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COMMUNICATION

N-Heterocyclic Carbenes Reduce and Functionalize Copper Oxide Surfaces in One Pot

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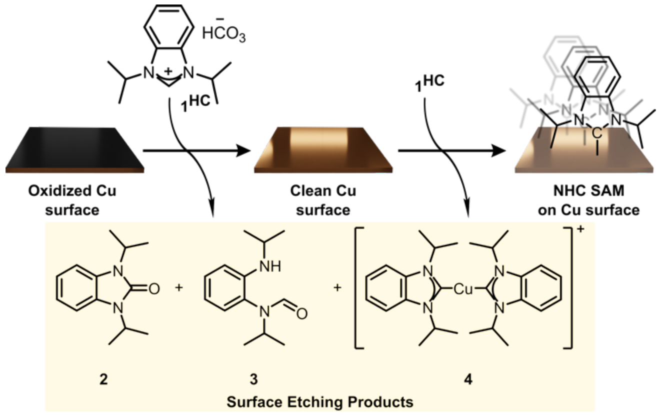
Abstract: Benzimidazolium hydrogen carbonate salts have been shown to act as N-heterocyclic carbene precursors which can remove oxide from copper oxide surfaces and functionalize the resulting metallic surfaces in a single step. Both the surfaces and the etching products are fully characterized by spectroscopic methods. Analysis of surfaces before and after NHC treatment by X-ray photoelectron spectroscopy demonstrates the complete removal of copper(II) oxide. Using ^{13}C-labelling, we determine that the products of this transformation include a cyclic urea, a ring-opened formamide and a bis-carbene copper(I) complex. These results illustrate the potential of NHCs to functionalize a much broader class of metals, including those prone to oxide treatment, greatly facilitating the preparation of NHC-based films on metals other than gold.

N-Heterocyclic carbenes (NHCs) are beginning to be recognized as powerful ligands for the stabilization of nanomaterials.[1] NHC–based monolayers have been reported to have considerably more thermal and chemical stability than thiol analogs,[2] and recent studies have shown that NHCs can also functionalize more reactive metal surfaces, including copper,[3] magnesium,[4] platinum[5] and silver.[3b]

Gold is the most widely employed metal in organic-on-metal type devices because of its high resistance to oxidation and ease of handling. However, more oxidation-sensitive metals often have superior properties and are typically much cheaper. For example, silver has a more sensitive surface plasmon response[6] and copper is widely applied in the semiconductor industry because of its conductivity and cost.[7]

Previous work from our groups[3a] and Papageorgiou and co-workers[3b] have shown that NHCs are fully capable of functionalizing metallic copper surfaces under ultra-high vacuum (UHV) conditions. Temperature programed desorption experiments demonstrated that the strength of the NHC–Cu bond is identical to that of the NHC–Au bond within error.[3a] However, handling copper surfaces in a typical laboratory environment is consistently challenged by the presence of surface oxide.

Herein, we describe the treatment of oxidized copper surfaces with common NHC precursors,[2b,8] resulting in removal of copper oxide and deposition of NHCs on the resulting metallic surface. Through several methods, we characterize the oxidation product of the NHC (Scheme 1). These results demonstrate that NHCs can be used not just to form monolayers on metal surfaces, but to remove oxide from reactive metals, and simultaneously functionalize the resulting metallic surfaces. This simple, straightforward method should significantly increase the ease with which more reactive, difficult to handle metals can be functionalized.



Scheme 1. Benzimidazolium hydrogen carbonate salts remove copper oxides and functionalize metallic copper surfaces. (NHC = 1,3-diisopropyl-benzimidazolylidene, **1**).

To examine the reaction of NHCs with copper oxide, polycrystalline copper surfaces were cleaned using *glacial* acetic acid and then oxidized using 30% H_2O_2.[9] The oxidized copper surfaces were then treated with 10 mM solutions of the NHC precursor, 1,3-diisopropylbenzimidazolium hydrogen carbonate (**1^{HC}**), in 1,2-dichloroethane at room temperature for 48 hours. Analysis of the resulting surfaces by X-ray photoelectron spectroscopy (XPS) confirmed the complete removal of CuO as seen by the loss of the Cu(II) shake-up peaks between 938.5 and 946.5 eV (compare Cu_{ox} and Cu_{ox}-**1^{HC}**, Figure 1a). The resulting Cu $2p_{3/2}$ XPS signal appears at 932.6 eV, in the region expected for a $Cu^{(0)}$ surface.[10] This signal appears at the same position as independently prepared $Cu^{(0)}$ surfaces, and is identical in intensity to NHC-modified $Cu^{(0)}$ surfaces prepared by either treatment with free NHC **1** ($Cu^{(0)}$-**1**) or hydrogen carbonate salt **1^{HC}** (Cu_{ox}-**1^{HC}**). This provides a preliminary indication that functionalization of the surface takes place after oxide etching (Figure 1a). It should be noted that thiols have also been shown to recued copper oxide

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surfaces, although this method would not be applicable to the formation of NHC-terminated surfaces.[11]

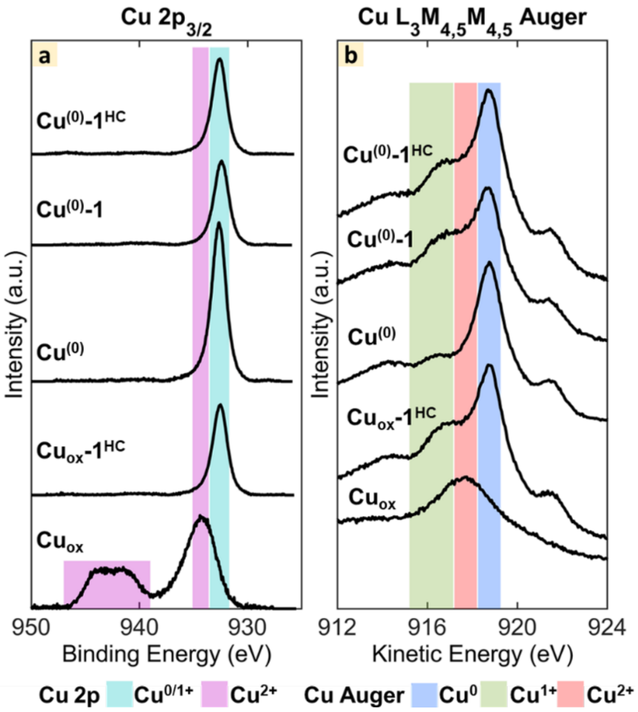


Figure 1. Stacked Cu 2p3/2 XPS (a) and Cu LMM Auger (b) plots illustrating the removal of metal oxides by treating cleaned (Cu(0)) and oxidized (Cu_{ox}) copper surfaces with solutions of the free NHC **1** or its hydrogen carbonate salt **1HC**.

While the data in Figure 1a show conclusively that Cu^{2+} species have been removed by treatment with **1HC**, the ability of the NHC to reduce Cu_2O cannot be assessed since the signals for Cu^{1+} and Cu(0) overlap in XPS.[12a] However, Auger spectroscopy in the Cu LMM region can give qualitative information about the presence of Cu^{1+} and Cu(0) species (Figure 1b).[12]

When analyzed by Auger spectroscopy, the oxidized sample (Cu_{ox}) exhibits a broad peak at 917.9 eV, characteristic of Cu^{2+}.[9b] By contrast, the Cu(0) sample exhibits a major peak at 918.8 eV, characteristic of metallic copper.[10, 13] Small amounts of Cu^{1+} species are also observed, which will be discussed below. Cu^{2+} species are not present.[14]

When Cu_{ox} is treated with **1HC**, the signal for Cu^{2+} at 917.8 eV is lost, consistent with the XPS results, and a new signals appears at 918.8 eV, corresponding to metallic copper (Figure 1b, Cu_{ox}-**1HC**).[15] Surprisingly, the signal at 916.9 eV attributed to Cu^{1+} species was enhanced. Interestingly, the same results were obtained when a metallic Cu surface was treated with **1** or **1HC** (Figure 1b). This led to the possibility that the observed Cu^{1+} signal results from sub-surface oxide revealed upon surface etching.

To address this, we performed XPS studies at glancing angles to differentiate between surface and bulk species. As shown in Fig S4, signals due to Cu_2O are only observed in bulk analysis, not at the more surface-sensitive glancing angles. (see supporting information). This indicates that these signals are likely due to sub-surface lattice Cu_2O, revealed by etching of the metal oxide/metal surface. Importantly, by studying direct reaction of NHC **1HC** with powdered Cu_2O, we are able to clearly demonstrate the ability of **1HC** to reduce this metal oxide.

The presence of NHC ligand on the surface after oxide removal was confirmed by analysis of the C 1s and N 1s XPS data. Although C 1s signals were not as helpful due to the presence of adventitious carbon, the change in the nitrogen region was highly diagnostic. As shown in Fig. 2a, Cu(0) modified with NHC **1** or precursor **1HC** were characterized by a strong signal at 400.0 eV, similar to what has been observed for NHC on Au.[2] The Cu_{ox} samples treated under the same conditions (Fig. 2b) also have a strong signal at 400.0 eV, identical to the functionalization of metallic surfaces. These observed changes strongly suggest that the removal of oxide from the surface is followed by protection of the newly revealed metallic surface with NHC.

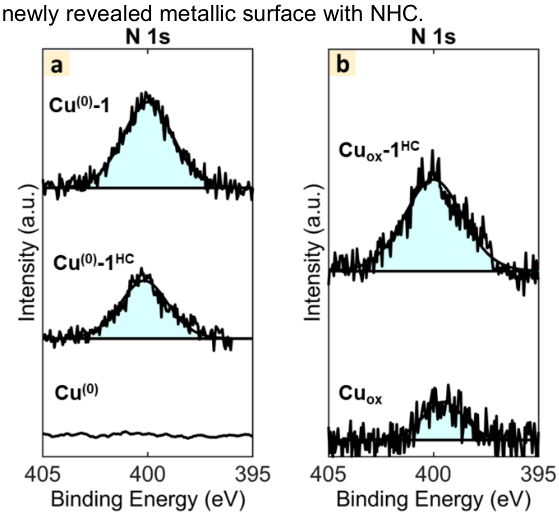
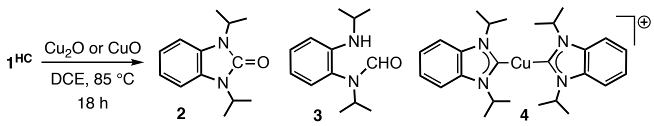


Figure 2. (a) Stacked N 1s XPS illustrating the functionalization of Cu(0) surfaces with NHC **1** and NHC precursor **1HC**, and (b) N 1s XPS plots illustrating the sample after treatment of Cu_{ox} surfaces with NHC precursor **1HC**. In both cases, treatment was accomplished with 10 mM DCE solutions of the hydrogen carbonate salt **1HC** or free NHC **1**.[16]

As shown in Table 1, treatment of bulk (powdered) Cu_2O and CuO with **1HC** afforded urea **2**, formamide **3** and copper complex **4** as confirmed by ^{1}H NMR spectroscopic analysis of the supernatant (Table 1).

Table 1. ^{1}H NMR (Cu_2O, CuO) and $^{13}C\{^1H\}$ NMR (Cu_{ox}, Cu(0)) spectroscopic yields[a,b] for copper etching with **1HC**.



Entry	Substrate	% Conv.[c]	2	3	4	% Rec.
1	Cu_2O	82 ± 2	33 ± 12	35 ± 9	10 ± 3	96 ± 1
2	CuO	84 ± 8	9 ± 2	64 ± 4	4 ± 4	94 ± 2
3	Cu_{ox}	63	9	46	7	99
4	Cu(0)	91	15	51	24	99

[a] Measured in CD_2Cl_2 and are relative to C_6Me_6 internal standard (0.5 mmol). Entries 1 and 2 are reported as an average of 3 replicates. [b] Entries 3 and 4 are given as relative yields for ^{13}C quantification with the assumption that all ^{13}C

labelled species originate from the starting material. [c] Remainder was determined to be unreacted **1^HC^**.

To confirm that the same species were observed in surface reactions, oxidized copper surfaces were treated with a labelled NHC precursor – namely **1^HC^** with a ^{13}C-label at the C(2) position. The supernatant was analyzed quantitatively using inverse-gated (IG) $^{13}C\{^1H\}$ NMR spectroscopy. As shown in Figure 4 and Table 1, urea **2** was again observed, along with remaining **1^HC^** and compound **3**, which results from hydrolysis of **1^HC^**, consistent with results obtained with bulk oxides.[18] In all cases, the spectroscopic assignment is based on the *de novo* synthesis of the compounds shown.[19] Mass spectrometry data also support these assignments (see the supporting information).

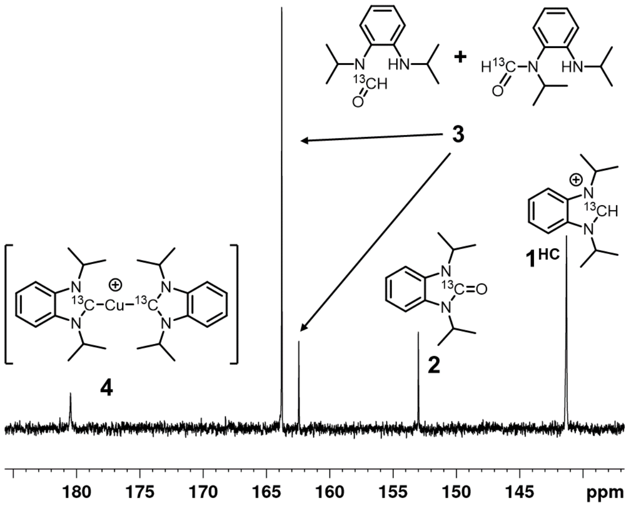
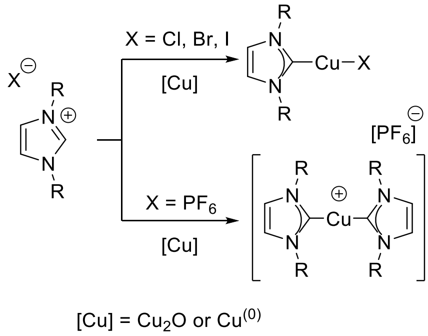


Figure 4. Quantitative IG-$^{13}C\{^1H\}$ NMR spectra of the supernatants obtained from Cu_{ox} etching experiments using ^{13}C-labelled **1^HC^**. $Cu^{(0)}$ etching is given in the supporting information. Yields are given in Table 1, entries 3-4.

Of the various compounds identified in the supernatants, urea **2** is the product of oxidation of carbene **1**. Importantly, this species is not observed upon inadvertent exposure of **1^HC^** to oxygen. Compound **3** results from hydrolysis of starting material **1^HC^**, a reaction that has been reported in rare cases,[20] but appears to be enhanced by the presence of surface metal hydroxides. Finally, along with unreacted starting material **1^HC^**, complex **4** is the only other organic species detected.

Complex **4** is an interesting by-product that results from abstraction of a copper atom from the surface. Previous work from our group and others have documented the ability of NHCs to lift metal atoms from metallic surfaces of Au, Cu and Ag resulting in surface-bound $M(NHC)_2$ species.[3,21] However, these compounds have not previously been observed in solution. Consistent with the suggestion that compound **4** arises from reaction with metallic copper,[23] a larger amount is observed from reaction with $Cu^{(0)}$ in comparison with oxidized copper (see supporting information).

These results can be compared with previous reports from the organometallic literature, which demonstrate that reaction between imidazolium salts and Cu_2O leads to NHC–Cu complexes.[22] The electrolysis of imidazolium salts in the presence of $Cu^{(0)}$ has also been shown to produce $[(NHC)_2Cu]^+$ species similar to compound **4** observed from reaction at the metallic surface.[23] To the best of our knowledge, this type of reactivity has not been applied to copper surfaces until now, and has not been employed to enable the reduction and functionalization of oxidized copper surfaces.



Scheme 3. Selected literature examples of imidazolium salts reacting with bulk Cu_2O and Cu.[22, 23]

In summary, we have shown that the interaction of NHCs with oxidized Cu surfaces reduces these surfaces to $Cu^{(0)}$, which then reacts with remaining NHC to yield an NHC-functionalized $Cu^{(0)}$ surface. Cyclic urea **2** is identified as the likely oxidation product arising from the reduction of the surface. Notably NHC complex **4** was also observed, illustrating the ability of the NHC to etch newly generated metallic copper. Consistent with this hypothesis, larger amounts of **4** are observed when starting with a primarily metallic copper surface. The results of this study provide the foundation for extending the use of NHC-based monolayers to more reactive metal substrates that are prone to oxidation. Finally, this work illustrates the ability of NHCs to act as chemical etchants, which may be used as an attractive alternative to other etchants, which are often unsafe or difficult to handle.

Acknowledgements

The Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canada Foundation for Innovation (CFI) are thanked for financial support of this work in terms of operating and equipment grants to CMC and JHH. AJV and MRN thank the Ontario government for OGS fellowships. AJV thanks NSERC for a Vanier Scholarship and also the Walter C. Sumner foundation for additional scholarship support.

Keywords: Carbenes • Copper • Monolayers • NMR spectroscopy • Photoelectron spectroscopy

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[14] The smaller signal with a kinetic energy of 921 eV arises from an unrelated Auger transition.[11]

[15] Note that the exact amounts cannot be quantified due to the qualitative nature of Auger spectroscopy, therefore we have not deconvoluted the signals.

[16] Reactivity between the free NHC **1** and DCE solvent was checked before deposition. No reaction was observed on the etching time scale at room temperature, however at 85 °C there was significant benzimidazolium salt formation, likely from HCl abstraction.[17] We also note that the nitrogen signal found in the bottom panel of 2b is from subsurface impurities as shown by angle resolved XPS. See supporting information for details.

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[18] The formamide **3** is observed as two signals because of restricted rotation about the amide bond.

[19] Although urea **2**, resulting from oxidation of the carbene, is the expected product, the formamide hydrolysis product **3** is actually the dominant species. We have observed this species to result from the reaction of $\mathbf{1^{HC}}$ with water in previous studies, but the amount observed here suggests that perhaps some surface copper hydroxide species promote this hydrolysis.

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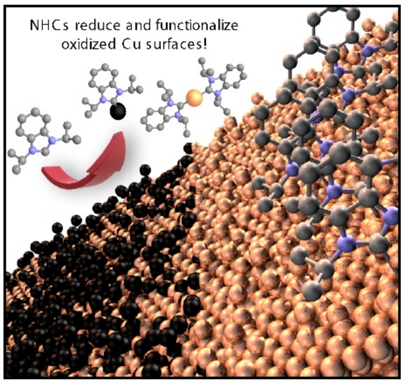

For the first time, a simultaneous etch-functionalize protocol has been developed for oxidized copper surfaces using N-heterocyclic carbenes. These results demonstrate the dual functionality of N-heterocyclic carbenes when applied to more reactive metal surfaces that are prone to oxidation and offers a new strategy for chemical etching that avoids dangerous reagents. This work also provides an opportunity to replace precious metals such as gold with more abundant metals like copper in organic-on-metal devices.

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