Pursuit of C-H borylation reactions with non-precious heterobimetallic catalysts: hypothesis-driven variations on a design theme

Noel J. Leon[a]
Hsien-Cheng Yu[a]
Thomas J. Mazzacano[a,†]
Neal P. Mankad*[a]

[a] Department of Chemistry, University of Illinois at Chicago, 845 W. Taylor St., Chicago, IL 60607, USA
[†] Current address: Intel Corporation.

npm@uic.edu

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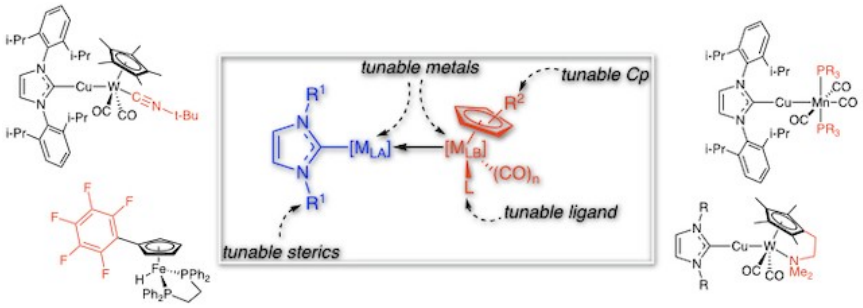

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Abstract This article presents a retrospective account of our group's heterobinuclear (NHC)Cu-[M_{CO}] catalyst design concept (NHC = *N*-heterocyclic carbene, [M_{CO}] = metal carbonyl anion), discovery of its application towards UV light-induced dehydrogenative borylation of unactivated arenes, and subsequent pursuit of thermal reaction conditions through structural modifications of the catalysts. The account highlights advantages of using a hypothesis-driven catalyst design approach that, while often fruitless with regard to the target transformation in this case, nonetheless vastly expanded the set of heterobinuclear catalysts available for other applications. In other words, curiosity-driven research conducted in a rational manner often provides valuable products with unanticipated applications even if the primary objective is viewed to have failed.

Key words catalysis, transition metals, copper, iron, tungsten, manganese, carbene complexes

1 Introduction to heterobinuclear catalysts for C-H borylation

Development of transition metal coordination compounds as catalysts in homogeneous solution has revolutionized complex molecule synthesis by enabling new C-C and C-X bond forming methods with tunable reactivity and selectivity patterns.[1–5] In fact, three Nobel Prizes have been won in this field just since 2000: for asymmetric catalysis (2001), olefin metathesis (2005), and Pd-catalyzed cross-coupling (2010). When one begins a new research group in this area, as two of us helped to do in 2012, it can be daunting to identify how to make original contributions of any significance. During those early days of our research group, we drew inspiration from the newly discovered[6] field of "frustrated Lewis pairs", or FLPs,[7,8] which had recently subverted the dominant paradigm for hydrogenation catalysis by delocalizing H-H bond activation across two reactive *p*-block sites, usually a bulky phosphine paired with a bulky borane (Figure 1a), rather than localizing oxidative addition at a single *d*-block metal site as usual. Realizing that the concept of cooperative bond activation need not be restricted just to *p*-block elements,[9,10] we sought to develop *d*-block analogues of FLPs. Such binuclear transition metal systems pairing a Lewis acidic metal with a Lewis basic metal had been studied for some time, but previous studies focused largely on structure/bonding elucidation and stoichiometric reactivity.[11–18] Comparatively little attention had been paid to catalytic applications of these transition metal Lewis acid/base pairs.[19] We dreamed of discovering heterobinuclear systems that were reactive enough to activate inert substrates such as CO_2 or C-H bonds (Figure 1b), yet still tunable enough that such bond activation processes could be incorporated into useful catalytic transformations.

Although we have yet to activate those "home run" substrates we dreamed of breaking open initially, this seed of an idea has blossomed into a full research program within our group.[20] Our plan became to construct our heterobinuclear catalysts by simple salt metathesis between anionic metal carbonyl complexes (the Lewis base partner) and transition metal halides (the Lewis acid partner), i.e. targeting L_nM-[M_{CO}] complexes derived from L_nMCl and Na[M_{CO}] precursors. Our first success came when we found that the most famous metal carbonyl anion, $[CpFe(CO)_2]^-$ or Fp^-,[21–23] reacted cleanly with copper carbenes[24] (NHC)CuCl to provide (NHC)CuFp derivatives featuring Cu-Fe bonds.[25] Soon after, we found that related Lewis acidic precursors $L_nZn^{II}Cl$ could be used in place of (NHC)CuCl, allowing for facile tuning of the Lewis acidic site.[25,26] More dramatically, seven different metal carbonyl anions could be used in place of Fp^-, thus providing a mini-library of (NHC)Cu-[M_{CO}] catalysts in which the NHC group could be used to tune steric properties and the [M_{CO}] group could be varied electronically.[27] In particular, we hoped (and continue to hope) that heterobinuclear reactivity patterns would correlate with known physical properties of the $[M_{CO}]^-$ groups such as

nucleophilicity[28] or pK_a.[29] As described below, we now know that further fine tuning can be attained through modification of the Cp group[30] within the [M$_{CO}$] unit or by substitution of one or more CO groups with other ligands (Figure 1c).[31] Are these systems frustrated like the *p*-block FLPs? Double-labeled crossover experiments indicated that, yes, the dative [M$_{CO}$]→Cu(NHC) bonds dissociate reversibly in solution even at room temperature.[27,32] In other words, while the neutral [M$_{CO}$]→Cu(NHC) forms of the complexes dominate both in solution and in the solid state, there is equilibrium speciation of [(NHC)Cu]$^+$/[M$_{CO}$]$^-$ Lewis acid/base pairs available in solution.

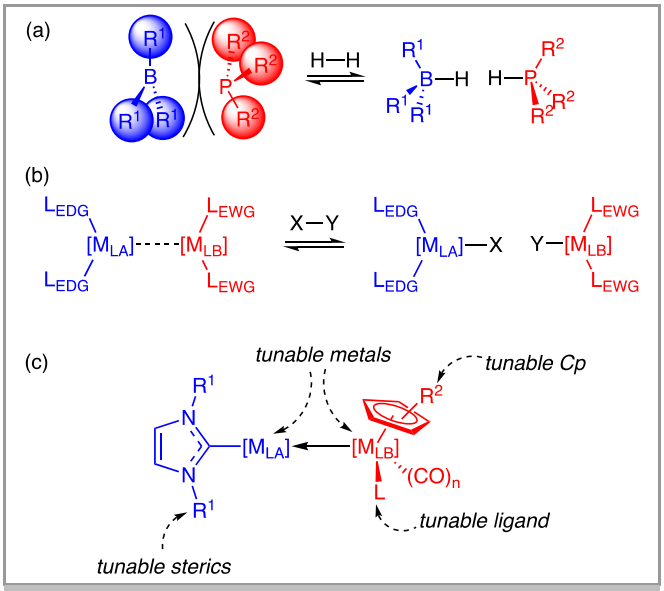
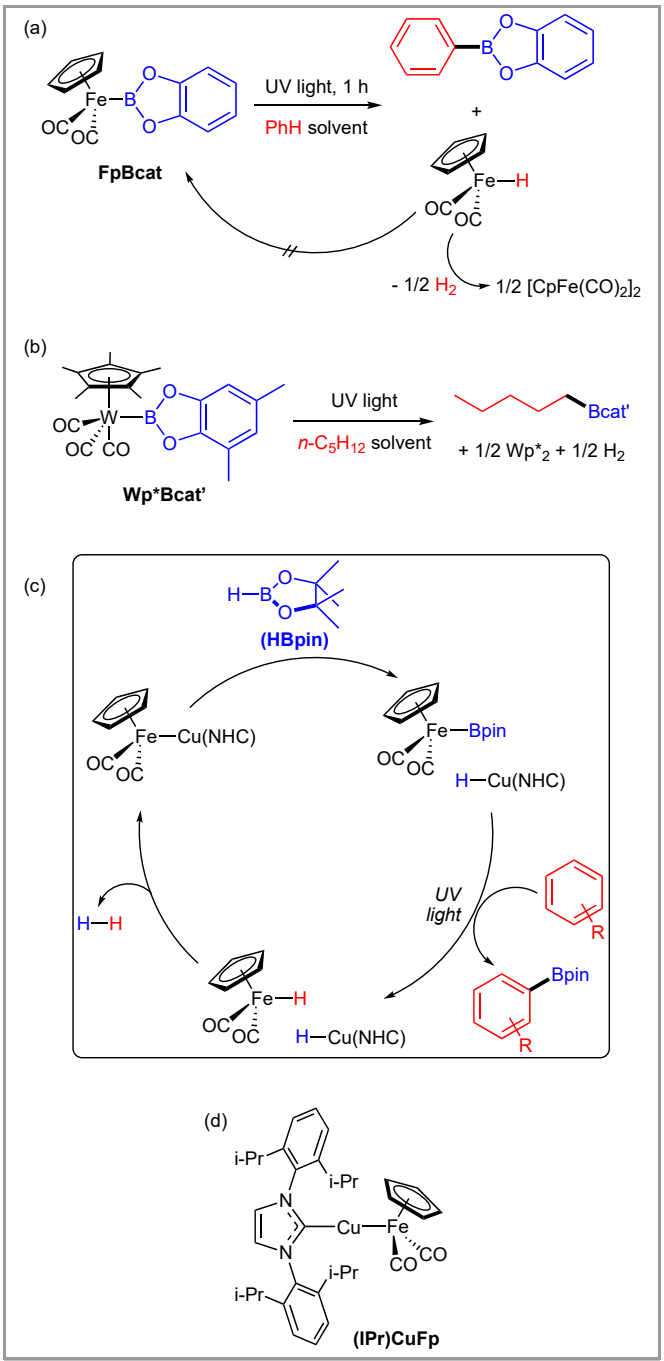


Figure 1 (a) Cooperative H_2 activation by *p*-block frustrated Lewis pairs; (b) hypothetical bond activation by binuclear transition metal catalysts; (c) summary of the tunable catalyst design used in this account.

With these new heterobinuclear catalysts in hand, the next step was to think of creative ideas for their use. Given the prolific applications of copper carbenes[24] in catalysis and of FpR complexes as stoichiometric reagents in synthesis,[21,22] we decided to focus initially on the (NHC)CuFp set of catalysts. Digging through the literature, we were intrigued by some historically important stoichiometric chemistry reported by Hartwig's group in the 1990s. During their studies of various [M$_{CO}$]B(OR)$_2$ complexes,[33] they found that the complexes [M$_{CO}$]Bcat (where [M$_{CO}$] = Fp, Mn(CO)$_5$, or Re(CO)$_5$ and cat = (O$_2$C$_6$H$_4$)$^{2-}$) would borylate unactivated C(*sp*^{2})-H bonds of aromatic solvents when exposed to UV light.[34,35] In particular, the FpBcat derivative gave high conversion to PhBcat when irradiated in benzene solvent. The presumed byproduct, FpH, is unstable under the photochemical conditions and was found to evolve H_2 and form inactive Fp$_2$. One could imagine a catalytic process emerging if FpH or Fp$_2$ could somehow be recycled back to FpBcat (Scheme 1a). Unfortunately, we have confirmed in our own lab that neither of these species react with HB(OR)$_2$ or B$_2$(OR)$_4$ reagents readily. Later, Hartwig also reported that unactivated alkane C(*sp*^{3})-H bonds were borylated in the same manner using Wp*B(OR)$_2$ reagents upon UV activation (Wp* = Cp*W(CO)$_3$, Scheme 1b).[36,37] Clearly, powerful chemistry is available if one can harness these metal-boryl intermediates. In fact, Hartwig, Smith, and others have developed an entire field of Ir-catalyzed C-H borylation chemistry[38,39] – more on that below.



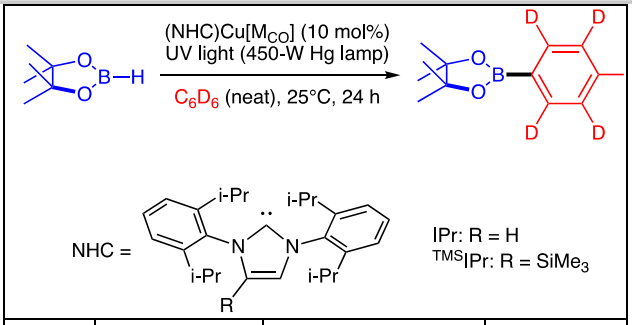
Scheme 1 Stoichiometric (a) C(*sp*^{2})-H and (b) C(*sp*^{3})-H borylation reactions reported by Hartwig;[34–37] (c) our original catalytic hypothesis; (d) a catalytically active Cu/Fe heterobinuclear catalyst.[26,32,40]

Our idea was to return to the original Fe-mediated borylation process and render it catalytic using cooperative heterobimetallic bond activation and formation steps.[40] Our hypothesis as originally formulated is shown in Scheme 1c, wherein cooperative Cu/Fe-mediated B-H activation continuously regenerates the active FpBpin intermediate catalytically, and cooperative Cu/Fe-mediated H_2 elimination turns the cycle over. To test this hypothesis, we proceeded to reproduce the reaction conditions reported in Hartwig's original paper[34] – down to every detail including purchasing the same UV

lamp! – but substituting the stoichiometric FpBcat reagent with HBpin and adding catalytic (NHC)CuFp (pin = (pinacolate)$^{2-}$). To our delight and amazement, we saw catalytic turnover, with (IPr)CuFp giving the best results at that time (Scheme 1d). More importantly, we showed that catalysis requires both metal sites to be present: control compounds (NHC)CuX, FpBpin, and Fp_2 did not catalyze C-H borylation of the benzene solvent under these conditions. This was our first successful example of catalysis that unequivocally requires heterobimetallic cooperation, and suffice to say it was a good day in the lab when our communication of these results was accepted for publication in a top journal.[26]

Following the progression laid out by Hartwig's stoichiometric work (Scheme 1a-b), we next targeted catalytic C(sp^3)-H borylation, hypothesizing that (IPr)CuWp* would show UV-induced activity towards alkanes in the same way that (IPr)CuFp succeeded for arenes. Here we reached an obstacle, because the neat reaction conditions reported by Hartwig for C(sp^3)-H borylation[36,37] were incompatible with the solubility properties of (IPr)CuWp*. Modification of the NHC ligand either by methylation of the imidazole backbone or through use of *N*-alkyl groups in place of *N*-aryl groups provided only minimal solubility in alkane solvents. Fortunately, reasonable catalyst concentrations in pentane solvent were achieved by silylation of the NHC backbone according to Robinson's procedure.[41] Sadly, attempts at UV-induced borylation of pentane solvent using HBpin and catalytic (^{TMS}IPr)CuWp* (10 mol%) resulted in only stoichiometric (<10%) conversion to (*n*-pentyl)Bpin.[42] To date, we have been unable to identify a heterobimetallic catalyst for C(sp^3)-H borylation.

Table 1 Effect of heterobinuclear catalyst structure on C-H borylation activity



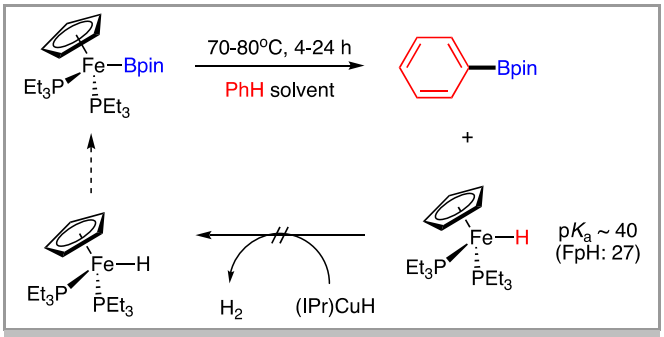
Entry	NHC	[M_{CO}]	Yield (%)[a]
1[b]	IPr	$FeCp^*(CO)_2$	24
2[b]	IPr	$FeCp(CO)_2$	71
3c	IPr	$WCp^*(CO)_3$	80
4[c]	^{TMS}IPr	$WCp^*(CO)_3$	92
5[c]	^{TMS}IPr	$FeCp(CO)_2$	96

[a] Determined by NMR integration against an internal standard. Temperatures were controlled using circulating chilled water. [b] From ref [26]. [c] From ref [42].

On the bright side, the catalyst modifications we introduced by following our hypotheses for C(sp^3)-H borylation inadvertently led us to discover more active catalysts for C(sp^2)-H borylation. As shown in Table 1, under identical conditions for benzene-d_6 borylation, catalytic activity follows the order (IPr)CuFp* < (IPr)CuFp < (IPr)CuWp* < (^{TMS}IPr)CuWp* < (^{TMS}IPr)CuFp, with the latter being the most active heterobinuclear catalyst for C(sp^2)-H we have identified to date.[42] Furthermore, the fact that the Cu/W catalysts are active for arene borylation indicates to us that the elementary steps needed for alkane borylation are, in fact, viable. Thus, the challenge for achieving alkane borylation is to further enhance catalytic rates such that the productive borylation pathways can outcompete unproductive decomposition pathways. For example, our working hypothesis is that the stoichiometric C-H borylation step is slower for alkanes than for arenes, making thermal decomposition of the (NHC)CuH partner[43,44] a more competitive unproductive pathway that depletes active catalyst in solution. As a corollary, the increased catalytic activity of the (^{TMS}IPr)Cu-[M_{CO}] catalysts compared to their (IPr)Cu-[M_{CO}] analogues likely results from increased (NHC)CuH stability with the more sterically bulky ^{TMS}IPr ligand.[45–47]

2 Pursuit of thermal borylation conditions

After obtaining the results described in the previous section, our next goal was to develop thermal rather than photochemical conditions for the heterobimetallic C-H borylation reaction. As we covered in our contemporaneous Synlett SYNPACTS article,[40] such a progression would reflect the history of precious metal-catalyzed C-H borylation, where photochemical C-H borylation with a metal-carbonyl catalyst, $Cp^*Re(CO)_3$,[48] was followed by thermal C-H borylation using CO-free Ir and Rh catalysts such as $Cp^*Rh(\eta^4\text{-}C_6Me_6)$,[49–51] ultimately paving the way for modern-day Ir-catalyzed C-H borylation methods that influence complex molecule synthesis in many venues.[39]



Scheme 2 Stoichiometric Fe-mediated C-H borylation under thermal conditions,[52] and lack of catalytic turnover due to insufficient [Fe]-H acidity.

Inspired by that history, we hypothesized that CO-free analogues of our catalysts may be active under thermal conditions. In particular, the mechanism of the stoichiometric C-H borylation step with [M_{CO}]B(OR)$_2$ complexes was established by Hartwig and Harris to involve reactive 16-electron metal-boryl intermediates generated transiently by UV-induced CO dissociation.[53] So, to test the validity of our hypothesis, we have long targeted heterobinuclear catalyst derivatives of (IPr)CuFp where one or both CO ligands are replaced with thermally labile groups. In pursuit of that hypothesis, we chose to initially examine just the stoichiometric C-H borylation step before tackling catalytic turnover. We were successful in synthesizing several $CpFe(PR_3)_2(Bpin)$ derivatives and found that $CpFe(PEt_3)_2(Bpin)$ was able to borylate arene solvents in the absence of light at temperatures as low at 70°C.[52] Unfortunately, catalysis was not possible in this case because the byproduct of C-H borylation, $CpFe(PEt_3)_2H$, was not observed to react with any (NHC)CuH partner (Scheme 2), thus eliminating the possibility of a thermal analogue of the cycle shown in Scheme 1c. The facile H_2 elimination reaction in our original system was driven by the hydridic character of (NHC)CuH complexes matching with the

protic character of FpH, whose pK_a value of 27.1 has been measured experimentally in acetonitrile solution.[54] By contrast, CpFe(PEt$_3$)$_2$H has an estimated pK_a value of 40 in acetonitrile,[55] and thus presumably lacks sufficient acidity to evolve H_2 with (NHC)CuH partners. Moving forward, the parameters of our design criterion became more well defined: we needed to identify a heterobinuclear catalyst whose corresponding metal-boryl intermediate was thermally labile while also giving rise to an acidic metal-hydride intermediate.

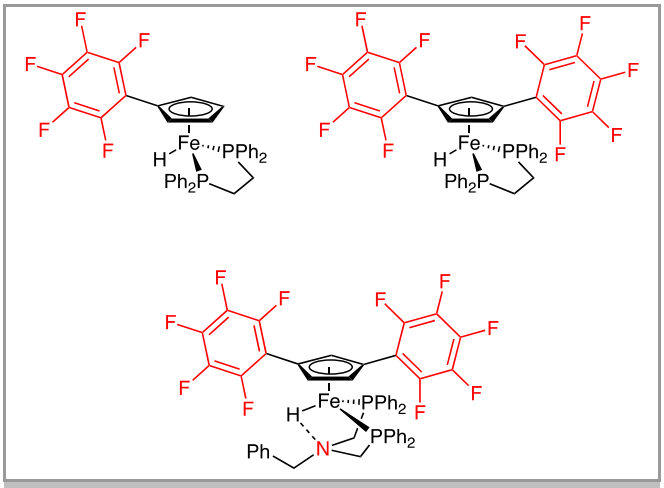


Figure 2 Attempts at identifying CO-free iron hydrides with sufficient acidity. None of these complexes would participate in the catalytically relevant H_2 evolution reaction.

Our first attempt at satisfying this criterion was to maintain the bis(phosphine) ligation that was working for thermal lability, but now to modify the cyclopentadienyl group to bring the iron-hydride pK_a down to a reactive range. To test the validity of this hypothesis, we synthesized model iron hydrides with fluorinated groups on the cyclopentadienyl ring based on literature precedents.[56] The impact of fluorinated cyclopentadienyl substituents on metal-hydride pK_a has not been studied quantitatively, so we needed to test out the H_2 evolution reaction first. We initially used chelating diphosphine ligands such as dppe to stabilize iron hydride intermediates for test reactivity (Figure 2), with the ultimate plan to replace these with monodentate phosphines or hemilabile chelating ligands should the idea prove promising. Unfortunately, none of the iron hydrides we tested showed any reactivity with (IPr)CuH, even with the presence of two electron-withdrawing C_6F_5 substituents as well as a secondary coordination sphere H^+ shuttle implemented recently by Bullock and Helm for Fe-mediated H_2 chemistry.[57,58] Apparently, no matter the modification, removal of both CO ligands from (IPr)CuFp was a step too far.

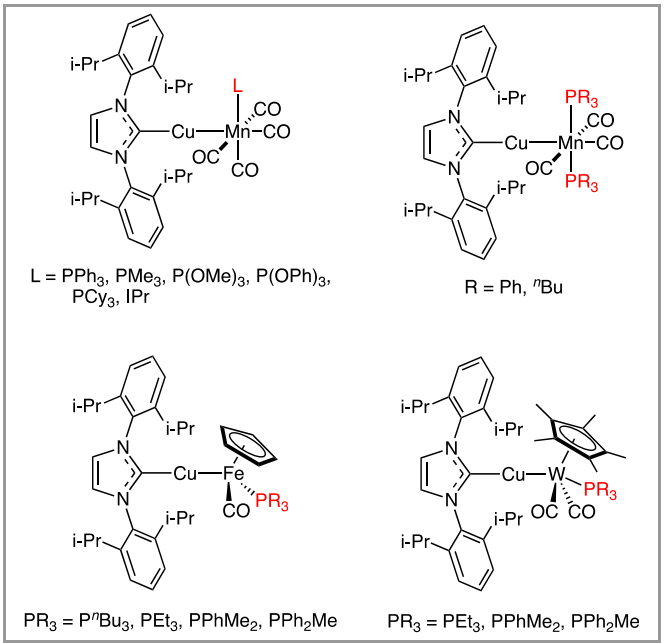


Figure 3 Mixed CO/PR$_3$ catalysts tested for thermal borylation activity.[31]

The logical next step was to target mixed CO/PR$_3$ systems, where in principle both thermal lability and metal-hydride acidity might be accessible. The challenge here was that, in many cases, the anionic metal-carbonyl precursors were not synthetically accessible. Inspired by our own heterobimetallic mechanism (Scheme 1c), we soon realized that an alternative synthetic method could involve reaction of the corresponding [M$_{CO}$]H conjugate acids with (NHC)CuH partners, a process which would not only represent a heterobinuclear synthetic method but also serve to validate whether new systems would be capable of H_2 evolution under catalytic scenarios. With this new synthetic method in hand, a series of mixed CO/PR$_3$ catalysts (NHC)Cu-Mn(CO)$_n$(PR$_3$)$_{5-n}$, (NHC)Cu-FeCp(CO)(PR$_3$), and (NHC)Cu-WCp*(CO)$_2$(PR$_3$) were developed (Figure 3), showing that the presence of even one CO ligand provides sufficient [M$_{CO}$]H acidity for H_2 evolution with (NHC)CuH.[31,42] Unfortunately, no significant catalytic activity was observed thermally, and only limited photochemical activity was observed in one case.[31] In part, this lack of activity is due to the instability of the mixed CO/PR$_3$ catalysts, some of which decompose at temperatures as low as 25°C unlike their more stable all-CO analogues. More importantly, we also synthesized metal-boryl intermediates Cp*W(CO)$_2$(P^{n}Bu$_3$)(Bpin) and *trans*-Mn(CO)$_3$(P^{n}Bu$_3$)$_2$(Bpin) and observed that neither exhibited stoichiometric borylation activity in the absence of UV light up to 110°C. So, even though the heterobinuclear B-H activation and H-H elimination steps are likely viable for these mixed CO/PR$_3$ catalysts, nonetheless they are not as thermally labile as the CpFe(PEt$_3$)$_2$(Bpin) derivative we had studied earlier.

Next, we hypothesized that thermal lability could be increased in comparison to our mixed CO/PR$_3$ complexes by using isocyanide ligands. Our thinking was that isocyanides could hit the sweet spot in terms of the design criteria we had identified, being more labile than CO ligands but still π-accepting enough to engender metal-hydride acidity. The Cu/Mn and Cu/W complexes shown in Figure 4a were successfully synthesized from known metal-isocyanide precursors.[59] Unfortunately, none of these complexes gave promising results in borylation reactivity. For example, an

attempt at catalyzing C-H borylation of benzene with HBcat under analogous conditions to our original Cu/Fe system instead produced catalyst decomposition products including $[Bcat_2]^-$ and unknown isocyanide reduction compounds with peaks in the N-$B(OR)_2$ region of the ^{11}B NMR spectrum. Similar isocyanide reduction was observed during attempts at independently synthesizing the $Cp^*W(CO)_2(CN^tBu)(Bcat)$ intermediate. Thus, we concluded that isocyanides are incompatible with any conditions involving borane reagents.

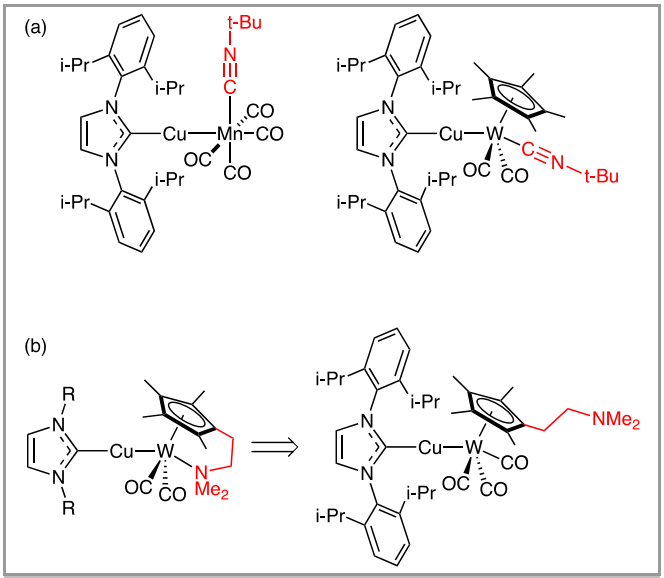


Figure 4 New catalyst designs with (a) isocyanide ligation, and (b) attempt at installing a hemilabile arm.

We also tried to incorporate a hemilabile amine arm into our catalyst design using a "tuck-in" cyclopentadienyl chelate (Figure 4b). Our hope here was to have the catalyst use reversible amine dissociation to reveal an open coordination site required for borylation activity, while still maintaining CO ligation needed for metal-hydride acidity. Having successfully synthesized a suitable "tuck-in" ligand based on literature precedent,[60] we went on to successfully synthesize the derivative of (IPr)CuWp* with a pendant amine arm, as shown in Figure 4b. Unfortunately, attempts to displace a CO ligand with the amine arm were unsuccessful. Furthermore, attempting to generate the relevant catalyst under benzene borylation conditions instead led to resonances in the C(sp^3)-$B(OR)_2$ region of the ^{11}B NMR spectrum and no observation of catalytic turnover. We concluded that the amine arm was undergoing borylation and resulting in rapid catalyst decomposition at a rate faster than external substrate borylation.

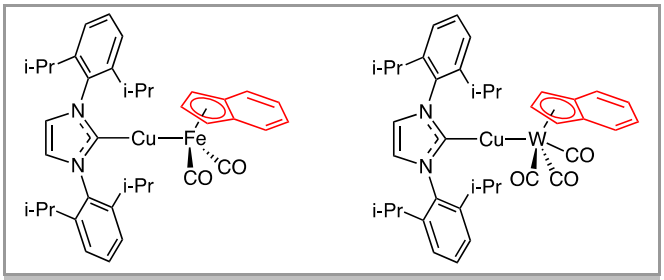
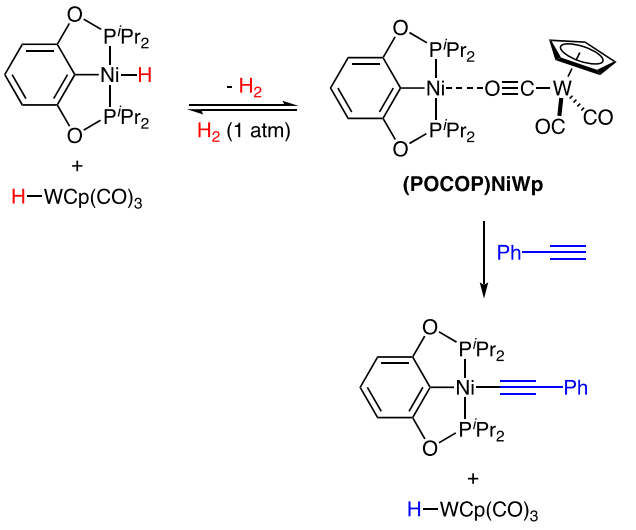


Figure 5 Heterobinuclear catalysts modified with indenyl groups for possible ring-slip isomerism.

One final hypothesis we pursued was to access reactive 16-electron intermediates not by ligand dissociation but by cyclopentadienyl ring slip. Thus, we synthesized Cu/Fe and Cu/W catalysts modified with indenyl groups (Figure 5), which are known to facilitate ring-slip equilibria.[61] Once again, no measurable borylation activity under thermal conditions was observed. We believe the problem here is the high barrier to ring slippage as we modeled computationally,[32] even for the indenyl system.

3 Catalysts beyond copper carbenes

Apart from small variations in NHC structure, up until now all of the major modifications to the initial (NHC)Cu-[M_{CO}] design had been on the metal-carbonyl side. Our original idea was to pursue [M_{LA}]-[M_{LB}] pairs where both metal sites are tunable (Figure 1b). Thus, we have recently initiated studies on modifying the Lewis acidic partner more significantly. Most of our published work in that direction has involved pursuing Ag and Au analogues to the Cu catalysts,[62–64] but can we get away from Group 11 and/or NHC ligands altogether? One foray in this direction has involved use of Ni(II) pincer complexes.[65] Exposing a (POCOP)Ni-H complex to H-$WCp(CO)_3$ (HWp) produced the heterobimetallic species (POCOP)NiWp (Scheme 3). This dehydrogenative synthesis was found to be reversible, as exposure of (POCOP)NiWp to H_2 regenerated (POCOP)NiH + HWp. Levina et al. made a closely related discovery while we were performing these experiments, further demonstrating that the reversible H_2 reaction proceeds through a fleeting [Ni]-H···H-[W] intermediate featuring a dihydrogen bonding interaction.[66] The structural chemistry of this Ni/W system truly highlights the analogy to FLP chemistry with which we began our program. Presumably due to steric repulsion, the Lewis acidic Ni(II) center and the Lewis basic W(0) center are not able to approach each other; instead a bridging isocarbonyl complex, [Ni]···OC-$WCp(CO)_2$, was characterized both by FT-IR spectroscopy and X-ray crystallography. The isocarbonyl bridge is presumably quite weak and can give rise to unmasked $[(POCOP)Ni]^+$ and $[Wp]^-$ equivalents. Indeed, we found that the heterobimetallic complex (POCOP)NiWp is reactive acetylenic C-H bonds, generating a nickel(II) acetylide complex along with HWp (Scheme 3).[65]



Scheme 3 Representative H-H and C-H bond activation chemistry of a frustrated Ni/W system.[65]

In line with the ability of (POCOP)NiWp to activate H-H and C-H bonds, we also observed its rapid reaction with hydroborane reagents HBpin and HBcat. Although the (POCOP)NiH complex was formed in these reactions as expected, no direct evidence for $WpB(OR)_2$ compounds was observed. At this time, we are unsure as to the fate of the tungsten component of the heterobinuclear pair. Thus, while we are excited to apply this new system to other catalytic transformations, unfortunately it seems to be incompatible with borylation chemistry.

4 Conclusions

During a typical research career, we often focus on achieving a desired target and lose sight of valuable lessons that emerge from our "failures". In the preceding account of our "failure" to construct a heterobinuclear catalyst for thermal C-H borylation, each attempt to tune our original Cu/Fe catalyst brought about a new synthetic method for manipulating catalyst structure, a new reactivity landscape to map out, and new information with which to refine our central design concept. Each step along the way was informed by a well-defined scientific hypothesis, which was tested using rigorous experiments each time. Results from each experiment, while often not giving the desired outcomes, still helped to formulate the next hypothesis in the sequence. Overall, this hypothesis-driven research approach provided valuable products which may have unanticipated applications even though the primary objective "failed". In our case, following the science where it led us in the pursuit of C-H borylation will ultimately impact our work in other arenas. For example, while all of the work described above was happening, our group members also found that our heterobinuclear catalysts show catalytic activity for CO_2 deoxygenation,[67] *trans*-selective alkyne semi-hydrogenation,[62,63,68] carbonylative Suzuki-Miyaura coupling,[69] and regiodivergent alkyne hydrostannylation.[70] Our research towards thermal C-H borylation, while narrowly "unsuccessful", inadvertently provided new fundamental knowledge about heterobinuclear chemistry and a dramatically expanded set of heterobinuclear catalysts that we can now apply to these other catalytic applications, or to find new ones.

Acknowledgment

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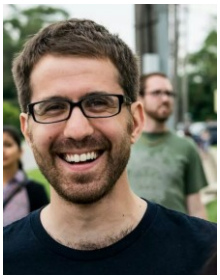
Biosketches

Noel J. Leon is a Chicagoland native and earned his undergraduate degree in chemistry from Northwestern University in 2013. He performed research in the Mirkin group, followed by a year of research at Ohmx Corporation, a biotech startup in Evanston, IL. In 2014, he started his graduate studies at the University of Illinois at Chicago under the leadership of Prof. Neal Mankad. His research focus is on synthesizing heterobimetallic complexes for small molecule activation and designing new electrolytes for beyond lithium batteries.

	In 2010, Hsien-Cheng Yu received his B.S. in chemistry from National Central University. In the same year, he continued his M.S. research in the Tsai group to study multinuclear and multiply-bonded metal complexes at National Tsing Hua University. In 2014, he started as a research associate at National Central University. In 2016, he began his Ph.D. degree at the University of Illinois at Chicago, working on the design and development of bimetallic catalysis under the supervision of Professor Neal Mankad.
	Thomas J. Mazzacano received his B.S. in Chemistry from University of Illinois at Urbana-Champaign in 2010. Afterwards, he joined Procter & Gamble as a Researcher studying surfactant chemistry. Thomas decided to forego industry and start his graduate career at the University of Illinois at Chicago in 2012. Under the advising of Professor Neal P. Mankad, he focused his research on synthesizing base metal heterobimetallic complexes to be used for new developments in C-H borylation. Thomas completed his Ph.D. 2017 and now continues his work in industry.
	Neal P. Mankad is an Associate Professor of Chemistry at the University of Illinois at Chicago. He earned a B.S. degree from MIT (2004), a Ph.D. from Caltech (2010), and conducted postdoctoral research at the University of California-Berkeley (2010-2012). Since 2012, his group at UIC has studied uses of multinuclear coordination complexes to solve challenging problems in the areas of organic synthesis, bioinorganic modeling, and energy storage and conversion.