

Concomitant Formation of N-Heterocyclic Carbene–Copper Complexes within a Supramolecular Network in the Self-Assembly of Imidazolium Dicarboxylate with Metal Ions

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A new building block containing an imidazolium salt was synthesized and used for the construction of supramolecular networks with metal ions. We discovered the concomitant formation of the N-heterocyclic carbene–copper complex (CN = 2) in the self-assembly of imidazolium dicarboxylates and copper nitrates in *N,N*-dimethylformamide under heating. The proton in the 2 position of the imidazolium salt was abstracted, and Cu^{II} was reduced to Cu^I during the self-assembly process.

Self-assembly using the “predesigned building block” is a powerful tool for the development of new solid materials because it yields self-assembled architectures not only with regular, well-defined inner structures but also with tailored functionalities.¹ In this regard, diverse functional building blocks were designed.^{1,2} Recently, the introduction of active metal sites into supramolecular networks has been an important task because the resultant networks have shown excellent interactions with small molecules such as hydrogen.³

N-Heterocyclic carbene (NHC) has been extensively studied in the field of organometallics⁴ as a ligand comparable to the conventional phosphine ligands capable of coordinating with a wide range of transition metals. Additionally, diverse

studies for applications of NHC–metal complexes have been conducted.^{4a} In this paper, we report on the synthesis and self-assembly of imidazolium-based building blocks and the unexpected concomitant formation of the NHC–copper complex within the supramolecular networks. As far as the authors are aware, this is the first example of the introduction of an organometallic NHC–metal complex within a supramolecular network (Scheme 1).

Scheme 2 shows the synthetic pathway for the building block **L** used in this study. First, the iodide group was introduced at the para position of 2,6-diisopropyl-1-aniline. Then, the diimine was prepared by reaction with 0.60 equiv of glyoxal. Two iodide groups were then replaced with CO₂Me groups through palladium catalysis. The successive hydrolysis produced the new building block, **L**, in good isolated yield.⁵ Diverse transition-metal salts such as zinc, manganese, cobalt, and cadmium nitrates have been screened as connectors in a variety of solvent systems to obtain the self-assembled crystalline solid.

Among these trials, in the case of cadmium nitrate, we could obtain a single-crystalline solid that formed the 1D chain, as shown in Figure 1, where two carboxylates were coordinated to a single cadmium ion and two chlorides functioned as bridging ligands between the cadmium units.⁶ Through this, the empty space was formed between the two building blocks (**L**; Figure 1a). The distances between the two imidazole rings and two cadmium connectors were 10.2 and 17.6 Å, respectively. Two *N,N*-dimethylformamide (DMF) molecules were also trapped inside this space (Figure 1b). The central imidazolium salts were intact, which indicates that further treatment with a base and coordination of the metal are needed for the introduction of the NHC–metal moiety into the supramolecular networks.

The most impressive structure was obtained using copper nitrate as a connector in DMF under heating at 110 °C. The assembled supramolecular structure is displayed in Figure 2.⁶

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(6) See the Supporting Information for crystallographic information.

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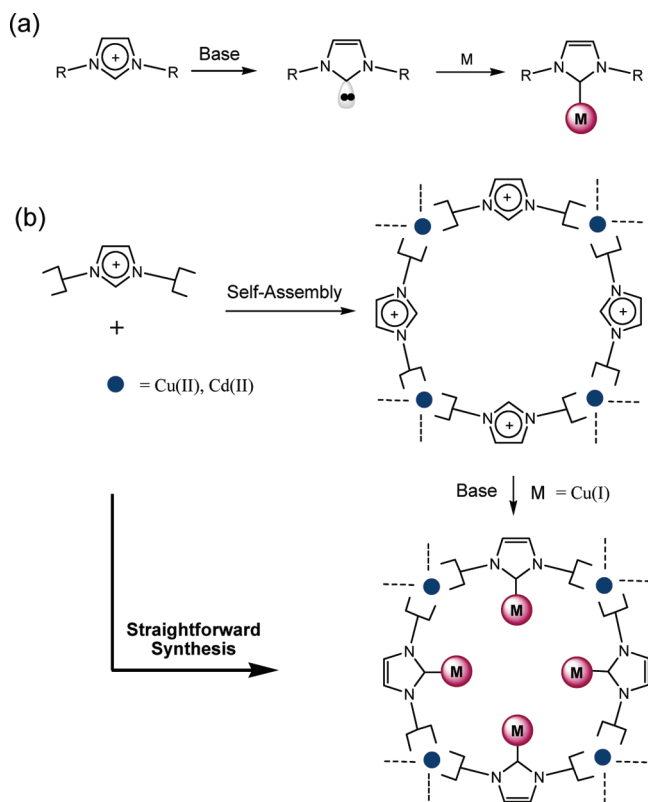
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(2) Selected examples: (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y.; Kim, K. *Nature* **2000**, *404*, 982. (b) Ma, L.; Lee, J. Y.; Li, J.; Lin, W. *Inorg. Chem.* **2008**, *47*, 3955. (c) Wu, C.-D.; Hu, A.; Lin, Z.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (d) Ma, L.; Mihalcić, D. J.; Lin, W. *J. Am. Chem. Soc.* **2009**, *131*, 4610.

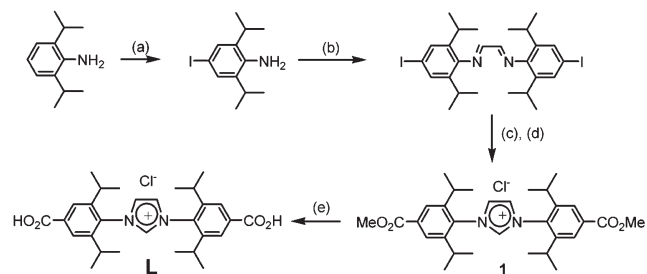
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Scheme 1. Conventional Route for the Formation of NHC–Metal Complexes from Imidazolium Salts (a) and Synthetic Pathways for Supramolecular Networks Bearing NHC–Metal Complexes (b)



Scheme 2. Preparation of Building Block **L**^a



^a (a) 1.1 equiv of I₂, diethyl ether, overnight, 2.0 equiv of K₂CO₃; (b) 0.60 equiv of glyoxal, catalyst formic acid, methanol, 36 h, room temperature; (c) 1.2 equiv of paraformaldehyde, 1.1 equiv of HCl (4.0 M aqueous solution), toluene, 110 °C, 2 h, room temperature, overnight; (d) 3 mol % Pd(OAc)₂, 12 mol % P(*o*-tolyl)₃, 3 atm of CO, MeOH, 2.0 equiv of NEt₃, 90 °C, 6 h; (e) excess (6 equiv) LiOH (0.10 M aqueous solution), methanol, room temperature, 4 h.

Interestingly, there were two kinds of copper species within the structure. The first was a copper paddlewheel structure that functioned as a connector of building block **L** (Figure 2a, b). The overall structure is the two-dimensional undulating grid structure, as shown in Figure 3a,b. The distances between the two imidazole rings on the long and short sides were 23.4 and 11.3 Å, respectively. The second copper species was copper(I) chloride coordinating to the NHC coordination mode in the center of building block **L**. It is quite interesting that the proton at the 2 position of the imidazolium salts in **L** was abstracted during the self-assembly process, concomitantly forming the organometallic NHC–copper units. A further interesting point is the reduction of the copper(II) species to a copper(I) species. We conducted a

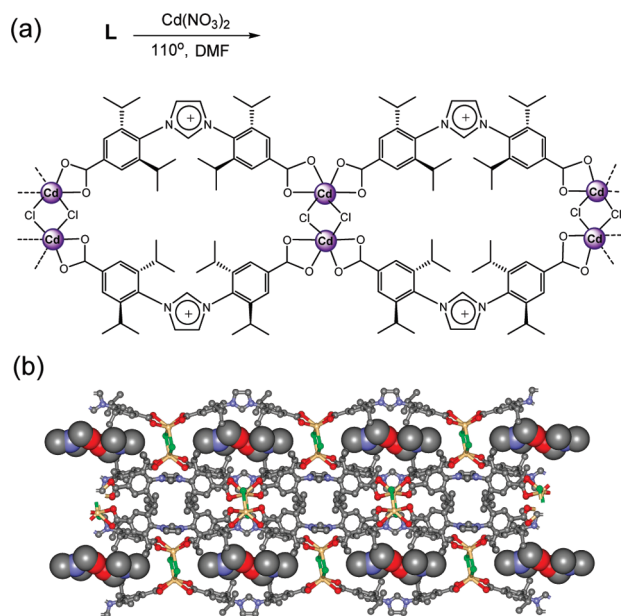


Figure 1. Self-assembled supramolecular structure between the building block **L** and cadmium(II) nitrate (a) in DMF and a single-crystalline X-ray structure (b) showing the trapping of two DMF molecules in the cavity.

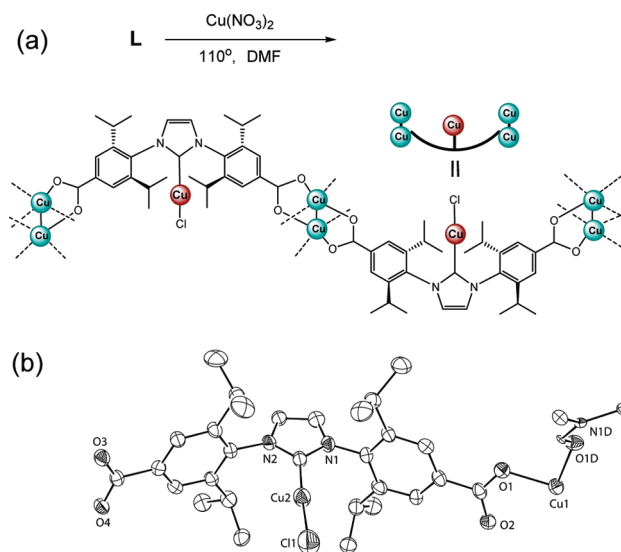


Figure 2. Self-assembled supramolecular structure between **L** and copper(II) nitrate in DMF: scheme of reaction (a); ORTEP drawing of the structural unit with 30% thermal ellipsoids (b).

simple model reaction between 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride and copper(II) nitrate (Scheme 3). As expected, NHC–copper(I) chloride (**2**) was formed in DMF under heating.⁷ Interestingly, the existence of halide as a counteranion was critical to obtaining the NHC–copper complexes.

It has been reported that reduction of the copper(II) species can be achieved via reaction of the amine under heating.⁸ To

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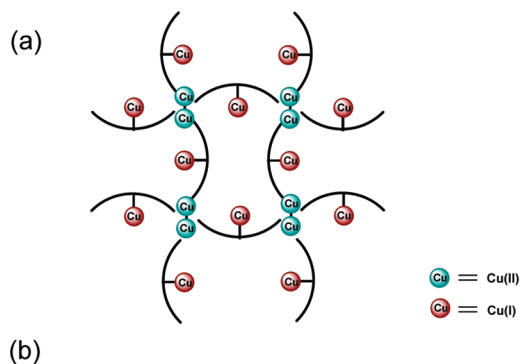


Figure 3. Cartoon of the supramolecular network structure formed by the assembly of **L** and copper(II) nitrate in DMF (a) and its X-ray structure (b).

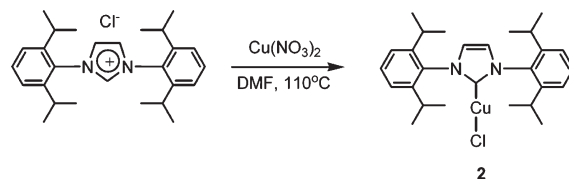
elucidate the chemical species playing the role of a reductant and base, more specific evidence is required. However, the above model reaction clearly verified that the reaction conditions (heating of the imidazolium chloride and copper nitrate in DMF) have a potential to generate the NHC–copper complex. It is common to form the copper paddlewheel by reaction of the carboxylate and copper ion.⁹ Thus, self-assembly of dicarboxylates having imidazolium chloride with copper nitrate in DMF is a good strategy to acquire a supramolecular structure containing the NHC–copper units.

Recently, new catalytic organic transformations based on NHC–metal complexes have been extensively studied.^{4,10}

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Scheme 3. Reaction of 1,3-Bis(2,6-diisopropylphenyl)imidazolium Chloride with Copper(II) Nitrate in DMF under Heating



Among them, copper catalysis using the NHC–copper complex has attracted continuous attention because cheaper copper catalysis is expected to replace palladium with the help of unprecedented electronic effects provided by NHC ligands.¹¹ In actuality, NHC–copper complexes have shown excellent catalytic activities in hydrosilylation, cycloaddition, enantioselective conjugated addition, and other such transformations.¹¹ On the other hand, to develop gas storage materials, the incorporation of an unsaturated metal site within the supramolecular network is important.³ However, because unsaturation usually implies an instability of the metal centers, their attainment can be capricious. To this point, the strong donor ability of the NHC ligands can be a good platform to incorporate and stabilize the unsaturated metal centers. Thus, we believe that the discovery of the concomitant formation of the NHC–copper complex (CN = 2) in the self-assembly of imidazolium dicarboxylates and copper nitrates in DMF under heating can be applied not only to form more diverse functional networks containing NHC–copper units by the design of new building blocks with diverse geometries but also to develop new heterogeneous catalysts and gas storage materials.

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Supporting Information Available: Experimental general procedures, detailed synthetic procedure of building block **L**, characterization data of new compounds, and crystallographic data (CCDC 719757 and 719758). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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