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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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
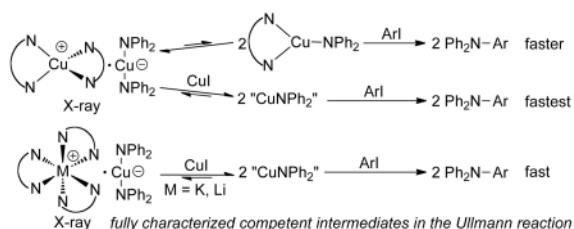
A series of Cu(I)-amido complexes both lacking ancillary ligands and containing 1,10-phenanthroline (phen) as ligand have been prepared. These complexes react with iodoarenes to form arylamine products, and these data are consistent with the intermediacy of such complexes in catalytic Ullmann amination 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 Cu(I)-amidates, -imidates and -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. DFT calculations of 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 with phen-ligated $LCuNPh_2$. The free energy barrier computed for reaction of PhI with $(DMSO)CuNPh_2$ was 21.8 kcal/mol, while the free energy barrier computed for 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 mediated 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 reported the coupling of arylamines with aryl iodides catalyzed by a combination of 1,10-phenanthroline (phen) and CuCl under

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mild conditions.3 Thereafter, a variety of ligands, such as 1,2-diamines,4 1,3-diketones,5 and others6 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 is available on the mechanism of this reaction. Ligandless "CuNPh$_2$" was proposed by Paine[7] in 1987 to be an intermediate in Ullman reactions catalyzed by CuI,[8] and tetramers of similar species [CuNR$_2$]$_4$ (R = alkyl) have been reported.[9] Ligated Cu(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*-aryl amides.[10,11] However, Cu(I)-amido complexes (LCuNR$_2$) containing a ligand that generates synthetically useful catalysts has not been characterized.[12]

Anionic copper(I) amides also could be intermediates in Ullman reactions. Organocuprates (MCuR$_2$) are among the most reactive nucleophiles in organic chemistry,[13] and similar cuprates have been proposed to form from the reaction of lithium amides with copper halides when the ratio of LiNR$_2$ to CuX is greater than one[14] (a condition that exists in the catalytic Ullmann reaction). However, amido cuprate complexes of the type MCu(NR$_2$)$_2$ have not been isolated, characterized or assessed as potential intermediates in the 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 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 ligate 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.

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 the ionic [Bu$_4$N][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*-octyl)$_4$N][Br] was 65.1 $\mu\Omega^{-1}$ cm^{-1} (0.99 Ω^{-1} cm^2 mol^{-1}) and that of a 65.5 mM 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 Cu(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.

The solid state structure of complex **3** contains two potassium cations ligated by six phenanthrolines and two bis-amidocopper anions (Figure 1). Two of the six phen ligands in

the dimer are shared by two potassium cations in which each nitrogen of the bridging ligand is coordinated to two potassium cations, such that each potassium cation is 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 (Table 1). Cuprates **2** and **3**, in which Li and K cations are ligated with phen, reacted similarly with *p*-iodotoluene in DMSO at 110 °C and 80 °C in 1 h and 3 h, respectively, to give one equivalent of **6** per copper in 84% and 90% yields. 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%). 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% yields, 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.

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 shows 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. The normalized concentration vs time plots overlap when the concentration of iodoarene is doubled, indicating that this process 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 occurred to form triarylamine **6** with a first order decay of **1** (Figure 2a). In contrast, this 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_{obs} = 3.1 × 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.
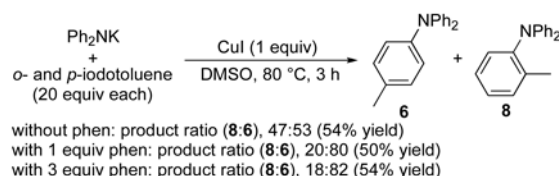
The effect of added phen on the reaction of complex **1** with *p*-iodotoluene was not straightforward. The reaction of complex **1** with *p*-iodotoluene in the presence of added phen was slower than that in the absence of added phen, but the reactions with 0.010 M and 0.020 M added phen occurred with identical rates (Figure 2b). The reaction at 80 °C with 0.010 M added phen was first order in **1**, with a half-life ($t_{1/2}$) of 32 min (k_{obs} = 3.6 × 10^{-4} s^{-1}). Thus, the slower rate with added phen does 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 that is generated in the absence of added phen and responsible for the autocatalysis and that the reaction occurs through the pathway lacking the autocatalysis in the presence of added phen. Reactions of **1** with varied concentrations of iodoarenes and added phen showed that the reaction was first order in this reagent.

Similar autocatalysis was observed for reactions of other copper amides. The reaction of cuprates **2** and **3** with *p*-iodotoluene occurred with sigmoidal reaction profiles (see 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_{obs} = 1.3 × 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_{obs} = 5.6 × 10^{-4} s^{-1}) at 80 °C.
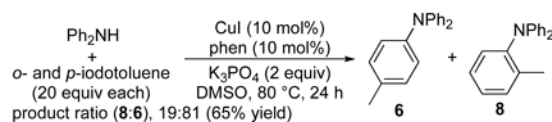
To assess the relationship between complexes **1–5** and intermediates in Ullmann reactions catalyzed by Cu(I)-phen species and to determine if the intermediates in the autocatalytic reactions are the same as those in reactions when free CuI is sequestered by added phen, we studied the selectivity of these complexes toward the sterically distinct *o*- and *p*-iodotoluenes. We then compared the distribution of products from these stoichiometric reactions in presence and absence of phen to those of catalytic reactions.

Results from these competitive reactions are provided in Table 2. The reaction of HNPh$_2$ with *o*- and *p*-iodotoluenes catalyzed by a 1:1 ratio of CuI to phen in the presence of K$_3$PO$_4$ formed a 19:81 ratio of **6** to **8**, and the reaction of KNPh$_2$ with *o*- and *p*-iodotoluenes in presence of stoichiometric amounts of a 1:1 ratio of CuI and phen formed an indistinguishable 20:80 ratio of these products (eq 1 and 2). A similar selectivity (14:86) was also observed at the early stage of the reaction of complex **1** with *o*- and *p*-iodotoluenes (2 min, 11% yield) when the concentration of free CuI was low and the autocatalytic pathway was not yet dominant. In contrast, the reaction of **1** with *o*- and *p*-iodotoluenes in the presence of CuI formed nearly equal amounts of the two amine products (49:51). This selectivity is similar to that of the reaction of KNPh$_2$ with stoichiometric CuI and no added phen (47:53).

The ratio of products from reaction of complex **1** with *o*- and *p*-iodotoluenes and no added phen (34:66) was between that of the reaction of HNPh$_2$ with *o*- and *p*-iodotoluenes catalyzed by a 1:1 ratio of CuI to phen in the presence of K$_3$PO$_4$ 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*-iodotoluenes in the presence of 1 equiv of phen to sequester free CuI formed a ratio (20:80) of the two products that is 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** or, more likely, the neutral form of **1** [Cu(phen)(NPh$_2$)], but the portion of the reaction of **1** with 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 generate a [CuNPh$_2$]$_n$ species lacking phen (Scheme 2).[17] This species is likely less selective than **1** because it contains a more open coordination sphere.

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)

(1)

(2)

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*-iodotoluenes in the presence of CuI were equally unselective. Thus, the reactions of

these cuprates in the presence of CuI generate the same species that we propose to be $[CuNPh_2]_n$.[18,19]

To probe the potential intermediacy of free aryl radicals during these reactions, we have 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 formed amine **10** in 16% yield with added phen and 60% yield without added phen. No detectable amount of cyclized **12** was observed by GC-MS in either reaction mixture (eq 3). Because our detection limit for **12** is 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, a bimolecular trapping of two reactive intermediates present in low concentrations is unlikely to occur on this timescale. Thus, the low selectivity from reaction without added phen and added CuI is unlikely to result from a pathway involving free aryl radicals and more likely from an open coordination sphere without a bidentate dative ligand.
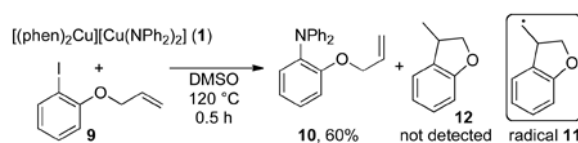
(3)

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 calculated with DFT the barriers for oxidative addition of iodobenzene to [(phen)Cu(I)(NPh$_2$)] and [(DMSO)Cu(I)NPh$_2$].[24,25] The formation of the Cu(III) species [(DMSO)Cu(NPh$_2$)(Ph)(I)] lacking a dative ligand is thermodynamically uphill of the combination of (DMSO)Cu(I)(NPh$_2$) and PhI by 17.1 kcal/mol and is formed with a $\Delta G^{\ddagger}$ of 21.8 kcal/mol at 25 °C.[26] This barrier is much lower than that for formation of [(phen)Cu(III)(NPh$_2$)(Ar)(I)], which was computed to be 33.4 kcal/mol (see 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 the phen-ligated LCuNPh$_2$ species 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 non-radical pathways[28] involving oxidative addition to form a Cu(III) intermediate (Scheme 3).[25,29] The radical mechanism is 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 Cu(II)-amide[21] to afford the arylated amine and regenerate the Cu(I) catalyst.

Previous theoretical studies and reactions of radical probes with isolated Cu(I)-amidate, -imidate and -phenoxide complexes 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, predicted barriers 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 the radical probe **9** suggest that the Cu(I)-catalyzed Ullmann reactions of diarylamines with iodoarenes do not proceed through free radial intermediates.[30]

We propose that the Ullmann reaction catalyzed by phenligated Cu(I) occurs by the pathway in Scheme 4. By this mechanism, the ligated CuI **13** is converted to the alkali metal cuprate **2** or **3** in the presence of excess amine and base. These cuprates then equilibrate 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 lithium and potassium amido cuprates **2** and **3**.

In summary, we have prepared and characterized a series of amido cuprates, 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 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 imply the reactions occur without Ph• intermediates, most likely through Cu(III) intermediates from oxidative addition of the iodoarene. DFT calculations further support the mechanism proceeding through Cu(III) intermediates since the formation of such Cu(III) species is predicted to occur with a low energy barrier.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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17. A referee asked if [CuNAr$_2$]$_n$ could be directly observed in this system. The ^{19}F NMR spectrum of the reaction of a *p*-fluoro analog of complex **1** with CuI in DMF-*d$_7$* at −50 °C contained a new signal, but the identity of the new species could not be determined unambiguously.

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

19. Tetrameric CuNR$_2$ complexes in which R = alkyl groups are known (see ref 9), and we found that they do not react with iodoarenes. The CuNPh$_2$ species generated *in situ* would have weaker bridging ligands and would be generated initially as a lower-coordinate species.

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26. DFT calculations suggested that both Cu(I) and Cu(III) species, [Cu(I)(NPh$_2$)] and [Cu(III)(NPh$_2$) (Ph)(I)], bind a single DMSO though oxygen.

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30. Because LCuNHMe is more electron-rich than LCuNPh$_2$, LCuNHMe could be more prone to engage in single electron transfer processes.
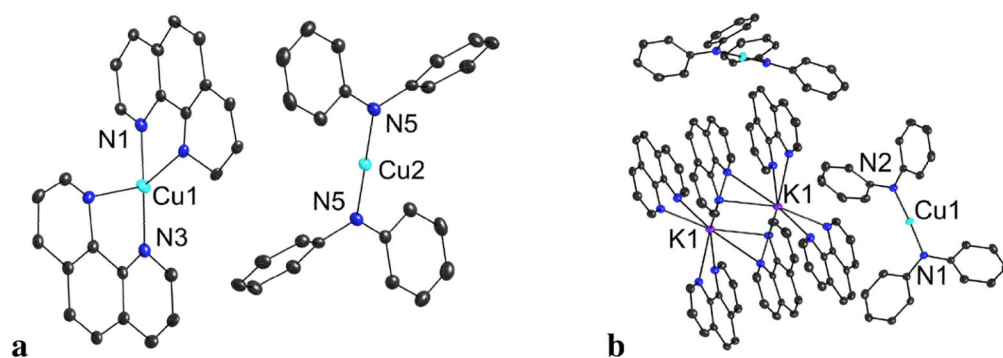
Figure 1.
(a) ORTEP drawings of **1** (a) and **3** (b) with 50% ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1** (a): Cu2-N5, 1.8659(15); N5-Cu2-N5, 180.0. Selected bond lengths (Å) and angles (deg) for **3** (b): Cu1-N1, 1.860(2); Cu1-N2, 1.879(2); N1-Cu1-N2, 176.45(10).
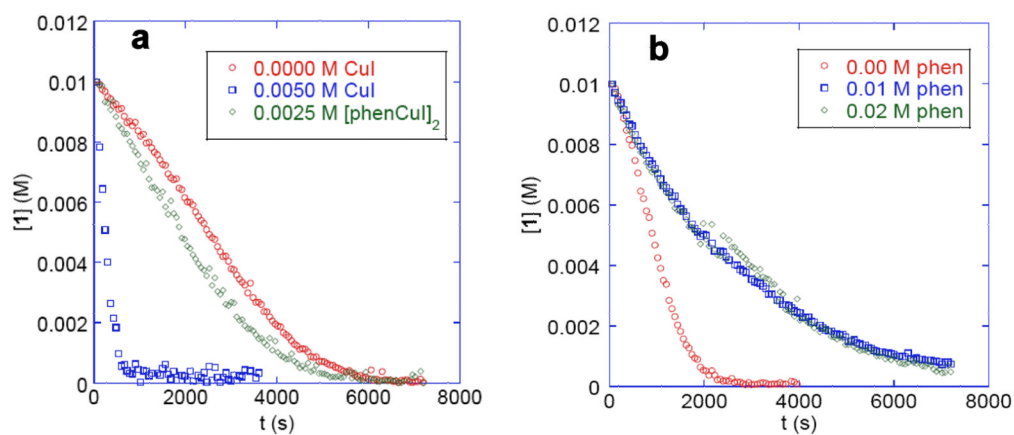
Figure 2.
a. Decay of complex **1** from reaction with *p*-iodotoluene alone (red), with added CuI (blue) or with added [phenCuI]$_2$ (green) at 60 °C. b. Decay of complex **1** from reaction with *p*-iodotoluene alone (red), with 0.010 M (blue) or 0.020 M (green) 1,10-phenanthroline at 80 °C.

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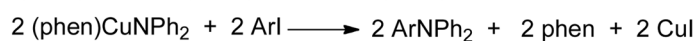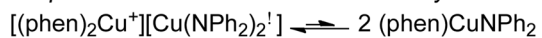**1**, 97%

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

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

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

$$\text{Ph}_2\text{NK} + \text{Ph}_2\text{NH} \xrightarrow[\text{THF, rt}]{\text{CuOtBu}} \text{K}[\text{Cu}(\text{NPh}_2)_2]$$
5, 76%
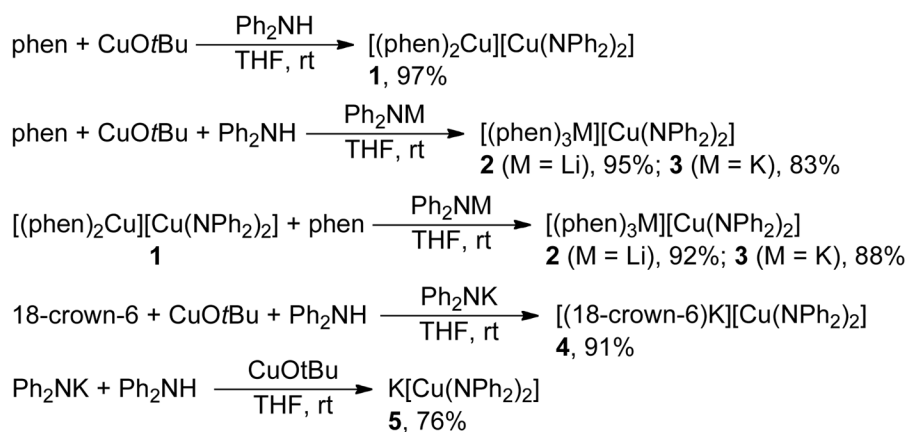
Scheme 1.

Proposed mechanism without autocatalysis

$[(phen)_2Cu^+][Cu(NPh_2)_2^!] \rightleftharpoons 2\ (phen)CuNPh_2$

$2\ (phen)CuNPh_2\ +\ 2\ ArI \longrightarrow 2\ ArNPh_2\ +\ 2\ phen\ +\ 2\ CuI$

Proposed autocatalytic mechanism

$[(phen)_2Cu^+][Cu(NPh_2)_2^-]\ +\ 2\ CuI \longrightarrow [(phen)_2Cu^+][CuI_2^-]\ +\ 2\ "CuNPh_2"$

$2\ "CuNPh_2"\ +\ 2\ ArI \longrightarrow 2\ ArNPh_2\ +\ 2\ CuI$

Scheme 2.

$$\text{ArNR}_2 + \text{Cu}^I\text{I} \longleftarrow \overset{\displaystyle \text{NR}_2}{\underset{\displaystyle \text{I}}{\text{LCu}^{III}\text{-Ar}}} \longleftarrow \text{LCuNR}_2 + \text{ArI} \longrightarrow \underset{\displaystyle \text{I}}{\text{LCu}^{II}\text{-NR}_2} + \text{Ar}^{\bullet} \longrightarrow \text{ArNR}_2 + \text{Cu}^I\text{I}$$

non-radical mechanism via Cu(III)   radical mechanism via Cu(II)
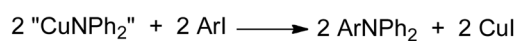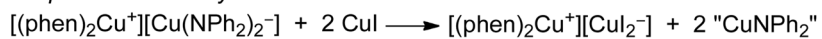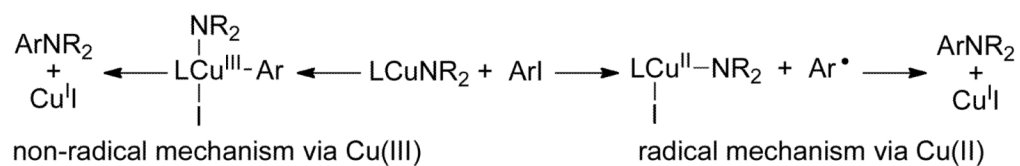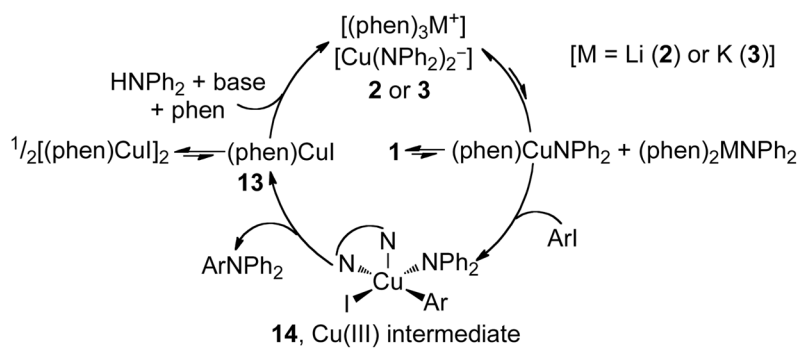
Scheme 3.

Scheme 4.
Proposed catalytic cycle without autocatalysis

Table 1

Reactivity of complexes **1–5** with *p*-iodotoluene.

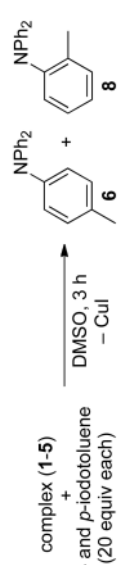| entry	complex	additive	temp (°C)	time (h)	% yield 6[a]	7/1–5[b]
1	**1**	none	80	1.5	95	-
2	**2**	none	110	1	84	1.14[c]
3	**3**	none	80	3	90	0.62
4	**4**	none	110	3	54	1.24[c]
5	**4**	phen (1 equiv)	80	2.5	>95	0.80
6	**5**	none	110	3	44	1.48[c]
7	**5**	phen (3 equiv)	80	3	56	1.24[c]

[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 reactions of **2–5** requires a proton from solvent or adventitious water;

[c]Each of complexes **1–5** contains two amido groups. In the balance equation, one amido group forms the triarylamine and one forms diarylamine. Some diarylamine is apparently formed in competition with the process that forms triarylamine, leading to a ratio that is greater than one.

Table 2

Selectivity of complexes **1–5** for *o-* and *p*-iodotoluenes.

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

[a] Combined GC yield of **6** and **8**; reactions of **2–5** also form Ph₂NH. See Table 1.

[b] 4 h.

[c] 2 min.