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Cu(I)−Amido Complexes in the Ullmann Reaction: Reactions of Cu(I)−Amido Complexes with Iodoarenes with and without Autocatalysis by CuI

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Abstract: A series of Cu(I)−amido complexes both lacking ancillary ligands and containing 1,10-phenanthroline (phen) as ancillary ligand have been prepared. These complexes react with iodoarenes to form arylamine products, and this reactivity is consistent with the intermediacy of such complexes in catalytic Ullmann amination reactions. The stoichiometric reactions of the Cu(I)−amido complexes with iodoarenes are autocatalytic, with the free CuI generated during the reaction serving as the catalyst. Such autocatalytic behavior was not observed for reactions of iodoarenes with copper(I) amidates, imidates, or phenoxides. The selectivity of these complexes for two sterically distinct aryl halides under various conditions imply that the autocatalytic reaction proceeds by forming highly reactive $[CuNPh_2]_n$ lacking phen. Reactions with radical probes imply that the reactions of phen-ligated Cu(I)−amido complexes with iodoarenes occur without the intermediacy of aryl radicals. Density functional theory calculations on the oxidative addition of iodoarenes to Cu(I) species are consistent with faster reactions of iodoarenes with $CuNPh_2$ species lacking phen in DMSO than reactions of iodoarenes with $LCuNPh_2$ in which L = phen. The free-energy barrier computed for the reaction of PhI with $(DMSO)CuNPh_2$ was 21.8 kcal/mol, while that for the reaction of PhI with $(phen)CuNPh_2$ was 33.4 kcal/mol.

A century has passed since the discovery of Ullmann reactions, in which arylamines couple with aryl halides through mediation by copper.[1] The synthetic scope of this process remained limited for many decades and often required stoichiometric amounts of copper and high reaction temperatures (typically 200 °C) to obtain satisfactory yields. More recently, copper catalysts containing ancillary ligands have been used, and these systems react with broader scope and at lower temperatures.[2] In 1999, Goodbrand and Hu[3] reported the coupling of arylamines with aryl iodides catalyzed by a combination of 1,10-phenanthroline (phen) and CuCl under mild conditions. Thereafter, a variety of ligands, such as 1,2-diamines,[4] 1,3-diketones,[5] and others[6] have been used with copper to promote the Ullmann amination reaction.

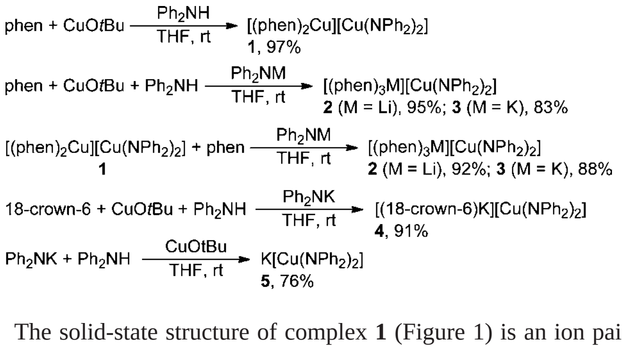
Despite significant improvements in the scope and conditions for the copper-catalyzed arylation of amines, little direct information on the mechanism of this reaction is available. Ligandless "$CuNPh_2$" was proposed by Paine[7] in 1987 to be an intermediate in Ullmann reactions catalyzed by CuI,[8] and tetramers of similar species, $[CuNR_2]_4$ (R = alkyl), have been isolated.[9] Ligated copper(I) phenoxides, amidates, and imidates have recently been characterized and shown to be likely intermediates in the Cu-catalyzed formation of biaryl ethers and *N*-arylamides.[10,11] However, Cu(I)−amido complexes ($LCuNR_2$) containing a ligand that generates synthetically useful catalysts have not been characterized.[12]

Anionic copper(I) amides also could be intermediates in Ullmann reactions. Organocuprates ($MCuR_2$) are among the most reactive nucleophiles in organic chemistry,[13] and the formation of similar cuprates from the reaction of lithium amides with copper halides when the ratio of $LiNR_2$ to CuX is greater than 1 (a condition that exists in the catalytic Ullmann reaction) has been proposed.[14] However, amidocuprate complexes of the type $MCu(NR_2)_2$ have not been isolated, characterized, or assessed as potential intermediates in Ullmann aminations.

We report the synthesis and characterization of a series of Cu(I)−amido complexes, some lacking additional ligands and some ligated by phen. These complexes are chemically and kinetically competent to be intermediates in the Ullmann amination or to lead to such intermediates. Under some conditions, these complexes react with iodoarenes by an autocatalytic process in which CuI serves as the catalyst. Our data imply that the autocatalysis occurs by generation of a highly reactive $[CuNPh_2]_n$ species lacking a phen ligand. Experimental and theoretical studies imply that these complexes react with iodoarenes without the intermediacy of aryl radicals, and this result implies the involvement of Cu(III) intermediates.[15,16]

Our synthesis of Cu(I)−amido complexes is outlined in Scheme 1. Phen-ligated complex **1** and cuprates **2**−**4** in which phen and a crown ether are ligated to K^+ or Li^+ were prepared by the reaction of CuO*t*Bu with $HNPh_2$ or a mixture of $HNPh_2$ and either $LiNPh_2$ or $KNPh_2$ in the presence of phen or 18-crown-6 in THF. Cuprates **2** and **3** were also prepared from phen, $LiNPh_2$ or $KNPh_2$, and double-salt **1** in THF. Finally, ligandless cuprate **5** was prepared from $HNPh_2$, $KNPh_2$, and CuO*t*Bu in the absence of any dative ligand. These complexes were characterized by elemental analysis and NMR spectroscopy. Solid-state structures of complexes **1** and **3** were determined by single-crystal X-ray diffraction.

Scheme 1



$$\text{phen} + \text{CuO}t\text{Bu} \xrightarrow[\text{THF, rt}]{\text{Ph}_2\text{NH}} [(\text{phen})_2\text{Cu}][\text{Cu}(\text{NPh}_2)_2] \quad \mathbf{1},\ 97\%$$

$$\text{phen} + \text{CuO}t\text{Bu} + \text{Ph}_2\text{NH} \xrightarrow[\text{THF, rt}]{\text{Ph}_2\text{NM}} [(\text{phen})_3\text{M}][\text{Cu}(\text{NPh}_2)_2] \quad \mathbf{2}\ (\text{M = Li}),\ 95\%;\ \mathbf{3}\ (\text{M = K}),\ 83\%$$

$$\underset{\mathbf{1}}{[(\text{phen})_2\text{Cu}][\text{Cu}(\text{NPh}_2)_2]} + \text{phen} \xrightarrow[\text{THF, rt}]{\text{Ph}_2\text{NM}} [(\text{phen})_3\text{M}][\text{Cu}(\text{NPh}_2)_2] \quad \mathbf{2}\ (\text{M = Li}),\ 92\%;\ \mathbf{3}\ (\text{M = K}),\ 88\%$$

$$\text{18-crown-6} + \text{CuO}t\text{Bu} + \text{Ph}_2\text{NH} \xrightarrow[\text{THF, rt}]{\text{Ph}_2\text{NK}} [(\text{18-crown-6})\text{K}][\text{Cu}(\text{NPh}_2)_2] \quad \mathbf{4},\ 91\%$$

$$\text{Ph}_2\text{NK} + \text{Ph}_2\text{NH} \xrightarrow[\text{THF, rt}]{\text{CuOtBu}} \text{K}[\text{Cu}(\text{NPh}_2)_2] \quad \mathbf{5},\ 76\%$$

The solid-state structure of complex **1** (Figure 1) is an ion pair consisting of a tetrahedral, cationic copper ligated by phen and a linear, anionic copper ligated by two amides. In DMSO, the molar conductivity of a 1.0 mM solution of **1** was high (16.9 Ω^{-1} cm^2 mol^{-1}) relative to that of a 1.0 mM solution of neutral ferrocene (0.3 Ω^{-1} cm^2 mol^{-1}) and similar to that of a 1.0 mM solution of $[Bu_4N][BPh_4]$ (23.5 Ω^{-1} cm^2 mol^{-1}). In THF, the conductivity of a 1.0 mM solution of **1** was 13.7 $\mu\Omega^{-1}$ cm^{-1} (13.7 Ω^{-1} cm^2 mol^{-1}), whereas the conductivity of a 65.5 mM solution of $[(n\text{-octyl})_4N][Br]$ was 65.1 $\mu\Omega^{-1}$ cm^{-1} (0.99 Ω^{-1} cm^2 mol^{-1}) and that of a 65.5 mM

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solution of ferrocene was 0.0 $\mu\Omega^{-1}$ cm^{-1} (0.0 Ω^{-1} cm^2 mol^{-1}). These data indicate that unlike ligated copper(I) amidates, imidates, and phenoxides, which vary in structure with the polarity of the solvent,[10] ligated Cu(I)−amido complexes are predominantly double salts in both polar and less polar solvents.

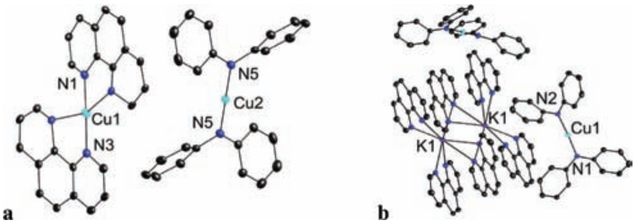
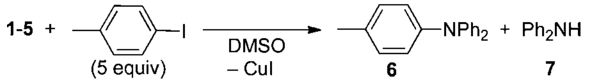


Figure 1. (a) ORTEP drawings of (a) **1** and (b) **3** with 50% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1**: Cu2−N5, 1.8659(15); N5−Cu2−N5, 180.0. For **3**: Cu1−N1, 1.860(2); Cu1−N2, 1.879(2); N1−Cu1−N2, 176.45(10).

The solid-state structure of complex **3** contains two K$^+$ ions ligated by six phens and two bisamidocopper anions (Figure 1). Two of the six phen ligands in the dimer are shared by two K$^+$ ions with each nitrogen of the bridging ligand coordinated to two K$^+$ ions, making each K$^+$ ions eight-coordinate.

The reactions of these Cu(I)−amido complexes with iodoarenes are summarized in Table 1. Phen-ligated complex **1** reacted with *p*-iodotoluene in DMSO at 80 °C to afford triarylamine **6** in 95% yield after 1.5 h. Cuprates **2** and **3**, in which Li$^+$ and K$^+$ ions are ligated with phen, reacted similarly with *p*-iodotoluene in DMSO at 110 and 80 °C in 1 and 3 h, respectively, to give 1 equiv of **6** per copper in 84 and 90% yield. The second amido group in **2** and **3** forms diphenylamine, presumably by abstracting a proton from DMSO. Cuprates **4** and **5**, which do not contain ancillary ligands to bind copper, did not react with *p*-iodotoluene when heated at 80 °C for 3 h; at 110 °C, they formed **6** in modest yields (54 and 44%, respectively). The combination of phen and complex **4** containing the crown ether and complex **5** containing no added ligand reacted with *p*-iodotoluene at 80 °C to give **6** in >95 and 56% yield, respectively. These results indicate that dative ligands such as phen can convert less reactive cuprates to a more reactive species, possibly by substitution of the phen for one of the two amido ligands to form a ligated copper amide.

Table 1. Reactivity of Complexes **1**−**5** with *p*-Iodotoluene



entry	complex	additive	temp (°C)	time (h)	% yield of **6**[a]	**7**/**1**−**5**[b]
1	**1**	none	80	1.5	95	−
2	**2**	none	110	1	84	1.14[c]
3	**3**	none	80	3	90	0.62
4	**4**	none	110	3	54	1.24[c]
5	**4**	phen (1 equiv)	80	2.5	>95	0.80
6	**5**	none	110	3	44	1.48[c]
7	**5**	phen (3 equiv)	80	3	56	1.24[c]

[a] Yield by GC with an internal standard. [b] Molar ratio of amine **7** formed relative to the starting complex **1**−**5**. The balanced equation for the reaction of **2**−**5** requires a proton from a solvent molecule or adventitious water. [c] Each of complexes **1**−**5** contains two amido groups. In the balanced equation, one amido group forms the triarylamine and the other forms the diarylamine. Some diarylamine is apparently formed in competition with the process that forms triarylamine, leading to a ratio that is greater than 1.

Although phen-ligated double salt **1** and cuprates **2** and **3** react with aryl halides to form triarylamines, monitoring of these reactions by ^{1}H NMR spectroscopy showed that the events during this process are complex. Figure 2 shows the profile of the decay of **1** from its reaction with 4-iodotoluene. This sigmoidal behavior is characteristic of an autocatalytic process. When normalized for the concentration of iodoarene, the plots of iodoarene concentration versus time for reactions with a two-fold difference in [ArI] overlapped. This result indicates that the reaction is first-order in iodoarene.

Further experiments showed that the autocatalysis results from the generation of CuI. The reaction of **1** with *p*-iodotoluene conducted with 0.5 equiv of added CuI was faster and formed triarylamine **6** with a first-order decay of **1** (Figure 2a). In contrast, this reaction was unaffected by added *ligated* copper iodide [phenCuI]$_2$. In the presence of 1 equiv of CuI, the reaction occurred at 30 °C with a first-order decay and a half-life ($t_{1/2}$) of 37 min ($k_{\text{obs}} = 3.1 \times 10^{-4}$ s^{-1}); no reaction of complex **1** with *p*-iodotoluene occurred at this temperature in the absence of added CuI. The reaction of **1** with *p*-iodotoluene in the presence of CuI was first-order in added CuI and in iodoarene.

The effect of added phen on the reaction of complex **1** with *p*-iodotoluene was not straightforward. The reaction of complex **1** with *p*-iodotoluene in the presence of added phen was slower than that in the absence of added phen, but the reactions with 0.010 and 0.020 M added phen occurred with identical rates (Figure 2b). The reaction at 80 °C with 0.010 M added phen was first-order in **1** with $t_{1/2} = 32$ min ($k_{\text{obs}} = 3.6 \times 10^{-4}$ s^{-1}). Thus, the lower rate with added phen did not result from reversible dissociation of phen to generate the active species, as is often concluded when a reduction in rate is observed with added ligand. Instead, these data imply that the added phen consumes the free CuI generated in the absence of added phen that is responsible for the autocatalysis and that the reaction occurs through a pathway lacking the autocatalysis in the presence of added phen. Reactions of **1** with various concentrations of iodoarene and added phen showed that the reaction is first-order in iodoarene.

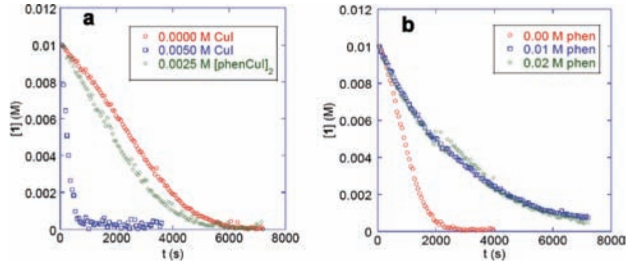


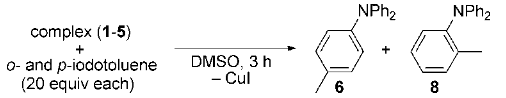
Figure 2. (a) Decay of complex **1** from reactions with *p*-iodotoluene alone (red), with added CuI (blue), and with added [phenCuI]$_2$ (green) at 60 °C. (b) Decay of complex **1** from reactions with *p*-iodotoluene alone (red) and with the addition of 0.010 M (blue) or 0.020 M (green) phen at 80 °C.

Similar autocatalysis was observed for reactions of other copper amides. The reactions of cuprates **2** and **3** with *p*-iodotoluene occurred with sigmoidal reaction profiles (see the Supporting Information), and the same reactions with added CuI were faster and occurred with an exponential decay. The reaction of **2** with 1 equiv of CuI occurred with $t_{1/2} = 9.1$ min ($k_{\text{obs}} = 1.3 \times 10^{-3}$ s^{-1}) at 100 °C, and the reaction of **3** with 2 equiv of CuI occurred with $t_{1/2} = 20.6$ min ($k_{\text{obs}} = 5.6 \times 10^{-4}$ s^{-1}) at 80 °C.

To assess the relationship between complexes **1**−**5** and intermediates in Ullmann reactions catalyzed by Cu(I)−phen species and to determine whether the intermediates in the autocatalytic reactions are the same as those in reactions in which free CuI is sequestered by added phen, we studied the selectivity of these complexes toward the sterically distinct aryl iodides *o*- and *p*-iodotoluene. We then compared the distribution of products from these stoichiometric reactions in the presence and absence of phen to those of the catalytic reactions.

Results from these competitive reactions are provided in eq 1−2 and Table 2. The reaction of HNPh$_2$ with *o*- and *p*-iodotoluene

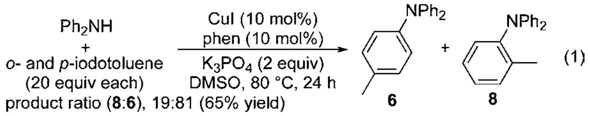
Table 2. Selectivity of Complexes **1**−**5** for *o*- and *p*-iodotoluene



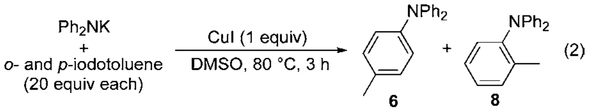
entry	complex	additive	temp (°C)	yield (%)[a]	product ratio (**8**/**6**)
1	**1**	none	80	11[b]	14:86[b]
2	**1**	CuI (1 equiv)	30	72	49:51
3	**1**	none	80	85	34:66
4	**1**	phen (1 equiv)	80	72[c]	20:80
5	**2**	none	100	82	15:85
6	**3**	none	80	92	10:90
7	**2**	CuI (4 equiv)	80	77	43:57
8	**3**	CuI (4 equiv)	80	84	43:57
9	**4**	CuI (1 equiv)	80	89	47:53
10	**5**	CuI (1 equiv)	80	80	47:53

[a] Combined GC yield of **6** and **8**; reactions of **2**−**5** also form Ph_2NH (see Table 1). [b] After 2 min of reaction. [c] Reaction time was 4 h.

catalyzed by a 1:1 ratio of CuI to phen in the presence of K_3PO_4 formed a 19:81 ratio of **8** to **6** (eq 1), and that of $KNPh_2$ with *o*- and *p*-iodotoluene in the presence of stoichiometric amounts of a 1:1 ratio of CuI to phen formed an indistinguishable 20:80 ratio of these products (eq 2):



product ratio (**8**:**6**), 19:81 (65% yield)



without phen: product ratio (**8**:**6**), 47:53 (54% yield)
with 1 equiv phen: product ratio (**8**:**6**), 20:80 (50% yield)
with 3 equiv phen: product ratio (**8**:**6**), 18:82 (54% yield)

A similar selectivity (14:86) was also observed at the early stage of the reaction of complex **1** with *o*- and *p*-iodotoluene (2 min, 11% yield) when the concentration of free CuI was low and the autocatalytic pathway was not yet dominant (Table 2, entry 1). In contrast, the reaction of **1** with *o*- and *p*-iodotoluene in the presence of CuI formed nearly equal amounts of the two amine products (49:51) (entry 2). This selectivity is similar to that of the reaction of $KNPh_2$ with stoichiometric CuI and no added phen (47:53) (eq 2).

The ratio of products from reaction of complex **1** with *o*- and *p*-iodotoluene and no added phen (34:66) (Table 2, entry 3) was between that of the reaction of $HNPh_2$ with *o*- and *p*-iodotoluene catalyzed by a 1:1 ratio of CuI to phen in the presence of K_3PO_4 base and the reaction of **1** and added CuI with the iodoarenes. However, the ratio of products from the reaction of **1** with *o*- and *p*-iodotoluene in the presence of 1 equiv of phen to sequester the free CuI formed a ratio of the two products (20:80) (entry 4) that was similar to that of catalytic reactions with added phen and the reaction of complex **1** before autocatalysis. Thus, we conclude that the reaction of **1** in the presence of phen occurs through complex **1**, most likely in its neutral form $[Cu(phen)(NPh_2)]$, but that the portion of the reaction between **1** and aryl iodide without added phen that is autocatalytic in CuI likely proceeds by the transfer of an amido group from the $Cu(NPh_2)_2^-$ unit to CuI to form a $[CuNPh_2]_n$ species lacking phen (Scheme 2).[17] This species likely is less selective than **1** because it contains a more open coordination sphere.

The reactions of cuprates **2** and **3**, which contain phen-ligated alkali-metal cations, and the reactions of cuprates **4** and **5**, which lack ancillary ligands capable of binding Cu(I), with *o*- and *p*-iodotoluene in the presence of CuI were equally unselective (eq 7−10). Thus, the reactions of these cuprates in the presence of CuI generate the same species, which we propose to be $[CuNPh_2]_n$.[18,19]

Scheme 2

Proposed mechanism without autocatalysis

$$[(\text{phen})_2\text{Cu}^+][\text{Cu}(\text{NPh}_2)_2^-] \rightleftharpoons 2\ (\text{phen})\text{CuNPh}_2$$

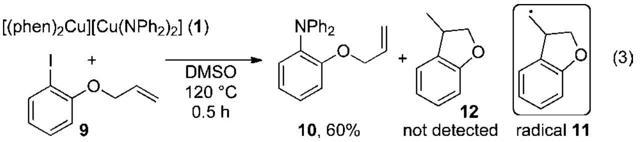
$$2\ (\text{phen})\text{CuNPh}_2\ +\ 2\ \text{ArI} \longrightarrow 2\ \text{ArNPh}_2\ +\ 2\ \text{phen}\ +\ 2\ \text{CuI}$$

Proposed autocatalytic mechanism

$$[(\text{phen})_2\text{Cu}^+][\text{Cu}(\text{NPh}_2)_2^-]\ +\ 2\ \text{CuI} \longrightarrow [(\text{phen})_2\text{Cu}^+][\text{CuI}_2^-]\ +\ 2\ \text{"CuNPh}_2\text{"}$$

$$2\ \text{"CuNPh}_2\text{"}\ +\ 2\ \text{ArI} \longrightarrow 2\ \text{ArNPh}_2\ +\ 2\ \text{CuI}$$

To probe the potential intermediacy of free aryl radicals during these reactions, we conducted the reaction of complex **1** with *o*-(allyloxy)-iodobenzene (**9**) in the presence and absence of phen. The aryl radical from this iodoarene is known to undergo cyclization to form the methyl radical **11** with $k_{obs} = 9.6 \times 10^9\ s^{-1}$ in DMSO, with subsequent formation of **12**.[20] Reaction of complex **1** with this arene (eq 3) formed amine **10** in 16% yield with added phen and 60% yield without added phen, and no detectable amount of cyclized **12** was observed by GC−MS in either reaction mixture.



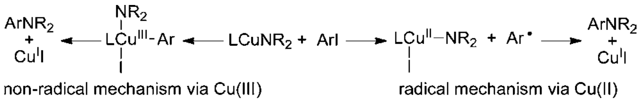
Because our detection limit for **12** was 0.1% of the amount of **10**, recombination would need to be >10^3 faster than cyclization. Thus, any free aryl radical must react with the copper(II) amide[21] to form the arylamine with a pseudo-first-order rate constant greater than 10^{13} s^{-1},[22] which is the lifetime of a transition state.[23] Clearly, bimolecular trapping of two reactive intermediates present in low concentrations is unlikely to occur on this time scale. Thus, the arylation of diarylamines catalyzed by Cu(I) and phen is unlikely to involve free aryl radicals.

Finally, to assess whether a copper amide lacking the phen ligand would be expected to add iodoarenes faster or slower than $[(phen)Cu(I)(NPh_2)]$, we used density functional theory (DFT) to calculate the barriers for oxidative addition of iodobenzene to $[(phen)Cu(NPh_2)]$ and $[(DMSO)Cu(NPh_2)]$.[24,25] The Cu(III) species $[(DMSO)Cu(NPh_2)(Ph)(I)]$ lacking a dative nitrogen ligand is computed to lie uphill of the combination of $(DMSO)Cu(NPh_2)$ and PhI by 17.1 kcal/mol and to be formed with a free energy of activation ($\Delta G^{\ddagger}$) of 21.8 kcal/mol at 25 °C.[26] This barrier is much lower than that for formation of $[(phen)Cu(NPh_2)(Ar)(I)]$, which was computed to be 33.4 kcal/mol (see the Supporting Information for details). These calculated barriers for oxidative addition are consistent with our proposal that the $CuNPh_2$ species lacking phen in DMSO is more reactive than $LCuNPh_2$, in which L = phen, and that the species lacking phen reacts with aryl halides when CuI is added.

Some authors have proposed that the mechanism of Cu(I)-catalyzed C−N and C−O coupling reactions of haloarenes occur by radical pathways,[7,27] and others have proposed that they occur by nonradical pathways[28] involving oxidative addition to form a Cu(III) intermediate (Scheme 3).[8b,25,29] The radical mechanism has been proposed to be triggered by electron transfer from copper to the haloarene to form a haloarene radical anion, which eliminates the halide to form a neutral aryl radical. The aryl radical would then combine with the copper(II) amide[21] to afford the arylated amine and regenerate the Cu(I) catalyst.

Previous theoretical studies and reactions of radical probes with isolated copper(I) amidate, imidate, and phenoxide complexes

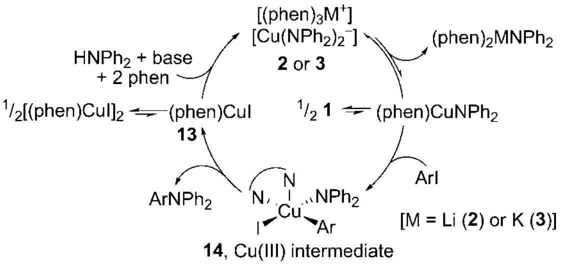
Scheme 3



provided evidence against the involvement of aryl radicals in Ullmann-type reactions.[10] This work provided some evidence for arylcopper(III) intermediates, and arylcopper(III) species have now been isolated.[15] However, the barriers predicted from Marcus theory using energies of reactants and products calculated by DFT led to the conclusion that the copper-catalyzed coupling of iodobenzene with methylamine as a representative alkylamine occurs by a radical path[22] and that the Cu(III) species [LCu(III)(NHMe)(Ph)(I)] lies at too high an energy to be an intermediate. Our results from the reactions of isolated amidocopper(I) intermediates with radical probe **9** suggest that the Cu(I)-catalyzed Ullmann reactions of diarylamines with iodoarenes do not proceed through free radical intermediates.[30]

We propose that the Ullmann reaction catalyzed by phen-ligated Cu(I) occurs by the pathway in Scheme 4. By this mechanism, phen-ligated CuI (**13**) is converted to alkali-metal cuprate **2** or **3** in the presence of excess amine and base. This cuprate then equilibrates with the neutral, monomeric form of **1**, which undergoes oxidative addition of the iodoarene to form Cu(III) species **14**. This Cu(III) species then reductively eliminates the amine product and regenerates **13**. The autocatalysis by free CuI observed in the reactions of complexes **1**−**3** with iodoarenes would not be expected to occur as part of this cycle because the excess amine and base would convert free CuI to the corresponding amidocuprate **2** or **3**.

Scheme 4. Proposed Catalytic Cycle without Autocatalysis



In summary, we have prepared and characterized a series of amidocuprates, some having phen-ligated Cu(I) countercations, some with phen-ligated alkali-metal cations, and some with alkali-metal cations lacking bound phen. Free CuI accelerates the reactions of each of these complexes. Double salt **1** was more reactive with iodoarenes than were the alkali-metal cuprates **2**−**5**. The relative reactivities in the presence of added CuI were **1** ≫ **3** > **2**. These rates relate to reactions of amines with aryl halides, base, and stoichiometric copper during which CuI would be generated. In the absence of added CuI, the relative rates for the reactions of the cuprates with iodotoluene were complicated by autocatalysis but followed the rough trend **1** > **3** > **1** + phen > **2** > **4** ≈ **5**. The low reactivity of cuprates **4** and **5**, which lack phen, implies that the reactions of **2** and **3** occur through a phen-ligated Cu(I) species, such as $[Cu(phen)(NPh_2)]$. The inherent reactivity of $[Cu(phen)(NPh_2)]$ with aryl iodides was assessed by conducting the reactions in the presence of added phen to sequester CuI, and these reactions occurred in high yields at 80 °C. The reaction of **1** with a radical probe implies that the reactions occur without Ph• intermediates, most likely through Cu(III) intermediates from oxidative addition of the iodoarene. DFT calculations further support a mechanism proceeding through Cu(III) intermediates, as the formation of such Cu(III) species is predicted to occur with a low energy barrier.

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Supporting Information Available: Experimental procedures, computational details, characterization of complexes, and crystallographic data (CIF) for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) This complex likely contains a DMSO ligand. Reactions in *t*BuS(O)Me occurred in lower yield than those in DMSO, suggesting that coordination of DMSO controls the reactivity of the unsaturated copper amide.
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