Synthesis and redox properties of Cu(I) complexes of tripodal tridentate ligands with tris(2-pyridyl)methane structure.

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Keywords: Cu(I) complex; Tripodal tridentate ligand; Disproportionation equilibrium; Cyclic voltammetry

Introduction. Reduction of CO_2 by using renewable energy sources is attracting attention as a technology that addresses both global warming and dependence on fossil fuels. Angamuthu et al. reported that a Cu(I) complex reduces CO_2 to $(COO)_2^{2-}$.[1] On the other hand, Donovan et al. reported that a Zn(II) complex with an uncoordinated lone pair can function as a catalyst for the electrolytic reduction of CO_2 to CO.[2] In this study, we synthesized two Cu(I) complexes with tris(2-pyridyl)methane structures that combine the features of these complexes and evaluated their redox properties (Fig.1).

Synthesis. The ligands were synthesized by the reaction of (6-bromo-2-pyridyl)bis(2-pyridyl)methoxymethane with an appropriate nucleophile in DMF under N_2. The complexes $[Cu(L_{SAr})]BF_4$ and $[Cu(L_{OMe})]BF_4$ were synthesized by the reaction of $[Cu(CH_3CN)_4]BF_4$ and the ligand in CH_3CN for 1 day (Fig.1).

Electrochemistry. The cyclic voltammetry measurements were performed under N_2 by using the complexes $[Cu(L_{SAr})]BF_4$ and $[Cu(L_{OMe})]BF_4$ (Fig.2). In both voltammograms, reduction waves were observed around -0.4 V, and redox waves around 0.15 V and 0.65 V. The reduction waves around -0.40 V were attributed to the reduction of $[Cu(L)_2]BF_4$. The redox waves around -0.15 V and 0.65 V were attributed to the redox of $[Cu(L)]BF_4$ and $[Cu(CH_3CN)_4]BF_4$, respectively.[3] These results mean that part of $[Cu(L)]BF_4$ is disproportionated to $[Cu(L)_2]BF_4$ and $[Cu(CH_3CN)_4]BF_4$ in solutions. In the ^1H NMR spectra, a single set of partly broadened signals was observed. This suggested that this disproportionation reaction was is reversible in the NMR time scale.

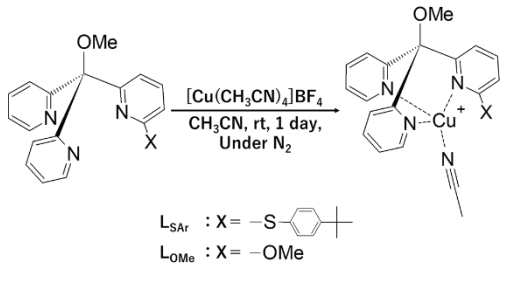

Figure 1. Synthetic scheme of Cu(I) complexes.

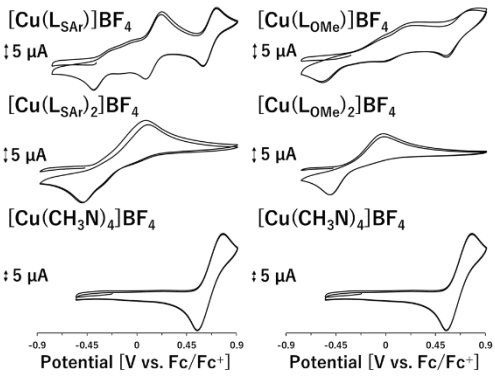

Figure 2. Voltammograms of Cu(I) complexes.

References. 1) R. Angamuthu, et al., *Science*, **2010**, *327*, 313-315. 2) E. S. Donovan, et al., *Chem. Commun.*, **2016**, *52*, 1685-1688. 3) R. T. Jonas, et al., *Inorg. Chem.*, **1998**, 37, 6615-6629.