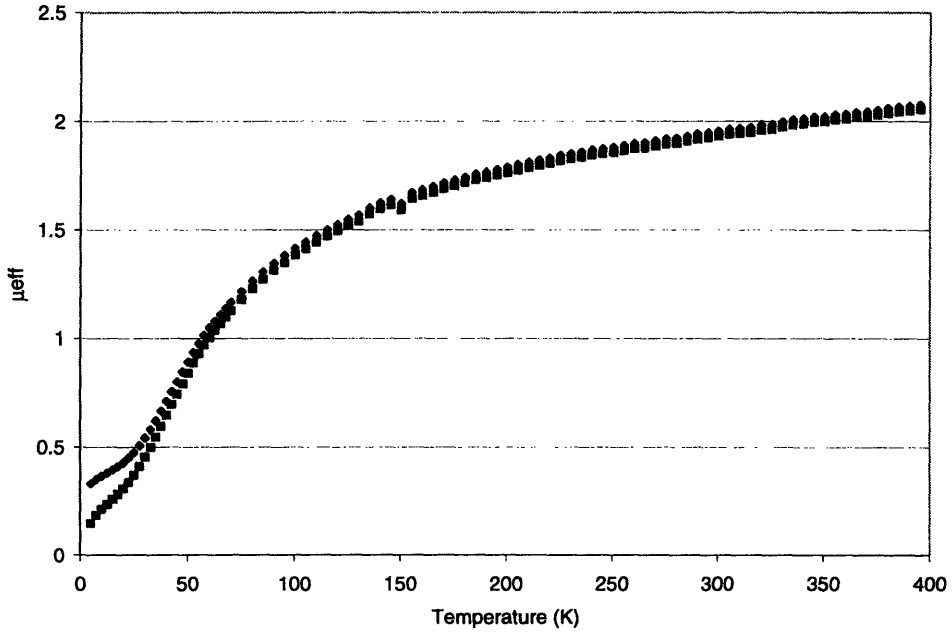


Figure 9. Plot μ_{eff} versus T(K). Experimental values corrected for a paramagnetic impurity are shown as squares, and uncorrected values are shown as diamonds.

Table 2. Crystallographic data for **2a**, **2c**, **3a**, **3b**, and **9**.

	2a	**2c**	**3a**	**3b**	**9**
empirical formula	$C_{27}H_{13}N_2F_{18}Cu$	$C_{57}H_{17}N_4F_{30}Cu$	$C_{48}H_{14}N_4O_2F_{42}Cu_2$	$C_{46}H_{24}N_4O_2F_{12}Cl_{12}Cu_2$	$C_{41.50}H_1N_5O_{0.50}F_{12}Cl_{12}Br_3Cu_2$
FW	770.93	1391.29	402.13	1445.17	1611.79
T, K	193(2)	193(2)	193(2)	193(2)	193(2)
Crystal syst	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$Ccca$	$C2/c$
a, Å	8.5814(14)	12.612(2)	14.102(7)	16.6596(5)	43.710(4)
b, Å	24.486(4)	14.303(2)	21.704(10)	13.4080(6)	12.6162(12)
c, Å	14.198(2)	16.034(3)	18.354(8)	20.9886(9)	22.241(2)
α, deg	90	111.794(3)	90	90	90
β, deg	100.135(3)	93.271(3)	99.907(7)	90	118.006(2)
γ, deg	90	100.767(3)	90	90	90
V, Å^3	2936.8(8)	2613.0(7)	5534(4)	5739.1(7)	10828.7(17)
ρ_{calc}, g/cm^{-1}	1.744	1.768	1.925	1.673	1.977
Z	4	2	4	4	8
μ, mm^{-1}	0.881	0.572	0.956	1.380	0.077
F(000)	1520	1372	3128	2856	6224
cryst size, mm^3	0.40 x 0.40 x 0.40	0.37 x 0.35 x 0.13	0.28 x 0.25 x 0.25	0.37 x 0.35 x 0.13	0.22 x 0.14 x 0.08
θ range, deg	2.21 to 25.00	2.22 to 23.30	2.21 to 23.30	2.21 to 23.29	3.39 to 23.33
no. of data/restraints/params	5138/0/544	5816 / 830 / 833	7963/ 1 / 969	2070 /79 /206	5999 /674/ 733
Total no. of reflns	13849	6467	22451	10970	11545
GOF on F^2	1.315	1.019	1.024	1.194	1.051
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0583 wR2 = 0.1215	R1 = 0.0324 wR2 = 0.0797	R1 = 0.0444 wR2 = 0.1153	R1 = 0.0447 wR2 = 0.1206	R1 = 0.0619 wR2 = 0.1465
R indices (all data)	R1 = 0.0611 wR2 = 0.1227	R1 = 0.0417 wR2 = 0.0843	R1 = 0.0568 wR2 = 0.1235	R1 = 0.0456 wR2 = 0.1213	R1 = 0.0857 wR2 = 0.1599

X-ray Crystallography

Crystals were transferred onto a microscope slide from a 20-mL scintillation vial and coated with STP. A crystal was selected, mounted on a glass fiber, and optically centered. The data were collected on a Siemens platform goniometer with a CCD detector. The data were integrated with SAINT (SHELXTL v5.1, Sheldrick, G. M. and Siemens Industrial Automation, 1997) and no absorption correction was applied. The structures were solved by direct methods in conjunction with standard difference Fourier techniques (SHELXTL v5.1, Sheldrick, G. M. and Siemens Industrial Automation, 1997). Non-hydrogen atoms were treated anisotropically, and hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 Å). CIF files for all unpublished structures are available at http://www.reciprocalnet.org/ [numbers 02133 (**3b**), 03145 (**2d**), 02171 (**9**)].

Complex 2a.

The fluorine atoms of the aryl trifluoromethyl groups were modeled over two positions each with half occupancy.

Complex 2d.

Crystals of complex **2d** diffracted poorly resulting in a low data to parameter ratio and rigid bond restraints for anisotropic displacement parameters were used.

Complex 3a

The fluorine atoms of certain thermally disordered trifluoromethyl groups [F(13)–F(15), F(25)–F(27), F(34)–F(36)] were modeled over two positions each with half-occupancy. The hydroxyl hydrogen was identified on the Fourier difference map and its bond distance was refined using a riding model.

Complex 3b

A toluene molecule located on a special position was found to be disordered. The symmetry constraints were relaxed and similarity restraints on 1–2 and 1–3 distances and displacement parameters were used. Rigid bond restraints for anisotropic displacement parameters were also used. The methyl group of the toluene molecule was not located on the Fourier difference map, and was modeled as a benzene molecule. The hydroxyl hydrogen atoms were identified on the Fourier difference map and their bond distances were refined using a riding model.

Complex 9

The fluorine atoms of a trifluoromethyl group [F(4)–F(6)] was disordered and modeled over two positions with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters. Rigid bond restraints for anisotropic displacement parameters were also used. The occupancies for the disordered parts were refined freely and converged at a ratio of 72:28. An acetone molecule located on a special position was also disordered. The symmetry constraints were relaxed and the acetone molecule was refined with restraints mentioned above.

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Research Advisor: Professor Joseph Sadighi

Graduate research has focused the synthesis of reactive Group 11 complexes and their use in catalysis. Synthetic routes to heavily fluorinated ligands were developed. Copper(I) complexes bearing these ligands make highly oxidizing species when exposed to molecular oxygen, capable of intramolecular hydroxylation of electron-poor aromatic C–H bonds. A series of Group 11 fluoride complexes, including the first isolable gold(I) fluoride, were synthesized and their reactivity towards C–F bond formation was assessed. The reactivity of the first well-characterized copper(I) boryl complex towards unsaturated molecules was explored. This complex catalyzes the deoxygenation of CO_2 using bis(pinacolato)diboron as the stoichiometric reductant. Copper(I) boryl species also catalyze the addition of diboron reagents across the C=O bond of aldehydes. The selectivity and mechanism of vinylarene insertion into Cu–B bonds was also examined.

University of Notre Dame — Notre Dame, Indiana
Position: Research Assistant — June 1998–June 2001
Research Advisor: Professor Seth N. Brown

Undergraduate research focused on the mechanism of oxygen atom transfer from metal oxo species to substrates and to other metal centers. The stoichiometric oxidation of triarylphosphines by $O{=}Ir(mes)_3$ was studied. The reaction showed a modest Hammett substituent effect and activation parameters for triphenylphosphine oxidation were determined.

Awards

Notre Dame Scholar — August 1997–1999

Publications

Laitar, D.S.; Sadighi, J. P. "The Insertion of CO_2 into Cu–Si bonds: A Synthetic and Mechanistic Investigation." Manuscript in preparation.

Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. "Efficient Diboration of Aldehydes Catalyzed by Copper(I) Boryl Complexes." Manuscript in preparation.

Akana, Jennifer A.; Hamilton, C. W.; Laitar, D. S.; Sadighi, J. P. "Copper(I)-Catalyzed Nitrene Transfer from Sulfonyl Azides to C–H Bonds." Manuscript in preparation.

Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. "The Insertion of Vinylarenes into a Cu–B bond." *Organometallics* **2006**, *25*, 2405–2408.

Laitar, D. S.; Müller, P.; Sadighi, J. P. "Efficient Homogeneous Catalysis in the Reduction of CO_2 to CO." *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197.

Laitar, D. S.; Müller, P.; Sadighi, J. P.; Gray, T. G. "A Carbene-Stabilized Gold(I) Fluoride: Synthesis and Theory." *Organometallics* **2005**, *24*, 4503–4505.

Mankad, N. P.; Laitar, D. S.; Sadighi, J. P. "Synthesis, Structure and Alkyne Reactivity of a Dimeric (Carbene)copper(I) Hydride." *Organometallics* **2004**, *23*, 3369–3371.

Hamilton, C. W.; Laitar, D. S.; Sadighi, J. P. "Oxidation-resistant, sterically demanding phenanthrolines as supporting ligands for copper(I) nitrene transfer catalysts." *Chem. Commun.* **2004**, 1628–1629.

Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. "Synthesis, Structure, and CO_2 — Reactivity of a 2-Coordinate (Carbene)copper(I) Methyl Complex." *Organometallics* **2004**, *23*, 1191–1193.

Laitar, D. S.; Mathison, C. J. N.; Davis, W. M.; Sadighi, J. P. "Copper(I) Complexes of a Heavily Fluorinated β-Diketiminate Ligand: Synthesis, Electronic Properties and Intramolecular Aerobic Hydroxylation." *Inorg. Chem.* **2003**, *42*, 7354–7356.

Jacobi, B. G.; Laitar, D. S.; Pu, L.; Wargocki, M. F.; DiPasquale, A. G.; Fortner, K. C.; Schuck, S. M.; Brown, S. N. *Inorg. Chem.* **2002**, *41*, 4815–4823.

Presentations

Laitar, D. S.; Müller, P.; Sadighi, J. P. "Catalytic Carbon Dioxide Deoxygenation by (NHC)copper(I) Boryl Complexes." 230th ACS National Meeting, Washington, DC, United States, Sept. 1, 2005.

Laitar, D. S.; Sadighi, J. P. "Group 11 Metal Fluoride Complexes of N-Heterocyclic Carbene Ligands: Synthesis, Structure and Reactivity." Invited presentation, Bruker/MIT Symposium, MIT, Jan. 15, 2005.

References

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