

Direct Observation of Reduction of Cu(II) to Cu(I) by Terminal Alkynes

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S Supporting Information

ABSTRACT: X-ray absorption spectroscopy and *in situ* electron paramagnetic resonance evidence were provided for the reduction of Cu(II) to Cu(I) species by alkynes in the presence of tetramethylethylenediamine (TMEDA), in which TMEDA plays dual roles as both ligand and base. The structures of the starting Cu(II) species and the obtained Cu(I) species were determined as (TMEDA)-CuCl₂ and [(TMEDA)CuCl]₂ dimer, respectively.

Among various transition metal catalysts, copper is considered as the most prominent and promising one because of its versatility, low cost, and low toxicity.¹ For example, Cu-mediated Glaser coupling reaction, which was first reported by Glaser in 1869, has been widely used in the synthesis of conjugated diynes.² Cu salts are also widely used in Sonogashira reaction, Huisgen cycloaddition, and Cadiot–Chodkiewicz coupling, etc.³ However, there have been surprisingly few mechanistic investigations toward Cu/alkyne chemistry.⁴ Various hypotheses regarding the oxidation state and structure of the Cu intermediates are usually proposed by different authors.⁵ Most studies have focused on the examination of different substrates, catalyst precursors, and additives. The fact that few *in situ* spectroscopic studies have been performed has led to controversial assignment of the oxidation state and structures of the intermediates.

Nuclear magnetic resonance (NMR), *in situ* infrared (IR) spectroscopy, and electrochemical methods have been widely used and provided meaningful structural information on reaction intermediates in various reactions.⁶ However, all of the three techniques have difficulties in studying the redox interaction between Cu catalyst and alkynes in solution. X-ray absorption spectroscopy (XAS) is a unique and powerful technique for probing local structures without requirement of long-range order. The oxidation state can be obtained from the X-ray absorption near-edge structure (XANES); while the information of coordination sphere can be extracted from the extended X-ray absorption fine structure (EXAFS). In addition, hard X-ray can be used for studying intermediates under reaction conditions. These advantages make XAS an excellent tool for *in situ* study of the structures of reaction intermediates.⁷ Herein, we communicate the observation of the reduction of Cu(II) to Cu(I) by terminal alkynes in the extensively used

Cu/alkyne/TMEDA (tetramethylethylenediamine) system utilizing *in situ* XAS and electron paramagnetic resonance (EPR) spectroscopy.

When XAS measurement was carried out to investigate the interaction between CuCl₂, TMEDA, and phenylacetylene under inert atmosphere, only Cu(I) species was observed (Figure 1). This interesting observation prompted us to probe the oxidation states of Cu species under various conditions.

As shown in Figure 1a, the XANES spectrum of the DMF solution of CuCl₂ gave a pre-edge at 8977.2 eV. Addition of phenylacetylene shifted the pre-edge by 0.1 eV, while addition of TMEDA shifted the pre-edge by 0.7 eV. However, all the pre-edge energies are in the typical range of Cu(II), which suggests that addition of TMEDA or phenylacetylene to the

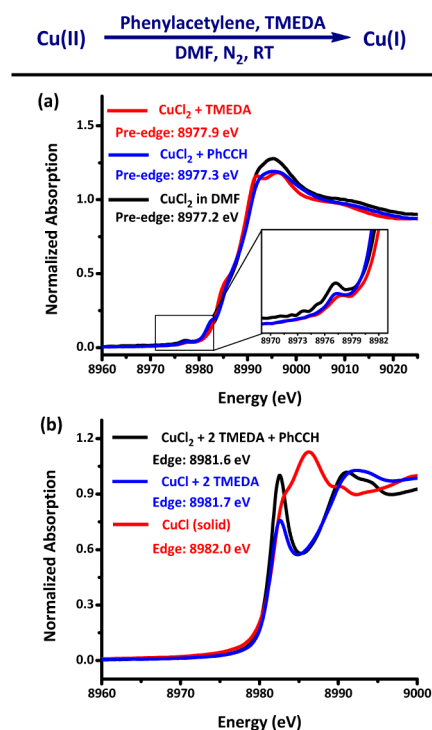


Figure 1. XANES spectra of various Cu species.

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DMF solution of CuCl_2 did not change the oxidation state of Cu.⁹ However, mixing phenylacetylene and TMEDA with CuCl_2 in DMF led to the formation of a new Cu species with the edge energy of 8981.6 eV, which is very close to those of CuCl (8982.0 eV) and DMF solution of CuCl/TMEDA (8981.7 eV) confirming the formation of Cu(I) (Figure 1b).¹⁰

EXAFS spectra were also taken to probe the local structures of the Cu species under different conditions. After addition of TMEDA to the DMF solution of CuCl_2 , a shorter average bond distance was observed compared with CuCl_2 (solid), which suggests the coordination of TMEDA to Cu(II) (Figure 2a). Fitting of the R-space EXAFS spectrum revealed that the obtained Cu(II) species had two N coordination atoms and two Cl coordination atoms in the first coordination sphere. The

Cu–N and Cu–Cl bond distances were determined as 2.00 and 2.29 Å, respectively (Table 1). The structure of the obtained

Table 1. Summary of XANES and EXAFS Results^a

	edge energy (eV)	OS	coordination atom	CN	<i>d</i> (Å)
$\text{CuCl}_2 + 2$ TMEDA in DMF ^b	8977.9 (pre-edge)	+2	N	1.9	2.00
			Cl	2.3	2.29
$\text{CuCl}_2 + 2$ TMEDA + PhCCH in DMF ^c	8981.6 (edge)	+1	N	2.4	2.01
			Cl	2.1	2.10

^aOS: oxidation state; CN: coordination number; *d*: bond distance. ^bFT range: 2.85–10.34 Å⁻¹; fitting range: 1.06–2.16 Å. ^cFT range: 3.37–10.66 Å⁻¹; fitting range: 1.33–2.09 Å.

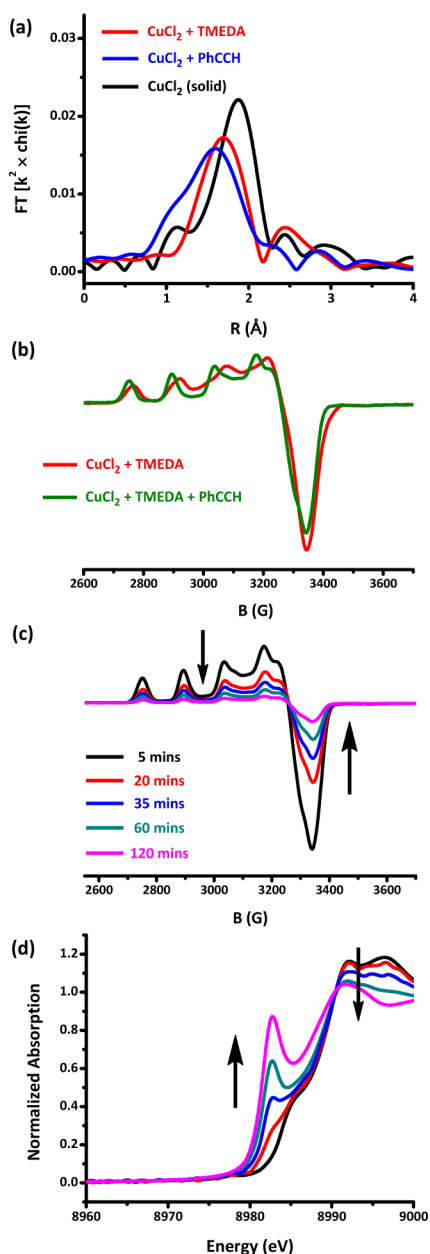


Figure 2. EXAFS and EPR spectra of various Cu species. (a) k^2 -weighted magnitude of the fourier transform (FT) of Cu(II) species. (b) EPR spectra measured at 160 K. (c) EPR spectra of the reduction process. (d) XANES spectra of the reduction process.⁸

Cu(II) species was thus assigned as $(\text{TMEDA})\text{CuCl}_2$. Upon addition of phenylacetylene to the DMF solution of CuCl_2 , the bond distance became even shorter (Figure 2a). In addition, an increased structural disorder was evidenced by the broadened R-space spectrum, which might be caused by the coordination of phenylacetylene to the Cu center. Low temperature EPR results suggested the coordination of phenylacetylene to Cu(II) even in the presence of TMEDA (Figure 2b). *In situ* EPR and XAS experiments were then carried out to monitor the reduction process. As shown in Figure 2c,d, decrease of the EPR signal was observed as the reaction proceeded. Consumption of Cu(II) and accumulation of Cu(I) were also confirmed by XANES spectra.

As shown in Figure S1 (Supporting Information), the EXAFS spectrum of the obtained Cu(I) species is very similar to that of $[(\text{Phen})\text{Cu}(\text{PPh}_3)_2]^+$ (Phen = phenanthroline, PPh_3 = triphenylphosphine), but showed a shorter average bond distance. Single crystal structure analysis of $[(\text{Phen})\text{Cu}(\text{PPh}_3)_2]^+$ has shown that Cu(I) has two N coordination atoms at an average distance of 2.08 Å and two P coordination atoms at an average distance of 2.26 Å.¹¹ These results suggest that the obtained Cu(I) species probably has two light coordination atoms (C/N/O) and two heavy ones (Cl). Further fitting of the EXAFS spectrum suggested that the Cu(I) metal center was surrounded by two N atoms at a distance of 2.01 Å and two Cl atoms at a distance of 2.10 Å. So the structure of the Cu(I) product was assigned as a dimer complex, $[(\text{TMEDA})\text{CuCl}]_2$.

Besides $[(\text{TMEDA})\text{CuCl}]_2$, the homocoupling product of phenylacetylene was also observed, and both aromatic and aliphatic alkynes could undergo the homocoupling smoothly. Various functional groups were well tolerated including ester, alkoxy, bromo, and hydroxyl groups (see Supporting Information for details). The role of TMEDA in the reaction was also investigated. In the presence of 2 equiv of TMEDA, the homocoupling product of phenylacetylene was obtained in excellent yield, while in the presence of 1 equiv of TMEDA, no homocoupling product was observed. When $(i\text{-Pr})_2\text{NH}$ or K_2CO_3 was used in combination with TMEDA, the reaction also took place smoothly (see Supporting Information for details). These results suggested that TMEDA could play dual roles as both ligand and base in this reaction. Further investigations suggested that O and P ligands do not promote the reaction, which highlighted the key role of TMEDA (see Supporting Information).

On the basis of the *in situ* EPR and XAS investigations, the reduction mechanism was proposed as shown in Figure 3.

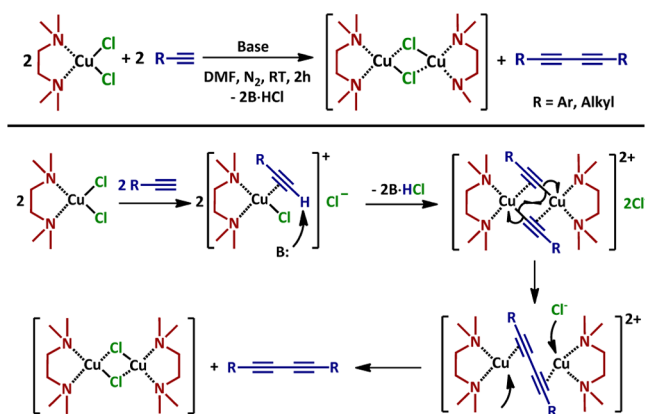


Figure 3. Proposed mechanism.

Coordination of C–C triple bonds to Cu(II) leads to activation of the C–H bond and thus facilitates the deprotonation in the presence of base and formation of Cu–C bonds. The subsequent innersphere electron transfer breaks the Cu–C bonds and forms the C–C bond. The attack of Cl[−] to Cu(I) releases the homocoupling product and forms [(TMEDA)CuCl]₂.

In conclusion, X-ray absorption spectroscopy and *in situ* electron paramagnetic resonance provided evidence for the reduction of Cu(II) to Cu(I) species by terminal alkynes in the presence of TMEDA. A wide range of aromatic and aliphatic terminal alkynes could be coupled in the presence of Cu(II) and TMEDA, where TMEDA plays dual roles as both ligand and base. The structures of the starting Cu(II) species and the obtained Cu(I) species were determined by EXAFS spectroscopy as (TMEDA)CuCl₂ and [(TMEDA)CuCl]₂ dimer complex, respectively. Given the extensive application of Cu/TMEDA/alkyne system, the oxidation state and structural information provided in the present work could shed light on Cu/acetylene chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The experimental procedure; XANES/EXAFS fitting results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (8) FT range of the EXAFS spectra are listed below. CuCl₂ + TMEDA: 2.85–10.34 Å^{−1}; CuCl₂ + PhCCH: 2.80–10.98 Å^{−1}; CuCl₂ (solid): 2.87–11.93 Å^{−1}.
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