I, Arundhoti Chakraborty, hereby submit this original work as part of the requirements for the degree of Doctor of Philosophy in Chemistry.

It is entitled:
Development of Copper Catalysts for the Reduction of Polar Bonds

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Development of Copper Catalysts for the Reduction of Polar Bonds

A Dissertation Submitted to the
Graduate School
of the University of Cincinnati
in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY (Ph.D.)

in the Department of Chemistry
of McMicken College of Arts and Sciences by

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ABSTRACT

This thesis focuses on the synthesis of new transition metal complexes that show metal–metal cooperativity and metal-ligand cooperativity. Late-late and early-late heterobimetallic complexes have been synthesized and employed in important chemical transformations like benzaldehyde (PhCHO) reduction under water-gas shift reaction (WGSR) conditions and reduction of an imine moiety respectively. A bifunctional hexameric copper hydride complex has also been isolated and utilized in the catalytic hydrogenation of aldehydes, ketones and CO₂.

I have synthesized late-late heterobimetallic complexes containing Fe–Cu bonds where the iron center is supported by a Knölker-type cyclopentadienone ligand and the copper center is ligated to a N-heterocyclic carbene. Reactions between the Knölker’s iron tricarbonyl complexes (SiMe₃ and tBu derivatives) and (IPr)CuOH lead to the formation of new Fe/Cu heterobimetallic complexes that contain a bridging hydride in the solid state. Solution IR, ¹³C{¹H} NMR analysis and variable temperature NMR suggest a dominant terminal iron hydride structure in solution for the SiMe₃ derivative.

Stoichiometric reactions of these Fe/Cu complexes with alkyl halides lead to the formation of new Fe/Cu halide complexes. Under a CO atmosphere, these Fe/Cu complexes generate the corresponding iron tricarbonyl species and the dimeric (IPr)CuH complex. Reduction of PhCHO to PhCH₂OH was successfully performed under water-gas shift reaction conditions. Both metal centers are necessary to carry out the reaction demonstrating the importance of metal–metal cooperativity. Isotope labelling studies performed with ¹³CO confirmed that the Fe/Cu catalyst is indeed active in WGSR.
In my second project I have synthesized and isolated a new copper hydride supported by a bis(phosphine)amine \[^{\text{iPr}}\text{PN(H)P}\] ligand with a hexameric copper core. The assignment of the hydride peak in the \(^1\text{H}\) NMR spectrum was confirmed by comparing the \(^1\text{H}\) NMR spectrum of the related copper deuteride complex. Benzaldehyde and acetophenone insert into the Cu–H bond to afford the corresponding copper alkoxide products. \(\text{CO}_2\) also undergoes a facile insertion into the Cu–H bond to form the corresponding copper formate species. Isotope labelling study indicates that the insertion is reversible but favors the formation of copper formate. Hydrogenation of aldehydes, ketones and \(\text{CO}_2\) has been carried out with the copper bromide precursor under mild conditions. The copper hydride complex also serves as an effective catalyst in the hydrogenation of benzaldehyde implying its direct involvement in the catalytic reaction. Catalytic inactivity of the copper bromide species containing the \[^{\text{iPr}}\text{(PN(Me)P}]\) ligand in the hydrogenation reaction implies a bifunctional mechanism; however, further investigation is needed to support this mechanism.

My third project focuses on the synthesis of early-late heterobimetallic complexes containing Cr–Cu bonds and the respective metal centers are supported by bulky \(\text{Cp}^*\) (\(\text{Cp}^* = 1,2,3,4,5\text{-cyclopentadienyl}\)) and \(N\)-heterocyclic carbene ligands. It was hypothesized that the polarity of the Cr–Cu bond and the steric crowding at the metal centers could assist in the activation of small molecules. Although activation of a variety of substrates such as \(\text{H}_2\), \(\text{CO}_2\) etc. proved unsuccessful, catalytic hydrogenation of an imine substrate led to the formation of the corresponding amine at higher temperature and pressure.
Preface

Part of this thesis has been adapted from an article co-written by the author. The following article was reproduced in part with permission from the American Chemical Society.

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ACKNOWLEDGEMENTS

I would like to express my immense gratitude toward my advisor Professor Hairong Guan for all his support and guidance throughout my PhD. He has been a source of constant inspiration and always provided me with insightful suggestions whenever I needed. He has taught me to be a better scientist, how to think independently and critically and that how important it is to be meticulous when we are either doing experiments or writing a manuscript. Besides being a great mentor, he has also been like a guardian to me. I am extremely grateful to him for being so understanding in my time of personal loss and letting me take some extra time off to be with my family when they needed me the most.

I was very fortunate to have Dr. William B. Connick and Dr. David B. Smithrud as my dissertation committee members. Their continuous helpful suggestions and critical questions have helped me evolve as a better scientist over the years. I also want to extend my gratitude toward all other faculty members of the Department of Chemistry at University of Cincinnati.

I would also like to thank our staff scientists Dr. Jeanette Krause who has helped me in solving my crystal structures which were very crucial to the growth and understanding of my projects and also Dr. Necati Kaval for repeatedly helping me with all my IR studies.

I want to thank my past and current group members without whom my PhD experience wouldn’t have been the same. I am extremely grateful to my senior group members Dr. Sumit Chakraborty who is also my husband, Dr. Sanjeewa Rodrigo and Dr. Anubendu Adhikary for teaching me the lab techniques to handle air sensitive compounds and also for offering me many useful suggestions in general. It was fun to work with Dr. Gleason Wilson, Dr. Papri Bhattacharya, Dr. Aaron Bailey and Becca Ransohoff. I would like to thank my current group members Nadeesha Wellala, Nathan Eberhardt, Yingze Li, Huiguang Dai, Becca Haley and our
current postdoc Dr. Jacek Pecyna. It has been so much fun to work with you all. Thank you Nadeesha for being such a great friend and for sharing so many good conversations. We had a lot of fun whenever we travelled to conferences together. I will always cherish those moments. Thank you Huiguang and Yingze for giving me ride to Kroger, Walmart and airport. I like to thank Nathan for being so helpful specially taking out his time to help me fix my vacuum pump. Becca Haley is one of the most generous people I have met in Cincinnati and I thank her for all the help as well. I have overlapped with Jacek only for a short period of time yet we have become such great friends and I love how he spoils us all with his delicious baked foods.

I am fortunate to have mentored very bright undergrads both from the REU program and from Inorganic Honors lab and I wish them all the best in their future endeavors.

Lastly, I would like to acknowledge and express my heartfelt gratitude toward my father Late Dhana Krista Goswami, my mother Anurupa Goswami and my husband Sumit Chakraborty. Without their unwavering support this thesis wouldn’t be complete. I can’t thank my mother enough for all the sacrifices she made for me, I am eternally grateful to her. Thank you Sumit for being so supportive and for being there through thick and thin of my life. Without your constant support and encouragement, I couldn’t have done this. My father has been the biggest motivation in my life and will always remain so. Even though he is not with us anymore, I know he would be extremely proud of me. His strong determination and passion for hard work has given me the courage to challenge my own boundaries. His dream was to see me earn the PhD degree and therefore with much love and affection I dedicate this dissertation to my beloved father.
Chapter 1

Introduction
1.1 INTRODUCTION

One of the major goals of the organometallic/catalysis community is to replace toxic, expensive, and precious metal-derived catalysts with those bearing base metals which are in general non-toxic, earth abundant, and inexpensive.\(^1\) However, because many catalytic transformations rely on two-electron redox processes, base metal complexes are usually inferior catalysts because of their tendency to undergo one-electron processes. In order to circumvent this issue, three main approaches have been developed to replace precious metal-based catalysts: (a) metal–ligand cooperativity,\(^2\) (b) metal–metal cooperativity,\(^3\) and (c) the Lewis acid–base cooperativity in Frustrated Lewis acid-base pairs (FLP, a non-metal approach).\(^4\) “Cooperativity” is broadly defined as interaction of molecules with synergistic action of two or more compounds or multiple components within one compound during a chemical reaction.\(^3\) In the following sections of this chapter, metal–metal cooperativity and metal–ligand cooperativity will be discussed in details as they form the basis of the following chapters of this dissertation. A brief description of the FLP systems will be given in Chapter 4 and therefore not covered in this chapter.

1.2 METAL–METAL COOPERATIVITY IN BIMETALLIC SYSTEMS

Cooperativity between two metal centers exists in both homobimetallic and heterobimetallic complexes. Discrete homobimetallic complexes have been studied in great


details and they have been successfully applied in many catalytic processes. In comparison, catalytic applications of heterobimetallic complexes, and those containing metal–metal bonds in particular, remain underdeveloped to date. A large number of heterobimetallic complexes are composed of electrophilic early-transition metals and nucleophilic late-transition metals. Traditionally, these type of complexes are called “early-late” heterobimetallic complexes. It is often postulated that bringing a nucleophilic late transition metal and an electrophilic early transition metal in proximity may form a polar metal–metal bond, which may activate substrates through different pathways (Scheme 1). The soft Lewis-basic late transition metal may show reductive reactivity (with respect to the substrate) while the hard Lewis-acidic early transition metal may aid in the oxidative of the substrate. The ability of the two metal centers to serve different roles during a concerted reaction or sequential steps of a reaction is often termed as “metal–metal cooperativity” and is a subject of study by many research groups.

Scheme 1. Modes of substrate-activation by the heterobimetallic metal-metal bonds.

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### 1.2.1 Stoichiometric Reactions of Early-Late Heterobimetallic Complexes

Some of the early work focusing on the reactivity of early-late heterobimetallic complexes was performed by the research groups of Bergman and Casey. Bergman and co-workers investigated the reactions of \( \text{Cp}_2\text{Zr}(\mu-N^\text{Bu})\text{IrCp}^* \) (1, \( \text{Cp} = \text{cyclopentadienyl, Cp}^* = 1,2,3,4,5\text{-pentamethylcyclopentadienyl} \)) with a variety of substrates including \( \text{H}_2, \text{CO}_2, \text{allenes}, \text{phosphines}, \text{alcohols, thiols}, \text{etc} \) (Scheme 2).\(^7\) The Casey group studied the reactivity of bimetallic \( \text{Cp}_2\text{XZr-Ru(CO)}_2\text{Cp} \) \( \text{(X = Me, Cl, O}^\text{Bu} \text{)} \) and trimetallic \( \text{Cp}_2\text{Zr[Ru(CO)}_2\text{Cp}_2 \) systems.\(^8\)

**Scheme 2.** Stoichiometric reactions of Bergman’s Zr/Ir heterobimetallic complexes.

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More recently, a broad range of stoichiometric reactions including C–H, CO and H₂ activation, and insertion into metal-alkyl and metal-hydride bonds were reported with early-late heterobimetallic complexes. For example, a Zr/Ir bridged polyhydride complex (2) was found to activate the \textit{ortho} C-H bonds of pyridine derivatives presumably via pre-coordination of the pyridine N-atom (Scheme 3, eq 1). Oishi and Suzuki demonstrated that \( \text{Bu}_2\text{Si}(\eta^5-\text{C}_5\text{H}_4)_2(\text{C}_6\text{H}_5)\text{Zr}(\mu-\text{H})_3\text{IrCP}^* \) (3) undergoes rapid H/D exchange with \( \text{C}_6\text{D}_6 \) involving the phenyl and bridging hydride ligands (Scheme 3, eq 2). A Ni/Mo complex \( \text{Cp}^*\text{Ni}=\text{Mo}(\mu-\text{CO})(\text{CO})_2(\text{Cp}) \) was applied in C–H activation of methyl acrylate. Heterolytic cleavage of H₂ was reported with a sulfide-bridged W/Ru complex \( \text{Cp}^*(\text{O})\text{W}(\mu-\text{S})_2\text{Ru}(\text{PPh}_3)_2\text{Cl} \) (4) in the presence of \( \text{NaBAR}_4^F \left( \text{Ar}^F = 3,5-\text{C}_6\text{H}_3(\text{CF}_3)_2 \right) \) to form \( [\text{Cp}^*(\text{OH})\text{W}(\mu-\text{S})_2\text{Ru(H)(PPh}_3)_2]\text{BAR}_4^F \) (Scheme 3, eq 3). Mechanistic studies showed that H₂ binds to the ruthenium center after initial chloride abstraction and is likely to be deprotonated by the basic W=O moiety. Thomas and co-workers reported a highly reduced Zr/Co heterobimetallic species capable of oxidatively adding two equivalents of dihydrogen. In addition to these reactions, migratory insertion of CO ligand into a Zr–C bond was observed for a \( \text{Me}Zr(\mu-\text{Cp}-\text{PPh}_3)_2(\text{CO})\text{Rh(PPh}_3) \) complex (5) to form an acyl-bridged Zr/Rh heterobimetallic complex (Scheme 3, eq 4). Several examples involving CO insertion into Pd–Me bonds of well-defined Fe/Pd complexes were documented as well. Insertion of a terminal alkyn PhC≡CH into the Pt–H bond of an Fe/Pt heterobimetallic complex (6) was also reported (Scheme 3, eq 5). The insertion product was identified to be \( \sigma \)-alkenyl complex stabilized by the

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14 Cornelissen, C.; Erker, G.; Kehr, G.; Frohlich, R. \textit{Organometallics} \textbf{2005}, \textit{24}, 214
coordination of a methoxysilyl group to the platinum center. In addition to the aforementioned studies, thiol (RSH), H\(_2\)S, halogen activation and C–C bond forming reactions have also been reported for early-late heterobimetallic complexes.\(^{3c}\)

**Scheme 3.** Stoichiometric reactions of early-late heterobimetallic complexes.

1.2.2 Catalytic Activity of Early-Late Heterobimetallic Complexes

Applications of early-late heterobimetallic complexes in homogeneous catalysis are rather limited compared to many examples of stoichiometric reactions as highlighted above. One of the major issues associated with the use of early–late heterobimetallic complexes in catalysis is the formation of thermodynamically robust early metal–heteroatom bonds (e.g., M–O, M–N, M–Cl, etc.) in potential intermediates. Catalysis is often inhibited as it is difficult to engage these robust intermediates in any further reactions. Nonetheless, catalytic applications of early-late heterobimetallic complexes have been demonstrated in hydrosilylation, hydrogenation, dehydrogenation and C–C bond forming reactions. A few selected examples highlighting the importance of metal–metal cooperativity are described hereafter. In a report by Ishii and co-workers, dithiolate-bridged Pt/Ir complexes were found to be active in the hydrosilylation of alkynes to form $\beta$-(Z) vinylsilanes selectively. A study by Nikonov and co-workers demonstrated that phosphide-bridged Nb/Rh heterobimetallic complexes were active in the hydrosilylation of both aldehydes and ketones. Interestingly, for the Nb/Rh system, the monometallic rhodium complex was found to be an equally effective hydrosilylation catalyst. A titanocene diphosphine $\text{Cp(C}_5\text{Me}_3\text{-1,2-(PPh}_2\text{)}_2\text{)}\text{TiCl}_2$ fragment connected to a cationic Rh(COD) (COD = 1,4-cyclooctadiene) moiety turned out to be a good hydrosilylation catalyst for aryl

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Catalytic Activity of Early-Late Heterobimetallic Complexes}
\end{figure}

ketones.\textsuperscript{19} The oxophilicity of titanium was hypothesized to be the origin of cooperativity in this bimetallic complex.

Homogeneous hydrogenation of CO\textsubscript{2} to formic acid and the reverse reaction, namely the dehydrogenation of formic acid, were shown to be catalyzed by Mo/Ru and W/Ru heterobimetallic complexes (Scheme 4).\textsuperscript{20} Individual monometallic fragments did not show any reactivity in these reactions, suggesting that defragmentation to monometallic species does not occur during the catalysis and both metals play a critical role during the reaction. In addition to the hydrogenation reactions, bimetallic complexes $EM(\mu$-Cp-P\textsubscript{2}El\textsubscript{2})\textsubscript{2}M'\textsuperscript{*Cp} (M = Zr, Hf; M' = Ru, Fe; E = Cl, Me, or NMe\textsubscript{2}) were found to be active catalysts for the dehydrogenation of dimethylamine-borane, a potential hydrogen-storage material (Scheme 5).\textsuperscript{21} Interestingly, monometallic Zr or Hf metallocenes were completely inactive and mononuclear Ru complexes exhibited much lower catalytic efficiency. Therefore a bimetallic cooperative pathway was proposed which involved a bridging Zr–H–Ru hydride as a catalytically active species. This species was presumably generated via the interaction of N–H moiety of the amine-borane with the heterobimetallic complex.

\textsuperscript{19} Comte, V.; Le Gendre, P.; Richard, P.; Moise, C. Organometallics \textbf{2005}, \textit{24}, 1439.

Scheme 5. Proposed cooperative mechanism for the dehydrogenation of amine-borane.

Proposed Mechanism
Heterobimetallic complexes have also been employed in C–C bond forming reactions. Lau and co-workers have unveiled discrete Ru/Mn complexes where an electrophilic Ru(II) center is linked to a highly nucleophilic Mn(−I) center. These complexes, which contain highly polar dative Mn–Ru bonds, effectively catalyze the reaction between epoxides and CO$_2$ to generate cyclic carbonates (Scheme 6). Monomeric Mn(−I) and Ru(II) species proved to be either less effective or completely inactive in this transformation. Computational studies supported an initial coordination of the epoxide moiety to the electrophilic ruthenium center, followed by epoxide ring opening assisted by the nucleophilic manganese center. A series of similar Re/Ru bimetallic complexes were examined in the catalytic addition reactions involving terminal alkynes and carboxylic acids to yield enol esters (Scheme 6). In addition to these applications, early-late heterobimetallic species have been reported for other catalytic processes such as hydroformylation, cross-coupling reactions and polymerization. 

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1.2.3 Stoichiometric and Catalytic Activity of Late-Late Heterobimetallic Complexes

As mentioned earlier, catalysis with early-late heterobimetallic complexes is often inhibited by the formation of strong bonds between the electrophilic early-transition metals and heteroatoms such as O, N and halogens. To circumvent this issue, much effort has been focused on heterobimetallic complexes in which the electrophilic early-transition metal is replaced by a late transition metal. These complexes are termed as “late-late” heterobimetallic complexes in the literature. In comparison to early-late complexes, heterobimetallic complexes containing electrophilic late-transition metal centers are much less common.\(^{27}\) However, the unique

structures and reactivity of such complexes unveiled by several research groups\textsuperscript{28,29} in recent years suggest that this has become an emerging and exciting field. In 2003, Morise and co-workers reported an Fe/Cu heterobimetallic catalyst bearing a phosphinoxazoline ligand for olefin cyclopropanation and Diels-Alder reactions. More recently, Mankad and co-workers studied the structures, bonding and reactivity of late-late heterobimetallic complexes containing unsupported Fe–Cu, Fe–Zn bonds. According to DFT (Density Functional Theory) analysis, these short metal–metal bonds are polarized (Fe\textsuperscript{δ}…Cu\textsuperscript{δ+}), and interestingly the Cu and Zn metals are found to be electrophilic whereas the Fe center is nucleophilic. Consistent with this polarity assignment, a reaction between (NHC)Cu–FeCp(CO)\textsubscript{2} (NHC = N-heterocyclic carbene) and Mel produced (NHC)CuI and MeFeCp(CO)\textsubscript{2} (eq 6).\textsuperscript{29}\textsuperscript{a} (NHC)Cu–FeCp(CO)\textsubscript{2} complex was also shown to react with CS\textsubscript{2} to form a dimeric CS\textsubscript{2}-bridged Fe\textsubscript{2}Cu\textsubscript{2} species with two types of binding modes observed for the CS\textsubscript{2} ligand (eq 7). A reaction of Fe/Cu complex with N\textsubscript{2}O resulted into a product where the cyclopentadienyl ligand migrated from iron to copper (eq 8).\textsuperscript{29}\textsuperscript{i} Activation of RCH\textsubscript{2}Cl (R = 4-F\textsubscript{3}CC\textsubscript{6}H\textsubscript{4}, 4-NCC\textsubscript{6}H\textsubscript{4}) by the Fe–Cu bond occurred to form the corresponding Fe–CH\textsubscript{2}R species


and \((\text{NHC})\text{CuCl}\) (eq 9). Using cyclopropylmethyl halide substrates demonstrated that alkyl halide activation occurs via a non-radical mechanism for alkyl bromides and chlorides but not for alkyl iodides.\(^{29d}\)

\[
\begin{align*}
\text{N} & \quad \text{Cu} \quad \text{Fe} \\
\text{N} & \quad \text{Cu} \quad \text{I} \\
\text{N} & \quad \text{Me} \quad \text{Fe} \\
\end{align*}
\]

\(\text{R} = \quad \text{and} \quad \text{and} \)

\[
\begin{align*}
\text{N} & \quad \text{Cu} \quad \text{Fe} \\
\text{N} & \quad \text{Cu} \quad \text{I} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{S} \\
\end{align*}
\]

\(\text{R} = \quad \text{and} \quad \text{and} \)

\[
\begin{align*}
\text{N} & \quad \text{Cu} \quad \text{Fe} \\
\text{N} & \quad \text{Cu} \quad \text{I} \\
\end{align*}
\]

\(+ \text{ intractable Fe species} \)
Mankad and co-workers have also demonstrated that (IPr)Cu−FeCp(CO)$_2$ (IPr = $N,N'$-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and (BDI)Zn−FeCp(CO)$_2$ (BDI = 2-(2,6-diisopropylphenyl)amido-4-(2,6-diisopropylimino)-2-pentene) complexes can catalyze C−H borylation of arenes under photochemical conditions (Scheme 7).$^{29b}$ At room temperature under neat conditions, several arene substrates including benzene were borylated by pinacolborane (H−Bpin) in the presence of 10 mol% (IPr)Cu−FeCp(CO)$_2$, and a 450 W-Hg lamp light source. Control studies with monometallic (IPr)CuCl and related iron complexes show minimal to no activity, highlighting the critical role of metal−metal cooperativity in this reaction. An analogous (IPr)Cu−FeCp*(CO)$_2$ complex was found to be less reactive than the Cp derivative. In a separate report, it was shown that the product selectivity for CO$_2$ reduction could be altered by employing monometallic and bimetallic catalysts. For example, hydroboration (H−Bpin) of CO$_2$ with (IPr)CuO$^t$Bu exclusively afforded boryl formate (pinB−OC(O)H) whereas the same reaction with (IPr)Cu−FeCp(CO)$_2$ and (IPr)Cu−MCp(CO)$_3$ (M = Mo, W) selectively produced CO and pinB−OC(O)H with a ratio of >20:1.$^{29j}$ Furthermore, the related (NHC)M−M′Cp(CO)$_2$ complexes (M = Cu, Ag and M′ = Fe, Ru) exhibited superior catalytic performance in the semi-hydrogenation
of internal alkynes to produce primarily $E$-selective alkenes under only 1 atm of H$_2$ pressure (eq 10).$^{29a}$

**Scheme 7.** C–H Borylation of arenes with Fe/Cu heterobimetallic catalysts.

In the field of synthetic organometallic chemistry, metals play crucial roles in breaking or forming chemical bonds by elementary reactions such as oxidative addition, reductive elimination and $\beta$-hydride elimination. Generally speaking, the ligands do not participate in the bond-breaking/making step. In contrast, bond activation in many enzymes occurs with active participation of both the metals and the ligands. For example, H$_2$ activation by hydrogenases.
typically proceeds via a cooperative mechanism where heterolytic activation of H−H bond takes place across the metal–ligand bond without a net change in metal’s oxidation state.\(^{30}\) Therefore, cooperating ligands may be defined as those which participate directly in the bond activation reaction. In such bifunctional systems the metal and the ligand act in a synergistic manner and their interplay facilitates a chemical reaction. Metal-ligand bifunctional catalysis has represented a new concept for the development of transition metal catalysts for a variety of chemical processes.\(^{31}\) One of the widely studied reactions that utilize bifunctional catalysis is the hydrogenation of polar, unsaturated carbon–heteroatom bonds. Among various cooperating ligands reported in the literature, amido ligands have received much attention for homogeneous hydrogenation of unsaturated substrates R(R')C=X, especially for aldehydes, ketones and imines (X = O, NR)\(^{1,32}\). Research in this area was sparked by the seminal discovery of Noyori’s chiral Ru(II) amido complexes for asymmetric hydrogenation of ketones that showed high activity (turnover frequency > 20000 h\(^{-1}\)) and enantioselectivity (ee > 98\%) (Scheme 8).\(^{33}\) The reaction mechanism involves heterolytic activation of H\(_2\) across the Ru–amido bond (A) to form an Ru-amino hydride complex (D). The substrate-binding occurs in the second coordination sphere through the interaction with the N−H\(^+\delta\) and Ru−H\(^-\delta\) moieties (E) and the hydrogen transfer proceeds in a concerted fashion. Grützmacher et. al. have developed an Rh(I)-amido complex with a sawhorse-type structure that cleaves H\(_2\) heterolytically across the Rh−N bond in a single step.\(^{34}\) The oxidative addition of H\(_2\) to the Rh(I) center to form a Rh(III)(H)\(_2\) species has a much

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higher activation barrier and is an endothermic process. Thus, this system also highlights the importance of metal–ligand cooperation in the activation of dihydrogen. During the past decade, several research groups have successfully utilized ruthenium–amido,\textsuperscript{35} osmium–amido\textsuperscript{36} and iridium–amido\textsuperscript{37} linkages as a means to catalytically hydrogenating C=O and C=N bonds (selected examples are shown in Figure 1) and have demonstrated metal–ligand cooperation in these systems.

**Scheme 8.** Catalytic Hydrogenation of Ketones with Noyori’s Ru-amido complexes.

![Scheme 8](image)

**Figure 1.** Selected examples of hydrogenation catalysts bearing Ru-amine linkages.


Our group has recently reported a series of iron complexes (7-9) supported by a bis(phosphino)amine \[{\text{Pr}PN(H)P}\] ligand (Scheme 9). These molecules were designed to incorporate the following features: (a) a bifunctional ligand that has a high binding affinity for iron and can deliver proton and hydride during hydrogenation processes, (b) a strong-field ligand such as CO to force iron to a low-spin state and (c) a strongly trans-directing ligand like hydride and borohydride to facilitate hydride transfer. Additionally, it was anticipated that an iron-amido bond would be generated to heterolytically cleave dihydrogen in a similar manner as its ruthenium analogues. The iron hydridoborate complex (8) was reported by both the Beller group and our group to be an efficient catalyst for the hydrogenation of esters under mild conditions. Remarkably, in addition to common aromatic and aliphatic esters, the iron catalyst could be employed to hydrogenate a mixture of long-chain fatty methyl esters to produce the corresponding fatty alcohols in high yields. The same iron catalysts showed superior catalytic activity in the hydrogenation of ketones and nitriles. Beller and co-workers showed that replacing the NH moiety with NMe resulted in an iron complex catalytically inactive for ester hydrogenation. This result suggests that the formation of iron-amido species during catalysis is critical. Interconversion between iron-amido and iron-amine species in the presence or absence of H\(_2\) was directly observed by NMR spectroscopy (Scheme 9).

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Scheme 9. Hydrogenation of esters with bifunctional iron catalysts.

Another well-known example of iron-based metal-ligand bifunctional catalysis was demonstrated by Casey and Guan in 2007. In this report, a hydroxycyclopentadienyl iron dicarbonyl hydride (10), first reported by the Knölker group,


catalyzed chemoselective hydrogenation of ketones (Scheme 10).

With aromatic aldehydes as the substrates for stoichiometric reduction reactions, cyclopentadienone Fe(0) alcohol complexes were successfully
synthesized, and one of the compounds was also studied by X-ray crystallography (12, Scheme 10). Isotope labeling experiments, reaction kinetics, and other mechanistic studies supported an outer sphere mechanism where the acidic hydrogen from the –OH group and the basic iron hydride are delivered to the C=O bond in a concerted fashion. This system demonstrates metal–ligand cooperativity via hapticity change of the cyclopentadienone moiety.

Scheme 10. Catalytic hydrogenation of ketones with the Knölker’s iron complex.

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1.4 GOALS OF THE RESEARCH PROJECTS

The goals of my dissertation research are twofold:

(a) Synthesize well-defined late-late and early-late heterobimetallic complexes and investigate their stoichiometric and catalytic activity towards small molecules. I have also focused my research on applying these heterobimetallic complexes in catalytic reduction of C=O and C≡N bonds.

(b) Synthesize new copper hydride complexes supported by cooperating ligands and employ them in catalytic hydrogenation of carbonyl groups.
Chapter 2

Cooperative Iron-Oxygen-Copper Catalysis in Reduction of Benzaldehyde Under the Water-Gas Shift Reaction Conditions
2.1 INTRODUCTION

Enzymes perform catalytic reactions in a remarkably efficient and selective manner by virtue of their ability to bind and activate substrates with synergistic action of amino acid side chains and cofactors.\(^1\) Inspired by the biological systems, synthetic chemists have successfully designed metal complexes, non-metal compounds, or the combination of thereof that can also activate molecules with multiple points of interaction.\(^2\) Recent advances in homogeneous catalysis have largely benefited from new strategies developed for small molecule activation, particularly utilizing the synergy between the two metals of a heterobimetallic complex,\(^3\) metal and a heteroatom (or a carbon atom) within a metal-ligand bifunctional catalyst,\(^4\) or a frustrated Lewis pair.\(^5\) More complex systems featuring the interaction of substrates with more than two


functional sites are being developed and showing great promise for homogeneous catalysis. Understanding the intricate role of each functional site of these well-defined systems is crucial to the rational design of new catalysts with improved efficiency and selectivity.

In recent years, a number of iron-based metal-ligand bifunctional catalysts have been developed for the reduction of carbonyl groups, a research area primarily driven by the interest in catalysis using earth-abundant metals such as iron. The first such catalyst is the Knölker complex (Figure 1), which was reported in 1999 but not known as a hydrogenation catalyst until Casey’s work published in 2007. Mechanistic studies have suggested that the acidic OH and hydridic FeH hydrogens are simultaneously transferred to a C=O bond, resulting in selective hydrogenation of aldehydes and ketones. Structural modifications to the Knölker complex have been made, including changing substituents on the cyclopentadienyl ring, substituting a chiral phosphoramidite for one of the CO ligands, and replacing the OH group with a silyl or germyl.

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These complexes and the related (cyclopentadienone)iron tricarbonyl 
complexes have been demonstrated as effective catalysts for a broad range of chemical 
transformations.

**Figure 1.** The Knölker complex and its derivatives (structural modifications highlighted in red).

We present here a new class of compounds bearing three potential functional sites as 
highlighted in Figure 2. Incorporating copper into the metal-ligand bifunctional system could 
create additional reaction pathways that are unavailable or inefficient with Knölker-type 
complexes alone. They also differ from the reported Fe-Cu heterobimetallic complexes whose

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15 Many (cyclopentadienone)iron tricarbonyl complexes were explored as precursors to Knölker-type 
complexes, although the proposed terminal iron hydride species were not isolated or spectroscopically 
Biomol. Chem.* **2012**, 10, 134. (c) Moulin, S.; Dentel, H.; Pagnoux-Ozherelyeva, A.; Gaillard, S.; Poater, 
Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, 52, 5120. (e) Johnson, T. C.; Clarkson, G. J.; Wills, M. 
reactivity is mainly governed by the polarization of the Fe–Cu bond.\textsuperscript{17} Our preliminary study shows that these “metal-ligand-metal trifunctional” catalysts, as one might call them, can promote the reduction of benzaldehyde under the water-gas shift reaction (WGSR) conditions. Reactivity exhibited by these new complexes versus the component complexes establishes the synergy of iron, oxygen and copper during the catalytic process.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{complex.png}
\caption{Heterobimetallic complexes with three potentially functional sites (L = ligand).}
\end{figure}

\section*{2.2 RESULTS AND DISCUSSION}

\subsection*{2.2.1 Synthesis and Characterization of Fe-Cu Heterobimetallic Complexes.}
According to Knölker’s original report,\textsuperscript{9} mixing a THF solution of iron tricarbonyl complex 1a with a 1 M aqueous solution of NaOH (NaOH/1a = 8.4) produces the Knölker complex 2a and its deprotonated form 3a in a 13 : 1 ratio (eq 1). This result implies that 3a reacts with water reversibly to yield 2a and NaOH, and the equilibrium lies to the 2a/NaOH side. We therefore surmised that, to synthesize the targeted Fe-Cu heterobimetallic complexes as illustrated in Figure 2, we could simply replace NaOH with a copper hydroxide complex (LCuOH) and carry out the reaction in a non-aqueous medium to avoid hydrolysis of the product.

In searching for copper hydroxide complexes, the one that caught our attention the most was Nolan’s (IPr)CuOH (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene), which was reported to react with a wide variety of molecules containing acidic hydrogens. Its hydroxide group is also nucleophilic, showing similar reactivity as NaOH when mixed with iron tricarbonyl complexes 1a-c in C₆D₆ (eq 2). At room temperature, 1a disappears completely after 48 h, providing a hydride species 4a with a characteristic ¹H resonance at –12.58 ppm. A similar reaction with 1b is much more sluggish; after 72 h, roughly 50% of 1b is converted to 4b (δH = –13.37 ppm). It is well known from other studies that the tendency for metal carbonyl complexes to undergo nucleophilic attack correlates with the force constants or stretching frequencies of the CO ligands. A lower force constant is indicative of a less positive charge on the carbon. Consistent with this analysis, the CO stretching frequencies of 1b (2057, 1997 and 1980 cm⁻¹, in CH₂Cl₂) were found to be lower than those of 1a (2064, 2008 and 1985 cm⁻¹, in CCl₄). In fact, the reaction of 1b with NaOH in THF/H₂O is sluggish too. Under reflux conditions for 16 h,

\[ \text{Fe} \left( \text{SiMe₃} \right)₂ \text{CO} + \text{NaOH} \rightarrow \text{Fe} \left( \text{SiMe₃} \right)₂ \text{H} + \text{Na}_2 \text{CO}_3 \]


only 14% of 1b is converted to the corresponding iron hydride species 2b. In contrast, the same reaction of 1a at room temperature reaches completion within 2.5 h (eq 1). Interestingly, the phenyl-substituted complex 1c reacts with (IPr)CuOH more rapidly, which is attributed to a less sterically demanding cyclopentadienone ring. The reaction is typically complete within 6 h, resulting in a new iron hydride \( \delta_H = -10.94 \text{ ppm} \) as confirmed by \(^1\text{H} \) NMR.

Complexes 4a and 4b can be isolated in an analytically pure form when the Hieber-type reaction is carried out overnight at 60 °C (Scheme 1). Unfortunately, isolating pure 4c is not possible due to its facile decomposition during work-up. This is not surprising considering that the related Knölker-type complex (i.e., replacing (IPr)Cu in 4c with H) is also short-lived. Compound 4a can be independently synthesized by reacting the Knölker complex 2a with (IPr)CuOH (or alternatively (IPr)CuO\( ^t\)Bu\(^23\)) for only 30 min. Because one equivalent of water is generated as the by-product, the success of this method suggests that these Fe-Cu heterobimetallic complexes are not as moisture sensitive as originally thought. On the contrary, they are very stable in the presence of water. Monitoring the mixture of 4a and 10 equiv of water (in C\(_6\)D\(_6\)) at 60 °C for 48 h shows no sign of any reaction, although at 100 °C, 4a starts to decompose to some black precipitate. Unlike the Knölker complex, which changes color under

\[ \text{Fe(CO)}_3(C_5H_5) + \text{Cu(OH)}_2 \rightarrow \text{FeH(CO)}_2(C_5H_5) \text{Cu} \]

\[ \text{FeH(CO)}_2(C_5H_5) \text{Cu} \]

\[ \delta_H = -10.94 \text{ ppm} \]

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22 The CO stretching frequencies of 1c (2065, 2010 and 1986 cm\(^{-1}\), in CCl\(_4\)) are almost identical to those of 1a. For details, see Ref. 21.

ambient fluorescent lighting.\textsuperscript{11a} 4a and 4b are not light sensitive.

**Scheme 1.** Synthetic routes to the Fe-Cu heterobimetallic complexes

![Scheme 1](image)

**2.2.2 Solid-State and Solution Structures.** Solid-state structures of the two isolated Fe-Cu heterobimetallic complexes were studied by X-ray crystallography. To our surprise, in both cases (IPr)Cu\(^+\) was found to bind to the Fe–H moiety rather than to the oxygen (Figure 3). The short C29–O1 distance [1.250(5) Å for 4a', 1.244(5) Å for 4b'] is best described as a C=O unit of a cyclopentadienone ligand, which adopts an envelope-shape conformation with C29 representing the flap. Like other cyclopentadienone iron complexes reported in the literature,\textsuperscript{13,14,15e-h,21,24} the Fe…C29 distance is 0.24-0.30 Å longer than the Fe–C bonds formed between iron and the cyclopentadienone ligand (Table 1). Compounds 4a' and 4b' can thus be viewed as (IPr)Cu–H being σ bonded to a formally 16-electron Fe(0) species.\textsuperscript{25} The Fe–Cu distance of 4a' [2.4959(9) Å] is comparable to those of many other Fe-Cu heterobimetallic complexes.


\textsuperscript{25} A better description of the heterobimetallic core is 3-center-2-electron Fe–H–Cu interaction. For details, see: Parkin, G. Struct. Bond 2010, 136, 113.

29
complexes;\textsuperscript{26} however, it is noticeably longer than the Fe–Cu distance of 4b' [2.4059(9) Å], (NHC)Cu–Fe(C₅R₅)(CO)₂ (R = H or Me) [2.3215(3)–2.3514(7) Å],\textsuperscript{17a,c} and (Ph₂EtP)₃Fe(μ-H)₃Cu(PEtPh₂) [2.319(2) Å],\textsuperscript{27} likely due to greater steric hindrance exerted by the SiMe₃ groups. In the case of 4a', the hydride was located from the difference map and shown to bridge both iron and copper. One of the CO ligands has close contact with copper [d(Cu–C) = 2.486(5) Å], which is similar to what was observed for (NHC)Cu–FeCp(CO)\textsubscript{2} \textsuperscript{17a} and categorized as a semibridging binding CO.\textsuperscript{28} Compared to 4a', the CO ligands in 4b' approach copper more closely, perhaps as a result of a shorter Fe–Cu bond. Consistent with the X-ray structure analysis, the FT-IR spectrum of each solid sample reveals two C=O bands (1967 and 1903 cm\textsuperscript{-1} for 4a', 1960 and 1896 cm\textsuperscript{-1} for 4b') and one C=O band (1577 cm\textsuperscript{-1} for 4a', 1582 cm\textsuperscript{-1} for 4b'). The bridging hydride band could be very weak. An attempt to locate its position by inspecting the IR spectrum of 4a'-D (made from 1a and (IPr)CuOD) was unsuccessful.


\textsuperscript{28} Parmelee, S. R.; Mankad, N. P. \textit{Dalton Trans.} 2015, 44, 17007.
Figure 3. ORTEP drawings of 4a' (left) and 4b' (right) at the 50% probability level. Several carbon atoms as well as the semibridging CO (C44–O3) of 4b' are disordered; only one component of each disordered group is shown. The bridging hydride of 4b' could not be located from the difference map.

Table 1. Selected Bond or Through-Space Distances (Å) and Angles (deg)

<table>
<thead>
<tr>
<th></th>
<th>4a'</th>
<th>4b'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Cu</td>
<td>2.4959(9)</td>
<td>2.4059(8)</td>
</tr>
<tr>
<td>Fe–C43</td>
<td>1.766(6)</td>
<td>1.761(4)</td>
</tr>
<tr>
<td>Fe–C44</td>
<td>1.767(6)</td>
<td>1.843(6), 2.049(19)</td>
</tr>
<tr>
<td>Cu…C43</td>
<td>2.901(5)</td>
<td>2.856(4)</td>
</tr>
<tr>
<td>Cu…C44</td>
<td>2.486(5)</td>
<td>2.279(5), 2.283(19)</td>
</tr>
<tr>
<td>Fe–H</td>
<td>1.78(4) N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu–H</td>
<td>1.73(4) N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>C29–O1</td>
<td>1.250(5)</td>
<td>1.244(5)</td>
</tr>
<tr>
<td>C43–O2</td>
<td>1.153(6)</td>
<td>1.148(5)</td>
</tr>
<tr>
<td>C44–O3</td>
<td>1.154(6)</td>
<td>1.177(7), 1.22(3)</td>
</tr>
<tr>
<td>Cu–C1</td>
<td>1.913(4)</td>
<td>1.903(3)</td>
</tr>
<tr>
<td>Fe–C28</td>
<td>2.131(4)</td>
<td>2.130(4)</td>
</tr>
<tr>
<td>Fe…C29</td>
<td>2.374(5)</td>
<td>2.376(4)</td>
</tr>
<tr>
<td>Fe–C30</td>
<td>2.126(4)</td>
<td>2.101(3)</td>
</tr>
<tr>
<td>Fe–C31</td>
<td>2.073(4)</td>
<td>2.091(4)</td>
</tr>
<tr>
<td>Fe–C32</td>
<td>2.072(4)</td>
<td>2.076(5)</td>
</tr>
<tr>
<td>Fe–Cu–C1</td>
<td>160.14(14)</td>
<td>166.49(11)</td>
</tr>
<tr>
<td>Fe–C43–O2</td>
<td>175.7(5)</td>
<td>177.9(4)</td>
</tr>
<tr>
<td>Bond</td>
<td>C–C44–O3</td>
<td>C–C44–O3</td>
</tr>
<tr>
<td>------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>Fe–C44–O3</td>
<td>172.5(4)</td>
<td>173.3(4)</td>
</tr>
<tr>
<td>Cu–C44–O3</td>
<td>117.9(4)</td>
<td>116.2(4)</td>
</tr>
<tr>
<td>Cu–Fe–C43</td>
<td>83.93(16)</td>
<td>85.04(13)</td>
</tr>
<tr>
<td>Cu–Fe–C44</td>
<td>68.91(16)</td>
<td>63.25(14)</td>
</tr>
</tbody>
</table>

Given the solid-state structures (4a' and 4b') revealed by X-ray crystallography, it is worth questioning if the Fe(μ-H)Cu core is intact in solution or actually breaks apart to form the terminal-hydride species (4a and 4b) as proposed in eq 2. In this particular case, because of the involvement of a d^{10} metal (i.e., Cu^{I}), chemical shift value for the hydride will not provide definitive information concerning its bonding mode. Nevertheless, the hydride resonance for 4a appears upfield of that for the Knölker complex 2a (Table 2). It is noted that deprotonation of the OH group of 2a shows a similar effect on the hydride resonance. The $^{13}$C{$^1$H} NMR spectra of these complexes are much more informative, especially the resonance for the cyclopentadienyl ring C29 carbon (referring to the numbering scheme in Figure 3) which reports the strength of the C–O bond. As expected, C–O bond order increases going from 2a to 3a to 1a, so does the chemical shift value for the C29 carbon (Figure 4). A solid sample of 4a', when dissolved in THF-$d_8$, displays a resonance at 168.10 ppm for the C29 carbon. This value is in between those of 2a and 3a, suggesting that in solution the Fe-Cu heterobimetallic complex adopts an analogous structure, hence a terminal hydride (4a). The close proximity to the value of 3a also indicates that the O–Cu bond has significant ionic character. Titrating a solution of 4a in C$_6$D$_6$ with DMSO (up to 20 equiv) results in a noticeable shift of the hydride resonance (from −12.58 to −12.82 ppm) as well as the imidazole resonance (from 6.28 to 6.61 ppm). It is possible that DMSO promotes the formation of a solvent-separated ion pair.


30 THF-$d_8$ was chosen as the solvent as it can dissolve all the iron complexes in Figure 4.
Table 2. $^1$H NMR Hydride Resonances of the Iron Complexes

<table>
<thead>
<tr>
<th></th>
<th>in C$_6$D$_6$ ($\delta$)</th>
<th>in THF-$d_8$ ($\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>-11.63</td>
<td>-12.00</td>
</tr>
<tr>
<td>3a</td>
<td>N.D.$^a$</td>
<td>-13.03</td>
</tr>
<tr>
<td>4a</td>
<td>-12.58</td>
<td>-13.26</td>
</tr>
</tbody>
</table>

$^a$ N.D. = not determined. 3a has poor solubility in C$_6$D$_6$.

Figure 4. Trend of the C29 resonance (in THF-$d_8$).

Additional evidence supporting 4a being the dominant solution structure comes from IR analysis of the solution samples. The strong C=O stretching band at 1577 cm$^{-1}$ is absent when 4a' is dissolved in toluene, THF, or cyclohexane. The two C=O bands, however, remain and are shifted to higher wavenumbers (by 8-14 cm$^{-1}$) from those observed for the solid sample. All in all, both isomers can be described as a tight ion pair of [3a minus Na$^-$] and [(IPr)Cu]$^+$ except that copper resides near oxygen in 4a while with the Fe–H bond in 4a' (eq 3). The energy difference between 4a and 4a' is probably small, so are the kinetic barriers for their interconversion. Crystal packing might provide sufficient driving force to shift the equilibrium to the more compact structure 4a' when the solvent is removed. Variable-temperature $^1$H NMR spectra of
4a' dissolved in toluene-$d_8$ show that the hydride resonance broadens significantly below 0 °C, coalesces around –30 °C, but becomes sharper when the temperature rises above 30 °C (see Supporting Information for details). These observations support a dynamic process in solution, which may involve a rapid interconversion between 4a and 4a'.

When 4b' is dissolved in toluene, it IR spectrum shows three C=O bands at 1973, 1960, and 1902 cm⁻¹ as well as one C=O band at 1611 cm⁻¹. The 1902 cm⁻¹ band is relatively broad, likely due to the presence of two overlapping bands. The C=O bands at 1960 and 1902 cm⁻¹ match reasonably well with those for the solid sample of 4b'. This result suggests that structures 4b' and 4b coexist in solution. Assuming similar molar absorptivities for the two isomers, the ratio between the two is estimated to be 2 : 1 favoring 4b'. The IR data for the sample dissolved in THF and cyclohexane are similar, except that in cyclohexane, the four C=O bands are better resolved. The estimated isomeric ratio of 4b' and 4b is 1 : 1 in both THF and cyclohexane.

Variable-temperature $^1$H NMR spectra of 4b' dissolved in toluene-$d_8$ also indicate some dynamic behavior, displaying a broad hydride resonance at low temperatures (below 0 °C) with a coalescence temperature of around –40 °C (see Supporting Information). At 30 °C or higher, the hydride resonance becomes sharp, similar to what has been observed with the trimethylsilyl derivative. The lack of synthetic routes to the mononuclear iron hydride 2b precludes a systematic comparison of the carbon resonances as made for the trimethylsilyl analog (Figure 4).
However, the C29 resonance of $4b/4b'$ in C$_6$D$_6$ (170.17 ppm) is quite close to the cyclopentadienone carbonyl resonance of $1b$ (173.73 ppm), consistent with the IR data showing that $4b'$ exists to a great extent in solution. Replacing the SiMe$_3$ groups in $4a'$ with less bulky 'Bu groups may reduce the steric repulsion with the IPr ligand and narrow the energy gap between the two isomers.

Given the structural elucidation described above, for the rest of the paper, we will use $4a$ and $4b/4b'$ to denote the species in solution, and $4a'$ and $4b'$ for the solid samples.

2.2.3 Stoichiometric Reactions of the Heterobimetallic Complexes. Having synthesized the Fe-Cu heterobimetallic complexes, we shifted our attention to the reactivity of these compounds towards various substrates. At room temperature, complex $4a$ reacts with HCO$_2$H readily to afford $2a^9$ and (IPr)CuOCHO$^{32}$ (eq 4). This process is analogous to the protonation of $3a$ with H$_3$PO$_4$ to yield $2a,^9$ except that the conjugate base generated here (i.e., HCO$_2^-$) is trapped by [(IPr)Cu]$^+$. The reaction of $4b/4b'$ with HCO$_2$H is similar, producing the tert-butyl analog of $2a$ and (IPr)CuOCHO within 15 min.

Complex $4a$ also reacts with organohalides such as CH$_3$I, PhCH$_2$Br, and PhCH$_2$Cl. In all cases, the hydride is delivered to the C–X carbon to form a dehalogenation product (CH$_4$ or PhCH$_3$). The reaction of $4a$ with CH$_3$I (3 equiv) is complete within 2 h, giving multiple organometallic products along with CH$_4$. The $^1$H NMR spectra suggest that the major copper-

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$^{31}$ Because $4b$ and $4b'$ undergo rapid interconversion, the observed C29 resonance should be the averaged resonance of the two isomers.

containing species (89%) bears a cyclopentadienyl or cyclopentadienone iron fragment. We tentatively assign this species as an Fe-Cu heterobimetallic iodide complex (5a) based on the fact that the Knöller complex 2a is converted to an iron iodide complex when mixed with 1-iodopentane (eq 5). While one of the minor copper-containing products (6%) has yet to be identified, NMR data of the other copper species (5%) match those of (IPr)CuI. Lalic and co-workers have recently reported catalytic dehalogenation of alkyl bromides and iodides with silanes through a transient (IPr)CuH intermediate. Thus, in addition to a direct H/I exchange between the Fe–H and CH₃–I moieties, 4a could first dissociate to form a 16-electron (cyclopentadienone)iron dicarbonyl species 6a and (IPr)CuH (Scheme 2). Subsequent dehydrogenation of CH₃I by (IPr)CuH followed by combination of 6a with the resulting (IPr)CuI would also yield 5a. We favor the direct H/I exchange pathway (highlighted in box) because 4a does not participate in other reactions that have been previously established for (IPr)CuH (vide infra). Extending the time for the reaction of 4a with CH₃I to 4 days increases the percentages of the unknown species and (IPr)CuI to 11% and 21%, respectively, at the expense of 5a. Dissociation of (IPr)CuI from 5a may occur slowly, and the iron moiety would be left as 6a, which is known to decompose into intractable products. Judging from the resonances in the upfield region that are characteristic of Me₃Si groups, there are at least three minor iron-containing species present along with 5a. In an attempt to trap 6a with MeCN to form a stable acetonitrile complex 7a, 5 equiv of MeCN was added at beginning of the reaction between 4a and CH₃I. The unknown copper species remains as a minor product (~4%), but the percentage of

33 We cannot rule out the possibility that the iodide ligand bridges iron and copper in a similar way as the hydride in 4a'.
36 An alternative pathway leading to (IPr)CuI involves alkylation of the oxygen with CH₃I; however, no CH₂O resonance could be found from the 'H NMR spectra.
(IPr)CuI has risen substantially (47% after 1 day and 65% after 4 days). The $^1$H NMR spectra show the growth of 7a as more 5a is converted to (IPr)CuI. Interestingly, the addition of MeCN does not appear to impact the rate of the dehalogenation of CH$_3$I, which is also consistent with the direct H/I exchange pathway.

**Scheme 2.** Reaction of 4a with CH$_3$I

The reaction of 4a with PhCH$_2$Br or PhCH$_2$Cl (1.5 equiv) gives two copper-containing products: a heterobimetallic halide complex analogous to 5a and (IPr)CuX (X = Br or Cl). The
minor iron-containing species are the same as those observed from the CH₃I reaction, implying that these are produced from the decomposition of 6a. As expected, PhCH₂Br is more reactive than PhCH₂Cl, requiring a shorter time to fully consume 4a (2 h vs. 36 h). Again, the addition of CH₃CN does not affect the rate of dehalogenation but accelerates the release of (IPr)CuX via the formation of 7a.

The tert-butyl derivative 4b/4b′ shows a similar reaction pattern as 4a. Its H/I exchange with CH₃I is, however, more sluggish, requiring >16 h to fully convert the hydride. The identifiable products are CH₄, a heterobimetallic iodide complex (5b) and (IPr)CuI. Also present are small amounts of an unknown copper species and several unidentified iron species. Adding CH₃CN does not affect the rate of the reaction but results in fewer organometallic products. After 3 days, the reaction mixture is composed of 5a, (IPr)CuI, and an iron acetonitrile complex (7b). Interestingly, 4b/4b′ reacts with PhCH₂Br at a rate comparable to 4a, giving a heterobimetallic bromide complex as well as (IPr)CuBr.

In contrast to facile insertion of alkynes²³,³⁷ and CO₂³² into (IPr)CuH, 4a is inert to PhC≡CPh and CO₂ (1 atm) at room temperature or 60 °C over a period of 2 days. The lack of reactivity with CO₂ was somewhat expected because CO₂ is a by-product formed during the synthesis of the heterobimetallic complexes (eq 2). On the other hand, this result suggests that under these conditions, dissociation of 4a to 6a and (IPr)CuH is not favorable. Complex 4a does not react with PhCHO at room temperature; however, at 60 °C, several benzoxide species (δ 5.07-4.30) including free PhCH₂OH appear after 4 h. The reaction is slow with ~50% of 4a remaining after a week. Although the insertion of aldehydes or ketones into (IPr)CuH has been

previously proposed\textsuperscript{38} and studied computationally,\textsuperscript{39} the reaction of 4a with PhCHO is more likely to proceed without the involvement of (IPr)CuH. If it were otherwise, 4a would react with PhC=CPh and CO\textsubscript{2} to generate insertion products and decomposition products of 6a. Perhaps 4a resembles the Knölker complex 2a, transferring hydride and copper to the aldehyde in a concerted manner\textsuperscript{11a} (Figure 5) to yield 6a and (IPr)CuOCH\textsubscript{2}Ph. The latter compound is available from a room temperature reaction of (IPr)CuOH with PhCH\textsubscript{2}OH, or alternatively from metathesis reaction between (IPr)CuCl and NaOCH\textsubscript{2}Ph. However, it is unstable at 60 °C, especially in the presence of water, reverting back to (IPr)CuOH and PhCH\textsubscript{2}OH.

\begin{center}
\textbf{Figure 5.} Proposed reduction of PhCHO by 4a.
\end{center}

Complex 4a reacts with 1 atm of CO at 60 °C, albeit at a slow rate (eq 6). The identifiable product is the iron tricarbonyl complex 1a, although the fate of the "(IPr)Cu" part is not clear to us. A control experiment shows that [(IPr)CuH]\textsubscript{2}\textsuperscript{23} the presumed copper product, is unstable under a CO atmosphere. The reaction of 4a with CO was investigated further under different conditions and the results are summarized in Table 3. Increasing the CO pressure from 1 atm to 6.4 atm results in a higher conversion of 4a to 1a (entry 3). Replacing C\textsubscript{6}D\textsubscript{6} with a more polar solvent THF-\textit{d}\textsubscript{8} has no effect on the rate of the reaction over 24 h (entry 4 vs. entry


1), but gives a slightly higher conversion over 72 h (entry 5 vs. entry 2). The tert-butyl derivative 4b/4b' is completely unreactive with CO under similar conditions.

![Image of a reaction scheme](image)

Table 3. Reactivity of the Fe-Cu heterobimetallic complexes towards CO

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Solvent</th>
<th>Temp.</th>
<th>pCO</th>
<th>Time</th>
<th>Conversiona</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>C₆D₆</td>
<td>60 °C</td>
<td>1 atm</td>
<td>24 h</td>
<td>17%</td>
</tr>
<tr>
<td>2</td>
<td>4a</td>
<td>C₆D₆</td>
<td>60 °C</td>
<td>1 atm</td>
<td>72 h</td>
<td>21%</td>
</tr>
<tr>
<td>3</td>
<td>4a</td>
<td>C₆D₆</td>
<td>60 °C</td>
<td>6.4 atm</td>
<td>48 h</td>
<td>71%</td>
</tr>
<tr>
<td>4</td>
<td>4a</td>
<td>THF-d₈</td>
<td>60 °C</td>
<td>1 atm</td>
<td>24 h</td>
<td>17%</td>
</tr>
<tr>
<td>5</td>
<td>4a</td>
<td>THF-d₈</td>
<td>60 °C</td>
<td>1 atm</td>
<td>72 h</td>
<td>30%</td>
</tr>
<tr>
<td>6</td>
<td>4b/4b'</td>
<td>THF-d₈</td>
<td>60 °C</td>
<td>1 atm</td>
<td>72 h</td>
<td>0%</td>
</tr>
</tbody>
</table>

a Determined by ¹H NMR.

2.2.4 Catalytic Reduction of PhCHO under the WGSR conditions. The reactivity of 4a towards PhCHO (Figure 5) and CO (eq 6), the hydrolysis of (IPr)CuOCH₂Ph, and how 4a is synthesized (eq 2) suggest that we can construct a catalytic cycle for the reduction of PhCHO using CO and H₂O, or under the WGSR conditions. Although homogeneous WGSR systems are well known in the literature, combining reduction of C=O bonds with the WGSR in one catalytic system is rare. Beller and co-workers have shown that at 80-100 °C, complex 1a

---

(0.5-5 mol%) catalyzes the reduction of PhCHO in DMSO/H₂O (1 : 1) under 5-10 bar of CO. This reaction requires at least 1 equiv of K₂CO₃ (with respect to PhCHO) as an additive; without a base, no alcohol product could be observed. In an aqueous alkaline medium, some if not all of 1a should be converted to 2a, which in turn reduces the aldehyde. In a related study, Wu et al. have also employed 1a as the catalyst (1-3 mol%) and 1 equiv of Na₂CO₃ as the additive for the reduction of PhCHO at 120 °C in DMSO/H₂O (1 : 1), in which case paraformaldehyde (10 equiv) is used as the surrogate for CO.

An external base is not required when Fe-Cu heterobimetallic complexes 4a and 4b/4b' are employed as the catalysts. The in-situ generated (IPr)CuOH should play the role as a base to regenerate the hydride species. Moreover, a less polar solvent can be used. In Beller’s work, switching the mixed solvent DMSO/H₂O (1 : 1) to toluene/H₂O (1 : 1) shuts down the catalysis completely. In contrast, in toluene, 4a alone is an effective catalyst for the reduction of PhCHO to PhCH₂OH by water (20 equiv) and CO (Table 4). At 100 °C and under a 6.4 atm of CO pressure, a nearly quantitative conversion can be achieved in 24 h with a catalyst loading of 1.5 mol% (entry 2). Lowering the loading to 1 mol % (entry 3) leads to a partial conversion of PhCHO, which is further compromised by reducing the CO pressure to 5 atm (entry 5).

Compared to 4a, the tert-butyl derivative 4b/4b' is a less active catalyst (entry 2 vs. entry 6). The reaction is also catalyzed by a 1 : 1 mixture of 1a and (IPr)CuOH with efficiency similar to that of 4a (entry 7). Interestingly, the mixture of 1b and (IPr)CuOH is more active than the heterobimetallic complex 4b/4b' (entry 8 vs. entry 4), suggesting that in this case it is more advantageous to keep the iron and copper fragments apart.

Table 4. Reduction of PhCHO Under the WGSR Conditions

\[
\text{PhCHO} + \text{H}_2\text{O} + \text{CO} \xrightarrow{\text{catalyst}} \text{PhCH}_2\text{OH} + \text{CO}_2
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>cat. loading (mol%)</th>
<th>(p_{\text{CO}}) (atm)</th>
<th>conversion (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>5</td>
<td>6.4</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>4a</td>
<td>1.5</td>
<td>6.4</td>
<td>&gt;99</td>
</tr>
<tr>
<td>3</td>
<td>4a</td>
<td>1</td>
<td>6.4</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>4a</td>
<td>5</td>
<td>5.0</td>
<td>&gt;99</td>
</tr>
<tr>
<td>5</td>
<td>4a</td>
<td>1</td>
<td>5.0</td>
<td>72</td>
</tr>
<tr>
<td>6</td>
<td>4b/4b'</td>
<td>1.5</td>
<td>6.4</td>
<td>40</td>
</tr>
<tr>
<td>7(^a)</td>
<td>1a + (IPr)CuOH</td>
<td>1.5</td>
<td>6.4</td>
<td>&gt;99</td>
</tr>
<tr>
<td>8(^a)</td>
<td>1b + (IPr)CuOH</td>
<td>1.5</td>
<td>6.4</td>
<td>62</td>
</tr>
</tbody>
</table>

\(^a\) The iron and copper species were mixed in a 1 : 1 ratio. \(^b\) NMR spectra showed no other products originated from PhCHO.

To gain a better understanding of the synergy between the iron and copper components, several control experiments were performed using monometallic iron or copper complexes (Scheme 3) under the catalytic conditions optimized for 4a (Table 4, entry 2). Iron complex 1a proves to be an inactive catalyst for the reduction of PhCHO. Iron hydride 2a shows very low catalytic activity, converting only 5% of PhCHO to PhCH\(_2\)OH. The small amount of alcohol was expected because 2a reacts with PhCHO stoichiometrically to generate a thermally unstable iron alcohol complex.\(^{11a}\) While the majority of this alcohol complex should be converted to 1a under CO, some may decompose to species that exhibit additional but limited catalytic activity. In any case, 4a is a significantly more active catalyst, confirming that the copper component is indispensable. Catalytic performance of copper-only complexes including (IPr)CuOH, [(IPr)CuH]\(_2\),\(^{23}\) and (IPr)CuOCH\(_2\)Ph was investigated similarly. In each case, the \(^1\)H NMR spectrum shows a mixture of unreacted PhCHO, PhCH\(_2\)OH, the Tischenko product PhCO\(_2\)CH\(_2\)Ph, and some unidentified products. In contrast, using 4a as the catalyst leads to a
clean conversion of PhCHO to PhCH$_2$OH. Taken together, these results suggest that the iron component enhances both the efficiency and the selectivity of the reaction.

**Scheme 3.** Control experiments with monometallic complexes

\[
\text{PhCHO} + \text{H}_2\text{O} + \text{CO} \xrightarrow{1.5 \text{ mol}\% \ [\text{Fe} \text{ or } \text{Cu}]} \text{toluene} 100^\circ \text{C}, 24 \text{ h} \rightarrow \text{PhCH}_2\text{OH} + \text{CO}_2
\]

Without PhCHO, 4a catalyzes the WGSR, although its catalytic activity has yet to be quantified. The formation of H$_2$ is confirmed by $^1$H NMR spectroscopy, when the reaction is carried out at 60 °C. Higher temperatures make it more difficult to detect H$_2$ because of lower solubility of the gas. A catalytic reaction performed under 1 atm of $^{13}$CO provides strong evidence for the formation of CO$_2$ (Scheme 4). The $^{13}$C{$^1$H} NMR spectrum displays resonances of both $^{13}$CO$_2$ ($\delta$ 124.88) and (IPr)CuO$^{13}$CHO ($\delta$ 167.44). The copper formate complex is likely to be generated from $^{13}$CO$_2$ insertion into (IPr)CuH. A control experiment of mixing (IPr)CuOH with CO rules out an alternative mechanism that involves CO insertion into (IPr)CuOH followed by isomerization of the resulting metallo-carboxylic acid. In addition to $^{13}$CO$_2$, (IPr)CuO$^{13}$CHO, and the unreacted $^{13}$CO ($\delta$ 184.52), 4a-$^{13}$CO and 1a-$^{13}$CO ($\delta$ 209.84)
are present in the reaction mixture. It should be mentioned that the Knölker complex 2a also exchanges with $^{13}$CO and at the same time is converted to $^{1}$a-$^{13}$CO via the loss of H$_2$.

**Scheme 4.** Catalytic WGSR using $^{13}$CO

\[
^{13}$CO + H$_2$O $\xrightarrow{5 \text{ mol\% 4a}}$ toluene-$d_8$ $\xrightarrow{100 \degree C, 1-4 \text{ d}}$ $^{13}$CO$_2$ + H$_2$
\]

**13C-labelled organometallic products**

![Chemical structures](image)

**2.2.5 Mechanisms for the Reduction of PhCHO.** On the basis of the stoichiometric reactions and labeling study, we propose two different catalytic cycles (Scheme 5, color coded in red and blue) that converge at the step to regenerate the heterobimetallic species (in magenta). Reduction of PhCHO by 4a via the transition state depicted in Figure 5 produces 6a and (IPr)CuOCH$_2$Ph. The separated iron and copper fragments independently react with CO and H$_2$O to give 1a and (IPr)CuOH, respectively. The catalytic cycle in red is completed by the reaction of 1a with (IPr)CuOH to release CO$_2$. Direct dissociation of 4a to 6a and (IPr)CuH is possible at 100 °C; however, this process is more favorable in the presence of CO, resulting in 1a and (IPr)CuH (the blue cycle). The copper hydride then reacts with PhCHO and H$_2$O sequentially to transform into (IPr)CuOH for the awaiting 1a.
Scheme 5. Catalytic cycles for the reduction of PhCHO with 4a under the WGSR conditions

We cannot rule out an alternative mechanism involving 4a-catalyzed WGSR followed by hydrogenation of PhCHO with H₂ generated from CO and H₂O. As a matter of fact, at 100 °C, 4a catalyzes the hydrogenation of PhCHO (in toluene) to PhCH₂OH under 6.4 atm of H₂ pressure. With a catalyst loading of 1.5 mol%, a quantitative conversion is achieved within 24 h. If the hydrolysis of (IPr)CuH (Scheme 5, highlighted in green) is more competitive than PhCHO insertion, WGSR would occur prior to the reduction of PhCHO. In an attempt to test the reactivity of (IPr)CuH towards water, [(IPr)CuH]₂ was generated in-situ from (IPr)CuO'Bu and (EtO)₃SiH as described in the literature. Unfortunately, subsequent addition of water resulting in a very complicated mixture, likely due to the interference from silicon-containing compounds.
The side reactions of (IPr)CuH with CO₂ and CO negatively impact the catalytic reaction. CO₂ inserts into (IPr)CuH to form (IPr)CuOCHO, which may re-enter into the catalytic cycle via deinsertion of CO₂ but reduces the steady-state concentration of the active (IPr)CuH. CO causes decomposition of (IPr)CuH, as confirmed by the control experiment. It is noted that as the catalytic reaction progresses, the color of the reaction mixture is darkening. To test the possibility of heterogeneous catalysis, a mercury poisoning experiment was conducted. Adding 100-fold excess of elemental mercury shows no retardation to 4a-catalyzed reduction of PhCHO under the WGSR conditions, suggesting that the catalytic reaction is homogenous.

2.3 CONCLUSIONS

We have successfully synthesized a unique class of Fe-Cu heterobimetallic complexes that preserve the core structure of the Knölker complex but incorporate an (NHC)Cu fragment. In solid state these complexes adopt a structure featuring a hydride bridging iron and copper; however, in solution they are present as both the bridging hydride and a terminal iron hydride that in a rapid equilibrium. The isomeric ratio depends on the substituents on the cyclopentadienone/cyclopentadienyl ring: the complex bearing bulky Me₃Si groups favors the terminal hydride species. These complexes show stoichiometric reactivity towards HCO₂H, CH₃I, PhCH₂Br, PhCH₂Cl, PhCHO and CO, and catalytic activity for the reduction of PhCHO under the WGSR conditions. Control experiments with monometallic iron or copper complexes have highlighted the importance of having both iron and copper components for the catalytic reaction to be efficient and selective. Compared to the catalytic system using iron complexes only,⁴¹ the heterobimetallic system does not require a large excess of base additive and avoids the use of a high-boiling polar solvent (i.e., DMSO). Though effective, the heterobimetallic
complexes and the copper component in particular decompose over the time. Our future efforts will be focused on building similar molecules with more robust ligand scaffolds.

2.4 EXPERIMENTAL SECTION

Materials and General Considerations. Unless otherwise mentioned, all air-sensitive compounds were handled under an inert atmosphere using standard Schlenk line and inert-atmosphere box techniques. Toluene, pentane, and THF were deoxygenated and dried in a solvent purification system by passing through an activated alumina column and an oxygen-scavenging column under argon. Cyclohexane, glyme, and water were degassed by bubbling argon or nitrogen through them for 30 min prior to use. C6D6 was distilled from Na and benzophenone under an argon atmosphere. Other deuterated solvents such as CDCl₃ and THF-d₈ (packed in an ampule) were used as received from commercial sources. Benzaldehyde was purchased from Sigma-Aldrich and purified by vacuum distillation prior to use. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with smart orbit diamond attenuated total reflectance (ATR) accessory. Complexes 1a, 44 2a, 9,45 and (IPr)CuOH 19 were synthesized according to the literature procedures.

45 Chakraborty, A.; Guan, H. Iron, dicarbonylhydro[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-2-hydroxy-1,3-bis(trimethylsilyl)-1H-inden-1-yl]. e-Encyclopedia of Reagents for Organic Synthesis, 2014.
Synthesis of 4a/4a'. Method A (from 1a): In a glove box, an oven-dried Schlenk flask equipped with a stir bar was charged with (IPr)CuOH (150 mg, 0.32 mmol), 1a (134 mg, 0.32 mmol), and 25 mL of toluene. The mixture was heated at 60 °C for 16 h, resulting in a yellow solution. After cooling to room temperature, the solution was filtered through a short plug of Celite and dried under the vacuum. The remaining sticky material was washed with a small amount of pentane (~ 5 mL) and further dried in vacuo to afford a yellow powder. The desired product was isolated in a pure form by recrystallizing this yellow powder from a saturated toluene solution layered with pentane and kept at −30 °C (124 mg, 46%). Method B (from 2a): In a glove box, an oven-dried Schlenk flask equipped with a stir bar was charged with (IPr)CuOH (186 mg, 0.40 mmol), the Knölker complex 2a (156 mg, 0.40 mmol), and 25 mL of toluene. The resulting yellow solution was stirred under argon for 30 min and then filtered through a short plug of Celite. The filtrate was concentrated under the vacuum to give a yellow solid, which was washed with pentane (5 mL) and further dried under the vacuum. The desired product was isolated as a yellow powder (201 mg, 60%).

1H NMR (400 MHz, C₆D₆, δ): 7.23 (t, 2H, 3J_H-H = 7.6 Hz, ArH), 7.08 (d, 4H, 3J_H-H = 7.6 Hz, ArH), 6.28 (s, 2H, NCH=CHN), 2.63-2.51 (m, 6H, CH(CH₃)₂ + CH₂), 2.25-2.21 (m, 2H, CH₂), 1.61-1.58 (m, 2H, CH₂), 1.37-1.35 (m, 14H, CH(CH₃)₂ + CH₂), 1.03 (d, 12H, 3J_H-H = 7.2 Hz, CH(CH₃)₂), 0.31 (s, 18H, Si(CH₃)₃), −12.58 (s, 1H, FeH).

13C {1H} NMR (101 MHz, C₆D₆, δ): 218.46 (Fe(CO)₂), 181.24 (CCu), 168.92 (CpCO), 145.60 (ortho-ArC), 135.15 (ipso-ArC), 130.85 (para-ArC), 124.61 (meta-ArC), 123.06 (NCH=CHN), 103.12 (CpC), 68.37 (CpC), 29.00 (CH(CH₃)₂), 26.49 (CH₂), 24.60 (CH(CH₃)₂), 24.26 (CH(CH₃)₂), 23.58 (CH₂), 1.65 (Si(CH₃)₃).

13C {1H} NMR (101 MHz, THF-
\[ \text{Synthesis of } \{2,5-(\text{Bu})_{2}-3,4-\{(\text{CH}_{2})_{4}\}(\eta^{4}-\text{C}_{4}\text{CO})\} \text{Fe}(\text{CO})_{3} \ (1b). \]

Under a nitrogen atmosphere, \( \text{BuCu}=\text{C}(\text{CH}_{2})_{4}\text{C}=\text{C}\text{Bu} \) (4.37 g, 20 mmol), Fe(CO)\(_5\) (5.26 mL, 40 mmol), and glyme (5 mL) were mixed in a Fisher-Porter glass tube. The reaction vessel was flushed with 3 atm of CO several times before disconnected from the CO source. The closed system was heated by a 120 °C oil bath for 22 h. After cooling, the reaction mixture was concentrated under the vacuum and the residue was subjected to purification by column chromatography (eluted with 1 : 1 hexanes/CH\(_2\)Cl\(_2\) first, and then with 1 : 1 hexanes/EtOAc). The desired product was isolated as an air-stable yellow solid (3.55 g, 46% yield). \( ^{1}H \) NMR (300 MHz, CDCl\(_3\), \( \delta \)): 2.88-2.75 (m, 2H, CH\(_2\)), 2.68-2.52 (m, 2H, CH\(_2\)), 1.82-1.73 (m, 4H, CH\(_2\)), 1.33 (s, 18H, CH\(_3\)). \( ^{1}H \) NMR (400 MHz, \( \text{C}_{6}\text{D}_{6} \), \( \delta \)): 2.45-2.38 (m, 2H, CH\(_2\)), 2.11-2.05 (m, 2H, CH\(_2\)), 1.36 (s, 18H, CH\(_3\)), 1.26-1.14 (m, 4H, CH\(_2\)). \( ^{13}C \) \( ^{1}H \) NMR (90 MHz, CDCl\(_3\), \( \delta \)): 210.53 (Fe(CO)\(_3\)), 173.25 (CpCO), 100.63 (CpC), 92.52 (CpC), 33.50 (C(CH\(_3\))\(_3\)), 30.22 (C(CH\(_3\))\(_3\)), 25.15 (CH\(_2\)), 22.32 (CH\(_2\)). \( ^{13}C \) \( ^{1}H \) NMR (101 MHz, \( \text{C}_{6}\text{D}_{6} \), \( \delta \)): 211.08 (Fe(CO)\(_3\)), 173.73 (CpCO), 100.57 (CpC), 92.66 (CpC), 33.62 (C(CH\(_3\))\(_3\)), 30.13 (C(CH\(_3\))\(_3\)), 25.00 (CH\(_2\)), 22.07 (CH\(_2\)). ATR-IR (solid, cm\(^{-1}\)): 2048 (v\( \text{C=O} \)), 1979 (v\( \text{C=O} \)), 1950 (v\( \text{C=O} \)), 1620 (v\( \text{C=O} \)). IR (toluene, cm\(^{-1}\)): 2055 (v\( \text{C=O} \)), 1996 (v\( \text{C=O} \)), 1975 (v\( \text{C=O} \)), 1644 (v\( \text{C=O} \)). IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\))
Synthesis of 4b/4b’. In a glove box, an oven-dried Schlenk flask equipped with a stir bar was charged with (IPr)CuOH (121 mg, 0.26 mmol), 1b (100 mg, 0.26 mmol), and 25 mL of toluene. The resulting mixture was heated at 60 °C for 18 h, and upon cooling to room temperature filtered through a short plug of Celite. Removal of the volatiles under the vacuum afforded a yellow residue, which was washed with a small amount of pentane (~ 5 mL) and then dried under the vacuum. An analytically pure product was obtained from recrystallization in toluene-pentane at -30 °C (102 mg, 49%). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), \(\delta\)): 7.26-7.07 (m, 6H, ArH), 6.33 (s, 2H, NCH=CHN), 2.67-2.62 (m, 6H, C\(_\text{H}_{\text{CH}_3}\)\(_3\)), 2.37-2.29 (m, 2H, CH\(_2\)), 1.45 (s, 18H, C(CH\(_3\))\(_3\)), 1.41 (d, 12H, \(^3J_{\text{H-H}} = 8.0\) Hz, CH(CH\(_3\))\(_2\)), 1.36-1.32 (m, 4H, CH\(_2\)), 1.04 (d, 12H, \(^3J_{\text{H-H}} = 10.4\) Hz, CH(CH\(_3\))\(_2\)), -13.37 (s, 1H, FeH). \(^{13}\)C\({}^1\)H NMR (101 MHz, C\(_6\)D\(_6\), \(\delta\)): 216.97 (Fe(\(\text{C}=\text{O}\)\)_2)), 182.39 (\(\text{CCu}\)), 170.17 (CpCO), 145.66 (orthoaRC), 135.14 (ipso-\(\text{ArC}\)), 130.79 (para-\(\text{ArC}\)), 124.46 (meta-\(\text{ArC}\)), 122.67 (NCH=CHN), 95.37 (Cp), 88.67 (CpC), 33.03 (C(CH\(_3\))\(_3\)), 31.14 (C(CH\(_3\))\(_3\)), 29.05 (CH(CH\(_3\))\(_2\)), 26.68 (CH\(_2\)), 24.51 (CH(CH\(_3\))\(_2\)), 24.23 (CH(CH\(_3\))\(_2\)), 23.19 (CH\(_2\)). ATR-IR (solid, cm\(^{-1}\)): 1960 (\(\nu_{\text{C}=\text{O}}\)), 1896 (\(\nu_{\text{C}=\text{O}}\)), 1582 (\(\nu_{\text{C}=\text{O}}\)). Transmission-IR (toluene, cm\(^{-1}\)): 1973 (\(\nu_{\text{C}=\text{O}}\)), 1960 (\(\nu_{\text{C}=\text{O}}\)), 1902 (\(\nu_{\text{C}=\text{O}}\)), 1611 (\(\nu_{\text{C}=\text{O}}\)). Transmission-IR (THF, cm\(^{-1}\)): 1972 (\(\nu_{\text{C}=\text{O}}\)), 1962 (\(\nu_{\text{C}=\text{O}}\)), 1903 (\(\nu_{\text{C}=\text{O}}\)), 1881 (\(\nu_{\text{C}=\text{O}}\)), 1606 (\(\nu_{\text{C}=\text{O}}\)). Transmission-IR (cyclohexane, cm\(^{-1}\)): 1978 (\(\nu_{\text{C}=\text{O}}\)), 1962 (\(\nu_{\text{C}=\text{O}}\)), 1905 (\(\nu_{\text{C}=\text{O}}\)), 1894 (\(\nu_{\text{C}=\text{O}}\)), 1618 (\(\nu_{\text{C}=\text{O}}\)). Anal. Calcd for C\(_{46}\)H\(_{63}\)N\(_2\)O\(_3\)FeCu: C, 68.09; H, 7.83; N, 3.45. Found: C, 67.86; H, 7.62; N, 3.23.
General Procedure for the Reduction of PhCHO under the WGSR Conditions. In a glove box, an oven-dried pressure tube equipped with a stir bar was charged with a 4.73 mM stock solution of 4a or 4b/4b' in toluene (3 mL, 14.2 µmol) and PhCHO (96.6 µL, 0.95 mmol, for a catalyst loading of 1.5 mol%). After mixing, the pressure tube was connected to a Fisher-Porter apparatus, which was subsequently attached to a Schlenk line filled with argon. Under a slightly positive argon pressure, degassed water (0.34 mL, 18.9 mmol, 20 equiv with respect to PhCHO) was added to the reaction vessel, and the system was flushed with 5 atm of CO for at least three times. The final CO pressure was set to 6.4 atm, and the Fisher-Porter apparatus was disconnected from the CO gas cylinder. The closed reaction system was heated at 100 °C with an oil bath. After 24 h, H₂ was slowly vented and the reaction mixture was cooled to room temperature. The resulting yellow solution was filtered through a Pasteur pipette packed with a short plug of silica gel, which was washed thoroughly with THF until the solution coming out of the pipette became almost colorless. Evaporation of the filtrate to dryness afforded an oily residue, which was dissolved in CDCl₃ and its ¹H NMR spectrum was recorded. The conversion from PhCHO to PhCH₂OH was calculated based on the ¹H NMR integrations of these two species. For reactions with a different catalyst loading, the volume of the catalyst stock solution (4.73 mM) was fixed at 3 mL. The amounts of PhCHO and water were varied but the PhCHO to water ratio was kept at 1 : 20. Control experiments using a complex bearing iron or copper only were conducted similarly. The concentration of the complex (1.5 mol% loading) was kept at 4.73 mM and the ratio between PhCHO and water was maintained at 1 : 20.

Protonation of the Fe-Cu Heterobimetallic Complexes with HCO₂H. In a glove box, 4a' or 4b' (25 µmol) was dissolved in ~0.6 mL of C₆D₆ and placed in a screw cap NMR tube. To the resulting solution was added HCO₂H (1.0 µL, 25 µmol) through the septum using a
microliter syringe. After 15 min, $^1$H NMR spectroscopy showed the formation of 2a or 2b as well as (IPr)CuOCHO.$^{46}$

**Reaction of the Fe-Cu Heterobimetallic Complexes with CH$_3$I.** In a glove box, 4a' (10.0 mg, 11.8 µmol) was dissolved in ~0.6 mL of C$_6$D$_6$ and placed in a J. Young NMR tube. To the resulting solution was added CH$_3$I (2.2 µL, 35.4 µmol) and the progress of the reaction was monitored by $^1$H NMR spectroscopy. The reaction was complete in 2 h, providing 5a, (IPr)CuI,$^{47}$ an unknown copper species, and at least three unknown iron species. $^1$H NMR of 5a (400 MHz, C$_6$D$_6$, $\delta$): 7.24 (t, 2H, $^3$J$_{H-H}$ = 7.6 Hz, ArH), 7.13 (d, 4H, $^3$J$_{H-H}$ = 7.6 Hz, ArH), 6.35 (s, 2H, NCH=CHN), 2.86 (sept, 4H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 2.35-2.07 (m, 2H, CH$_2$), 1.53 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.25-1.07 (m, 2H, CH$_2$), 1.07 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 0.15 (s, 18H, Si(CH$_3$)$_3$). Selected $^1$H NMR data of the unknown species (400 MHz, C$_6$D$_6$, $\delta$): 6.33 (s, NCH=CHN of a Cu species), 0.34 (s, Si(CH$_3$)$_3$ of an Fe species), 0.29 (s, Si(CH$_3$)$_3$ of an Fe species), 0.12 (s, Si(CH$_3$)$_3$ of an Fe species).

The NMR reaction was also carried out in the presence of MeCN (3.1 µL, 59.2 µmol) following otherwise the same procedure. In addition to the products mentioned above, 7a,$^{48}$ was generated and became the major iron-containing product after 3 days.

The NMR reactions of 4b/4b' with CH$_3$I were carried out similarly. After 16 h, ~15% of 4b/4b' remained unreacted. In the absence of MeCN, after 3 days, the reaction yielded CH$_4$ ($\delta$ 0.15), 5b (48% of all Cu species), (IPr)CuI (41% of all Cu species), an unknown copper species (11% of all Cu species), and two unknown iron species. In the presence of MeCN, after 3 days, the reaction yielded CH$_4$ ($\delta$ 0.15), 5b (9% of all Cu species), (IPr)CuI (91% of all Cu species),


and an iron acetonitrile complex 7b. Selected $^1$H NMR data of 5b (400 MHz, C$_6$D$_6$, δ): 6.39 (s, 2H, NCH=CHN), 2.82 (sept, 4H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.54 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.26 (s, 18H, C(CH$_3$)$_3$), 1.07 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$). Selected $^1$H NMR data of 7b (400 MHz, C$_6$D$_6$, δ): 1.55 (s, 18H, C(C$_3$H$_3$)$_3$), 0.74 (s, 3H, CH$_3$CN).

Reaction of the Fe-Cu Heterobimetallic Complexes with PhCH$_2$X (X = Br, Cl). In a glove box, 4a' or 4b' (11.8 µmol) was dissolved in ~0.6 mL of C$_6$D$_6$ and placed in a J. Young NMR tube. To the resulting solution was added PhCH$_2$X (17.7 µmol) and the progress of the reaction was monitored by $^1$H NMR spectroscopy. While the reaction with PhCH$_2$Br was complete in 2 h, the reaction with PhCH$_2$Cl took 36 h to reach completion. In each case, the products were PhCH$_3$ (δ 2.10), the bromide or chloride derivative of 5a or 5b, (IPr)CuX, and two unknown iron species. The $^1$H NMR spectra of the heterobimetallic bromide and chloride complexes derived from 4a are almost indistinguishable. Selected data (400 MHz, C$_6$D$_6$, δ): 6.33 (s, 2H, NCH=CHN), 2.88 (sept, 4H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 2.25-2.18 (m, 2H, CH$_2$), 1.99-1.93 (m, 2H, CH$_2$), 1.53 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.27-1.09 (m, 4H, CH$_2$), 1.07 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 0.13 (s, 18H, Si(C$_3$H$_3$)$_3$). Selected $^1$H NMR data of the chloride derivative of 5b (400 MHz, C$_6$D$_6$, δ): 6.37 (s, 2H, NCH=CHN), 2.83 (sept, 4H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 2.39-2.33 (m, 2H, CH$_2$), 2.03-1.96 (m, 2H, CH$_2$), 1.55 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$), 1.24 (s, 18H, C(CH$_3$)$_3$), 1.08 (d, 12H, $^3$J$_{H-H}$ = 7.2 Hz, CH(CH$_3$)$_2$).

The NMR reactions were also carried out in the presence of MeCN (3.1 µL, 59.2 µmol) following otherwise the same procedure. In addition to the products mentioned above, 7a or 7b was generated.
Synthesis of (IPr)CuOCH\textsubscript{2}Ph. Under an argon atmosphere, complex (IPr)CuOH (200 mg, 0.43 mmol) was added to a 50 mL oven-dried Schlenk flask, followed by the addition of THF (15 mL) to dissolve the solid. To this solution was added PhCH\textsubscript{2}OH (44 µL, 0.43 mmol), and the reaction mixture was stirred at room temperature for 30 min. Removal of the solvent under the vacuum afforded a white powder, which was washed with pentane (6 mL x 3) and then dried. The titled compound was isolated as a white solid (96 mg, 40% yield). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 7.37 (d, 2H, \(3J_{H-H} = 7.6\) Hz, ArH), 7.20-7.13 (m, 4H, ArH), 7.10-7.03 (m, 5H, ArH), 6.40 (s, 2H, NCH=C=CHN), 4.83 (s, 2H, CH\textsubscript{2}), 2.53-2.48 (m, 4H, CH(CH\textsubscript{3})\textsubscript{2}), 1.29 (d, 12H, CH(CH\textsubscript{3})\textsubscript{2}), 1.05 (d, 12H, \(3J_{H-H} = 6.8\) Hz, CH(CH\textsubscript{3})\textsubscript{2}); one of the resonances for the phenyl group was overlapped with the solvent resonances. The elemental analysis results were unsatisfactory despite repeated trials. Anal. Calcd for C\textsubscript{34}H\textsubscript{43}N\textsubscript{2}OCu: C, 73.02; H, 7.75; N, 5.01. Found: C, 68.53; H, 7.80; N, 4.71. HRMS-ESI (m/z): [M+Cu(IPr)]\textsuperscript{+} calcd for C\textsubscript{61}H\textsubscript{79}N\textsubscript{4}OCu\textsubscript{2}, 1011.48395; found, 1011.48252.

For comparison, \textsuperscript{1}H and \textsuperscript{13}C {\textsuperscript{1}H} NMR spectra of PhCH\textsubscript{2}OH were recorded. \textsuperscript{1}H NMR of PhCH\textsubscript{2}OH (400 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 7.17-7.06 (m, 5H, ArH), 4.30 (s, 2H, CH\textsubscript{2}), 1.34 (s, 1H, OH). \textsuperscript{13}C {\textsuperscript{1}H} NMR of PhCH\textsubscript{2}OH (101 MHz, C\textsubscript{6}D\textsubscript{6}, \(\delta\)): 141.62 (ArC), 128.58 (ArC), 127.47 (ArC), 127.21 (ArC), 64.71 (CH\textsubscript{2}).

**Reaction of 4a with CO (1 atm).** In a glove box, 4a' (10.0 mg, 11.8 µmol) was dissolved in ~0.6 mL C\textsubscript{6}D\textsubscript{6} (or THF-d\textsubscript{8}) and placed in a J. Young NMR tube. The resulting
solution of 4a was degassed by three freeze-pump-thaw cycles and then exposed to 1 atm of CO. The NMR tube was either heated by a 60 °C oil bath or left at room temperature (22 °C) and the progress of the reaction was monitored by 1H NMR spectroscopy. Conversions were calculated based on the integrations of the Si(CH₃)₃ resonances of 4a and 1a. The reaction of 4b/4b' (in THF-d₈) with CO (1 atm) was conducted following the same procedure.

**Reaction of 4a with CO (6.4 atm).** In a glove box, an oven-dried Fisher-Porter tube equipped with a stir bar was charged with 4a' (10.0 mg, 11.8 µmol) and 1 mL of C₆H₆. The tube containing the solution of 5a was taken outside the glove box, flushed with CO several times, and placed under 6.4 atm (or 80 psig) of CO. The CO cylinder was disconnected from the tube and the closed system was heated at 60 °C using an oil bath. After 48 h, CO was slowly vented, and the reaction mixture was cooled to room temperature before being filtered using a Pasteur pipette with a cotton plug. The resulting clear solution was evaporated to dryness and the residue was dissolved in C₆D₆ for NMR analysis. Conversions were calculated based on the integrations of the Si(CH₃)₃ resonances of 4a and 1a.

**Mercury Poisoning Experiment.** Reduction of PhCHO was performed using 4a (10.0 mg, 11.8 µmol, 5 mol% catalyst loading), PhCHO (24.1 µL, 237 µmol), elemental mercury (237 mg, 1.18 mmol), degassed water (4.3 µL, 237 µmol), and 3 mL of toluene under 6.4 atm of CO. The general procedure for the reduction under the WGSR conditions was followed using a catalyst loading of 5 mol%.

**Hydrogenation of PhCHO Catalyzed by 4a.** In a glove box, to an oven-dried pressure tube equipped with a stir bar was added 4a (10.0 mg, 11.8 µmol, 5 mol% catalyst loading), PhCHO (24.1 µL, 237 µmol) and 3 mL of toluene. After mixing, the pressure tube was connected to a Fisher-Porter apparatus, which was subsequently connected to a CO cylinder.
The reaction vessel was flushed with H₂ several times and the final H₂ pressure was set to 6.4 atm. This closed system was heated at 100 °C using an oil bath. After 24 h, H₂ was slowly vented and the reaction mixture was cooled to room temperature. The resulting yellow solution was filtered through a Pasteur pipette with a cotton plug, which was washed thoroughly with THF until the solution coming out of the pipette became almost colorless. The obtained solution was evaporated to dryness and the oily residue was dissolved in CDCl₃ for NMR analysis.

**X-ray Structure Determination.** Single crystals of 4a' were grown from a toluene solution layered with pentane. Single crystals of 4b' were obtained from evaporation of an NMR sample in C₆D₆, but can also be grown from a toluene solution. Crystal data collection and refinement parameters are summarized in Tables S1 and S6. Intensity data were collected at 150K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, λ = 1.54178 Å. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. The bridging hydride of 4a' was located directly from the difference map; the coordinates were refined. The remaining H-atoms were calculated and subsequently treated with a riding model. Complex 4a' crystallizes with toluene in the lattice while complex 4b' crystallizes with C₆D₆ in the lattice. In 4a'•C₇H₈, the toluene of crystallization shows some disorder. A few isopropyl group carbon atoms also show some anisotropic displacement parameter enlargement. However, in neither case was the disorder modeled as two-components. In 4b'•C₆D₆, several carbon atoms as well as the semibridging CO are disordered; two-
component disorder models for the disordered are presented; major conformers are in the 60-80% occupancy range.

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Chapter 3

Synthesis and Reactivity of a New Hexameric Copper Hydride Complex Supported by a (bisphosphino)amine Ligand
3.1 INTRODUCTION

Copper hydrides are key intermediates in many copper-catalyzed organic reactions.\textsuperscript{1} Although copper hydride chemistry has been known for a long time,\textsuperscript{2} examples of well-characterized copper hydride complexes are exceedingly rare in the literature (Figure 1). One of the best known copper hydrides is the hexameric copper cluster, [(PPh\textsubscript{3})CuH]\textsubscript{6}, which was originally synthesized by Osborn, Churchill, and co-workers.\textsuperscript{3} Later on, the Stryker group has demonstrated that catalytic hydrogenation of \(\alpha,\beta\)-unsaturated ketones with [(PPh\textsubscript{3})CuH]\textsubscript{6} leads to chemoselective reduction of C=C double bonds over C=O bonds.\textsuperscript{4} Caulton and co-workers discovered that a dimeric copper hydride could be formed if a bulky tripodal phosphine ligand (MeC[CH\textsubscript{2}PPh\textsubscript{2}]\textsubscript{3}) is employed.\textsuperscript{5} Interestingly, one of three P-arms of the tripodal ligand does not coordinate to the copper center presumably because of the strong Cu\textsubscript{2}(\(\mu\)-H)\textsubscript{2} core. In stark contrast to [(PPh\textsubscript{3})CuH]\textsubscript{6}, Caulton’s [(tripodal)CuH]\textsubscript{2} catalyzes selective hydrogenation of C=O bonds in the presence of C=C bonds.\textsuperscript{6} Recently, Norton and co-workers have isolated a trinuclear copper hydride complex bearing a diphosphine (dpbbz = 1,2-bis(diphenylphosphino)benzene) ligand and have studied its electron-transfer reactions.\textsuperscript{7} In

addition to the aforementioned copper hydrides, octameric\(^8\) and pentameric copper hydrides\(^9\) and copper clusters with interstitial hydrides\(^10\) have also been reported in the literature.

\[ \text{[(PPh}_3\text{)CuH]}_6 \]

Osborn, 1971  
[Cu\(\mu\)-H\(\mu\)-Cu] \[ \text{Caulton, 1986} \]

\[ \text{[(IPr)CuH]}_2 \]

Norton, 2013

**Figure 1.** Selected Examples of Isolated Copper Hydride Complexes Supported by Phosphine Ligands.

Bulky \(N\)-heterocyclic carbene (NHC) ligands are also known to stabilize copper hydrides complexes with low nuclearity (Figure 2). Sadighi and co-workers have isolated a copper hydride complex supported by an IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) ligand, and X-ray crystallography reveals a dimeric \{Cu\(\mu\)-H\(\mu\)]\(2\) core in the solid-state structure.\(^11\) [(IPr)CuH]\(2\) undergoes clean insertion with 3-hexyne to form the corresponding copper alkenyl complex, as established by NMR spectroscopy. Bertrand et al. have shown that using a more sterically crowded alkylaminocarbene ligand, the thermodynamic stability of the dimeric copper hydride complex could be greatly enhanced.\(^12\) Studies by Schomaker and co-workers have demonstrated that substitution of the isopropyl groups in the IPr ligand with more

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bulky 3-pentyl or 4-heptyl moieties also increases the stability of the dimeric copper hydride complex. More recently, Sadighi et al. have synthesized dimeric copper hydrides bearing six and seven-membered NHC ligands that are stable at ambient temperatures in both solid and solution states. Solution IR spectrum suggests that the dimeric \( \{ \text{Cu}_2(\mu-H)_2 \} \) core remains intact in solution. Stoichiometric insertion reactions of these new copper hydrides with alkenes and isonitriles have been investigated.

![Selected Examples of Isolable Copper Hydrides Bearing N-Heterocyclic Carbene Ligands.](image)

**Figure 2.** Selected Examples of Isolable Copper Hydrides Bearing N-Heterocyclic Carbene Ligands.

Our group has been interested in catalytic reduction of C=O bonds with \( \{ \text{RPN(H)P} \} \)-based iron, cobalt and nickel pincer complexes. It has prompted us to synthesize analogous

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copper hydride complexes bearing $[^{10} \text{PN}(\text{H})\text{P}]$ ligands and investigate their stoichiometric and catalytic reactions. To the best of our knowledge, copper hydride complexes supported by a tridentate ligand with a protic N–H moiety has not been reported prior to our study. Herein we report the isolation of a new hexameric copper hydride complex stabilized by a $[^{1\text{Pr}} \text{PN}(\text{H})\text{P}]$ ligand. We also demonstrate its reactivity in catalytic hydrogenation of aldehydes, ketones, and CO$_2$. Catalysis could be performed either by generating this copper hydride species in-situ from the corresponding copper halide complexes or directly employing the copper hydride in the reaction. Preliminary results suggest that hydrogenation of C=O bonds proceed via a bifunctional pathway that involves the participation of the N–H moiety in the tridentate ligand.

3.2 RESULTS AND DISCUSSION

3.2.1 Synthesis of $[^{10} \text{PN}(\text{H})\text{P}]\text{CuX}$ (X = Br, BH$_4$) Complexes. Treatment of the $[^{10} \text{PN}(\text{H})\text{P}]$ (R = Cy, ‘Bu) ligand with CuBr in tetrahydrofuran afforded the corresponding $[^{10} \text{PN}(\text{H})\text{P}]\text{CuBr}$ species (1b: R = Cy, 1c: R = ‘Bu) in good isolated yields (50-58%, Scheme 1). Related $[^{1\text{Pr}} \text{PN}(\text{H})\text{P}]\text{CuBr}$ complex (1a), previously reported by Arnold and co-workers, was synthesized according to the literature procedure. Compounds 1b and 1c were isolated as white powders and characterized by $^1\text{H}$ NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, IR spectroscopy, elemental analysis, and single-crystal X-ray crystallography. The phosphorous atoms are equivalent in these complexes, showing one signal by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.


Interestingly, chemical shift for the tert-butyl-substituted phosphorous atoms in complex 1c appeared much downfield (δ 14.97) compared to the cyclohexyl (δ –4.00) and isopropyl (δ 2.91) analogues. The N–H stretching frequencies for complexes 1a and 1b were observed near 3230 cm\(^{-1}\). In contrast, \(v_{\text{N-H}}\) was found to be shifted to a higher value (3271 cm\(^{-1}\)) for 1c. These spectroscopic differences indicated that the tert-butyl-substituted copper bromide complex could be structurally unique. This hypothesis was supported by the X-ray crystallographic study (Figure 3), which shows that the N–H moiety of the ligand is not coordinated to the copper. The copper center adopts a distorted trigonal geometry with average Cu–P bond distance of 2.26 Å.

We believe that bulky tert-butyl groups on the phosphorous atoms prevent the N–H coordination to copper and therefore the metal center cannot attain the anticipated tetrahedral geometry. In contrast, X-ray structure of the cyclohexyl-substituted copper complex (1b, Figure 4) showed N–H coordination to copper. The N–Cu bond distance is found to be 2.290 Å and the N–H and Cu–Br bonds have syn spatial orientation. Other structural features of complex 1b are similar to 1a, as reported by Arnold et al.\(^{19}\) X-ray crystal data and refinement parameters for 1b and 1c are given in Table 1.

In addition to the copper bromide complexes, related copper hydridoborate complexes (1a-BH\(_4\) and 1b-BH\(_4\)) have also been synthesized and characterized by multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis. Treatment of 1a-b with an excess of NaBH\(_4\) in ethanol generated the copper hydridoborate complexes as the sole products. Solid-state IR spectrum of 1a-BH\(_4\) complex showed two B-H stretching frequencies: \(v(\text{B–H}_\text{terminal}) = 2352\) cm\(^{-1}\) and \(v(\text{B–H}_\text{bridging}) = 2021\) cm\(^{-1}\). A broad quartet for the BH\(_4\) resonance was observed at δ 1.90-1.30 by \(^1\)H NMR spectroscopy. Similar spectroscopic features were observed with the cyclohexyl analogue.
**Scheme 1.** Synthesis of $^R \text{PN}(\text{H})\text{P} \text{CuX}$ (X = Br, BH$_4$) Complexes

$$ \text{R}_2\text{P} - \text{N} - \text{PR}_2 \xrightarrow{\text{CuBr}} \begin{array}{c} \text{H} \\ \text{R} = \text{Cy, } ^{1}\text{Pr} \end{array} \xrightarrow{\text{THF}, \text{rt, overnight}} \begin{array}{c} \text{H} \\ \text{R} = \text{Cy, } ^{1}\text{Pr}, \text{reported} \end{array} \xrightarrow{\text{NaBH}_4 \text{ (xs)}} \begin{array}{c} \text{H} \\ \text{R} = \text{Cy, } 50\% \text{ yield} \end{array} \xrightarrow{\text{EtOH, rt, 16 h}} \begin{array}{c} \text{H} \\ \text{R} = \text{Cy, } 30\% \text{ yield} \end{array}$$

**Figure 3.** X-ray Crystal Structure of 1c (50% probability level). Selected bond lengths (Å) and angles (deg): Cu–P(1) 2.2617(4), Cu–P(2) 2.2583(4), Cu–Br(1) 2.4196(3), P(1)–Cu–P(2) 133.629(17), P(1)–Cu–Br(1) 112.365(13), P(2)–Cu–Br(1) 113.942(13).
Figure 4. X-ray Crystal Structure of 1b (50% probability level). Selected bond lengths (Å) and angles (deg): Cu–P(1) 2.2247(16), Cu–P(2) 2.2416(15), Cu–N(1) 2.290(5), Cu–Br(1) 2.4164(9), P(1)–Cu–P(2) 132.05(6), N(1)–Cu–P(1) 83.95(13), N(1)–Cu–P(2) 85.73(12), N(1)–Cu–Br(1) 113.25(12), P(1)–Cu–Br(1) 115.10(5), P(2)–Cu–Br(1) 112.00(5).

Table 1. Crystal Data and Refinement Parameters for 1a and 1b.

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<th>1b</th>
<th>1c</th>
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<td>C_{28}H_{45}NP_{2}BrCu</td>
</tr>
<tr>
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3.2.2 Synthesis of $^{R}[PN(H)P]$ Ligated Copper Hydride Complexes. With a flexible tridentate ligand that supports both the tetrahedral and trigonal geometry around copper, we anticipated that the corresponding copper hydride complex could be formed and would have sufficient stability for isolation. Different methods have been reported in the literature for the synthesis of copper hydride species from copper precursors. In Osborn’s original report, a DMF solution of [PPh$_3$CuCl]$_4$ was treated with sodium trimethoxyborohydride at room temperature, which generated deep red crystals of hexameric copper hydride complex. Using a different strategy, Caulton et al. demonstrated that hydrogenolysis of the Cu–O bond of (CuO'Bu)$_4$ in the presence of a tripodal MeC(CH$_2$PPh$_3$)$_3$ ligand afforded the dimeric $\{[\kappa^2$-MeC(CH$_2$PPh$_3$)$_3$]$_2$Cu$_2$(μ-H)$_2$\} as shown in Figure 1. Norton and co-workers also used the hydrogenolysis route in order to form the trinuclear [(dppbz)$_3$Cu$_3$(μ-H)$_3$] species. Sadighi and co-workers demonstrated that reactions of (NHC)Cu-O'Bu species with tertiary silanes or boranes rapidly generate the corresponding copper hydride compounds that are typically intense yellow in color. The formation of strong Si–O and B–O bonds is likely the thermodynamic driving force in these reactions.

In order to synthesize $^{R}[PN(H)P]$-supported copper hydride complexes, we planned to utilize the hydrogenolysis route reported by Caulton and Norton groups. The presence of the acidic NH moiety on the [PN(H)P] ligand posed difficulties to isolate the corresponding Cu-O'Bu species via a salt metathesis reaction. Instead, 1a was mixed with KO'Bu in toluene under 40 psig H$_2$ (Scheme 2), which resulted in an intense orange-red color solution. An orange solid was isolated after washing the crude product with acetonitrile. Alternatively, the same complex can be synthesized directly by mixing iPr$_2$[PN(H)P] ligand, anhydrous KO'Bu and anhydrous CuBr in a 1 : 2 : 2 ratio at room temperature under 40 psig H$_2$ pressure. The isolated product is
extremely air and temperature sensitive and readily decomposes upon exposure to air; however, it can be stored under an inert atmosphere at –30 °C for days. $^1$H NMR spectrum of the isolated compound (2a) in C$_6$D$_6$ (Figure 5) shows characteristic hydride resonance at $\delta$ 2.07 ($J_{\text{H-P}} = 8.0$ Hz), consistent with the chemical shift values ($\delta$ 0.60-2.67) reported for other copper hydride complexes.$^{3-14}$ The resonance at $\delta$ 2.07 disappeared for the corresponding copper deuteride (2a-D) species, further confirming the assignment for the hydride resonance (see Appendix). The N-H resonance was also located at $\delta$ 3.56 by $^1$H NMR spectroscopy, which is significantly shifted from that of the parent copper bromide complex ($\delta$ 2.67). When an excess of D$_2$O was added to a C$_6$D$_6$ solution of 2a, H/D exchange reaction occurred only to the NH moiety not to the CuH resonance, suggesting that the NH moiety is acidic. Four sets of CH$_2$ peaks and four sets of CH$_3$ peaks are found in the $^1$H NMR spectrum, indicating a lower symmetry in the copper hydride species. More interestingly, based on the integrations of the hydride ligand and $[^{15}\text{P} \text{PN}(\text{H})\text{P}]$ ligand; it was evident that two hydride ligands were present per $[^{15}\text{P} \text{PN}(\text{H})\text{P}]$ ligand. Although $^1$H NMR spectrum of 2a suggested a low symmetry structure, $^{31}$P{$^1$H} NMR spectrum showed a single resonance at $\delta$ 0.99 indicating that all the phosphorous resonances are equivalent. Infrared spectra of solid samples reported for Sadighi’s$^{11,14}$ and Caulton’s$^5$ dimeric copper bridging hydride species showed moderately strong $\nu$(CuH) bands near 881-912 cm$^{-1}$ and 950 cm$^{-1}$, respectively. On the other hand, $\nu$(CuH) bands were not observed for Norton’s trimeric$^7$ and Osborn’s$^3$ hexameric copper bridging hydrides, suggesting that $\nu$(CuH) bands for {Cu$_n$H$_n$} clusters (where n$\geq$3) are significantly weaker in the IR spectra. Unfortunately, the $\nu$(CuH) band could not be conclusively assigned from the IR spectrum of complex 2a. Comparing the IR spectrum of 2a with that of 2a-D (prepared using D$_2$ instead of H$_2$) did not show any band with the anticipated isotopic shift (see Appendix). On the basis of $^1$H NMR integrations and the
absence of a ν(CuH) band in the IR spectrum, we expected that the structure of 2a would be described by a general formula of \( \{iPr(PNHP)_{n/2}Cu_nH_n\} \) (where \( n \geq 3 \)).

**Scheme 2. Synthesis of Copper Hydride Complex 2a**

**Figure 5.** \(^1\text{H}\) NMR Spectrum of 2a in \( C_6D_6 \).
Single crystals of 2a were grown by layering a saturated toluene solution of 2a with acetonitrile and studied by X-ray crystallography. Consistent with NMR and IR spectroscopy, preliminary X-ray crystal structure (Figure 6) suggests a hexameric \{Cu_6(\mu-H)_6\} core supported by three iPr[PN(H)P] ligands. In this structure, six copper centers form an octahedron and the six hydride ligands are presumably situated at six out of eight faces of the octahedron. Unlike the copper bromide complex 1a, the two phosphorous donors of each [PN(H)P] ligand in 2a are bonded to two different copper centers. This structural pattern suggests that the hydride bridges in the core are sufficiently stronger than a potential second Cu–P bond formation. This is reminiscent to Caulton’s dimeric copper hydrides structure\(^5\) where the third Cu–P bond of the tripodal ligand was displaced by the hydride bridge. It is also interesting to note that in 2a the N–H moiety of the iPr[PN(H)P] ligand is no longer bonded to the copper center.
3.2.3. Stoichiometric Reactions of 2a with Compounds Containing C=O Bonds.

(a) Insertion of PhCHO. Next, stoichiometric reactions of 2a with carbonyl substrates including benzaldehyde, acetophenone and carbon dioxide were investigated. When ten equivalents of benzaldehyde were mixed with 2a in C₆D₆, facile insertion occurred within a few minutes and the original intense orange color of the hydride solution faded to yellow (eq 1). ¹H NMR spectrum of the resulting solution showed complete disappearance of the starting copper hydride resonance at δ 2.07 and formation of a new copper species that is assigned to the copper benzyloxide complex, [iPrPN(H)P]CuOCH₂Ph (3). In the ¹H NMR spectrum, complex 3 shows a characteristic singlet resonance at δ 5.15 for the methylene protons of the benzyloxide moiety.
bonded to the copper. $^{31}$P{$^1$H} NMR spectrum of 3 depicts a single resonance at $\delta$ 4.28. Despite several attempts, isolation of 3 in an analytically pure form via an independent route (eq 2) proved unsuccessful owing to its high moisture sensitivity.

\[
\text{(1)}
\]

(b) Insertion of Acetophenone. The success of aldehyde insertion prompted us to explore similar insertion chemistry with a ketone. A much slower insertion of PhC(O)CH$_3$ into the Cu–H bond of 2a was observed, forming a product consistent with $\{^{iPr}PN(H)P\}$Cu-OCH(Me)Ph (4, eq 3). Based on the $^{31}$P{$^1$H} NMR, 2a was fully converted over a period of two hours. Characteristic resonances of complex 4 include a quartet at $\delta$ 5.07 ($J = 12$ Hz) for the CH and a doublet at $\delta$ 1.63 ($J = 4$ Hz) for the CH$_3$ protons of the benzyloxide group. In addition to complex 4, several other unidentified copper species were detected as minor products of the insertion reaction.
(c) Insertion of CO$_2$. Insertion of CO$_2$ into an M–H bond represents a fundamentally important step in transition metal-catalyzed reduction of CO$_2$.\textsuperscript{20} Despite high thermodynamic and kinetic stability of CO$_2$, we observed that the reaction of 2a with CO$_2$ (\textasciitilde1 atm) proceeded rapidly at ambient temperature to afford copper formate complex 5 as the sole product (Scheme 3). Complex 5 was isolated as a light yellow powder (22\% isolated yield) and characterized by $^1$H, $^{31}$P{$^1$H}, $^{13}$C{$^1$H} NMR spectroscopy and IR spectroscopy. $^1$H NMR spectrum of 5 in C$_6$D$_6$ shows a broad singlet at $\delta$ 9.50 assigned to the formate (Cu-OCHO) proton resonance. $^{31}$P{$^1$H} NMR spectrum depicts a single phosphorus resonance at $\delta$ 7.38 indicating two equivalent phosphorus atoms in the molecule and the formate carbon resonance (Cu-OCHO) was observed at $\delta$ 168.86 in the $^{13}$C{$^1$H} NMR spectrum. Infrared spectrum of 5, recorded in the solid state, shows a strong $\nu$(CO) band at 1588 cm$^{-1}$ and the $\nu$(NH) band is located at 3210 cm$^{-1}$. These spectroscopic data are consistent with other reported copper formate complexes containing a terminally bound formate group.\textsuperscript{21}


**Scheme 3. Synthesis of the Copper Formate Complex 5**

\[
egin{array}{c}
{[\text{IPrPN(H)P]}_3Cu_6H_6 + CO_2} \\
\text{rt, } <5 \text{ min} \\
\rightarrow 5 \\
\text{added, rt, } <5 \text{ min} \\
\text{HCO}_2\text{H} \\
\text{rt, } <5 \text{ min} \\
\rightarrow {[\text{IPrPN(H)P]}_3Cu_6H_6} \\
\end{array}
\]

Although CO₂ insertion into 2a favors the formation of 5, this process is reversible. This was confirmed by performing an isotope labeling experiment with ^{13}CO₂. When ^{13}CO₂ (~1 atm) was introduced to a C₆D₆ solution of 5 at room temperature, after seven days, 40% of 5 was converted to the ^{13}C-labelled copper formate complex 5' (eq 4). The formate resonance of 5' appeared as a doublet (\(J_{C-H} = 188\) Hz) centered at δ 9.60.

\[\begin{array}{c}
\text{5} \\
\text{added, rt, } 7 \text{ d} \\
\Rightarrow \text{5'} (40\% \text{ conversion})
\end{array}\]

### 3.2.4 Catalytic Hydrogenation of Aldehydes, Ketones and CO₂.

Catalytic hydrogenation of carbonyl substrates to produce alcohols is an important process and compared to the stoichiometric reduction with reactive metal hydrides (e.g., NaBH₄ and LiAlH₄) hydrogenation is more atom economical. Although precious metal-based homogeneous catalysts dominate the hydrogenation field, over the last two decades, a great amount of research has been done focusing on the development of catalysts that contain inexpensive, earth-abundant first-row transition metals. Although copper-based heterogeneous
catalysts are routinely employed for the hydrogenation of CO$_2$ and esters, examples of homogeneous copper catalysts for hydrogenation reactions are rare in the literature. In a recent study by Sawamura and co-workers, a homogeneous (IPr)CuO'Bu pre-catalyst was employed in the semihydrogenation of internal alkynes to produce alkenes with high Z-selectivity. (IPr)CuH has been proposed as the active catalytic intermediate, which is presumably generated via hydrogenolysis of (IPr)CuO'Bu.

Having synthesized well-defined copper hydride and copper halide complexes and having successfully demonstrated stoichiometric reactions of 2a with PhCHO, PhC(O)Me and CO$_2$, we seek the possibility of utilizing these complexes for catalytic hydrogenation reactions. It was hypothesized that reactions of dihydrogen with copper alkoxide and formate complexes would regenerate the active copper hydride species, thereby releasing the reduced organic products.

(a) Hydrogenation of Aldehydes and Ketones. Because the copper bromide complexes are more air-stable, readily accessible, we first employed 1a-c as catalysts for the hydrogenation of PhCHO and PhC(O)Me. Gratifyingly, we observed that PhCHO was quantitatively converted to PhCH$_2$OH at room temperature within one day when a mixture of 2 mol% of 1a, 2.4 mol% KO'Bu and PhCHO in THF were stirred under 50 psig H$_2$ pressure (eq 5). Under the same catalytic conditions except with a slightly higher H$_2$ pressure (80 psig), PhC(O)Me was also reduced to the corresponding alcohol in a quantitative yield (eq 6). As a comparison, 1b (2 mol%) gave a quantitative conversion of PhC(O)CH$_3$ to PhCH(OH)CH$_3$ but 1c turned out to be

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completely inactive. The lack of N–Cu interaction in 1c and the failure to form the corresponding copper hydride species under the catalytic conditions could explain its inactivity in the hydrogenation reaction. Reducing the catalyst loading of 1a from 2 mol% to 1 mol% resulted in only 60% conversion of acetophenone to the alcohol under 80 psig H₂ pressure. Control studies performed without KO'Bu and 1a afforded 0% and 4% of reduced alcohols, respectively, suggesting that the reaction is indeed catalytic in copper. Catalyst-poisoning study was carried out in the presence of an excess of elemental mercury, which did not affect the hydrogenation activity of 1a.

Because complexes 1a and 1b show similar catalytic activity and because the copper hydride derived from 1a is better established, we decided to use 1a to investigate substrate scope for the copper-catalyzed hydrogenation reaction (Table 2). Aldehydes with either an electron-donating or an electron-withdrawing group reacted smoothly to yield the corresponding alcohols in high GC yields (>99%). No apparent rate difference was observed between PhCHO, 4-
fluorobenzaldehyde and 4-methoxybenzaldehyde (entries 1-3) as all of these substrates afforded the corresponding alcohols in >99% yield in a day. In contrast, both electron-deficient ketones such as benzophenone (entry 6) and electron-rich aliphatic ketones such as cyclohexanone (entry 7) reacted slower than acetophenone and after one day yielded 81% and 65% of products, respectively. No other side product was detected in the crude reaction mixture. Surprisingly, acetophenone derivative containing a CO₂Me group at the para position (entry 8) did not produce any alcohols under these conditions. 2-pyridyl ketone in which an N-heterocycle is present also failed to generate the corresponding alcohol, perhaps because of inhibition of the catalyst by the coordination pyridine ring to copper (entry 9).

Table 2. Substrate Scope for the Catalytic Hydrogenation of Aldehydes and Ketones

<table>
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<tr>
<th>entry</th>
<th>substrate</th>
<th>product</th>
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<th>yield (%)</th>
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<td><img src="image2" alt="image" /></td>
<td>50</td>
<td>&gt;99</td>
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Next, we turned our attention to utilizing 2a directly in catalytic hydrogenation of PhCHO. Under base-free conditions, 77% of PhCH₂OH was produced when 2 mol% of 2a was employed and the catalytic reaction was carried out under 50 psig H₂ pressure for one day (eq 7). This observation supports the involvement of the copper hydride complex in the hydrogenation reaction and therefore bears mechanistic significance.

\[
\begin{align*}
\text{entry} & & \text{substrate} & & \text{product} & & \text{pH₂} & & \text{yield} \\
5 & & \text{Ph-CHO} & & \text{Ph-OH} & & 80 & & >99 \\
6 & & \text{Ph₂-CHO} & & \text{Ph₂-OH} & & 80 & & 81 \\
7 & & \text{cyclohexanone} & & \text{cyclohexanol} & & 80 & & 65 \\
8 & & \text{CO₂Me-CHO} & & \text{CO₂Me-OH} & & 80 & & 0 \\
9 & & \text{Pyridine-CHO} & & \text{Pyridine-OH} & & 80 & & 0
\end{align*}
\]

\[(\text{b) Catalytic Hydrogenation of CO₂.})\text{ An increase in the atmospheric CO₂, a greenhouse gas, has detrimental effects on our environment. One way to reduce the amount of CO₂ in the}\]

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atmosphere is to utilize CO\textsubscript{2} in the production of C\textsubscript{1} based chemicals, which can be used as alternative fuels. Therefore there is a growing interest in the development of homogeneous catalysts for the reduction of CO\textsubscript{2} to produce formates\textsuperscript{25,26a-j}, formic acid\textsuperscript{26a-b} and methanol.\textsuperscript{27} These chemicals have high hydrogen contents and can be implemented as hydrogen storage material,\textsuperscript{28} especially considering that transporting these liquid fuels is less costly and safer than transporting hydrogen itself. To date, the most active catalysts for the hydrogenation of CO\textsubscript{2} to formates are based on ruthenium\textsuperscript{29} and iridium,\textsuperscript{30} and the development of catalysts based on inexpensive and earth abundant metals would be more desirable. Recently, several catalysts containing iron\textsuperscript{31} or cobalt\textsuperscript{32} have been reported for the hydrogenation of CO\textsubscript{2}. Appel and co-workers have demonstrated the use of a homogeneous copper catalyst bearing a triphos ligand

\textsuperscript{28} Ohl, G. A. Angew. Chem., Int. Ed. 2013, 52, 104.
for the homogeneous hydrogenation of CO$_2$ to formate salt using an excess of 1,8-diazabicylcoundec-7-ene (DBU) as the base.$^{33}$

Given the insertion of CO$_2$ into 2c and catalytic activity of 1c in hydrogenation of carbonyl compounds, we decided to carry out copper-catalyzed hydrogenation of CO$_2$ to produce formate salts. Preliminary results demonstrate that at 94 °C in the presence of 2 mol% of 1a and 100 mol% of KO'Bu, a 1 : 1 mixture of CO$_2$ and H$_2$ (total pressure = 300 psig) in THF is converted to potassium formate salt with 16% conversion in a day. When the same catalytic reaction was performed in 1,2-dimethoxyethane (glyme), NMR yield of potassium formate increased to 31% (eq 8). In contrast to the catalytic system developed by Appel and co-workers, DBU is not an effective base in our system as only <5% of potassium formate was obtained even with a higher catalyst loading (5 mol %) and higher total pressures (600 psig). We are currently in the process of optimizing the catalytic conditions for the hydrogenation of CO$_2$.

**3.2.5 Mechanism**

A proposed catalytic cycle for the hydrogenation of carbonyl compounds including aldehydes and ketones is shown in Scheme 4. A copper hydride species is generated in solution when 1a is treated with KO'Bu and H$_2$. Although a hexanuclear structure was observed for the solid sample of copper hydride 2a, this species may exist in a different form ([LCu-H]$_n$) in solution during catalysis. Rapid insertion of C=O groups into the Cu–H bond has been observed

experimentally and therefore it is likely that under the catalytic conditions copper alkoxide complexes form rapidly as well. Two pathways are possible for the release of the reduced organic product: (a) direct hydrogenolysis of the Cu–OR bond and (b) elimination of ROH from the Cu–OR and NH moieties, followed by H₂ activation by the N–Cu bond. To test the possibility of the hydrogenolysis mechanism, complex 4 was first generated in-situ via the reaction between 2a and an excess of acetophenone, and then exposed to 1 atm H₂ pressure (Scheme 5). Monitoring the reaction by ¹H NMR spectroscopy showed that the CH resonance of 4 (δ 5.07) slowly disappeared and a new CH resonance appeared at δ 4.84, which is consistent with the formation of free PhCH(OH)Me. When the reaction mixture was spiked with an authentic sample of PhCH(OH)Me, resonances originated from the hydrogenolysis product and those of the added alcohol overlapped with each other.
In order to test if the NH moiety of the tridentate ligand is actively participating in the hydrogenation reaction, the related N(Me) derivative of the copper bromide complex (1a-Me) was synthesized by reacting \(^{\text{IPr}}\text{PN(Me)}\text{P}\) ligand with anhydrous CuBr in THF (eq 9). This complex was isolated in 40% yield and characterized by \(^1\text{H}, \ ^{31}\text{P}\{^1\text{H}\}, \ ^{13}\text{C}\{^1\text{H}\}\) NMR and IR.
spectroscopy. The N-CH₃ resonance appeared at δ 2.42 in the ¹H NMR spectrum and a single phosphorous resonance was observed by ³¹P{¹H} NMR spectroscopy. The solid-state structure of this complex was established by X-ray crystallography (Figure 5). X-ray structure of 1a-Me shows that the N-Me and Cu-Br bonds are oriented *syn* to each other. Crystal data and refinement parameters for complex 1a-Me are given in Table 3.

![Chemical structure diagram](image)

**Figure 7.** X-ray Crystal Structure of 1a-Me (50% probability level). Selected bond lengths (Å) and angles (deg): Cu–P(1) 2.2400(6), Cu–P(2) 2.2363(6), Cu–N(1) 2.2364(19), Cu–Br(1) 2.4118(4), P(1)–Cu–P(2) 125.39(2), N(1)–Cu–P(1) 85.11(5), N(1)–Cu–P(2) 85.41(5), N(1)–Cu–Br(1) 108.87(5).
Table 3. Crystal Data and Refinement Parameters for 1a-Me.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>empirical formula</td>
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</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P2_1/n</td>
</tr>
<tr>
<td>a, Å</td>
<td>7.77892(2)</td>
</tr>
<tr>
<td>b, Å</td>
<td>19.3323(5)</td>
</tr>
<tr>
<td>c, Å</td>
<td>14.9717(4)</td>
</tr>
<tr>
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<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>99.7043(8)</td>
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<tr>
<td>γ, deg</td>
<td>90</td>
</tr>
<tr>
<td>Volume, Å³</td>
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</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
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<tr>
<td>no. of unique data, R_{int}</td>
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</tr>
<tr>
<td>R1, wR2 (I &gt; 2σ(I))</td>
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</tr>
<tr>
<td>R1, wR2 (all data)</td>
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</tr>
</tbody>
</table>

In the presence of KO{\textsuperscript{t}}Bu, when 2 mol\% of 1a-Me was employed in the catalytic hydrogenation of acetophenone, no PhCH(OH)Me was formed after one day (eq 10), suggesting that ketone hydrogenation likely proceeds via a bifunctional mechanism involving the participation of the NH moiety of the [PN(H)P] ligand. It is worth to note that under H\textsubscript{2} pressure the solution turned bright orange, which indicated that the corresponding copper hydride species was formed during the reaction.

\[ \text{PhCOCH}_2\text{Me} + \text{H}_2 (80 \text{ psig}) \xrightarrow{\text{KO}^t\text{Bu}(2.4 \text{ mol}\%)} \xrightarrow{\text{THF, rt, 1 d}} \text{PhCH(OH)Me} \text{ (10)} \]

0% conversion
3.3 CONCLUSIONS

A series of $^r$[PN(H)P]CuX ($R = ^{i}$Pr, Cy, $^t$Bu; $X = Br, BH_4$) complexes have been synthesized and employed in the catalytic reduction of C=O bonds. Hydrogenation reactions of aldehydes and ketones have been achieved under relatively mild conditions. A hexameric copper hydride, a key intermediate in the copper catalyzed hydrogenation reactions, has been isolated and directly utilized as the catalyst in these reactions. Stoichiometric studies carried out with the copper hydride provided further mechanistic insight. Precatalyst $^{ipr}$[PN(H)P]CuBr in presence of excess base has also been exploited in CO$_2$ hydrogenation reaction and shows promising results. Further investigations are underway to optimize the catalytic conditions and the corresponding $^{ipr}$ {PN(H)P} CuOCHO will also be employed for catalytic CO$_2$ hydrogenation.

3.4 EXPERIMENTAL SECTION

General Experimental Information. Unless otherwise mentioned, all air-sensitive compounds were handled under an inert atmosphere using standard Schlenk line and inert-atmosphere box techniques. Toluene, pentane and THF were deoxygenated and dried in a solvent purification system by passing through an activated alumina column and an oxygen-scavenging column under argon. Acetonitrile was dried over calcium hydride. C$_6$D$_6$ was distilled from Na and benzophenone under an argon atmosphere. Other deuterated solvents such as CDCl$_3$ and THF-$d_8$ (packed in an ampule) were used as received from commercial sources. All liquid aldehydes were freshly distilled prior to use. Liquid ketone substrates were degassed and dried over molecular sieves. Unless otherwise noted, $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR were recorded on a Bruker AV 400MHz spectrometer. $^{31}$P NMR spectra were referenced externally to 85% H$_3$PO$_4$ which appears at 0 ppm. $^2$H NMR spectra were recorded in a Bruker Avance-500
MHz instrument. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with smart orbit diamond attenuated total reflectance (ATR) accessory.

Synthesis of \( \{\text{CyPN(H)P}\text{CuBr} \text{(1b)} \). Under an inert atmosphere, an oven-dried Schlenk flask equipped with a stir bar was charged with bis[2-(dicyclohexylphosphinoethyl)]amine ligand (206 mg, 0.442 mmol) and CuBr (56 mg, 0.402 mmol), followed by the addition of 20 mL of THF. The resulting mixture was stirred overnight and then filtered through a plug of Celite to give a colorless solution. The filtrate was dried under vacuum and the residue was washed with pentane (3 × 7 mL). Further evaporation of the volatiles in vacuo afforded the desired product as a white solid (116 mg, 50% yield). X-ray quality single crystals were grown at −30 °C from a saturated solution of the product in THF layered with pentane. \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), δ): 2.38–2.35 (m, CHCy, 4H), 2.26 (br, PNHP, 1H), 1.88–1.91 (br m, PNPC\(_H_2\), 8H), 1.81–1.69 (br m, CH\(_2\), 10H), 1.64 (br, 5H), 1.59–1.43 (br m, 8H), 1.35 (br, 4H), 1.29–1.15 (br m, 13H). \(^{13}\)C\(^{\{1\}H}\) NMR (101 MHz, C\(_6\)D\(_6\), δ): 45.58 (br, NCH\(_2\)), 34.56 (t, \(J_{C-P} = 7.07\) Hz, PCHCH\(_2\)), 30.06 (s, CyC), 29.80 (s, CyC), 27.96 (t, \(J_{C-P} = 5.05\) Hz, CyC), 27.65 (t, \(J_{C-P} = 5.05\) Hz, CyC), 26.63 (s, CyC), 23.63 (t, \(J_{C-P} = 7.07\) Hz, PCH\(_2\)). \(^{31}\)P\(^{\{1\}H}\) NMR (162 MHz, C\(_6\)D\(_6\), δ): −4.00 (s). ATR-IR (solid): \(\nu(\text{N-H}) = 3234\) cm\(^{-1}\). Anal. Calcd for C\(_{28}\)H\(_{53}\)BrCuNP\(_2\): C, 55.21; H, 8.77; N, 2.30. Found: C, 55.36; H, 8.78; N, 2.31.

Synthesis of \( \{\text{tBuPN(H)P}\text{CuBr} \text{(1c)} \). Under an inert atmosphere, an oven-dried Schlenk flask with a stir bar was charged with bis[2-(di-tert-butylphosphino)ethyl]amine ligand (267 mg, 0.738 mmol), CuBr (96 mg, 0.671 mmol) and 20 mL of THF. This mixture was stirred overnight and then filtered through a
plug of Celite to give a colorless solution. The filtrate was dried under vacuum and the residue was washed with pentane (3 × 7 mL). Further evaporation of the volatiles in vacuo afforded the desired product as a white solid (216 mg, 58% yield). X-ray quality single crystals were grown at −30 °C from a saturated solution of THF layered with pentane. 

\[ ^1H \text{NMR (400 MHz, C}_6\text{D}_6, \delta): \]
2.56 (br, NCH₂, 4H), 1.35 (br, PCH₂, 4H), 1.25 (t, CH₃, 36H). 

\[ ^13C\{^1H\} \text{NMR (101 MHz, C}_6\text{D}_6, \delta): \]
44.41 (br, NC₇H₂), 33.54 (t, Jc-p = 6.06 Hz, C(CH₃)₃), 29.83 (t, Jc-p = 4.04 Hz, C(CH₃)₃), 19.19 (br, PCH₂). 

\[ ^31P\{^1H\} \text{NMR (162 MHz, C}_6\text{D}_6, \delta): \]
14.97 (s). 

ATR-IR (solid): \( \nu (N-H) = 3271 \text{ cm}^{-1} \).

**Synthesis of \{iPr(PN(H)P)_3Cu}_6H_{0}\} (2a).** Method A: Inside a glovebox, an oven dried Fischer-Porter glass tube equipped with a stir bar was charged with 1a (220 mg, 0.446 mmol), which was dissolved in 5 mL of toluene. KO'Bu (55 mg, 0.490 mmol) was then added, followed by the addition of 2 mL of toluene to rinse the Fischer-Porter tube. The tube was then connected to the Fischer-Porter adapter and taken out of the glovebox. Outside the glovebox, the apparatus was purged with hydrogen gas several times and finally the pressure of H₂ was adjusted to 40 psig. The resulting mixture was stirred at room temperature for 1 h while the reaction vessel was wrapped with an aluminum foil. Within 10 min the color of the reaction mixture turned to bright orange and remained orange during the course of the reaction. After 1 h, H₂ was vented and the apparatus was brought back to the glovebox. This orange solution was quickly filtered through a short plug of Celite and the filtrate was concentrated under vacuum until ~1 mL of the solvent remained. Acetonitrile was added to the concentrated solution,
resulting in an orange precipitate. The orange precipitate was collected and dried under vacuum to afford the desired product 2a. **Method B:** Inside a glove box, a Fischer-Porter bottle with a stir bar was charged with $^{iPr}{\text{PN(H)P}}$ ligand (355 mg, 1.16 mmol), CuBr (333 mg, 2.32 mmol), KOtBu (261 mg, 2.32 mmol) and 6 mL of toluene. The bottle was taken out of the glovebox, purged with H$_2$ several times and then placed under 40 psig of H$_2$. The color of the solution changed from light yellow to bright orange and the work up was carried out in a similar fashion as method A. 2a was obtained as a bright orange color powder (300 mg, 20% yield). 

$^{iPr}{\text{PN(H)P}}_3\text{Cu}_6\text{D}_6$ (2a-D) was synthesized in a similar fashion from $^{iPr}{\text{PN(H)P}}\text{CuBr}$, KOtBu and ~1 atm D$_2$. Crystals of 2a were grown from a saturated toluene solution layered with acetonitrile and kept at −30 °C. $^1$H NMR (400 MHz, C$_6$D$_6$, δ): 3.53-3.60 (m, NH, 1H), 2.90-3.08 (m, CH(CH$_3$)$_2$, 4H), 2.04-2.09 (m, $J_{H\cdot P} = 8$ Hz, CuH, 2H), 1.89-1.96 (m, CH$_2$, 2H), 1.73-1.82 (m, CH$_2$, 4H), 1.61-1.66 (m, CH$_2$, 2H), 1.40-1.46 (m, CH(CH$_3$)$_2$, 6H), 1.17-1.30 (m, CH(CH$_3$)$_2$, 18H). $^{31}$P{^1}H NMR (162 MHz, C$_6$D$_6$, δ): 0.99 (s). ATR-IR (solid): ν(N-H) = 3190 cm$^{-1}$.

**Synthesis of $^{iPr}{\text{PN(H)P}}\text{Cu(OCHO)}$ (5).** Under an inert atmosphere, an oven-dried Schlenk flask equipped with a stir bar was charged with 2a (700 mg, 0.539 mmol) and 10 mL of toluene. CO$_2$ (~1 atm) was introduced to the reaction and the resulting mixture was stirred for one hour. During the course of the reaction, the color changed from orange to yellow and a brownish residue was observed at the bottom of the flask. After one hour, the solution was filtered through a glass cannula and the clear yellow filtrate was evacuated under vacuum to obtain an oily residue. Trituration of the residue with ~5 mL pentane afforded a yellow powder, which was further dried in vacuo to yield the desired product (50 mg, 22% yield). $^1$H NMR (400 MHz, C$_6$D$_6$, δ): 9.50 (s, OCHO, 1H), 5.07 (t, NH,
1H), 2.38 (br, NCH₂, 4H), 1.67 (br, PCH(CH₃)₂, 4H), 1.33 (br, PCH₂, 4H ), 1.00-1.05 (m, CH(CH₃)₂, 24H). ¹³C {¹H} NMR (101 MHz, C₆D₆, δ): 168.86 (s, C=O), 45.00 (t, J_C-P = 3.53 Hz, NCH₂), 25.21 (t, J_C-P = 8.58 Hz, PCH(CH₃)₂), 23.74 (t, J_C-P = 6.56 Hz, PCH₂), 19.82 (t, J_C-P = 3.03 Hz, CH(CH₃)₂), 19.67(t, J_C-P = 3.53 Hz, CH(CH₃)₂). ³¹P {¹H} NMR (162 MHz, C₆D₆, δ): 7.38 (s). ATR-IR (solid): ν (N-H) = 3210 cm⁻¹, ν (C=O) = 1588 cm⁻¹.

**Synthesis of {³¹PrPN(H)P}Cu(HBH₃) (1a-BH₄).** Under an argon atmosphere, a flame-dried Schlenk flask equipped with a stir bar was charged with 1a (200 mg, 0.445 mmol) and NaBH₄ (84 mg, 2.23 mmol). To this mixture, 30 mL of degassed EtOH was slowly added at 0 °C and the reaction mixture was gradually warmed to room temperature and stirred for 16 h. Removal of the volatiles under vacuum afforded a colorless oily residue. Extraction of the residue with toluene followed by filtration through Celite gave a colorless solution. Removing the solvent under vacuum and washing the residue with pentane afforded the desired product as a white solid (60 mg, 35%). ¹H NMR (400 MHz, C₆D₆, δ): 2.44-2.53 (m, NCH₂, 4H), 1.90-1.31 (br q, CuBH₄, 4H), 1.69-1.77 (m, PCH(CH₃)₂, 4H), 1.13-1.22 (m, PCH(CH₃)₂ + PCH₂, 16H), 0.88-0.93 (m, PCH(CH₃)₂, 12H ). ¹³C {¹H} NMR (101 MHz, C₆D₆, δ): 44.11 (t, J_C-P = 2.52 Hz, NCH₂), 24.03 (t, J_C-P = 9.59 Hz, PCH(CH₃)₂), 19.63 (t, J_C-P = 5.55 Hz, PCH₂), 19.01 (t, J_C-P = 3.53 Hz, CH(CH₃)₂), 18.16 (br t, CH(CH₃)₂). ³¹P {¹H} NMR (162 MHz, C₆D₆, δ): 2.41 (s). ATR-IR (solid): ν (N-H) = 3304 cm⁻¹, ν (B-Hterminal) = 2352 cm⁻¹, ν (B-Hbridging) = 2021 cm⁻¹. Anal. Calcd for C₁₆H₄₁BCuNP₂: C, 50.07; H, 10.77; N, 3.65. Found: C, 50.01; H, 10.86; N, 3.59.
Synthesis of \(\{\text{CyPN(H)}\text{P}\}\text{Cu(HBH}_3\}) (1b-\text{BH}_4)\). Synthesis of 1b-BH\(_4\) was carried out in a similar fashion as 1a-BH\(_4\) and isolated as a white powder (30% yield). \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), \(\delta\)): 2.58-2.66 (m, NCH\(_2\), 4H), 2.00 (d, \(J_{\text{H-P}} = 12\) Hz, PCH\(_2\)(Cy)\(_2\), 4H), 1.59-1.71 (m, PCH\(_2\) +CyCH\(_2\) + BH\(_4\), 26H), 1.09-1.38 (m, PCH\(_2\) + CyH, 22H). \(^{13}\)C\(^{1}\)H NMR (101 MHz, C\(_6\)D\(_6\), \(\delta\)): 44.50 (br, NCH\(_2\)), 33.91 (t, \(J_{\text{CP}} = 9.09\) Hz, PCH\(_2\)(Cy)\(_2\), 28.91 (d, \(J_{\text{CP}} = 10.60\) Hz CyC), 27.54-27.40 (m, \(J_{\text{CP}} = 5.05\) Hz, CyC), 26.59 (s, CyC), 20.08 (t, \(J_{\text{CP}} = 5.55\) Hz, PCH\(_2\)). \(^1\)P\(^{1}\)H NMR (162 MHz, C\(_6\)D\(_6\), \(\delta\)): –18.43 (s).

ATR-IR (solid): \(\nu\) (N-H) = 3303 cm\(^{-1}\), \(\nu\) (B-H\(_{\text{terminal}}\)) = 2345 cm\(^{-1}\), \(\nu\) (B-H\(_{\text{bridging}}\)) = 2021 cm\(^{-1}\). Anal. Calcd for C\(_{28}\)H\(_{57}\)BCuNP\(_2\): C, 61.81; H, 10.56; N, 2.57. Found: C, 61.60; H, 10.53; N, 2.55.

Synthesis of \(\{\text{iPrPN(Me)}\text{P}\}\text{CuBr} (1a-\text{Me})\). Under an inert atmosphere, an oven dried Schlenk flask equipped with a stir bar was charged with 2-[bis(1-methylethyl)phosphine]-N-[2-[bis(1-methylethyl)phosphino]ethyl]-N-methyl (217 mg, 0.679 mmol), CuBr (88 mg, 0.617 mmol) and 20 mL of THF. The resulting mixture was stirred overnight and was then filtered through a plug of Celite to give a colorless solution, which was concentrated under vacuum. The obtained residue was washed with pentane and further evacuated to dryness to afford the desired product as a white solid (115 mg, 40% yield). X-ray quality single crystals were grown from a saturated solution of THF layered with pentane and kept at –30 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 2.51 (m, NCH\(_2\), 4H), 2.42(s, NCH\(_3\), 3H), 2.04 (m, PCH(CH\(_3\))\(_2\), 4H), 1.76 (m, PCH\(_2\), 4H), 1.25 (m, PCH(CH\(_3\))\(_2\), 24H). \(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\), \(\delta\)): 54.47 (t, \(J_{\text{CP}} = 3.03\) Hz, NCH\(_2\)), 44.57 (s, NCH\(_3\)), 24.00 (t, \(J_{\text{CP}} = 7.57\) Hz, PCH(CH\(_3\))\(_3\)), 22.32 (t, \(J_{\text{CP}} = 7.07\) Hz, PCH\(_2\)), 19.71 (t, \(J_{\text{CP}} = 2.52\) Hz, PCH(CH\(_3\))\(_2\)), 19.46 (t, \(J_{\text{CP}} = 2.52\) Hz, PCH(CH\(_3\))\(_2\)).
= 3.03 Hz, PCH(CH₃)₂). ³¹P{¹H} NMR (162 MHz, C₆D₆, δ): 14.97 (s). ATR-IR (solid): ν (N-H) = 3271 cm⁻¹. Anal. Calcd for C₁₇H₉BrCuNP₂: C, 44.11; H, 8.49; N, 3.03. Found: C, 43.86; H, 3.07; N, 8.36.

**Stoichiometric Reaction between 2a and Acetophenone.** In an oven-dried J. Young NMR tube, 2a (16 mg, 12.5 µmol) and acetophenone (14.6 µL, 125 µmol) were mixed in ca. 0.6 mL of C₆D₆. Formation of the insertion product 4 was observed by ¹H and ³¹P{¹H} NMR spectroscopy. The color of the solution changed from orange to yellow within 2 h. The following resonances were tentatively assigned to complex 4. ¹H NMR (400 MHz, C₆D₆, δ): 5.07 (q, J = 6 Hz, CuOCH(CH₃)Ph, 1H), 1.63 (d, J = 4 Hz, CuOC(H)(CH₃)Ph, 3H). ³¹P{¹H} NMR (162 MHz, C₆D₆, δ): 3.11 (major peak after one day). Note: besides the insertion product, other minor species were also present that are not yet identified.

**Stoichiometric Reaction between 2a and Benzaldehyde.** In an oven dried J. Young NMR tube, 2a (16 mg, 12.5 µmol) and freshly distilled benzaldehyde (12.7 µL, 125 µmol) were mixed in ca. 0.6 ml of C₆D₆. Within a few minutes of mixing, the color of the reaction mixture turned from orange to yellow, giving rise to a new species assigned to the insertion product 3. At that point, the resonances for the starting hydride 2a disappeared completely. ¹H NMR (400 MHz, C₆D₆, δ): 5.15 (s, CuOCH₂Ph, 2H). Keeping the reaction mixture for a few hours resulted in color change from yellow to black, indicating the decomposition of 3. This is also evident from the broadening of the peaks in the ¹H NMR spectrum.

**Reaction of 2a with CO₂ (1 atm).** A solution of 2a (10 mg, 7.7 µmol) in ~ 0.6 mL of C₆D₆ was prepared inside a glove box. The solution was degassed by freeze-pump-thaw cycles followed by the addition of ~1 atm of CO₂. Within several minutes after CO₂ addition, the color of the solution changed from intense orange to pale yellow. ¹H NMR spectrum indicated
complete disappearance of the starting copper hydride species and the formation of the copper formate species 5. $^1$H NMR (400 MHz, C$_6$D$_6$, δ): 9.48 (s, OCHO, 1H), 5.41 (br, NH, 1H), 2.38 (br, NCH$_2$, 4H), 1.66 (br, PCH(CH$_3$)$_2$, 4H), 1.33 (br, PCH$_2$, 4H), 1.00-1.05 (m, CH(CH$_3$)$_2$, 24H). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$, δ): 10.23.

**Reaction of 2a with formic acid.** Inside a glove box, a dry screw-cap NMR tube was charged with 2a (15 mg, 11.5 µmol), which was dissolved in ~ 0.6 mL of C$_6$D$_6$. The NMR tube was taken outside the glovebox and degassed formic acid (stored over 4Å molecular sieves) (2.18 µL, 2.66 mg) was added. There was an instant reaction between these two reagents with a color change from bright orange to pale yellow and rapid gas evolution was observed. $^1$H NMR spectrum recorded at this point confirmed the formation of the corresponding copper formate species 5. The $^1$H NMR data were consistent with those of the copper formate described above from the reaction between 2a and CO$_2$.

**Reaction of 2a with D$_2$O.** In an oven dried screw-cap NMR tube, 2a (15 mg, 11.6 µmol) was dissolved in ~0.6 mL C$_6$D$_6$ followed by the addition of degassed water (7.31 µL, 405 µmol). The reaction was monitored by $^1$H NMR spectroscopy. The NH resonance at δ 3.56 was shifted to δ 5.21 presumably because of the hydrogen bonding with D$_2$O and it became very broad implying H/D exchange. The sample turned black and decomposed over a period of one day. Note: the copper hydride resonance remained intact which suggests that the hydride does exchange with D$_2$O.

**Exchange reaction between 5 and $^{13}$CO$_2$.** To a C$_6$D$_6$ solution of 5 (generated in-situ from 2a (15 mg, 11.6 µmol) and CO$_2$) was added $^{13}$CO$_2$ (1 atm). The progress of the reaction was monitored by $^1$H NMR spectroscopy over a period of 7 days. $^1$H NMR spectrum showed
that after one day there was only 9% conversion to the labeled formate species, which increased to 40% after 7 days at room temperature (d, 9.60 ppm, $J_{C-H} = 188$ Hz).

**Hydrogenolysis of 4.** In a dry J. Young NMR tube, 2a (16 mg, 12.5 µmol) and acetophenone (7.3 µL, 62.5 µmol) were mixed in 0.6 mL of C$_6$D$_6$. The reaction was monitored by $^1$H NMR spectroscopy. Upon completion of the insertion reaction, the solution was first degassed by freeze-pump-thaw cycles and then H$_2$ (~1 atm) was introduced into the NMR tube. New resonances corresponding to the free alcohol started to grow in the $^1$H NMR spectrum and it was confirmed by adding 1-phenylethanol to the solution. The increase in intensity for the quartet at $\delta$ 4.84 and the doublet at $\delta$ 1.46 suggests that these are methine and methyl resonances of the free alcohol.

**General Procedure for the hydrogenation of aldehydes and ketones.** In a glove box, an oven-dried Fischer-Porter bottle equipped with a stir bar was charged with 1a (9.0 mg, 0.020 mmol), KOtBu (3.0 mg, 0.024 mmol) and 3 mL of THF. To the resulting faint yellow solution was added 1 mmol of the aldehyde or ketone substrate. The sealed tube was taken outside the glove box and flushed with H$_2$ three times, after which the pressure was set to the appropriate value according to the substrate (50 psig for aldehydes and 80 psig for ketones). The reaction was stirred at room temperature for 24 h, and then the reaction was stopped, H$_2$ was vented slowly and an internal standard$^{34}$ was added so that substrate to internal standard ratio was kept at 1 : 1. For GC yields, 100 µL of aliquot was taken and diluted with ethyl acetate, passed through a small plug of Celite to remove the catalyst and analyzed by gas chromatography. For NMR yields, the reaction mixture was dried under vacuum, and the obtained residue was mixed

$^{34}$ Tridecane was used as the internal standard for benzaldehyde and acetophenone hydrogenation reactions while optimizing the reaction conditions. Hexadecane was used for all other substrates for which GC yields were obtained. Mesitylene or durene was used for calculating the NMR yields.
with a measured amount of internal standard in CDCl₃ before NMR analysis. Hydrogenation of benzaldehyde with 2a was carried out in the same way.

**Hg Poisoning Experiment.** In a Fischer-Porter tube, elemental Hg (635 mg, 3.165 mmol) was added to a reaction mixture of 1a (14 mg, 0.03165 mmol), KO'Bu (4 mg, 0.0379 mmol) and PhCHO (161 µL, 1.582 mmol) in 3 mL of THF. The Fischer-Porter tube was sealed and brought outside the glovebox, purged with H₂ three times and the reaction was carried out under 50 psig at room temperature for 24 h. Upon completion of the reaction, the solution was passed through a small plug of silica gel, washed thoroughly with a plenty of THF and dried under vacuum. ¹H NMR of the residual colorless oil in CDCl₃ showed a quantitative conversion of PhCHO to benzyl alcohol.

**Synthesis of tBu{PN(H)P}Cu(HBH₃).** Under an argon atmosphere, a flame-dried Schlenk flask equipped with a stir bar was charged with 1c (100 mg, 0.198 mmol) and NaBH₄ (37 mg, 0.99 mmol). To this mixture, 30 mL of degassed ethanol was added at 0 °C and the reaction mixture was gradually warmed to room temperature and stirred for 16 h. Removal of the volatiles under vacuum afforded a colorless oily residue. Extraction of the residue with toluene followed by filtration through Celite gave a colorless solution. Removing the solvent under vacuum and washing the residue with pentane (3 × 5 mL) yielded the desired product as a white solid (60 mg, 35%). ¹H NMR (400 MHz, THF-d₈, δ): 2.88-2.77 (m, NCH₂, 4H), 1.88-1.85 (m, PCH₂, 4H), 1.30 (t, J = 6.0 Hz, C(CH₃)₃, 36H), 0.86 {br q, CuBH₄, 4H, a range could not be given as the farthest left peak is overlapped with other resonances}. ¹³C{¹H} NMR (101 MHz, THF-d₈, δ): 45.08 (t, J_C-P = 3.03 Hz, NCH₂), 33.77 (t, J_C-P = 5.05 Hz, C(CH₃)₃), 29.83 (t, J_C-P = 4.04 Hz, C(CH₃)₃), 20.27 (t, J_C-P = 4.04 Hz, PCH₂). ³¹P{¹H} NMR (162 MHz, THF-d₈, δ): 15.56 (s) (data acquired using an
AMX 400 Mz spectrometer). ATR-IR (solid): ν (N-H) = 3299 cm$^{-1}$, ν (B-H$_{\text{terminal}}$) = 2353 cm$^{-1}$, ν (B-H$_{\text{bridging}}$) = 2058 cm$^{-1}$.

**Synthesis of Copper Hydride bearing the [iPrPN(Me)P] ligand.** Inside a glovebox, an oven dried Fischer-Porter glass tube equipped with a stir bar was charged with 1a–Me (150 mg, 0.3240 mmol), which was dissolved in 5 mL of toluene. KO'Bu (54 mg, 0.486 mmol) was then added, followed by the addition of 2 mL of toluene to rinse the Fischer-Porter tube. The tube was then connected to the Fischer-Porter adapter and taken out of the glovebox. Outside the glovebox, the apparatus was purged with hydrogen gas several times and finally the pressure of H$_2$ was adjusted to 80 psig. The resulting mixture was stirred at room temperature for 1 h while the reaction vessel was wrapped with an aluminum foil. Within 10 min the color of the reaction mixture turned to bright orange and remained orange during the course of the reaction. After 1 h, H$_2$ was vented and the apparatus was brought back to the glovebox. This orange solution was quickly filtered through a short plug of Celite and the filtrate was concentrated under vacuum until ~1 mL of the solvent remained. Acetonitrile was added to the concentrated solution, resulting in an orange precipitate. The orange precipitate was collected and dried under vacuum to afford the desired product. $^1$H NMR (400 MHz, THF-$d_8$, δ): 2.59-2.40 (m, CuH, 2H), 2.30-2.13 (m, CH(CH$_3$)$_2$, 4H), 1.95 (s, NCH$_3$, 3H), 1.90-1.44 (m, CH$_2$, 8H), 1.29-1.06 (m, CH(CH$_3$)$_2$, 24H).
Chapter 4

Synthesis and Reactivity of Early-Late Heterobimetallic Complexes

Containing Cr–Cu Bonds
4.1 INTRODUCTION

Heterobimetallic complexes with polar metal–metal bonds often show interesting reactivity towards both polar and non-polar substrates. The former interact favorably with the polar metal–metal bonds, resulting in substrate-activation through polarity match. In case of non-polar substrates, the metal–metal bonds first polarize the non-polar substrates, which then become more susceptible to the attack by other polar moieties.\(^1\)\(^2\) Although there have been continuing efforts to utilize metal–metal cooperativity of heterobimetallic complexes in catalysis, to date this remains an underdeveloped area of research. In contrast, catalytic reactions that benefit from metal–metal cooperativity in homobimetallic complexes\(^3\) or electrophile-nucleophile interactions in main-group-based Frustrated Lewis Pairs (FLP)\(^4\) have been studied in great details. Heterobimetallic complexes with a polar metal–metal bond are often formed by combining a complex containing an electrophilic, early-transition metal with one containing a nucleophilic, late-transition metal.\(^1\) Generally, in these “early-late” heterobimetallic complexes, the early-transition metal bears a partially positive charge while the late-transition metal bears a partially negative charge because of the electronegativity difference. In addition to the early-late heterobimetallic complexes, polar metal–metal bonds containing two different late-transition


metals (e.g., Fe and Cu) have been recently studied.\(^5\) In heterobimetallic complexes, polarity of the metal–metal bonds govern the reactivity of the complexes. FLPs are consisted of a pair of compounds that also show nucleophile/electrophile cooperativity and give rise to new mode of reactivity in both stoichiometric and catalytic reactions.\(^4\) However, their mode of substrate-activation depends greatly on the steric factors. Sterically crowded electrophilic and nucleophilic counterparts remain in close proximity without forming a chemical bond and can release steric strain through the activation of substrates. We have been intrigued by the mechanistic differences between early-late heterobimetallic complexes and FLPs and have planned to design early-late heterobimetallic complexes with sterically demanding ligands with the objective to incorporate both types of substrate-activation modes.

As \(N\)-heterocyclic carbene (NHC) ligands are known to support two-coordinate, late-transition metal complexes, especially compounds of Group 11 metals,\(^6\) we planned to utilize the [(NHC)Cu]\(^+\) fragment as the nucleophilic building block for the construction of an early-late heterobimetallic compound. In addition, as the structures of NHC ligands are highly modular, we anticipated that steric and electronic properties of the resulting heterobimetallic complexes could be readily tuned by using different NHC ligands. Group 6 metals (i.e., Cr, Mo, W) are usually electrophilic and their metal complexes are also well studied in the literature.\(^7\) Therefore, for the initial study, I have focused on a Cp*-supported chromium species (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) as the early-transition metal fragment for synthesizing the early-


late heterobimetallic complexes. It was anticipated that the Cr–Cu bond would be sufficiently polar to activate small molecules. Moreover, the steric crowding near the Cr–Cu bond engendered by bulky Cp* and NHC ligands would result in substrate activation via the FLP-type mechanism.

4.2 RESULTS AND DISCUSSION

4.2.1 Synthesis and Characterization of Cr-Cu Heterobimetallic Complexes. Often the metal-metal bond in a heterobimetallic complex is constructed by reacting an electrophilic metal center with a nucleophilic metal counterpart. It has been recently shown that this synthetic strategy can be used to prepare not only early-late heterobimetallic complexes but also late-late heterobimetallic complexes. For example, heterobimetallic complexes featuring Cu–Fe and Zn–Fe bonds were prepared by Mankad and co-workers by adding [CpFe(CO)₂]⁻ to copper and zinc complexes supported by N-heterocyclic carbene ligands. These complexes show interesting stoichiometric reactions with small molecules, and can be applied for catalytic borylation of arene C–H bonds. Using the same method, early-late heterobimetallic complexes containing Cu–M bonds (M = W, Mo, Cr, Mn) were synthesized via reactions of (IPr)CuCl with a stoichiometric amount of Na’[LnM]⁻ (Scheme 1).

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Scheme 1. Synthesis of Heterobimetallic Complexes through the Combination of Electrophilic-Nucleophilic Metal Fragments

![Scheme 1 diagram]

We have adopted a different synthetic strategy to gain access to early-late heterobimetallic complexes containing a metal-metal bond. It was hypothesized that reactions of acidic Group 6 (Cr, Mo, W) metal hydrides with a basic late-transition metal hydroxide complex (M−OH) would form the corresponding heterobimetallic compounds through the release of H₂O. In fact, when Cp*Cr(CO)₃H (1)⁹ and (IPr)CuOH (2)¹⁰ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) were mixed in a 1 : 1 ratio, heterobimetallic complex Cp*(CO)₃Cr−Cu(IPr (3) was produced at room temperature (eq 1). A similar reaction between 1 and (SIPr)CuOH (4) (SIPr = 1,3-bis(diisopropylphenyl)imidazolidin-2-ylidene) generated Cp*(CO)₃Cr−Cu(SIPr complex (5, eq 2). These compounds were isolated as yellow powders in good yields (76-84%) and are stable for a long period of time under an inert atmosphere.

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Both complexes have been characterized by multinuclear nuclear magnetic resonance ($^1$H and $^{13}$C($^1$H) NMR) spectroscopy, FT-IR spectroscopy (solid samples) and elemental analysis. The $^1$H NMR spectrum of 3 shows only two methyl resonances for the four $^i$Pr moieties, indicating a free, rapid rotation of the Cu–Cr bond on the NMR time scale. A single methyl resonance was observed at δ 1.55 for the Cp* ligand. In the $^{13}$C($^1$H) NMR spectrum of 3, a single carbon resonance was observed at δ 241.7 for the three CO ligands. Three $\nu$(CO) vibrational bands were located at 1905, 1805 and 1761 cm$^{-1}$ for the solid sample of complex 3. These $\nu$(CO) bands match well with the terminal CO bands present in [CpCr(CO)$_3$]$^-$(1900, 1800 and 1752 cm$^{-1}$)$^{11}$ and therefore they are assigned as terminal CO vibrations. A related

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Cp(CO)$_3$Cr–Cu(IPr) complex (Cp = cyclopentadienyl), reported by Mankad et al., also shows terminal $\nu$(CO) vibrations near this region (1914, 1822 and 1792 cm$^{-1}$). Complex 5 shows similar spectroscopic features (see Experimental Section for details).

Solid-state structure of 3 was determined by X-ray crystallography (Figure 1). X-ray quality single crystals of 3 were grown from a saturated dichloromethane solution layered with pentane and kept at $-30^\circ$C. The Cr–Cu bond distance was found to be 2.4635(5) Å which is in good agreement with the reported Cr–Cu distance for Mankad’s Cp(CO)$_3$Cr–Cu(IPr) complex. However, it is interesting to note that even though Cp$^*$ is more bulky than Cp and expected to have a more severe steric clash with the $^1$Pr moieties on the NHC ligand, it does not significantly impact the Cr–Cu bond distance in complex 3. Although all three CO ligands in Cp$^*(CO)_3$Cr–Cu(IPr) complex display an almost linear geometry around the carbon centers (Cr–C–O bond angles, 169-178°), two CO ligands were found to be in close proximity to the copper center and exhibited a semi-bridging interaction with copper. An average Cu…CO distance of 2.176 Å was observed for these semi-bridging interactions. In comparison, the Cu…CO distance for the terminal CO ligand was found to be much longer, 3.582 Å. Crystal data and refinement parameters for complex 3 are given in Table 1.
Figure 1. X-ray Crystal Structure of 3 (50% probability level). Selected bond lengths (Å) and angles (deg): Cu–C(1) 1.920(3), Cu–Cr 2.4635(5), Cu…C(39) 2.168(3), Cu…C(40) 2.183(3), Cu…C(38) 3.582, C(2)–C(3) 1.343(4), Cr–C(38) 1.842(3), Cr–C(39) 1.840(3), Cr–C(40) 1.847(3), C(38)–O(1) 1.153(4), C(39)–O(2) 1.168(4), C(40)–O(3) 1.164(4), Cr–Cu–C(1) 170.98(8), Cr–C(38)–O(1) 178.4(3), Cr–C(39)–O(2) 171.9(2), Cr–C(40)–O(3) 169.6(3), Cu–Cr–C(38) 111.79(10), Cu–Cr–C(39) 58.38(8), Cu–Cr–C(40) 58.79(8).

Table 1. Crystal Data and Refinement Parameters for 3.

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#### 4.2.2 Stoichiometric and Catalytic Activity

Having synthesized well-defined early-late heterobimetallic complexes containing a Cr−Cu bond, we aimed to utilize these compounds for small molecule activation. Based on the electronegativity difference between chromium (1.6) and copper (1.9) metals, we expected that the Cr−Cu bond is likely to be polarized (Crδ⁺−Cuδ⁻) and therefore would interact with polar molecules (Scheme 2). However, when 1 equivalent of PhCHO, in which a polar C=O bond is present, was added to a C₆D₆ solution of 3 and heated to 60 °C, no net reaction was observed even after 24 h based on ¹H NMR spectroscopy. It is noteworthy that the heterobimetallic complex 3 did not undergo decomposition under this condition, suggesting that the complex is thermally robust. No reaction was observed either with N₂O (~1 atm) when the reaction mixture was heated at 60 °C for days. Likewise, complex 3 was found to be unreactive towards H₂O, phenyl acetylene and PhSiH₃. Furthermore, activation of non-polar substrates such as CO₂ and H₂ could not be achieved with 3, once again demonstrating high inertness of the Cr−Cu bond. Despite the presence of bulky ligands on chromium and copper, the Cr−Cu bond might be still too strong to react.
Although complex 3 was found to be unreactive towards dihydrogen under atmospheric pressure, we hoped that the Cr−Cu bond could still be cleaved by H<sub>2</sub> under higher H<sub>2</sub> pressures and high temperatures. We hypothesized that hydrogenolysis of the Cr−Cu bond would generate the corresponding chromium and copper hydride species that would react with polar C=O, C=N bonds. These steps could be combined in a catalytic process as shown in Scheme 3. It is well-known in the literature that Group 6 metal hydrides, including Cp(CO)<sub>3</sub>CrH (<i>pKa</i> = 13.3 determined in MeCN),<sup>12</sup> are acidic in nature. On the other hand, late-transition metal hydrides are generally hydridic (basic).<sup>12</sup> Based on the orthogonal nature of Cr−H<sup>δ+</sup> and Cu−H<sup>δ−</sup> species, we envisioned a sequential H<sup>+</sup>/H<sup>−</sup> addition-type mechanism for the reduction of C=O or C=N bonds. Guided by this mechanistic hypothesis, we pursued catalytic hydrogenation of PhCHO and PhCH=NHPh by employing complex 3 as the catalyst. Unfortunately, PhCHO could not be hydrogenated to PhCH<sub>2</sub>OH using 3 (10 mol%) and under 6.4 atm H<sub>2</sub> pressure (eq 3). Perhaps

catalysis might have been inhibited by the formation of intermediates with strong Cr–O bonds. In contrast, when PhCH=NHPh was used as the substrate and the catalytic reaction was performed with 10 mol% of 3 and under 6.4 atm H₂ pressure, after 68 h at 100 °C, the reduced product amine was formed with a 78% conversion (eq 4). Surprisingly, under the same catalytic conditions but replacing toluene with THF as the solvent, only 9% conversion to the amine was observed. Using 1,4-dioxane as the solvent resulted in no hydrogenation product. A control experiment was carried out with 5 mol% of [(IPr)CuH]₂, which was generated in-situ from (IPr)Cu–O'Bu (10 mol%) and (EtO)₃SiH (12 mol%),¹³ producing the amine product with only 9% conversion (eq 5). Although catalytic hydrogenation of the imine proceeded with a slow rate (turnover frequency = 0.11 h⁻¹), the reaction conditions could be further optimized (i.e., higher H₂ pressure, higher temperatures, different solvents, with base additives) to obtain a faster rate. These studies will be carried out in the future.

**Scheme 3. Mechanistic Hypothesis for the Hydrogenation of Polar Bonds**

![Mechanistic Hypothesis](image)

To gain the mechanistic insights into this catalytic reaction, an experiment was performed where [(IPr)CuH]₂ and Cp*Cr(CO)₃H were added sequentially to PhCH=NH(Ph) (Scheme 4) and the reaction mixture was analyzed by ¹H NMR spectroscopy. When 1 equiv of PhCH=NH(Ph) was added to the in-situ generated [(IPr)CuH]₂ (formed by mixing (IPr)Cu-O'O'Bu
with triethoxysilane), the bright yellow color of the copper hydride species disappeared instantly and the hydride resonance at δ 2.63 was no longer present in the ${}^1$H NMR spectrum. Meanwhile, a very small amount of the reduced amine product (δ 6.44 and δ 6.71) was observed at this time. The methylene resonance of the amine is possibly overlapped with those of the ethoxide moieties originated from (EtO)$_3$SiH. The amine product might have been produced by the hydrosilylation (with residual triethoxysilane) of the imine, followed by hydrolysis by the adventitious water. Addition of Cp*(CO)$_3$CrH complex to this solution resulted in the formation of 3 as evidenced by ${}^1$H NMR spectroscopy (Scheme 5). However, the amount of the amine product did not increase during the process.

**Scheme 4.** Sequential Addition of Metal Hydrides to Imine (Hypothesis)

\[
\frac{1}{2} [(IPr)CuH]_2 + \quad \text{N}^\text{Ph}_{\text{Ph}} \quad \text{C}_6\text{D}_6, \text{rt} \rightarrow \quad (IPr)Cu-N_{\text{Ph}}_{\text{Ph}}_{\text{H}} \\
H_{\text{Ph}}_{\text{Ph}}_{\text{H}} + \quad \text{Cp}^*\text{Cr(CO)}_3\text{H} \\
3 \quad \text{C}_6\text{D}_6, \text{rt} \quad \text{H}_2\text{O} \\
\]

**Scheme 5.** Sequential Addition of Metal Hydrides to Imine (Observed)

\[
(IPr)Cu-O^\text{Bu} \quad (\text{EtO})_3\text{SiH} \quad \text{C}_6\text{D}_6, \text{rt} \rightarrow \frac{1}{2} [(IPr)CuH]_2 \\
H_2\text{O} \rightarrow (IPr)Cu-O^\text{OH} \\
(IPr)Cu-O^\text{Bu} \quad (\text{EtO})_3\text{SiH} \quad \text{C}_6\text{D}_6, \text{rt} \rightarrow \text{Cp}^*\text{Cr(CO)}_3\text{H} \\
(IPr)Cu-O^\text{Bu} \quad (\text{EtO})_3\text{SiH} \quad \text{C}_6\text{D}_6, \text{rt} \rightarrow \text{Cp}^*\text{Cr(CO)}_3\text{H} \\
\]

4.3 CONCLUSIONS

In conclusion, early-late heterobimetallic complexes containing a Cr–Cu bond have been successfully synthesized by mixing an acidic chromium hydride with basic copper hydroxide complexes. Cp* and NHC ligands are used to support the chromium and copper centers, respectively. These compounds have been characterized by NMR and FT-IR spectroscopy. Solid-state structure of Cp*(CO)₃Cr–Cu(IPr) complex has been studied by X-ray crystallography. Two CO ligands remain within the Van der Waals range of the copper center with much shorter Cu…CO distances compared to the distance from the remaining CO ligand to copper. Attempted stoichiometric reactions have shown that Cp*(CO)₃Cr–Cu(IPr) fails to activate polar and non-polar molecules including PhCHO, N₂O, H₂O, phenylacetylene, H₂, and CO₂. However, catalytic hydrogenation of PhCH=NH(Ph) proceeded at 100 °C in the presence of 10 mol% of Cp*(CO)₃Cr–Cu(IPr) and under 6.4 atm H₂ pressure. After 68 h, 78% of starting imine was converted to the desired amine.

4.4 EXPERIMENTAL SECTION

General Experimental Information. Unless otherwise mentioned, all air-sensitive compounds were handled under an inert atmosphere using standard Schlenk line and inert-atmosphere box techniques. Toluene, pentane and THF were deoxygenated and dried in a solvent purification system by passing through an activated alumina column and an oxygen-scavenging column under argon. C₆D₆ was distilled from Na and benzophenone under an argon atmosphere. Other deuterated solvents such as CD₂Cl₂, CDCl₃ and THF-d₈ (packed in an ampule) were used as received from commercial sources. Unless otherwise noted, ¹H and ¹³C{¹H} were recorded on a Bruker AV 400MHz spectrometer. Infrared spectra were recorded
on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with smart orbit diamond attenuated total reflectance (ATR) accessory. PhCH=NNPh was prepared following a literature procedure.\textsuperscript{15}

\textbf{Synthesis of Cp*Cr(CO)\textsubscript{3}−Cu(IPr) (3).} In the glovebox under an argon atmosphere, an oven dried Schlenk flask with a stir bar was charged with 1 (58 mg, 0.213 mmol) and 2 (100 mg, 0.213 mmol) and 5 mL of toluene. The resulting yellow color solution was stirred for 30 min under argon and then concentrated under vacuum. The obtained residue was washed with pentane (3 x 4 mL) and dried under vacuum to afford the desired product as a yellow powder (136 mg, 84\% isolated yield). X-ray quality crystals were grown from a solution of 3 in CH\textsubscript{2}Cl\textsubscript{2} layered with pentane and kept at –30 °C. \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 400 MHz, \(\delta\) ppm): 7.48 (t, \(J_{H-H} = 8\) Hz, Ar-\textit{CH}, 2H), 7.31 (d, \(J_{H-H} = 8.0\) Hz, Ar-\textit{CH}, 2H), 7.16 (s, imid-\textit{CH}, 2H), 2.73–2.67 (m, \(J_{H-H} = 6.8\) Hz, \textit{iPr}-\textit{CH}, 4H), 1.55 (s, Cp*\textit{H}, 14H), 1.29 (d, \(J_{H-H} = 6.8\) Hz, \textit{iPr}-\textit{CH}, 12H), 1.18 (d, \(J_{H-H} = 6.8\) Hz, \textit{iPr}-\textit{CH}, 12H). \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (101 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \(\delta\)): 241.58 (s, CO), 181.42 (s, NCCu), 146.23 (s, ArC), 135.61 (ArC), 130.41 (s, imidC), 124.47 (s, ArC), 123.43 (s, ArC), 96.13 (s, Cp*C), 29.07 (s, \textit{iPrC}), 24.92 (s, \textit{iPrC}), 23.76 (s, \textit{iPrC}), 10.86 (s, Cp*\textit{CH}). ATR-IR (cm\textsuperscript{-1}): 1905, 1805, 1762. Anal. Caled for C\textsubscript{40}H\textsubscript{51}CrCuN\textsubscript{2}O\textsubscript{3}: C, 66.41; H, 7.11; N, 3.87. Found: C, 64.88; H, 7.11; N, 3.90. The carbon analysis is low, possibly due to the formation of chromium carbide during the combustion of the sample.

Synthesis of Cp*Cr(CO)\(_3\)-Cu(SIPr) (5). In the glovebox, an oven dried Schlenk flask with a stir bar was charged with 1 (58 mg, 0.213 mmol) and 2 (100 mg, 0.213 mmol) and 5 mL of toluene. The resulting yellow color solution was stirred for 30 min under argon and then concentrated under vacuum. The obtained residue was washed with pentane (3 × 4 mL) and dried under vacuum to afford the desired product as a yellow powder (122 mg, 76% isolated yield). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz, δ ppm): 7.38 (t, \(J_{H-H} = 8\) Hz, Ar-CH, 2H), 7.25 (d, \(J_{H-H} = 8.0\) Hz, Ar-CH, 4H), 4.03 (s, 4H, imid-CH), 3.21–3.14 (m, \(J_{H-H} = 6.7\) Hz, \(^{i}\)Pr-CH\(_3\), 4H), 1.52 (s, Cp*H, 14H), 1.36 (d, \(J_{H-H} = 8\) Hz, \(^{i}\)Pr-CH\(_3\), 12H). \(^{13}\)C{\(^1\)H} NMR (101 MHz, CD\(_2\)Cl\(_2\), δ): 202.78 (s, NCCu), 147.53 (s, ArC), 135.77 (ArC), 129.80 (s, ArC), 124.85 (s, ArC), 96.15 (s, Cp*C), 54.22 (s, imid C) 29.35 (s, \(^{i}\)PrC), 25.26 (s, \(^{i}\)PrC), 24.94 (s, \(^{i}\)PrC), 10.88 (s, Cp*CH\(_3\)). ATR-IR (cm\(^{-1}\)): 1903, 1804, 1767.

Synthesis of (SIPr)CuOH (4). (SIPr)CuCl (100 mg, 0.204 mmol) and anhydrous CsOH (68 mg, 0.408 mmol) were dissolved in 5mL of THF and the resulting mixture was stirred for 20 h. The yellow solution was filtered through a plug of Celite and concentrated to 1 mL. The residue was washed with pentane (3 × 5 mL) and dried under vacuum to afford the desired product as a white powder (78 mg, 81% yield). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz, δ): 7.44 (t, \(J_{H-H} = 8\) Hz, Ar-CH, 2H), 7.28 (d, \(J_{H-H} = 8.0\) Hz, Ar-CH, 4H), 3.98 (s, imid-CH, 4H), 3.11–3.04 (m, \(J_{H-H} = 6.7\) Hz, \(^{i}\)Pr-CH, 4H), 1.35 (t, \(J_{H-H} = 6\) Hz, \(^{i}\)Pr-CH\(_3\), 24H), −1.33 (s, CuOH, 1H).
Hydrogenation of imine. In a glove box, an oven-dried Fischer-Porter bottle equipped with a stir bar was charged with 3 (10 mg, 0.0133 mmol), benzeneamine-N-(phenyl methylene) (24 mg, 0.133 mmol) and 2 mL of toluene. The sealed bottle was taken outside the glove box and flushed with H₂ three times, after which the pressure was set to 80 psig. After stirring at 100 °C for 68 h, the reaction was stopped and cooled to room temperature, and then H₂ was vented slowly. The solution was passed through a short plug of silica gel and washed with toluene to elute all the organic compounds. The collected solution was evaporated to dryness and the residue was dissolved in CDCl₃ for NMR analysis. Based on NMR integrations, the conversion was calculated to be 78% (Figure 2). ¹H NMR of the amine product (CDCl₃, 400 MHz, δ): 7.39-7.16 (m, ArH, 7H), 6.74-6.63 (m, ArH, 3H), 4.33 (d, JₜH-ₜH = 5.6 Hz, CH₂), 4.03 (br, NH, 1H).

Figure 2. ¹H NMR spectrum of the crude product from the hydrogenation reaction
Attempted stoichiometric reactions with H₂, CO₂ and N₂O. A solution of 3 (10 mg, 13.27 µmol) in ~ 0.6 mL of THF-d₈ was prepared inside a glove box and placed in a J. Young NMR tube. The solution was degassed by three freeze-pump-thaw cycles followed by the addition of ~1 atm of H₂, CO₂ or N₂O. No change in color of the solution was observed after passing any of these gases. ¹H NMR spectra indicated no reaction even after heating the solution at 60 °C for 4 days.

Attempted stoichiometric reactions with PhCHO, Phenylacetylene and Phenylsilane. Compound 3 (10 mg, 13.27 µmol) and an equimolar amount of the substrate (phenylacetylene, phenylsilane or benzaldehyde) were mixed in ~ 0.6 mL of THF-d₈ (C₆D₆ for PhCHO) inside a glove box. The reactions were monitored by ¹H NMR at room temperature for several days followed by heating at 60 °C; however, no new species were observed indicating that there was no reaction between any of the substrates and 3.

Addition of water to 3. Compound 3 (10 mg, 13.27 µmol) and degassed water (4.77 µL, 265 µL) were mixed in ~0.6 mL of THF-d₈ and the progress of the reaction was monitored by ¹H NMR spectroscopy for several days. There was no change in the NMR resonances even under the heating at 60 °C; however, some greenish precipitate could be seen.

Synthesis of Cp(CO)₃Mo—Cu(IPr). A flame dried Schlenk flask with a stir bar was charged with CpMo(CO)₃H (48 mg, 0.106 mmol, based on 55% purity of the hydride), 2 (50 mg, 0.106 mmol) and 5 mL of toluene. The resulting solution was stirred for 1 h under argon and then concentrated under vacuum. The obtained residue was washed with pentane (3 × 4 mL) and dried under vacuum to afford the desired product as a yellow powder (49
mg, 68% isolated yield). $^1$H NMR (CD$_2$Cl$_2$, 400 MHz, δ ppm): 7.23 (t, $J_{\text{H-H}} = 8$ Hz, Ar-CH, 2H), 7.13 (d, $J_{\text{H-H}} = 8.0$ Hz, Ar-CH, 4H), 6.36 (s, imid-CH, 2H), 4.76 (s, Cp), 2.81–2.71 (m, $J_{\text{H-H}} = 8$ Hz, iPr-CH, 4H), 1.46 (d, $J_{\text{H-H}} = 8$ Hz, iPr-CH$_3$, 12H), 1.06 (d, $J_{\text{H-H}} = 8$ Hz, iPr-CH$_3$, 12H).
APPENDIX 1

Characterization and Reactivity Data of Chapter 3
AC3061
Group Guan

$^1$H NMR of 1b in C$_6$D$_6$
$^{13}$C($^1$H) NMR 1b in C$_6$D$_6$
$^{31}$P{H} NMR of 1b in C$_6$D$_6$
Solid IR of 1b
$^1$H NMR of 1c in C$_6$D$_6$
$^{13}\text{C} \{^1\text{H}\}$ of 1c NMR in C$_6$D$_6$
$^{13}$C 135 DEPT NMR of 1c in C$_6$D$_6$
$^{31}$P{^1}H NMR of 1c in C₆D₆
Solid IR of 1c
$^1$H NMR of $2a \{^{iPr}PN(H)P\}_3Cu_6H_6$ in C$_6$D$_6$
$^{31}$P $^1$H NMR of $\{^{iPr}PN(H)P\}_3Cu_6H_6$ in $C_6D_6$
$^1$H NMR of $\{^{i\text{Pr}}\text{PN(H)}\text{P}\}_3\text{Cu}_6\text{H}_6$ mixed with 10 equiv of D$_2$O in C$_6$D$_6$
Solid IR of $\{^{18}\text{PN(H)P}\}_3\text{Cu}_6\text{H}_6$
$^{1}$H NMR of 5 in C$_6$D$_6$
$^{13}$C $^{1}$H NMR of 5 in C$_6$D$_6$
$^{31}\text{P}^{1\text{H}}$ NMR of 5 in C$_6$D$_6$
Soild IR of 5
$^1$H NMR of 1a-Me in CDCl$_3$
\[ ^{13} \text{C} \{ ^{1} \text{H} \} \text{ NMR of 1a-Me in CDCl}_3 \]
$^1$H NMR 1b-BH$_4$ in C$_6$D$_6$
$^{31}$P-{H} NMR of 1b-BH$_4$ in C$_6$D$_6$
13C{1H} NMR of 1b-BH₄ in C₆D₆
$^1\text{H NMR}$ of 1a-BH$_4$ in C$_6$D$_6$
$^{31}\text{P}^1\text{H}$ NMR of 1a-BH$_4$ in C$_6$D$_6$
$^{13}$C$^{1}$H} NMR of 1a-BH$_4$ in C$_6$D$_6$
Aldehyde insertion

\[ \{^\text{iPrPN(H)P}_3\}CuH + \text{PhCHO} \xrightarrow{\text{rt, <10 min}} \text{H-N-OCH}_2\text{Ph} \]

\[ \text{iPr[^\text{PN(H)P}]CuOCH}_2\text{Ph} \]

CuH disappeared
$^{31}$P{$^1$H} NMR after 10 min of reaction
Acetophenone insertion into CuH after 2 h, rt. $^1$H NMR in C$_6$D$_6$
Acetophenone insertion into CuH after 2 h, rt. $^{31}$P-$^1$H NMR in C$_6$D$_6$
Acetophenone insertion into CuH after 1 d, rt. $^1$H NMR in C$_6$D$_6$
Acetophenone insertion into CuH (2a) after 1 d, rt. $^{31}\text{P}^{[\text{H}]}$ NMR in C$_6$D$_6$
Insertion of acetophenone into 2a followed by hydrogenation
\[
\text{(iPrPNNHN)}_3\text{Cu}_6\text{H}_6 + \text{PhCHO} \quad \text{10 eq} \quad \text{C}_6\text{D}_6 \quad \text{rt} \quad \rightarrow \quad \text{PhCH}_3
\]
$^1$H NMR of 1c-BH$_4$ in THF-$d_8$
$^{13}$C{¹H} NMR in THF-$d_8$
$^1$H NMR of iPr[PNMe]P]CuH in THF-$d_8$
APPENDIX 2

Characterization Data of Chapter 4
$^1$H NMR of Cp*Cr(CO)$_3$-Cu(IPr) in CD$_2$Cl$_2$
$^{13}\text{C}^{1\text{H}}$ NMR of Cp*Cr(CO)$_3$-Cu(IPr) in CD$_2$Cl$_2$
Solid IR of Cp*Cr(CO)₃-Cu(IPr)
$^{1}$H NMR of Cp*Cr(CO)$_3$-Cu(SIPr) in CD$_2$Cl$_2$
$^{13}\text{C}^{1}\text{H}$ of $\text{Cp}^*\text{Cr(CO)}_3-\text{Cu(SiPr)}$ NMR in CD$_2$Cl$_2$
Solid IR of Cp*Cr(CO)$_3$-Cu(SiPr)
(SIPr)CuOH in CD$_2$Cl$_2$
AC2130/3
$^1$H NMR of CpMo(CO)$_3$—Cu(IPr) in C$_6$D$_6$. 

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