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Cu_2O: A Versatile Reagent for Base-Free Direct Synthesis of NHC-Copper Complexes and Decoration of 3D-MOF with Coordinatively Unsaturated NHC-Copper Species

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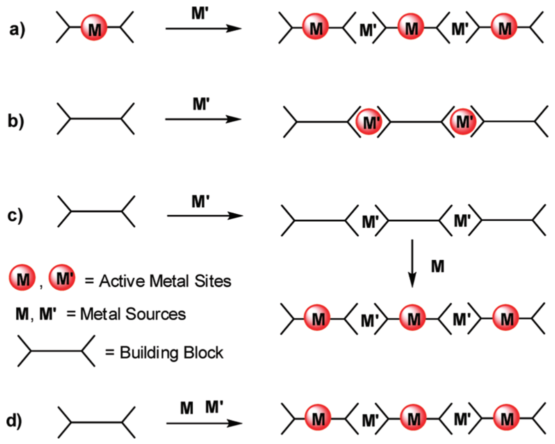
Summary: A new and direct synthetic route for N-heterocyclic carbene (NHC)-copper complexes was disclosed by heating imidazolium halides with Cu_2O. The related synthetic procedure was quite simple and the product easily separable from the reaction mixture by simple filtration. Ultimately, this reaction was successfully applied to decorate three-dimensional (3D)-metal organic frameworks (MOFs) with coordinatively unsaturated NHC-copper species.

Incorporation of unsaturated metal sites into supramolecular networks is an important issue because the resultant metal-decorated networks can be applied as specific catalysts[1] or gas-storage materials.[2] Typically, in the literature, three approaches have been applied to achieve this goal.[3−5] As illustrated in Scheme 1, the first method involves preparation of unsaturated metal-containing building blocks with additional free coordination modes and construction of the supramolecular networks through a self-assembly process[3] (Scheme 1a). In this case, significant time is required for synthesis of the delicately designed building blocks, and the prepared building blocks must be stable in the self-assembly process. In the second method, during assembly of the supramolecular networks between the conventional building blocks and metal connectors, active metal sites are generated in the nodes of the supramolecular networks[4] (Scheme 1b). However, obtainment of such active metal sites within the supramolecular networks is seldom predictable. In the third method, after obtaining the porous networks without active metal sites, the supramolecular networks are post-treated with target metal sources.[5] In this case, homogeneous distribution of the active metal sites requires clarification, as the unidentified metal solids can be deposited either inside or on the surface of the supramolecular networks. In addition, the supramolecular networks should be stable enough during the reaction with metal sources (Scheme 1c). An alternative and ideal route would be *in situ* decoration of supramolecular networks with metal sites during the construction process of networks, as displayed in Scheme 1d. Usually, more than two kinds of metal sources have been used to achieve the active metal site-decorated networks. However, known examples of this approach are quite rare.[6]

Scheme 1. Synthetic Approach for Active Metal Site-Containing MOFs: (a) Assembly of the Active Metal Site-Containing Building Blocks; (b) Formation of the Active Metal Sites at Nodes in the Self-Assembly Process; (c) Post-treatment of MOF with Metal Reagents; (d) *in Situ* Formation of Active Metal Sites during Construction of MOFs Using Two-Metal Sources



Recently, we reported the formation of a 2D-supramolecular network via assembly of 1,3-bis(4-carboxy-2,6-diisopropylphenyl)imidazolium chloride, **L1**, with copper(II) nitrate.[7] During the assembly process, copper ions formed a paddle wheel structure and functioned as the connector. In addition, copper(II) ions were converted to the copper(I) species, while unexpectedly, N-heterocyclic carbene (NHC)-copper complexes formed within the network. The resultant basic skeleton of the network was

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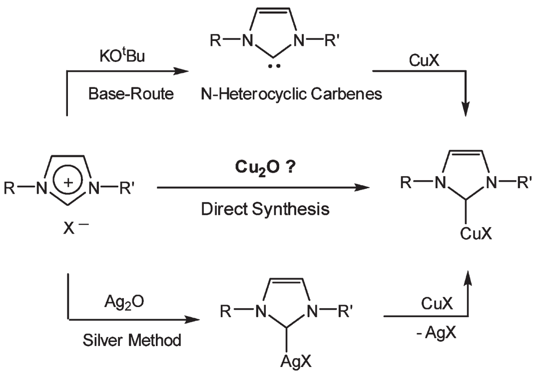
strictly limited to a 2D-network due to the unique chemical properties of the copper(II) nitrate as connector. Hence, to achieve more diverse structures and a more generalized synthetic route for active metal site-containing networks, an improved and systematic protocol was needed. To this end, it was rationalized that two kinds of independent metal sources were compulsory: the first to induce construction of the supramolecular networks by connecting the building blocks, and the second to form the active metal sites by reaction with the building blocks (Scheme 1d).

To realize this approach, new copper reagents having reasonable reactivity toward imidazolium salts were requisite to form the NHC-copper complex. Usually, in the literature, NHC-copper complexes are prepared via two synthetic routes:[8,9] (i) treatment of imidazolium salts with an appropriate base and sequential reaction with copper sources to yield the NHC-copper complexes;[8] (ii) reaction of silver oxide (Ag_2O) with imidazolium salts to form the NHC-silver complex, whereby silver moieties are replaced with copper sources to form the NHC-copper complexes[9] (Scheme 2).

In contrast to the literature methods, during the screening of the reactivity of diverse copper reagents toward imidazolium salts in the absence of base, we found that Cu_2O reacted directly with the imidazolium salts to form the NHC-copper complex.[10] As far as we are aware, this discovery was not reported in the literature and can be applied as a new and more general synthetic route for copper-NHC complexes. Table 1 summarizes the reactivity of Cu_2O toward several imidazolium salts to form the corresponding NHC-copper complexes.

Cu_2O showed very similar chemical properties to Ag_2O toward the imidazolium salts. It has been well established that Ag_2O possess good reactivity toward imidazolium halides in the absence of base to form NHC-silver halide complexes.[11] As shown in entries 1−5 in Table 1, when the counterions were halides, the NHC-copper complexes were successfully formed in good yields, indicating that the copper−halide bond formation is an important driving force in this reaction. It is noteworthy that the same behavior was observed for Ag_2O.[11] Powdery Cu_2O is not soluble in conventional organic solvents; thus, isolation of the product from the reaction mixture was quite straightforward: simple filtration to remove the unreacted Cu_2O and evaporation of the solvent to result in formation of microcrystalline solids. Recently, 1,3-bis(2,6-diisopropylphenyl)imidazoline-copper halides, denoted as **(IPr)CuX**, have shown unprecedented reactivity in diverse organic transformations.[12] Presently, 1,3-bis(2,6-diisopropylphenyl)imidazoline-copper halides are also commercially available.[13] Thus, we believe that Cu_2O routes can be effectively applied for mass production of these complexes. In addition, in this work, two new NHC-copper complexes (compounds **1** and **2**), in entries 6 and 7 in Table 1, were prepared and fully characterized.[10] Figure S1 in the Supporting Information shows the single-crystal X-ray structure of compound **2**.[14]

Scheme 2. Synthetic Routes for NHC-Copper Complexes



Next, we applied the reaction between imidazolium salts and Cu_2O for the decoration of a 3D-supramolecular network with coordinatively unsaturated NHC-copper moieties. Using Cu_2O as an NHC-Cu inducing reagent in the self-assembly process of **L1**, the systematic approach for decoration of supramolecular networks with NHC-copper species was developed; Scheme 3 summarizes the overall observations.

During screening of the diverse cationic connectors in the self-assembly of **L1**, a 3D-network was formed when cerium(III) nitrate was used as a connector.[15] As shown in Figure 1, two cerium ions coordinate to eight carboxylate groups in the building block. Four carboxylates were coordinated to one cerium ion, and the other four carboxylates functioned as bridging ligands by coordinating with the two cerium ions. The coordination pattern of the eight building blocks resulted in formation of four helical chains around two cerium ions.

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(10) Typical procedure for the synthesis of NHC-copper complexes: imidazolium salt (0.19 mmol) and Cu_2O (0.14 mmol) in 4 mL of dioxane were heated at 100 °C for 16 h. Then the reaction mixture was cooled to room temperature. The unreacted Cu_2O was removed by filtration, and the remaining solvent was evaporated to form precipitates. The solid was washed with water to remove any salts and then dried under vacuum. The spectroscopic characterization data of **(IPr)CuX** in entries 1−3 matched well with those in the literature (ref 12). Characterization data of compound **1**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 4H), 7.11 (s, 2H), 2.45 (septet, J = 6.9 Hz, 4H), 1.27 (d, J = 6.9 Hz, 12H), 1.20 (d, J = 6.9, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.6, 147.8, 134.2, 133.9, 123.4, 97.6, 28.8, 24.7, 23.8 ppm. Anal. Calcd for $C_{27}H_{34}N_2I_2CuCl$: C, 43.86; H, 4.63. Found: C, 43.91; H, 4.48. Characterization data of compound **2**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 4H), 7.19 (s, 2H), 4.00 (s, 6H), 2.58 (septet, J = 6.9 Hz, 4H), 1.33 (d, J = 6.6 Hz, 12H), 1.27 (d, J = 6.9, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2, 166.4, 146.2, 137.9, 132.3, 125.8, 123.3, 52.5, 29.0, 24.7, 23.8 ppm. Anal. Calcd for $C_{31}H_{40}O_4N_2CuCl$: C, 61.68; H, 6.68. Found: C, 61.70; H, 6.60.

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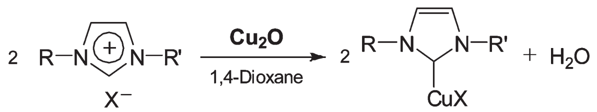
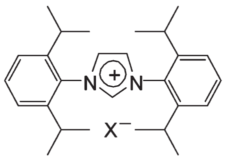
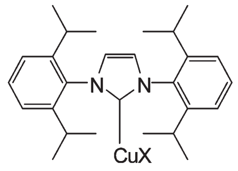
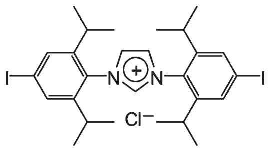
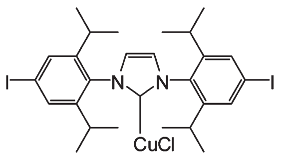
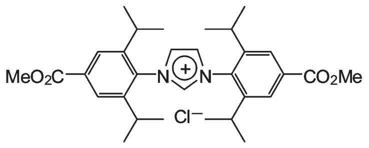
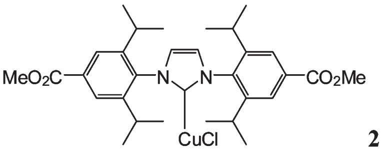
(13) Catalogue of Aldrich Chemical Co. and STREM Chemicals Inc.

(14) The crystals of compound **1** have a plate-like morphology and were not suitable for single-crystal X-ray analysis. Crystallographic data for compound **2**: M_r = 603.64, monoclinic, space group $C2/c$, a = 15.847(4) Å, b = 9.503(2) Å, c = 21.959(4) Å, β = 106.577(6)°, V = 3170(1) Å^3, Z = 4, ρ = 1.265 g cm^{-3}, completeness 96.3%, 13 113 collected reflections, 3818 crystallographically independent reflections (R_{int} = 0.0560), R1 = 0.0557 ($I > 2\sigma(I)$), wR2 = 0.1509 (all data).

(15) **L1** (0.113 g, 0.220 mmol) and cerium nitrate (0.115 g, 0.265 mmol) were dissolved in DMF (4 mL), and the reaction mixture was heated at 110 °C for 3 days. The colorless crystal was formed on the wall of the vial. Crystal data for (**L1**-Cl)$_2$CeNO$_3$: M_r = 1153.31, monoclinic, space group $P2_1/c$, a = 14.868(4) Å, b = 25.174(6) Å, c = 22.523(6) Å, β = 98.458(4)°, V = 8338(4) Å^3, Z = 4, ρ = 0.919 g cm^{-3}, completeness 99.1%, 30 887 collected reflections, 8508 crystallographically independent reflections (R_{int} = 0.0794), R1 = 0.0500 ($I > 2\sigma(I)$), wR2 = 0.1446 (all data).

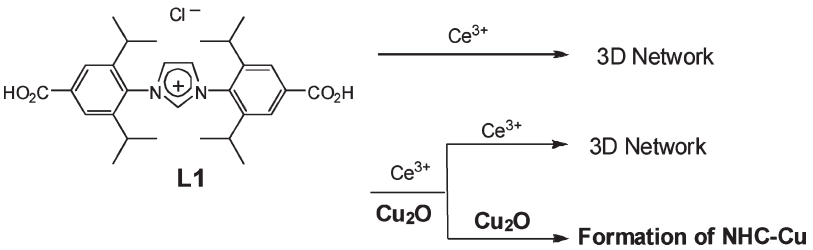
Table 1. Direct Synthesis of the NHC-Copper Complexes by Reaction of Imidazolium Salts with Cu_2O[a]



Entry	Imidazolium Salts	Product	Yield (%)[b]
1	X = Cl 		74
2	X = Br		92
3	X = I		88
4	X = BF_4		N.R.[c]
5	X = PF_6		N.R.
6		 1	84
7		 2	64

[a] Reaction conditions: 0.19 mmol of imidazolium salts, 0.75 equiv of Cu_2O, 5 mL of dioxane, 100 °C, 16 h. [b] Isolated yield. [c] No reaction.

Scheme 3. Systematic Approach for Decoration of the 3D-Supramolecular Network with NHC-Copper Moieties



A more detailed structure of the helical chains is displayed in Figure S2 in the Supporting Information. Interestingly, between the helical chains, big channels were formed, as shown in Figure 2. The imidazolium salts in the building blocks were intact during the self-assembly process. The two cerium ions, eight carboxylates, and four imidazolium salts have +6, −8, and +4 charges, respectively. For the charge balance, two nitrates having a −2 charge per two cerium ions existed in the channels to compensate for the positive charge of the basic network skeleton, which was supported by elemental analysis.

Finally, an attempt was made to construct 3D-supramolecular networks using **L1** and cerium nitrate in the presence of Cu_2O. The observed network was nearly identical to the structure formed without Cu_2O. However, NHC-copper species were formed inside the 3D supramolecular networks.[16] The incorporated copper species are displayed as blue balls in Figure 3. Although the channel structure is not simple due to the helical framework, the narrowest pore size was calculated as ca. 6.5 × 8.4 Å.

Interestingly, the NHC-copper moieties were formed for every two building blocks (not all building blocks) in each helical chain. This can be rationalized considering the charge balance. In the original 3D-network formed by assembly of Ce^{3+} with **L1**, the network skeleton has a positive charge, which was compensated for by incorporation of nitrates inside the channels. By formation of an NHC species for every two building blocks in the network, all positive charges of the skeleton were compensated; two cerium ions (+6); eight carboxylates (−8); two imidazolium ions (+2); two NHC-copper moieties (0). If NHC-copper moieties were formed at every building block, the network skeleton should have a negative total charge, which implies that there should be suitable countercations inside the network for compensation of the negative charge.

In conclusion, we found a new and direct synthetic route for the synthesis of NHC-copper halide complexes using

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(16) Cu_2O (11.7 mg, 0.081 mmol), **L1** (0.113 g, 0.220 mmol), and cerium nitrate (0.115 g, 0.265 mmol) were suspended in DMF (4 mL), and the reaction mixture was heated at 110 °C for 3 days. The pale brown, transparent crystals were formed on the wall of the vial. Crystal data for (**L1**-Cl)(**L1**-Cl-H)CeCuCl: M_r = 1189.28, monoclinic, space group $P2_1/c$, a = 15.483(2) Å, b = 24.962 2) Å, c = 22.355(2) Å, β = 99.575(6)°, V = 8519(1) Å^3, Z = 4, ρ = 0.927 g cm^{-3}, completeness 98.2%, 28 417 collected reflections, 5003 crystallographically independent reflections (R_{int} = 0.1078), R1 = 0.0666 ($I > 2\sigma(I)$), wR2 = 0.1892 (all data).

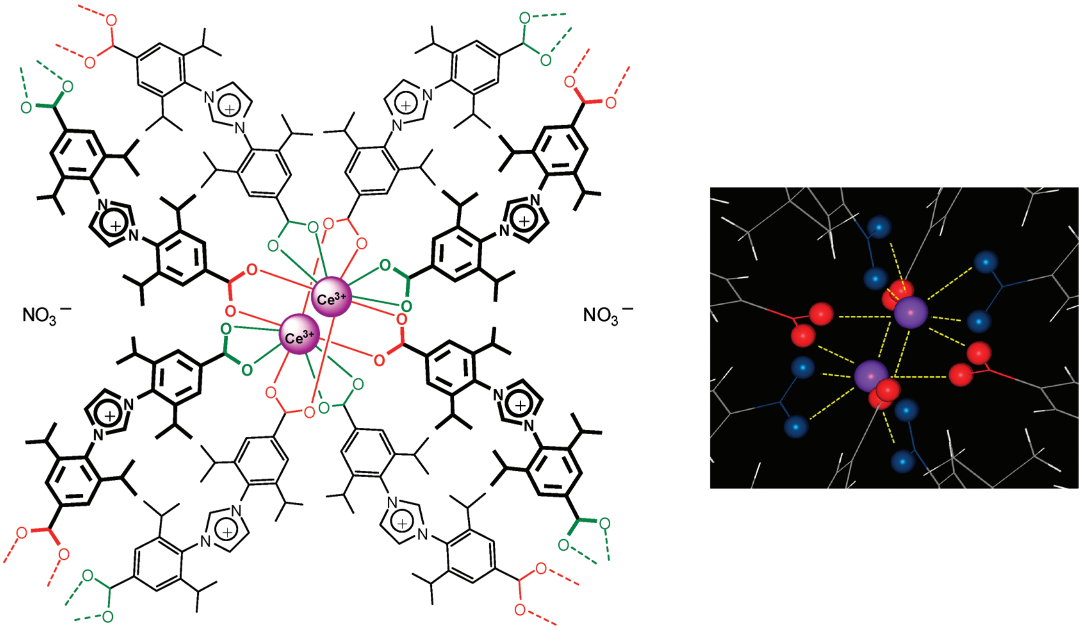

Figure 1. 3D-network structure formed by assembly of **L1** and Ce^{3+} (the bridging and nonbridging carboxylates were differentiated by red and green colors, respectively).

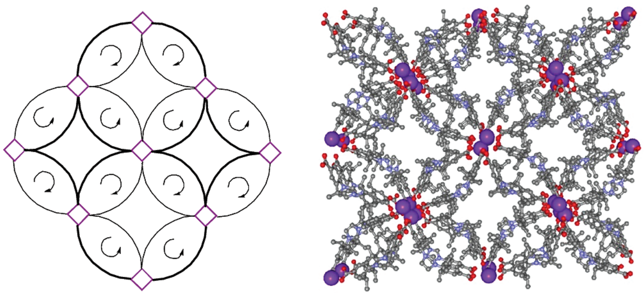

Figure 2. Cartoon and X-ray structure of the 3D-supramolecular network formed by self-assembly of **L1** with Ce^{3+}. Violet balls indicate cerium ions. Nitrate ions were omitted for clarity.

Cu_2O and successfully applied it to the incorporation of coordinatively unsaturated NHC-copper species inside the supramolecular structure. The self-assembly between cerium nitrates and imidazolium dicarboxylates resulted in the formation of a 3D porous supramolecular structure. Using two kinds of metal sources, cerium nitrates and Cu_2O, the porous structure was *in situ* decorated with NHC-copper species during the construction process of the network. We believe that the strategy in this study can be extended to the construction of more diverse supramolecular systems by designing appropriate building blocks containing imidazolium halides.

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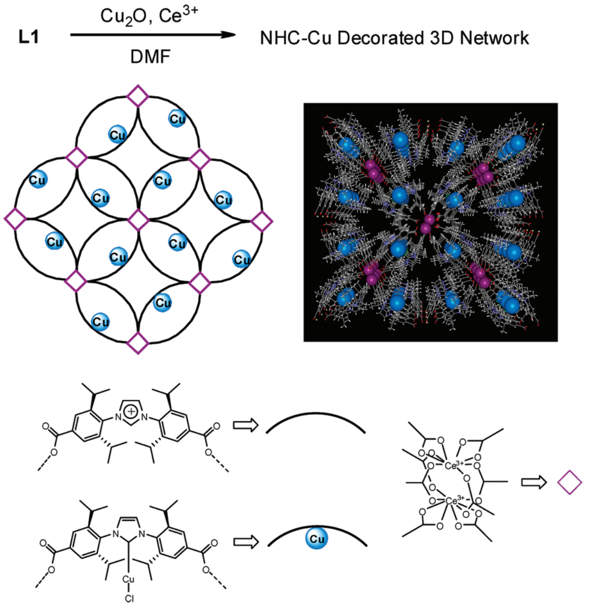

Figure 3. Cartoon and X-ray structures of the NHC-copper decorated 3D-network. Blue and violet balls indicate incorporated copper in building blocks and cerium connectors, respectively.

Supporting Information Available: X-ray structure of compound **2**, cartoon of helical chain and crystallographic data (CCDC 745333, 745334, and 745622). This material is available free of charge via the Internet at http://pubs.acs.org.