C−N Bond Formation from a Masked High-Valent Copper Complex Stabilized by Redox Non-Innocent Ligands

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Abstract: *The reactivity of a stable copper(II) complex bearing fully oxidized iminobenzoquinone redox ligands towards nucleophiles is described. In sharp contrast with its genuine low-valent counterpart bearing reduced ligands, this complex performs high-yielding C−N bond formations. Mechanistic studies suggest that this behavior could stem from a mechanism akin to reductive elimination occurring at the metal center but facilitated by the ligand: it is proposed that a masked high oxidation state of the metal can be stabilized as a lower copper(II) oxidation state by the redox ligands without forfeiting its ability to behave as a high-valent copper(III) center. These observations are substantiated by a combination of advanced EPR spectroscopy techniques with DFT studies. This work sheds light on the potential of redox ligands as promoters of unusual reactivities at metal centers and illustrates the concept of masked high-valent metallic species.*

The advent of catalytic manifolds relying on highly oxidized organometallic species is currently an area of acute interest in catalysis. The rich opportunities offered by such metallic complexes have been showcased in the case of several metals and among the most promising so far are copper(III),[1,2] palladium(III) and palladium(IV),[1,3] as well as nickel(III) and nickel(IV)[4] derivatives. These high-valent molecular edifices display distinct selectivity from their lower valent counterparts and can perform catalytically notoriously challenging events.[5] Mechanistic studies on these species are difficult and stoichiometric studies of these high-valent complexes can provide fundamental insights towards the rationalization of their reactivity. High-valent species are typically generated upon oxidation of a metal center with strong oxidants such as hypervalent iodine and/or CF_3^+ or F^+ sources.[4b,d, 6]

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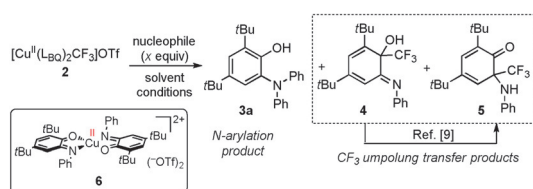13397 Marseille cedex 20 (France)

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So-called non-innocent or redox ligands[7] are molecular scaffolds which are able to delocalize spin density in metal complexes, and this specific behavior could lead to the stabilization of formal higher metallic oxidation states through electronic redistribution.[7d] Focusing on the well-established family of amidophenolate and related ligands,[8] we have recently reported[9] (Scheme 1) that oxidation of the
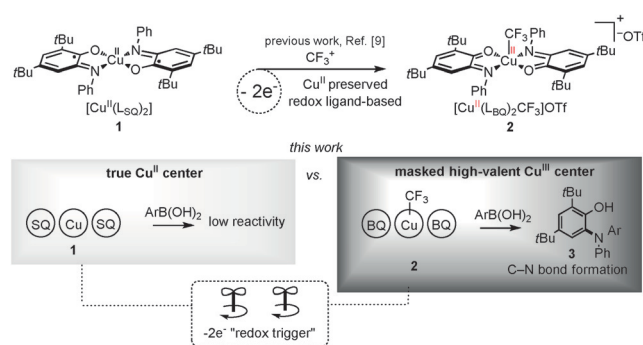
Scheme 1. Distinct reactivity from two copper(II) centers. SQ: iminosemiquinone ligand, BQ: iminobenzoquinone ligand. Tf = trifluoromethanesulfonyl.

copper(II) complex **1**[10] with an electrophilic source of CF_3^+ [S-(trifluoromethyl)-dibenzothiophenium triflate; TDTT] affords the complex **2** in which the copper oxidation state has been preserved as copper(II) while the $2e^-$ oxidation is sustained by the ligands (see the Supporting Information for computational data). While originating from a CF_3^+ source, **2** undergoes internal transfer of CF_3^- in solution at electrophilic sites, thus suggesting that the redox ligands can perform a formal umpolung of the CF_3 moiety. Furthermore, in the presence of a radical acceptor, ligand-based single-electron transfer (SET) in **1** allows the controlled generation of $CF_3^•$ radicals, thus enlarging the synthetic potential of this family of complexes.[11]

We reasoned that the propensity of these ligands to promote ligand-based (as opposed to metal-based) redox events could be interfaced with the reactivity of metallic high-valent oxidation states. Interestingly, redox non-innocent ligands have already been used in a related but opposite strategy aiming at preparing masked palladium(0) complexes.[12] Metallic high-valent oxidation states are known to behave as electrophiles and, upon investigating the reactivities of **1** and **2** towards nucleophiles, we found that while being spectroscopically identified as a copper(II) complex, **2** behaves as a high-valent copper(III) species and performs high-yielding C−N bond formations with carbon nucleophiles

to yield the N-arylated products **3**. This reactivity is in stark contrast with that of **1**, which exhibits lower reactivity (Scheme 1). The highly oxidized state of the ligands is therefore key to the enhanced reactivity of **2**.[8c,k]

Copper-catalyzed or copper-mediated formation of C−O and C−N bonds involving an aryl electrophile and an amine is known as the Ullmann coupling.[13] The mechanism of this transformation is still a topic of investigation. This reaction was shown to involve high-valent copper(III) species and recent reports showed that a radical pathway is possible under photoinduced conditions.[14] Copper(III) species have also been postulated in the related Chan–Lam–Evans reaction, an oxidative coupling which involves reverse electronics with a carbon nucleophile and either an amine or alcohol.[15] Although often invoked as intermediates in copper-catalyzed transformations such as C−H activation and cross-coupling, transient copper(III) species are mostly elusive and difficult to characterize.[2] However, detailed studies based on well-defined stable macrocyclic aryl/copper(III) complexes have provided a wealth of reactivity and mechanistic insights on these copper-catalyzed transformations.[16] Notably, these studies have shown that the reductive elimination step from aryl/copper(III) complexes with a nucleophile occurs easily. These results have unambiguously established the viability of aryl/copper(III) intermediates in Ullmann reactions, and suggest they could also be operative in the Chan–Lam–Evans coupling, a reaction our transformation is reminiscent of.

Preparation of **2** was previously reported by our team by oxidation of **1** with TDTT.[9] However, an optimized synthesis was devised based on the use of non-commercially available but easily synthesized 3-cyclopropyl-1-trifluoromethylbenzothiophenium triflate (see the Supporting Information).[17] Optimization studies for the N-arylation reaction were conducted (Scheme 2; see Table S1 in the Supporting Infor-
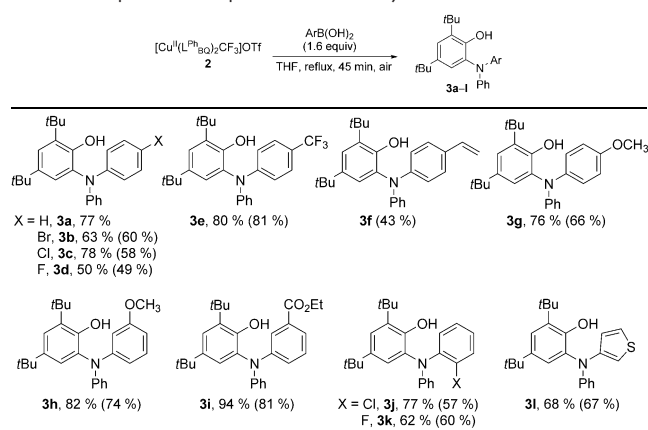
mation) as the expected product **3a** is obtained along with the products **4** and **5**, which were previously reported and arise from internal CF$_3^-$ transfer on either of the proximal carbon atoms to the copper center.[9] The compound **5** is the most stable and prolonged heating of **4** in acetonitrile results in full conversion into **5**. Initial attempts with phenyl potassium trifluoroborate showed that the reaction occurs in either THF or AcOEt (albeit in lower yield) but that acetonitrile inhibits the formation of **3a** (Table S1, entries 1–3). The reaction can be carried out under either argon or air, and increasing the amount of the nucleophile to 1.6 equivalents afforded a higher yield (entry 4) while using 2 equivalents did not produce significantly better results (entry 6). Time optimiza-

tion revealed that the reaction is complete after 45 minutes (entry 5, almost full conversion observed after 10 min). Substituting PhBF$_3$K with phenylboronic acid gave good yield and fewer by-products (entry 7), and was therefore selected for the rest of our study. Related complexes **1** [Cu^{II}(L$_{SO}$)$_2$] and **6** [Cu^{II}(L$_{BQ}$)$_2$(OTf)$_2$] (Scheme 2; see the Supporting Information for preparation) were found to give much lower yields (Table S1, entries 8 and 9) for this transformation. This outcome is expected in the case of **1**, which is not electrophilic enough, but in the case of **6** it is an indication that a high oxidation state of the ligands alone cannot account for the observed reactivity, and underlines the importance of the CF$_3$ moiety in this reactivity.

Structural confirmation of the N-arylation products **3d**, **3f**, **3g**, and **3h** (Table 1) was obtained through single-crystal X-ray diffraction (Figure 1; see the Supporting Information). However, switching to Csp^3 partners (alkyl boronic acids) was not successful. The influence of different electronic substitutions on the redox ligand was investigated (Table 2) by preparing analogues of **2** bearing diverse aryl substitutions on the nitrogen center (**7**–**10**: Ar = 4-CH$_3$(C$_6$H$_4$): **7**; 4-CF$_3$(C$_6$H$_4$): **8**; 4-Cl(C$_6$H$_4$): **9**; 3,5-(MeO)$_2$(C$_6$H$_3$): **10**). The resulting N-arylated products (**3c**, **3e**, **11**, and **12**) were isolated and the best yields were observed for electron-deficient aryl moieties (**3c** and **3e**).

The reaction is complete in around 45 minutes. Investigation of the reaction medium at 70 °C by UV-vis studies (see Figure S1) showed consumption of **2**, followed by an intensity increase around $\lambda = 270$ nm, thus suggesting formation of new

Scheme 2. Product distribution arising from N-arylation reaction.

Table 1: Scope of nucleophiles for the N-arylation reaction.

X = H, **3a**, 77 %
Br, **3b**, 63 % (60 %)
Cl, **3c**, 78 % (58 %)
F, **3d**, 50 % (49 %)

3e, 80 % (81 %)

3f (43 %)

3g, 76 % (66 %)

3h, 82 % (74 %)

3i, 94 % (81 %)

X = Cl, **3j**, 77 % (57 %)
F, **3k**, 62 % (60 %)

3l, 68 % (67 %)

Yields were determined by ^{1}H NMR spectroscopy. Yields of isolated products given within parentheses.
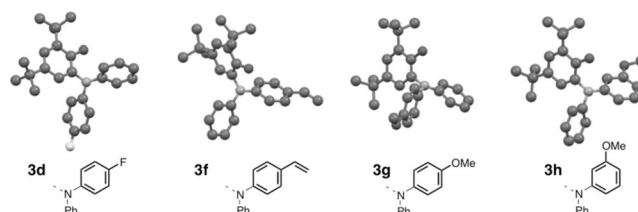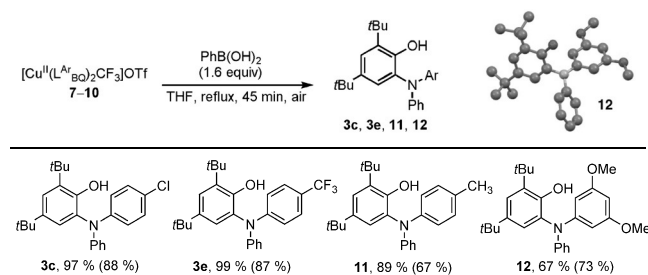
Figure 1. X-ray structures of compounds **3d**, **3f**, **3g**, and **3h**. Hydrogen atoms are omitted for clarity.

Table 2: Variation of the aryl substitution on the redox ligand and X-ray structure of **12**.

Yields were determined by ^{1}H NMR spectroscopy. Yields of isolated products given within parentheses. Hydrogen atoms are omitted for clarity.

aromatic species. From a mechanistic point of view the reaction of a carbon nucleophile to form a C−N bond through direct S_N2 attack seems very unlikely as the nitrogen atom in **2** does not bear electrophilic reactivity. Other mechanistic possibilities for this transformation include an outer-sphere radical-type mechanism. However, when adding up to 5 equivalents of TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl radical), the N-arylation product was isolated in 74% yield, thus suggesting that the reaction does not involve

substrate-based radicals. Besides, **2** alone does not react with TEMPO,[11] thus ruling out the possibility of an initial electron transfer between TEMPO and **2**. Mass spectrometry performed on the reaction mixture allowed the observation of a species corresponding to [(L$_{BO}$)$_2$Cu(CF$_3$)(Ph)] (see the Supporting Information). The molecular formula was validated by high-resolution MS (HRMS, observed: *m/z* 799.34831, calculated: *m/z* 799.35062) and proves the incorporation of the nucleophilic aryl moiety in the complex, thus providing strong evidence for an inner-sphere mechanism. Competition experiments were performed with added exogenous ligands and addition of increasing amounts of triphenylphosphine was found to inhibit the reaction. This observation suggests that a lack of available coordination sites on the copper center shuts down the reaction and further supports an inner-sphere mechanism.

This reaction involves several paramagnetic species and EPR spectroscopy can provide useful insights on the mechanisms at stake in homogeneous catalysis with paramagnetic complexes bearing redox non-innocent ligands.[18] EPR studies were first performed on a solution of **2** alone, which undergoes intramolecular CF$_3$ transfer to afford **5** (Scheme 3).[9] Interestingly, small changes of its room-temperature EPR signature are observed between dichloromethane and THF solutions, thus indicating that coordination of an
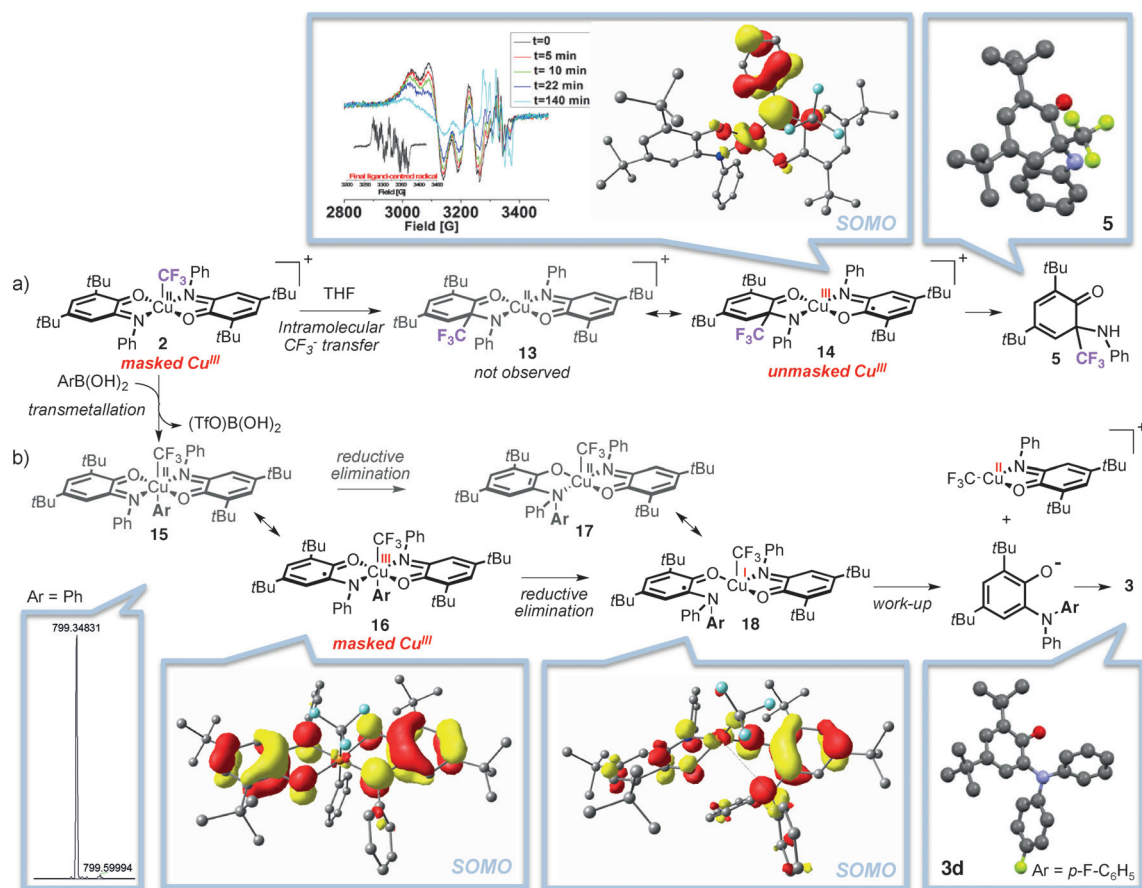
Scheme 3. Proposed mechanisms rationalizing the observed masked high-valent reactivity of **2** in a) an intramolecular CF$_3$ transfer (insets: EPR and DFT studies on the intermediate **14** and X-ray structure of **5**) and b) the N-arylation reaction (insets: HRMS, and DFT studies on the intermediates **16** and **18**, and X-ray structure of **3d**. Hydrogen atoms are omitted for clarity.

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exogeneous ligand, here THF, on the copper center is probable. Indeed, the main features of the THF spectrum remain characteristic of a copper(II) species in solution, with the typical four lines resulting from the hyperfine coupling of $S = 1/2$ (d^9 Cu^{II}) with its nuclear spin I = 3/2. A g_{iso} value of 2.11 and hyperfine coupling $A_{Cu} = 68$ G respectively are measured. The spectral shape observed is due to the tumbling effect.[19] Similar signals are measured in DCM solution. Additionally, a weak quadruplet signal (intensity 1:3:3:1, centered at $g = 2.003$) overlaps with the copper signal in THF.

Upon heating (60°C), we can first observe a decrease of copper(II) signal without any change in g and A values, thus indicating that only redox reactions occur with no symmetry change. Over the course of time at 60°C (see Figure S2), we can observe a growing signal ($g = 2.010$) resulting from the formation of a ligand-based organic radical, while the quadruplet signal disappears. The hyperfine structure of this new ligand-based signal is more complex (insert), and its simulation [$(^{14}N) = 17.55$ G, $A(^1H) = 38.94$ G and $A(^1H)_{tBu} = 2.93$ G; see Figure S3] is in agreement with an N-centered iminosemiquinone radical species (**14**), presumably still coordinated to the copper center, and resulting from the intramolecular CF$_3^-$ attack onto the other L$_{BQ}$ ligand (Scheme 3a). DFT calculations confirmed that the electronic structure of **14** is consistent with a copper(III) center bearing an L$_{SQ}$ ligand and that this species is found to be 8.8 kcal mol^{-1} higher in energy with respect to **2**. The structure of **5** was confirmed by single-crystal X-ray diffraction.

Addition of PhB(OH)$_2$ in the solution does not modify the spectrum recorded at room temperature. However, upon heating at 60°C, evolutions are observed. In the first stage, over about a 15 minute timespan, modification of the copper-(II) species spectrum is observed, notably with the disappearance of the copper signal at $g_{iso} \approx 2.09$ along with conformational changes and a $g_{iso} \approx 2.15$ at the final state (see Figure S4). No changes are measured for copper hyperfine coupling. The weak quadruplet signal at $g \approx 2.003$ also quickly disappears and no signature of organic radical is detected. The remaining copper(II) signature then progressively diminishes in intensity, and almost completely vanishes after an hour. These data clearly show that upon reaction, the copper species is modified and ultimately degraded. No transient ligand-based radical copper species could be detected, probably because of the faster reaction kinetics with the boronic nucleophile.

Accordingly, a plausible pathway based on a coordination/reductive elimination mechanistic manifold is proposed (Scheme 3b). Initial transmetalation of **2** with phenylboronic acid gives rise to a [(L$_{BQ}$)$_2$Cu(CF$_3$)(Ph)] species where the phenyl is bound to the copper center in a *trans* relative position to the trifluoromethyl group. DFT studies performed on the resulting [(L$_{BQ}$)$_2$Cu(CF$_3$)(Ph)] species support this putative geometry, which is formed with an energetic cost of 16.9 kcal mol^{-1} and leads to a copper(III) center with a radical ligand (**16**) rather than a copper(II) center with closed-shell iminobenzoquinone ligand (**15**). The intermediate **16** can be best described as a fully delocalized π-radical which is equally distributed on both sides of the ligand. This species then undergoes C−N bond-forming reductive elimination to yield

the copper(I) species **18**. DFT calculations also support this copper(I)/radical SQ ligand electronic state in **18** rather than a copper(II) center with a closed-shell BQ ligand species **17**. The intermediate **18** is characterized by the decoordination of the amine bearing the phenyl and is 3.0 kcal mol^{-1} higher in energy compared to **16**. The alternative geometry in which the phenyl would bind the oxygen center, **18***, has also been considered but was found to be unfavorable. Final decoordination of the N-arylated amidophenolate occurs along with the formation of an unidentified copper(II) species. Similarly, transmetalation of a boronic acid occurring at a copper(III) center followed by reductive elimination, was recently reported by Grushin and co-workers.[20] In that case, the geometry of the intermediate allows Ph−CF$_3$ reductive elimination to occur, a step which is not possible in our present system because of the relative *trans* positions of the phenyl and CF$_3$ moieties. Also, iminosemiquinone ligands have been implicated in Ph−Ph reductive elimination from a zirconium (Zr^{IV}) complex.[8i,21]

In conclusion, we have shown that **2**, spectroscopically a copper(II) complex bearing fully oxidized iminobenzoquinone ligands, behaves as a copper(III) species towards carbon nucleophiles, thus performing C−N bond formation. The reactivity exhibited by **2** can be rationalized through ligand-based redox mechanisms implicating masked high-valent intermediates and arising from initial oxidation of **1** with a CF$_3^+$ source. The role of electrophilic fluorination sources as by-standers in the oxidation of metallic centers and promoting reductive elimination has been rationalized by Yu and co-workers in the context of palladium and gold chemistry.[6] The present work hints at a similar behavior as evidenced by EPR measurements and DFT calculations. The complex **2** is a rare example of a stable, masked, high-valent copper complex and this unprecedented reactivity opens the way towards new developments in high-oxidation-state copper chemistry.

Experimental Section

Acknowledgments

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