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Unexpected $C_{carbene}$−X (X: I, Br, Cl) Reductive Elimination from N-Heterocyclic Carbene Copper Halide Complexes Under Oxidative Conditions

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Summary: The non-spectator roles of NHC ligands have attracted wide attention due to their important implications for reaction mechanisms and subsequent impact on catalyst design. Herein, we report facile $C_{carbene}$−halogen reductive eliminations from NHC copper halide complexes at RT under oxidative conditions. Density functional calculations on a simplified model system suggest that the reactions occur through oxidation of Cu(I) species to Cu(III) species followed by $C_{carbene}$−halogen reductive eliminations from NHC Cu(III) halide complexes. Remarkably short $C_{carbene}$−chloride contacts and rare interactions between the chloride lone pair electrons and the $C_{carbene}$ p_π orbital were found for the calculated NHC Cu(III) chlorides. The facile $C_{carbene}$−X reductive elimination reported here warrants consideration as a potential decomposition pathway in reactions involving NHC-supported high-valent metal complexes, especially with late transition metals.

N-Heterocyclic carbene (NHC) metal complexes are used widely as catalysts in organic reactions.[1] Compared to other neutral type ligands, NHCs usually form stronger bonds with metals due to excellent σ-donating ability. The conjugation between the carbene carbon ($C_{carbene}$) p_π orbital and nitrogen lone pair electrons in the heterocycle further stabilizes the metal−$C_{carbene}$ bonds. As a result, NHCs are often better at suppressing catalyst decompositions. The metal−$C_{carbene}$ bonds are remarkably inert compared to other metal−carbon bonds at catalytic metal centers, which are prone to undergo various reactions such as migratory insertion and olefin metathesis.[1] In contrast, only a small number of elementary organomellic reactions, mostly limited to $C_{carbene}$−C reductive elimination and ligand dissociation/displacement, are documented with the metal−$C_{carbene}$ bonds.[2−4]

Carbon−halogen (C−X) reductive elimination of metal−C_{alkyl} or metal−C_{aryl} bonds is an important elementary organometallic reaction,[5] but no well-defined example is reported for $C_{carbene}$−X reductive elimination from NHC metal halide complexes,[6] although such complexes are ubiquitous in NHC chemistry.[1] Herein, we report facile formation of 2-haloimidazoliums from NHC Cu(I) halide complexes at room temperature (RT) under oxidative conditions as well as computational evidence to support a mechanism involving $C_{carbene}$−X reductive elimination from NHC Cu(III) halide complexes.

As a part of our continuing efforts in the characterization of reactivity of Cu(III) complexes,[7] we postulated that NHC

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(6) Halogenolysis of the metal−$C_{carbene}$ bonds to form $C_{carbene}$−X bonds does occur, presumably through either direct electrophilic cleavage of metal−$C_{carbene}$ bonds by X_2 or oxidative addition of X_2 followed by $C_{carbene}$−X reductive elimination. DFT calculations support a direct electrophilic cleavage of the Pd−$C_{carbene}$ bond by I_2.[9f] (a) Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1283–1291. (b) Liu, S.-T.; Ku, R.-Z.; Liu, C.-Y.; Kiang, F.-M. *J. Organomet. Chem.* **1997**, *543*, 249–250. (c) Cole, M. L.; Davies, A. J.; Jones, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2451–2452. (d) Fooladi, E.; Dalhus, B.; Tilset, M. *Dalton Trans.* **2004**, 3909–3917. (e) Heckenroth, M.; Neels, A.; Garnier, M. G.; Aebi, P.; Ehlers, A. W.; Albercht, M. *Chem.—Eur. J.* **2009**, *15*, 9375–9386. (f) Lee, E. Ph.D. Dissertation, Stanford University, Stanford, CA, 2009.

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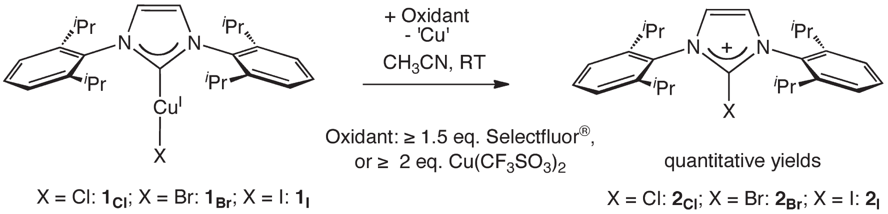
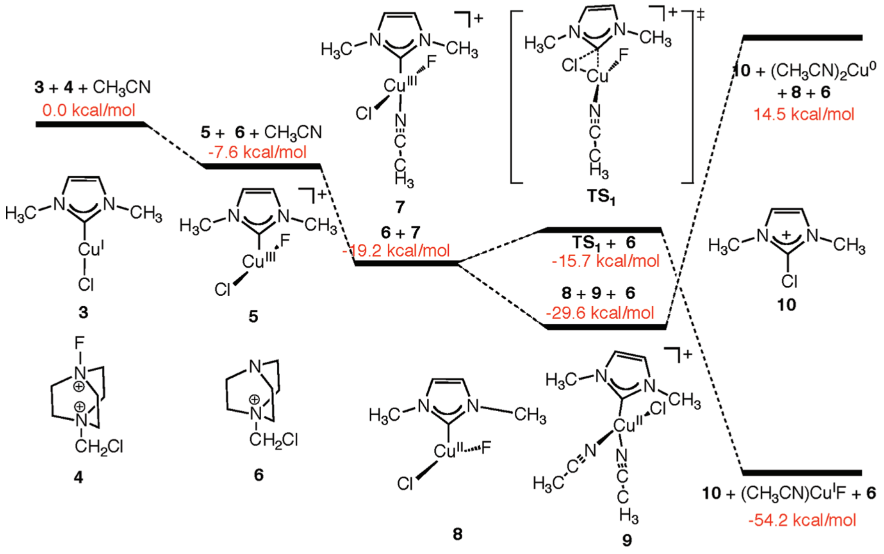
Scheme 1



Scheme 2



Relative free energies in kcal/mol.

Cu(III) complexes might be isolable because of the relatively inert Cu−C$_{\mathrm{carbene}}$ bond. In that regard, oxidations of IPr-Cu$^{\mathrm{I}}$Cl (**1**$_{\mathrm{Cl}}$, IPr: 1,3-bis(2, 6-diisopropylphenyl)imidazol-2-ylidene) by various oxidants were investigated. No significant reaction was observed between **1**$_{\mathrm{Cl}}$ and $[\mathrm{Ph_2I}]^+\mathrm{PF_6}^-$ or $[\mathrm{Cp_2Fe}]^+\mathrm{PF_6}^-$ (0.64 V vs NHE)[8] in acetonitrile (MeCN). By contrast, mixing **1**$_{\mathrm{Cl}}$ with Selectfluor (≥1.5 equiv) or Cu$^{\mathrm{II}}$(CF$_3$SO$_3$)$_2$ (≥2.0 equiv, 1.30 V vs NHE)[9] in MeCN at RT rapidly and quantitatively forms 2-chloroimidazolium **2**$_{\mathrm{Cl}}$ (Scheme 1).[10] Quantitative formation of 2-halo-imidazolium **2**$_{\mathrm{Br}}$ or **2**$_{\mathrm{I}}$ was realized for IPrCu$^{\mathrm{I}}$Br (**1**$_{\mathrm{Br}}$) or IPrCu$^{\mathrm{I}}$I (**1**$_{\mathrm{I}}$) under similar conditions.[11]

These reactions appear to occur through either an inner- or outer-sphere oxidation followed by C$_{\mathrm{carbene}}$−X reductive elimination. An outer-sphere oxidation is supported by the ca. 80% formation of **2**$_{\mathrm{Cl}}$ by reacting **1**$_{\mathrm{Cl}}$ with [(1,10-phenanthroline)$_3$Fe$^{\mathrm{III}}$]$^{3+}$ (≥2 equiv, 1.22 V vs NHE)[12] in MeCN at RT.[13] However, all these reactions are fast even at low temperatures ($t_{1/2} \approx$ seconds at ca. −40 °C), and no intermediate species could be detected by UV−vis spectroscopy on a time scale of seconds.

DFT calculations provide mechanistic insights into the oxidation by Selectfluor. The calculated free-energy profiles corresponding to C$_{\mathrm{carbene}}$−X reductive elimination from either a Cu(II) or Cu(III) species using a simplified model system (**3**) are shown in Scheme 2.[14] The oxidation of **3** by Selectfluor to form **5**, a three-coordinate Cu(III) species, is thermodynamically favorable.[15] The Cu(III) species is further stabilized by coordination of an MeCN ligand to form **7**.[16]

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(10) **2**$_{\mathrm{Cl}}$ was characterized by NMR (^{1}H, ^{13}C, and ^{19}F), mass spectroscopy, and X-ray crystallography (**2**$_{\mathrm{Cl}}$·SbF$_6$·CH$_2$Cl$_2$).[19] Reactions with lesser amounts of oxidants led to unreacted **1**$_{\mathrm{Cl}}$ and lower yields of **2**$_{\mathrm{Cl}}$. The amounts of oxidant and the color of the reaction solution suggest that the side product is Cu(II) (blue) and Cu(I) (colorless) species for the reaction with Selectfluor and Cu$^{\mathrm{II}}$(CF$_3$SO$_3$)$_2$, respectively.

(11) **2**$_{\mathrm{Br}}$ and **2**$_{\mathrm{I}}$ were characterized by NMR (^{1}H, ^{13}C, and ^{19}F), mass spectroscopy, and X-ray crystallography (**2**$_{\mathrm{Br}}$·CF$_3$SO$_3$·CH$_2$Cl$_2$ and **2**$_{\mathrm{I}}$·I$_3$).[19] The reaction of IPrCu$^{\mathrm{I}}$F with Cu$^{\mathrm{II}}$(CF$_3$SO$_3$)$_2$ led to the formation of IPrCu$^{\mathrm{I}}$(CF$_3$SO$_3$) (a crystal structure was obtained),[19] while the reaction with Selectfluor afforded a species with broad ^{1}H NMR signals similar to that of a reported NHC-ligated Cu(II) dimer,[20b] suggesting that C−F formation is slower than the comproportionation between Cu(I) and Cu(III).

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(13) Protonolysis of the Cu−C$_{\mathrm{carbene}}$ bond was also observed, leading to ca. 20% yield of the corresponding imidazolium. In addition, no well-defined oxidation occurs with **1**$_{\mathrm{Cl}}$ by cyclic voltammetry at low temperatures (ca. −40 °C).

(14) All calculations were performed at the level of B3LYP/6-311+G** by the Gaussian 03 program. The solvation effect was estimated by the PCM/UA0 model. Relative free energies are used in the computational discussion. See Supporting Information for more detailed descriptions of the computational methods. (a) Frisch, M. J.; et al. *Gaussian03*, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2004. (b) The gas-phase entropies were converted to corresponding entropies[19] (1 M in CH$_3$CN) according to the method in: Wertz, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 5316–5322.

(15) A 12.8 kcal mol^{-1} activation free energy was calculated for this step (fluorine transfer) at a lower-level method (B3LYP/6-311+G**//B3LYP/ LANL2DZ).[19]

(16) **6** is proposed as an intermediate in the reaction. It might ligate to copper in the final uncharacterized Cu(II) product. Coordination of MeCN to **3** might facilitate the oxidation. However, the corresponding three-coordinate species could not be located computationally.

The activation barrier for $C_{carbene}$−Cl reductive elimination from **7** via $\mathbf{TS_1}$ to form 2-chloroimidazolium **10** is remarkably low at 3.5 kcal mol^{-1}.[17] The overall reaction is favorable by −54.2 kcal mol^{-1}. Other possible Cu(III) species[18] are less stable than **7** and lead to higher activation barriers. Alternatively, **7** could react with another equivalent of **3** to form Cu(II) intermediates **8** and **9**, the two most stable Cu(II) species.[19] Although no transition state from **9** to **10** could be located (the energy monotonically increases as the $C_{carbene}$−Cl separation shortens), the lower limit of its activation barrier can be estimated by the corresponding reaction free energy, 44.1 kcal mol^{-1}, the least endothermic among various Cu(II) species.[19] Therefore, the calculations on the simplified model system favor a mechanism of $C_{carbene}$−Cl reductive elimination from NHC Cu(III) chloride complexes for the oxidation of $\mathbf{1_{Cl}}$ by Selectfluor.

The thermodynamically unfavorable $C_{carbene}$−Cl reductive elimination from **9** is consistent with isolable NHC Cu(II) chloride complexes.[20] On the basis of these results, we prefer a mechanism with two sequential inner- or outer-sphere 1e^- oxidations followed by $C_{carbene}$−Cl reductive elimination from NHC Cu(III) chloride complexes for the reaction with $Cu(CF_3SO_3)_2$,[21] although the detailed mechanism is still unclear. Furthermore, the quantitative formation of $\mathbf{2_{Cl}}$ instead of IPrCu(II) chloride complexes from the reaction of $\mathbf{1_{Cl}}$ and Selectfluor suggests that $C_{carbene}$−Cl reductive elimination from IPrCu(III) chloride complexes is much faster than reactions of $\mathbf{1_{Cl}}$ to form IPrCu(II) halide complexes. This reactivity is consistent with the calculated 3.5 kcal mol^{-1} activation barrier from **7** to **10**. Such a low barrier is probably a consequence of the electrophilic nature of a Cu(III) center that renders the NHC $C_{carbene}$ susceptible to nucleophilic attack, as suggested by the remarkably close $C_{carbene}$−Cl contacts (ca. 2.7 Å) in **5** and **7** (Figure 1) as well as the interactions between the chloride lone pair electrons and the $C_{carbene}$ p_π orbital (Figure 2). A similar interaction has been invoked to rationalize the short $C_{carbene}$−Cl contact (ca. 2.85 Å) in NHC $V^V(O)Cl_3$.[22] In contrast, no evidence of such an interaction exists for **8** (Figure 1).

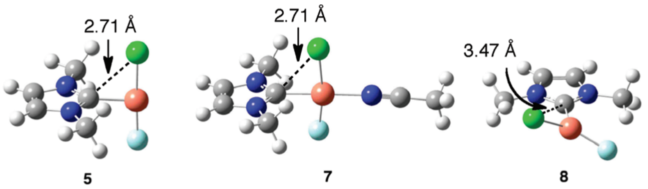

Figure 1. Optimized structures of **5**, **7**, and **8**.

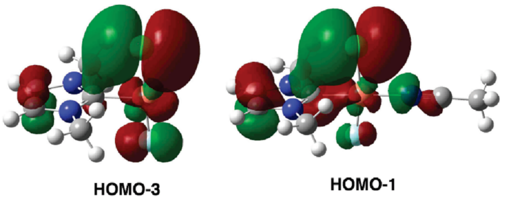

Figure 2. HOMO−3 of **5** and HOMO−1 of **7**.

In summary, we have demonstrated that $C_{carbene}$−halogen reductive eliminations readily occur from NHC copper halides at RT under oxidative conditions. These reactions provide new examples for the well-known oxidation-induced reductive eliminations. DFT calculations on a simplified model system suggest that the involvement of NHC Cu(III) halides is essential for these reactions and the reductive eliminations might be facilitated by the interaction between $C_{carbene}$ and the halogen lone pair. Given the ubiquity of NHC metal halide complexes, the facile $C_{carbene}$−X reductive elimination reported here warrants consideration as a potential decomposition pathway in reactions involving NHC-supported high-valent metal complexes, especially with late transition metals under oxidative conditions.

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Supporting Information Available: Detailed experimental and calculational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] η^2-Arene-coordination intermediates have been reported in a related computational study for oxidative addition of Ph−Br to various Cu^I species. Zhang, S.-L.; Liu, L.; Fu, Y.; Guo, Q.-X. *Organometallics* **2007**, *26*, 4546–4554. By contrast, no analogous intermediate was located computationally for our system.

[18] These include two isomers of **7**, one five-coordinate Cu(III) species, and a complex with **6** coordinated to **5**.[19]

[19] See Supporting Information.

[20] (a) Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2004**, 1612–1613. (b) Larsen, A. O.; Leu, W.; Oberhuber, C. N.; Campbell, J. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 11130–11131.

[21] Previous work indicated that $AgSbF_6$ (1.35 V vs NHE)[8] can oxidize Cu^{II}-Salen to $[Cu^{III}\text{-Salen}](SbF_6)$ in CH_2Cl_2.[7g] Therefore, the oxidation of $\mathbf{1_{Cl}}$ to Cu(III) by $Cu^{II}(CF_3SO_3)_2$ (1.30 V vs NHE)[9] seems possible.

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