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Communication

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Three Coordinate Copper(II) Aryls: Key Intermediates in C-O Bond Formation

Subrata Kundu,[a] Christine Greene,[a] Kamille D. Williams,[a] Tolani K. Salvador,[a,b] Jeffery A. Bertke,[a] Thomas R. Cundari,*[,c] and Timothy H. Warren*[,a]

[a]Department of Chemistry, Georgetown University, Box 571227-1227, Washington, D. C. 20057 United States

[b]Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, United States

[c]Department of Chemistry, Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, TX 76203, United States

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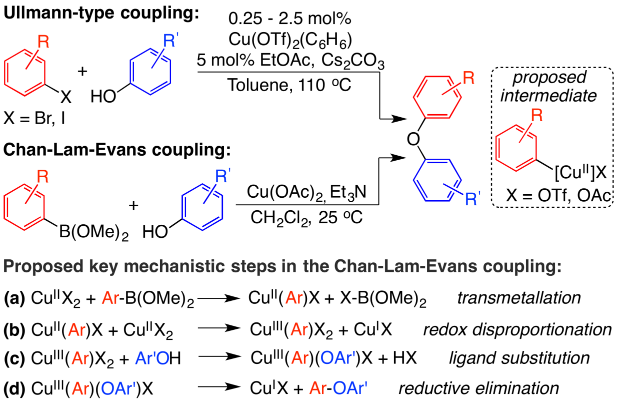
ABSTRACT: Copper(II) aryl species have been proposed as key intermediates in copper-catalyzed cross coupling reactions. Novel three coordinate copper(II) aryls $[Cu^{II}]$-C_6F_5 supported by ancillary β-diketiminate ligands form in reactions between copper(II) alkoxides $[Cu^{II}]$-O^tBu and $B(C_6F_5)_3$. Crystallographic, spectroscopic, and DFT studies reveal the geometric and electronic structures of these unusual copper(II) organometallic complexes. Reaction of $[Cu^{II}]$-C_6F_5 with the free radical $NO_{(g)}$ results in C-N bond formation to give $[Cu](\eta^2$-$ONC_6F_5)$. Most remarkably, addition of the phenolate anion PhO^- to $[Cu^{II}]$-C_6F_5 directly affords the diaryl ether PhO-C_6F_5 with concomitant generation of the copper(I) species $[Cu^I]$(solvent) and $\{[Cu^I]$-$C_6F_5\}^-$. Experimental and computational analysis supports a redox disproportionation between $[Cu^{II}]$-C_6F_5 and $\{[Cu^{II}](C_6F_5)(OPh)\}^-$ to give $\{[Cu^I]$-$C_6F_5\}^-$ and $[Cu^{III}](C_6F_5)(OPh)$ unstable towards reductive elimination to $[Cu^I]$(solvent) and PhO-C_6F_5.

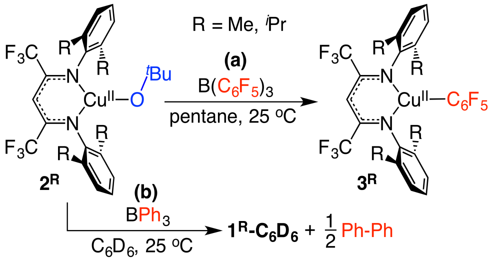
Copper-catalyzed cross coupling reactions offer significant cost and environmental benefits as compared to more traditionally employed Pd variants.[1] Over a hundred years ago, Ullmann *et al.* reported Cu-mediated homo- and hetero-coupling reactions to afford biaryls, diaryl amines, and diaryl ethers.[2] Methodologies for copper catalyzed C-, N-, O-, and S-aryl bond formation have since experienced remarkable improvements, offering broad synthetic scope under ambient reaction conditions (Scheme 1).[1] In particular, revolutionary developments by Chan, Lam, and Evans led to a complementary strategy that employs aryl boronic acids ($ArB(OH)_2$) with amine (RNH_2) or alcohol (ROH) based nucleophiles for the formation of Ar-NHR and Ar-OR bonds (Scheme 1).[3]

The success of copper-catalyzed coupling reactions motivates an understanding of the active species to further improve and expand these synthetic methodologies. Based on oxidative addition/reductive elimination steps involving Pd-aryl intermediates in Pd cross-coupling catalysis,[4] Cu-aryl intermediates have been envisioned in Cu catalyzed protocols.[5] While a d^8/d^{10} redox couple would correspond to Cu^{III}/Cu^I intermediates,[6] the ability of first-row transition metals to participate in single electron transformations raises the possibility of copper(II) aryls as intermediates (Scheme 1).[6c] Examples of well-characterized copper(II) aryl and copper(III) aryl complexes, however, are rare.[7,8,9] Notably, most form via copper-mediated C-H bond activation of ancillary macrocyclic ligands that kinetically stabilize the Cu-aryl linkage.[7,8] Recently, Tilley and coworkers demonstrated the activation of an arylborato anion BAr_4^- by a dicopper(I) complex to provide a $\{[Cu^I]_2(\mu$-$Ar)\}^-$ species that undergoes reversible one-electron oxidation to afford the corresponding mixed-valent $[Cu^{II,I}]_2(\mu$-$Ar)$ complex.[9] Inspired by the Chan-Lam-Evans coupling in which a copper-aryl intermediate is thought to form between $Cu(OAc)_2$ and $ArB(OH)_2$,[10] we targeted discrete, mononuclear copper(II) aryls $[Cu^{II}]$-Ar.

Scheme 1. Representative examples and proposed mechanism[6] of copper catalyzed diaryl ether synthesis.



Scheme 2. Transarylation of $[R_2NN_{F6}]Cu^{II}$-O^tBu (2^R).



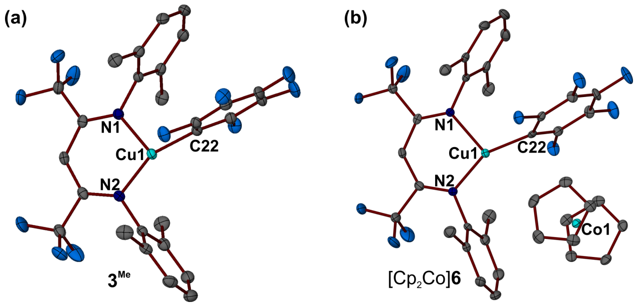


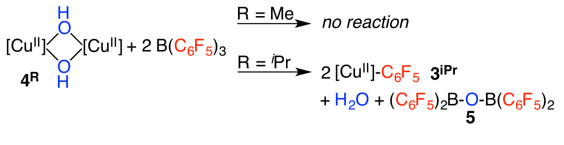
Figure 1. X-ray structures of (a) copper(II) aryl (3^{Me}) and (b) copper(I) arylate (6) with cobaltocenium counterion.

In analogy to the reaction of many copper(I) β-diketiminates [Cu^{I}] with ^{t}BuOO^{t}Bu that form three coordinate copper(II) *tert*-butoxide complexes [Cu^{II}]-O^{t}Bu,[11] reaction of [Me$_2$NN$_{F6}$]Cu(NCMe)[12] (**1^{Me}-MeCN**) with ^{t}BuOO^{t}Bu provides [Me$_2$NN$_{F6}$]Cu^{II}-O^{t}Bu (**2^{Me}**). Since related [Cu^{II}]-O^{t}Bu species undergo transesterification with acyl-protected phenols AcOAr to give copper(II) aryloxides [Cu^{II}]-OAr,[11d] we anticipated a related transarylation reaction with the highly Lewis acidic tris(pentafluorophenyl)borane B(C$_6$F$_5$)$_3$. Addition of B(C$_6$F$_5$)$_3$ to [Me$_2$NN$_{F6}$]Cu^{II}-O^{t}Bu (**2^{Me}**) in pentane at room temperature results in a rapid color change from brownish-purple to dark violet (Scheme 2a). Crystallization from pentane provides dark violet [Me$_2$NN$_{F6}$]Cu-C$_6$F$_5$ (**3^{Me}**) in 63% yield. In contrast, addition of BPh$_3$ to **2^{Me}** results in rapid formation of the biaryl Ph-Ph with reduction to copper(I) (Scheme 2b).

X-ray diffraction reveals a short Cu-C$_{aryl}$ distance of 1.9290(14) Å (Figure 1a). The sum of angles around the copper center in **3^{Me}** is 359.77(6)°, indicating trigonal planar coordination at copper. A T-shaped distortion is observed, however, with two distinct N$_{\beta\text{-dik}}$-Cu-C22 angles of 110.39(6)° and 153.56(6)°. This results in a corresponding disparity in Cu-N$_{\beta\text{-dik}}$ distances of 1.9241(12) and 1.8611(12) Å, respectively, with the shorter Cu-N distance essentially *trans* to the aryl group. The T-shaped geometry in the solid state structure of **3^{Me}** could gain stabilization from π-stacking between the electron-rich N-aryl ring and electron deficient pentafluorophenyl ring.[13] An unrestricted DFT geometry optimization at the BP86/6-31+G(d)/gas//BP86+GD3BJ/6-311++G(d,p)/SMD-benzene level of theory on **3^{Me}**, however, leads to a Y-shaped trigonal planar geometry (N$_{\beta\text{-dik}}$-Cu-C22 = 132.1°) with a Cu-C22 distance of 1.951 Å. Nonetheless, these DFT calculations predict a very low free energy difference between the Y- and T-shaped geometries (0.3 kcal/mol; Figures S44-S45).

To more closely model transarylation via air-stable [Cu^{II}]-OH intermediates[14] in the Chan-Lam-Evans coupling (Scheme 1, step a), we examined the reaction between {[Me$_2$NN$_{F6}$]Cu}$_2$(μ-OH)$_2$ (**4^{Me}**)[12] and B(C$_6$F$_5$)$_3$. Unfortunately, no reaction occurred, perhaps due to very tight interactions between two [Cu^{II}]-OH moeties (Cu•••Cu= 3.0195(6) Å).[12] Employing a more sterically demanding ligand that possesses *o*-^{i}Pr N-aryl β-diketiminate substituents, {[^{i}Pr$_2$NN$_{F6}$]Cu}$_2$(μ-OH)$_2$ (**4^{iPr}**) (Cu•••Cu= 3.112(1) Å) can be synthesized by exposing a pentane solution of [^{i}Pr$_2$NN$_{F6}$]Cu(η^2-benzene)[15] (**1^{iPr}-C$_6$H$_6$**) to air at room temperature. **4^{iPr}** undergoes smooth transmetallation with B(C$_6$F$_5$)$_3$ in pentane to give violet [^{i}Pr$_2$NN$_{F6}$]Cu-C$_6$F$_5$ (**3^{iPr}**) along with the colorless borinic acid anhydride (C$_6$F$_5$)$_2$B-O-B(C$_6$F$_5$)$_2$ (Scheme 3). [^{i}Pr$_2$NN$_{F6}$]Cu-C$_6$F$_5$ (**3^{iPr}**) possesses a similar, planar T-shaped structure as **3^{Me}** with a slightly longer Cu-C$_{aryl}$ distance of 1.955(3) Å (Figure S38). The borinic acid anhydride occurs from rapid dehydration of the borinic acid (C$_6$F$_5$)$_2$B-OH produced upon transmetallation. [^{i}Pr$_2$NN$_{F6}$]Cu-C$_6$F$_5$ (**3^{iPr}**) may also be prepared in the reaction of [^{i}Pr$_2$NN$_{F6}$]Cu-O^{t}Bu (**2^{iPr}**) and B(C$_6$F$_5$)$_3$ (Scheme 2a). The greater thermal sensitivity of [^{i}Pr$_2$NN$_{F6}$]Cu-C$_6$F$_5$ (**3^{iPr}**) relative to **3^{Me}** has hindered the isolation of analytically pure **3^{iPr}**. Thus we performed further characterization and reactivity studies with **3^{Me}**.

Scheme 3. Transmetallation of {[R$_2$NN$_{F6}$]Cu^{II}}$_2$(OH)$_2$ (4^{R}, R = Me, ^{i}Pr).



The cyclic voltamogram of [Me$_2$NN$_{F6}$]Cu-C$_6$F$_5$ (**3^{Me}**) in fluorobenzene at room temperature exhibits a quasi-reversible reduction wave centered at -420 mV *vs* Cp$_2$Fe$^+$/Cp$_2$Fe (Figure S3). Cobaltocene reduction of [Me$_2$NN$_{F6}$]Cu-C$_6$F$_5$ (**3^{Me}**) in fluorobenzene allows for isolation of the corresponding copper(I) arylate [Cp$_2$Co]$^+${[Me$_2$NN$_{F6}$]Cu-C$_6$F$_5$}$^-$ ([Cp$_2$Co]**6**) in 61% yield. X-ray analysis reveals only modestly altered bond distances and angles in the copper(I) arylate **6** as in the copper(II) analogue **3^{Me}** (Figure 1b). The Cu-C$_{aryl}$ distance (1.928(3) Å) in this T-shaped copper(I) aryl is essentially identical to that in the copper(II) aryl (Cu-C$_{aryl}$ = 1.9289(14) Å), while the Cu-N$_{\beta\text{-dik}}$ distances increase to 2.056(2) and 1.928(2) Å, which reflect the anionic charge and lower Cu oxidation state in **6**. The N$_{\beta\text{-dik}}$-Cu-C22 angles in anion **6** of 110.05(9) and 153.11(9)°, respectively, are almost unchanged from those in neutral **3^{Me}**. DFT optimized geometries predict a similar trend in the variation of Cu-N$_{\beta\text{-dik}}$ distances in **6** and **3^{Me}** (Figures S44 and S46). NMR spectra in THF-*d$_8$* exhibit sets of ^{1}H and ^{19}F resonances that fully support the diamagnetic nature of **6** including sharp, distinct ^{19}F resonances arising from backbone CF$_3$ and terminal C$_6$F$_5$ groups (Figures S10 and S11).

To provide insight into the electronic structure of these novel copper(II) aryl complexes **3**, we carried out EPR, UV-vis, and DFT studies. The isotropic X-band EPR spectrum of **3^{Me}** in heptane at 293 K exhibits a four-line signal characteristic of a S = ½ copper(II) site (Figure S28). Simulation of the isotropic EPR spectrum provides g_{iso} = 2.093 with A_{iso}(Cu) = 175 MHz. The frozen glass EPR spectrum of **3^{Me}** in heptane at 80 K provides a rhombic signal and its simulation gives g_1 = 2.115, g_2 = 2.099, g_3 = 2.062 with A_1(Cu) = 95, A_2(Cu) = 290, A_3(Cu) = 110 MHz (Figure S29). Notably, EPR spectra for these Cu^{II}-aryls are not axially biased ($g_1 \approx 2.20$, $g_{2,3} \approx 2.05$) as found in related three coordinate [Cu^{II}]-X species (X = amide, alkoxide, thiolate, halide).[11,16] The UV-vis spectrum of [Me$_2$NN$_{F6}$]Cu^{II}-C$_6$F$_5$ (**3^{Me}**) in heptane at 25 °C shows a strong optical band at λ_{max} = 565 nm (4150 M^{-1}cm^{-1}) with a less intense, very broad feature at 910 nm (405 M^{-1}cm^{-1}) (Figure S2). The UV-vis spectrum of **3^{iPr}** is similar to that of **3^{Me}** (Figures S2 and S7).

DFT studies suggest that the SOMO for [Cu^{II}]-aryl species **3** results from a π-interaction between the Cu d orbital destabilized via σ-donation by the β-diketiminate N-donors and the π-system of the C$_6$F$_5$ ring. This interaction shifts e$^-$ spin density onto the C$_6$F$_5$ ring (0.12 e$^-$ total) away from the formally d^9 Cu^{II} center (0.34 e$^-$) (Figures 2 and S68, Table S6). The precise spin distribution depends on the energy levels of the [Cu] and Ar fragments. For instance, raising the energy of the aryl-based orbitals places these MOs closer in energy to the Cu-C π* SOMO and enhances the aryl group contribution. Thus, we predict and compute considerably higher electron spin on the aryl group in the putative [Me$_2$NN$_{F6}$]Cu-C$_6$H$_5$ (0.23 e$^-$ total) (Figure S69) relative to its perfluorophenyl congener. Interestingly, enhanced spin density on the Cu-bound aryl correlates with decreasing Cu-aryl bond strength. While DFT predicts the Cu-aryl bond dissociation free energy (BDFE) in [Cu^{II}]-C$_6$F$_5$ (**3^{Me}**) to be 56.2 kcal/mol, the predicted BDFE for [Me$_2$NN$_{F6}$]Cu-C$_6$H$_5$ is much lower at 36.0 kcal/mol (Table S7). This difference likely contributes to the

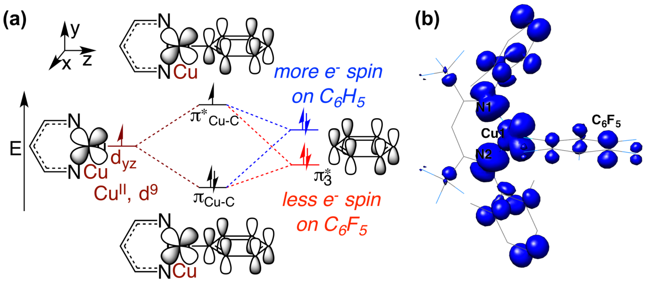
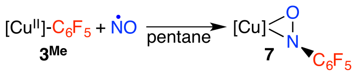


Figure 2. (a) Qualitative frontier orbital interactions in trigonal copper(II)-C_6F_5/C_6H_5 species. (b) Spin density plot for 3^{Me}.

markedly lower thermal stability of $[Me_2NN_{F6}]Cu-Ph$ whose attempted synthesis results in the biaryl Ph-Ph (Scheme 2b). Nonetheless, these BDFEs for dissociation of an aryl radical Ar• from $[Cu^{II}]-C_6F_5$ or $[Cu^{II}]-Ph$ are too high to allow for such a dissociation to readily proceed around room temperature; we instead consider a redox disproportionation (Scheme 6b).

Illustrating the reactivity of $[Me_2NN_{F6}]Cu-C_6F_5$ (**3^{Me}**) with radicals, addition of 1 equiv. $NO_{(g)}$ to **3^{Me}** in pentane results in C-N coupling to provide the diamagnetic C-nitroso complex $[Me_2NN_{F6}]Cu(\eta^2-ONC_6F_5)$ (**7**) in 77% isolated yield (Scheme 4). X-ray crystallographic analysis reveals η^2-O,N coordination of the C_6F_5NO ligand to the β-diketiminato Cu center (Figure S40) similar to the previously reported $[Me_2NN_{F6}]Cu(\eta^2-ONPh)$.[17] Unfortunately, attempts at C-O bond formation with sterically hindered, O-based free radicals such as TEMPO or 2,4,6-$^tBu_3C_6H_2O$• failed and led to formation of the biaryl $F_5C_6-C_6F_5$ in 21% and 38% yields, respectively.

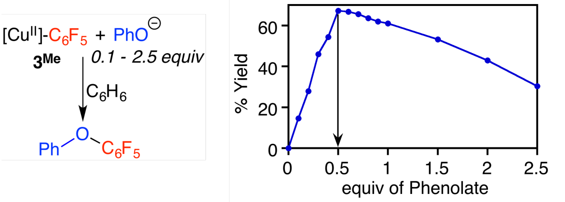
Scheme 4. Reductive nitrosylation of $[Me_2NN_{F6}]Cu^{II}-C_6F_5$ (3^{Me}).



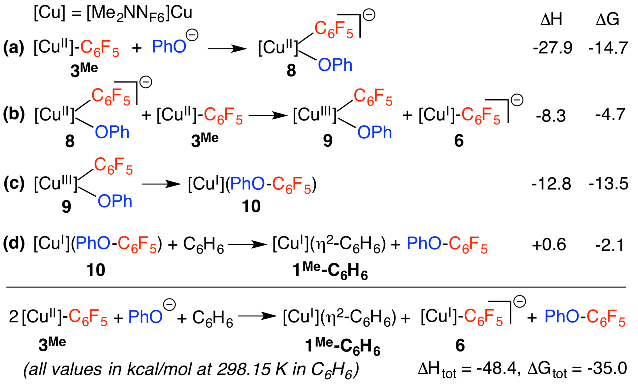
Remarkably, addition of the phenoxide anion in $[Bu_4N]OPh$ to $[Me_2NN_{F6}]Cu-C_6F_5$ (**3^{Me}**) in benzene at room temperature results in immediate formation of $PhO-C_6F_5$ (Scheme 5). A plot of the yield of $PhO-C_6F_5$ vs. different equivalents of phenolate anion exhibits a maximum at 0.5 equiv. phenolate anion / Cu (Scheme 5, Table S2). This suggested 2:1 reaction stoichiometry between **3^{Me}** and phenolate is also confirmed by a Job plot (Figure S18). In the addition of 1 equiv. PhO^- to 2 equiv. $[Cu^{II}]-C_6F_5$ (**3^{Me}**) in benzene-d_6, ^1H and ^{19}F NMR analyses indicate the formation of $PhO-C_6F_5$ (45% yield based on 1 equiv. **3^{Me}**) along with $[Me_2NN_{F6}]Cu(\eta^2\text{-benzene})$ (**$1^{Me}-C_6D_6$**) and anionic $\{[Me_2NN_{F6}]Cu-C_6F_5\}^-$ (**6**) in 49% and 38% yields, respectively (Figures S19 and S20). A small amount of the biaryl $F_5C_6-C_6F_5$ (5-15%) also forms in these experiments (Figure S20).

Based on the reaction stoichiometry which requires two $[Cu^{II}]-C_6F_5$ for each PhO^- along with the formation of the copper(I) arylate anion $\{[Cu^I]-C_6F_5\}^-$ (**6**), we propose that PhO^- coordinates to $[Cu^{II}]-C_6F_5$ followed by a redox disproportionation of resulting anion $\{[Cu^{II}](C_6F_5)(OPh)\}^-$ (**8**) and $[Cu^{II}]-C_6F_5$ (**3^{Me}**) (Scheme 6 and S70). Examined computationally at BP86/6-31+G(d)/gas//BP86+GD3BJ/6-311++G(d,p)/SMD-benzene level of theory, coordination of PhO^- to $[Cu^{II}]-C_6F_5$ (**3^{Me}**) results in the copper(II) aryl phenolate complex $\{[Cu^{II}](C_6F_5)(OPh)\}^-$ (**8**) (Scheme 6a). Reductive elimination of C_6F_5-OPh from **8** would give the monoanionic, zero-valent copper complex $\{[Me_2NN]Cu\}^-$ which is uphill by 38.5 kcal/mol in free energy (Table S7). Instead, DFT studies reveal this more electron-rich, anionic species **8** to be susceptible towards electron transfer to the more electron-poor $[Cu^{II}]-C_6F_5$ (**3^{Me}**) to give the copper(III) aryl phenolate $[Cu^{III}](C_6F_5)(OPh)$ (**9**) and the copper(I) arylate anion $\{[Cu^I]-C_6F_5\}^-$ (**6**) (Scheme 6b). Driven by phenolate coordination, this redox disproportionation is predicted to be favorable by 4.7 kcal/mol. Facile reductive elimination from $[Cu^{III}](C_6F_5)(OPh)$ (**9**) to the diaryl ether-bound copper(I) complex $[Cu^I](PhOC_6F_5)$ (**10**) (ΔG = -13.5 kcal/mol) proceeds through a low energy transition state with $\Delta G^{\neq}$ = 16.5 kcal/mol (Scheme 6c and 70; Figure S55). Displacement of the sterically hindered diaryl ether product from the copper(I) center by benzene gives the observed $[Cu^I](\eta^2\text{-benzene})$ (**$1^{Me}-C_6H_6$**) (ΔG = -2.1 kcal/mol; Scheme 6d). The overall transformation that delivers the diaryl ether product along with two reduced copper species is highly favorable from an enthalpy (ΔH_{total} = -48.4 kcal/mol) and free energy (ΔG_{total} = -35.0 kcal/mol) perspective.

Scheme 5. Analysis of reaction stoichiometry for the reaction of $[Cu^{II}]-C_6F_5$ (3^{Me}) with phenolate anion.



Scheme 6. DFT calculated thermodynamics of each individual mechanistic step in C-O coupling mediated by $[Me_2NN_{F6}]Cu^{II}-C_6F_5$ (3^{Me}) in benzene.

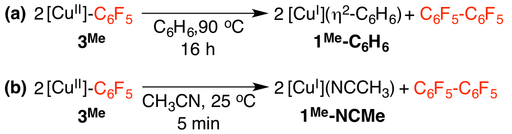


(all values in kcal/mol at 298.15 K in C_6H_6) ΔH_{tot} = -48.4, ΔG_{tot} = -35.0

BP86/6-31+G(d)/gas//BP86+GD3BJ/6-311++G(d,p)/SMD-benzene

In the absence of a covalently bound coupling partner, $[Me_2NN_{F6}]Cu-C_6F_5$ (**3^{Me}**) is stable at room temperature in nonpolar solvents such as pentane, benzene, and toluene for several days. At elevated temperature (90 °C) in benzene, however, **3^{Me}** decays over a period of 16 hours to give decafluorobiphenyl ($F_5C_6-C_6F_5$) in 73% yield. ^{19}F NMR analysis reveals the formation of the copper(I) complex $[Cu^I](\eta^2\text{-benzene})$ (**$1^{Me}-C_6H_6$**) in 78% yield, indicating that $[Cu^I]$ forms along with C-C coupling of the copper-bound aryl group (Scheme 7). Most interestingly, coordinating solvents such as acetonitrile dramatically accelerate the decay of $[Cu^{II}]-C_6F_5$ (**3^{Me}**) to cleanly provide $[Cu^I]-NCMe$ (**$1^{Me}-NCMe$**) and $F_5C_6-C_6F_5$ in quantitative yield (NMR and GC-MS, Figures S23-S25). Acceleration by addition of a Lewis base would seem to rule out the intermediacy of simple bimolecular intermediates $[Cu^{II}]_2(\mu-C_6F_5)_2$, since such dimerization should be even less favored upon binding of an additional Lewis base to the $[Cu^{II}]$ center. Moreover, spontaneous loss of $•C_6F_5$ radicals is also unlikely due to the high BDFE of $[Cu^{II}]-C_6F_5$ (56.2 kcal/mol) along with the absence of any C-O coupled product in the addition of TEMPO or $^tBu_3C_6H_2O$• to $[Cu^{II}]-C_6F_5$. We currently are considering a related redox disproportionation mechanism that generates $\{[Cu^{III}](Ar)(L)\}^+$ / $\{[Cu^I]-Ar\}^-$ that may promote the formation of transient $[Cu^{III}](C_6F_5)_2$. Computational studies reveal that $[Cu^{III}](C_6F_5)_2$ is exceedingly unstable towards

Scheme 7. [Me$_2$NN$_{F6}$]Cu^{II}-C$_6$F$_5$ ($\mathbf{3^{Me}}$) mediated homocoupling reactions.



reductive elimination to give F$_5$C$_6$-C$_6$F$_5$ and [Cu^{I}] (Figures S65 and S66, Table S7) with a reductive elimination free energy barrier of ~ 2 kcal/mol. The [Cu^{III}](C$_6$F$_5$)$_2$ intermediate could not be optimized without constraint of either the Cu-C$_{aryl}$ or C$_{aryl}$-C$_{aryl}$ bond lengths, consistent with facile ligand-induced C-C coupling chemistry experimentally observed.

Transmetallation of copper(II) alkoxides or hydroxides [Cu^{II}]-OR (R = alkyl, H) with the electron-deficient borane B(C$_6$F$_5$)$_3$ provides entry into an unprecedented family of three coordinate copper(II) aryls [Cu^{II}]-C$_6$F$_5$. Facile reduction of [Cu^{II}]-C$_6$F$_5$ ($\mathbf{3^{Me}}$) to the copper(I) arylate complex {[Cu^{I}]-C$_6$F$_5$ (**6**) ($E_{1/2}$ = -420 mV vs. Fc$^+$/Fc) enables redox disproportionation upon coordination of the phenolate nucleophile to provide [Cu^{III}](C$_6$F$_5$)(OPh) that reductively eliminates PhO-C$_6$F$_5$, coupling the incoming phenolate nucleophile with the bound Cu-aryl. These mechanistic findings provide insight into the mechanism of C-O coupling in the Chan-Lam-Evans coupling and support a redox disproportionation pathway that involves Cu^{I}, Cu^{II}, and Cu^{III} organometallic intermediates.[6] Ongoing studies probe the reactivity of other nucleophiles Nu (e.g. amides, thiolates) with these novel copper(II) aryls [Cu^{II}]-Ar for Nu-Ar coupling.

ASSOCIATED CONTENT

Supporting Information. Experimental, characterization, and computational details (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

thw@georgetown.edu (T.H.W.); t@unt.edu (T.R.C)

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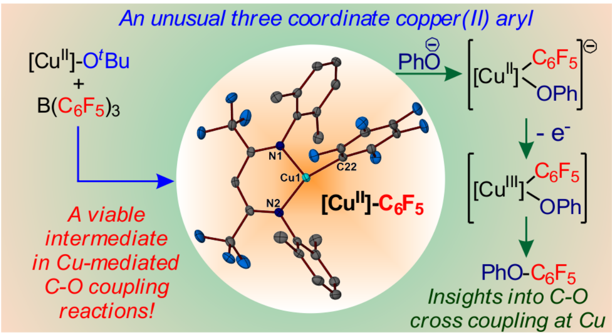
An unusual three coordinate copper(II) aryl
[Cu^{II}]-O^{t}Bu
+
B(C$_6$F$_5$)$_3$
A viable intermediate in Cu-mediated C-O coupling reactions!
N1
Cu1
C22
N2
[Cu^{II}]-C$_6$F$_5$
PhO$^{\ominus}$
[Cu^{II}] C$_6$F$_5$ OPh
- e$^-$
[Cu^{III}] C$_6$F$_5$ OPh
PhO-C$_6$F$_5$
Insights into C-O cross coupling at Cu