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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 Cu^{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 formation. 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 Cu^{II} oxidation state by the redox ligands without forfeiting its ability to behave as a high-valent Cu^{III} center. These observations are substantiated by a combination of advanced EPR spectroscopy techniques with DFT studies. This work sheds light on the potentialities 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 Cu^{III},^[1,2] Pd^{III} and Pd^{IV},^[1,3] Ni^{III} and Ni^{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 CF₃⁺ or F⁺ sources.^[4b,d,6]

So-called non-innocent or redox ligands^[7] are molecular scaffolds 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 Cu^{II} complex **1**^[10] with an electrophilic source of CF₃⁺ (S-(trifluoromethyl)-dibenzothiophenium triflate TDTT) affords complex **2** in which the copper oxidation state has been preserved as Cu^{II} while the 2e[−] oxidation is sustained by the ligands (see SI for computational data). While originating from a CF₃⁺ source, complex **2** undergoes internal transfer of CF₃[−] in solution at electrophilic sites, thus suggesting that the redox ligands can perform formal umpolung of the CF₃ moiety. Furthermore, in the presence of a radical acceptor, ligand-based single-electron transfer (SET) in complex **1** allows the controlled generation of CF₃[•] 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 Pd⁰ complexes.^[12] Metallic high-valent oxidation states are known to behave as electrophiles and, investigating the reactivity of complexes **1** and **2** towards nucleophiles, we found that while being spectroscopically identified as a Cu^{II}, complex **2** behaves as a high-valent Cu^{III} species and performs high-yielding C–N bond formation with carbon nucleophiles to yield N-arylated product **3**. This is in stark contrast with complex **1**, which exhibits lower reactivity (Scheme 1). The highly oxidized state of the ligands is therefore key to the enhanced reactivity of complex **2**.^[8c,k]

Scheme 1. Distinct reactivity from two Cu^{II} centers. Color code for ligands: green petal stands for iminosemiquinone (SQ) ligand while orange petal refers to iminobenzoquinone (BQ) ligand.

Copper-catalyzed or mediated formation of C–O and C–N bonds involving an aryl electrophile and an amine is known as Ullmann coupling.^[13] The mechanism of this transformation is still a topic

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of investigation. This reaction was shown to involve high-valent Cu^{III} species and recent reports showed that a radical pathway is possible under photoinduced conditions.^[14] Implication of Cu^{III} species has also been postulated in the related Chan-Lam-Evans reaction, an oxidative coupling which involves reverse electronics with a carbon nucleophile and an amine or alcohol.^[15] Although often invoked as intermediates in copper-catalyzed transformations such as C–H activation and cross-coupling, transient Cu^{III} species are mostly elusive and difficult to characterize.^[2] However, detailed studies based on well-defined stable macrocyclic aryl- Cu^{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- Cu^{III} complexes with a nucleophile occurs easily. These results have unambiguously established the viability of aryl- Cu^{III} intermediates in Ullmann reactions, and suggest they could also be operative in the Chan-Lam-Evans coupling, of which our transformation is reminiscent.

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

Preparation of complex **2** was previously reported by our team by oxidation of the complex **1** with TDDT.^[9] However, an optimized synthesis was devised based on the use of non commercially available but easily synthesized 3-cyclopropyl-1-trifluoromethylbenzothiophenium triflate (see SI).^[17] Optimization studies for the N-arylation reaction were conducted (Scheme 2 and Table S1) as the expected product **3a** is obtained along with products **4** and **5**, previously reported and arising from internal CF_3^- transfer on either of the proximal carbons to the copper center.^[9] Compound **5** is the most stable and prolonged heating of **4** in acetonitrile results in full conversion into compound **5**. Initial attempts with phenyl potassium trifluoroborate showed that the reaction occurs in THF or AcOEt (albeit in lower yield) but that acetonitrile inhibits the formation of compound **3a** (Table S1, entries 1–3). The reaction can be carried out under Ar or air and increasing the amount of nucleophile to 1.6 equiv. afforded a higher yield (entry 4) while using 2 equiv. did not produce any significantly better results (entry 6). Time optimization revealed that the reaction is complete after 45 min (entry 5, almost full conversion is already observed after 10 min.). Substituting PhBF_3K with phenylboronic acid gave good yield and less by-products (entry 7) and was therefore selected for the rest of our study. Related complexes **1** [$\text{Cu}^{\text{II}}(\text{L}_{\text{SQ}})_2$] and **6** [$\text{Cu}^{\text{II}}(\text{L}_{\text{BQ}})_2(\text{OTf})_2$] (see SI for preparation) were found to give much lower yields (entries 8 and 9) for this transformation. This is expected in the case of complex **1**, which is not electrophilic enough but, in the case of complex **6**, 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.

Table 1. Scope of nucleophiles for the N-arylation reaction. Yields were determined by ^1H NMR spectroscopy, isolated yields in brackets.

Figure 1. X-ray structures of compounds **3d**, **3f**, **3g** and **3h**. Hydrogen atoms are omitted for clarity.

Structural confirmation of the N-arylation products **3d**, **3f**, **3g** and **3h** was obtained through single crystal X-ray diffraction (Figure 1, SI for detailed description of the structures). However, switching to Csp^3 partners (alkyl boronic acids) was not successful. The influence of electronic substitution on the redox ligand was investigated (Table 2) by preparing analogues of complex **2** bearing diverse aryl substitutions on the nitrogen (complexes **7–10**). The resulting N-arylated products (**3c**, **3e**, **11** and **12**) were isolated and the best yields were observed for electrodeficient aryl moieties (**3c** and **3e**).

Table 2. Variation of the aryl substitution on the redox ligand and X-ray structure of compound **12**. Yields were determined by ^1H NMR spectroscopy, isolated yields in brackets. Hydrogen atoms are omitted for clarity.

The reaction is complete in around 45 min. Investigation of the reaction medium at 70°C by UV-vis studies (Fig. S1) showed consumption of complex **2**, followed by an intensity increase around 270 nm, suggesting formation of new aromatic species. From a mechanistic point of view, the reaction of a carbon nucleophile to form a C–N bond through direct $\text{S}_{\text{N}}2$ attack seems very unlikely as the nitrogen atom in complex **2** does not bear electrophilic reactivity. Other mechanistic possibilities for this transformation include outer-sphere radical type mechanism.

However, when adding up to 5 equiv. 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, complex **2** alone does not react with TEMPO,^[11] thus ruling out the possibility of an initial electron transfer between TEMPO and complex **2**. Mass spectrometry performed on the reaction mixture allowed the observation of a species corresponding to $[(L_{BQ})_2Cu(CF_3)(Ph)]$ (see SI for selected spectra). 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 grounds 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 (see SI for details). 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.

Scheme 3. Proposed mechanisms rationalizing the observed masked high-valent reactivity of complex **2** in a) intramolecular CF_3 transfer with inserts of EPR and DFT studies on intermediate **14** and X-ray structure of compound **5** and b) *N*-arylation reaction with inserts of HRMS, DFT studies on intermediates **16** and **18** and X-ray structure of compound **3d**. Hydrogen atoms are omitted for clarity.

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 complex **2** alone, which undergoes intramolecular CF_3 transfer to afford compound **5**.^[9] Interestingly, small changes of its room temperature EPR signature are

observed between dichloromethane and THF solutions, indicating that coordination of an exogenous ligand, here THF, on the copper center is probable. Indeed, the main features of the THF spectrum remain characteristic of a Cu^{II} species in solution, with typical four lines due to 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 Cu^{II} signal without any change in g and A values, indicating that only redox reactions occur with no symmetry change. Over the course of time at 60°C (Fig. S2), we can observe a growing signal ($g=2.010$) due to 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 ($A(^{14}\text{N}) = 17.55$ G, $A(^1\text{H}) = 38.94$ G and $A(^1\text{H})_{\text{Bu}} = 2.93$ G, Fig. S3) is in agreement with an N-centered iminosemiquinone radical species **14**, presumably still coordinated to the Cu center, resulting from the intramolecular CF₃[•] attack onto the other L_{BQ} ligand (Scheme 2a). DFT calculations confirmed that the electronic structure of **14** corresponds to a Cu^{III} center bearing an L_{SQ} ligand (see SI for details) and that this species is found to be 8.8 kcal/mol higher in energy with respect to **2**. The structure of final product **5** was confirmed by single crystal X-ray diffraction (Scheme 2a).

Addition of PhB(OH)₂ in the solution does not modify the spectrum recorded at RT. However, upon heating at 60°C, evolutions are observed. In a first stage, over about a 15 min timespan, modification of the Cu^{II} species spectrum is observed, notably with the disappearance of the copper signal at $g_{\text{iso}} \approx 2.09$ along with conformational changes with a $g_{\text{iso}} \approx 2.15$ at the final state (Fig. 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 Cu^{II} signature then progressively diminishes in intensity, and has almost completely vanished 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 due to the faster reaction kinetics with the boronic nucleophile.

Accordingly, a plausible pathway based on a coordination/reductive elimination mechanistic manifold is proposed (Scheme 2b). Initial transmetalation of complex **2** with phenylboronic acid gives rise to a [(L_{BQ})₂Cu(CF₃)(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})₂Cu(CF₃)(Ph)] species support that this putative geometry that is formed with an energetic cost of 16.9 kcal/mol leading to a Cu^{III} center with radical ligand **16** rather than a Cu^{II} center with closed-shell iminobenzoquinone ligands **15** ligand (see SI for details). 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 Cu^I species **18**. DFT calculations also support this Cu^I/radical SQ ligand electronic state in **18** rather than a Cu^{II} center with a closed-shell BQ ligand species **17** (see SI for details). Intermediate **18** is characterized by the decoordination of the amine bearing the phenyl and is 3.0 kcal/mol 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 (see SI for details). Final decoordination of the N-arylated amidophenolate occurs along

with the formation of an unidentified Cu^{II} species. Similarly, transmetalation of a boronic acid occurring at a Cu^{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–CF₃ reductive elimination to occur, which is not possible in our present system due to the relative trans positions of the phenyl and CF₃ 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 complex **2**, spectroscopically a Cu^{II} complex bearing fully oxidized iminobenzoquinone ligands, behaves as a Cu^{III} species towards carbon nucleophiles, performing C–N bond formation. The reactivity exhibited by complex **2** can be rationalized through ligand-based redox mechanisms implicating masked high-valent intermediates and arising from initial oxidation of complex **1** with a CF₃⁺ source. The role of electrophilic fluorination sources as by-standing oxidants allowing 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. 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

CCDC 1471618 (**3d**), 1471619 (**3f**), 1471620 (**3g**), 1471621 (**3h**), 1471622 (**12**) and CCDC 1472428 (**5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: copper • redox-active ligand • non-innocent ligand • Cu^{III} • high-valent oxidation state • masked high-valent reactivity

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