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STEM

An Investigation of Multi-Electron Copper Reactions Using Redox Active Ligands

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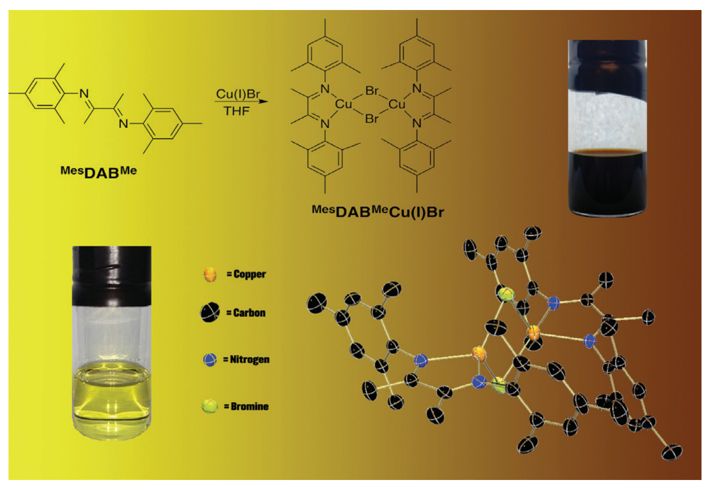
A catalyst is a substance that allows a chemical reaction to proceed at a faster rate than normally possible. Worldwide industry is dependent on catalysis to produce many products, such as plastics, hygiene products, and fertilizers. Precious metals like platinum and palladium are widely used in catalysis. These metals work very well due to their ability to accept and supply electrons (known as reduction/oxidation, or redox), but are rare, expensive, and often toxic. Copper is an inexpensive and nontoxic alternative that can be manipulated to exhibit electronic properties similar to those of precious metals. Copper already has a place in catalytic chemistry in the fields of medicine, synthesis, and materials science. Our lab binds copper to specialized ligands (a ligand is a molecule bound to the surface of a metal) to undergo redox chemistry similar to that of a precious metal. We believe that the large ligand $^{Mes}DAB^{Me}$ will serve to support stable copper hydrides, which are reactive in organometallic transformations but are relatively unstable.

$^{Mes}DAB^{Me}$ was easily prepared as yellow crystals and metallated by stirring with a single equivalent of CuBr, generating the $[(^{Mes}DAB^{Me})CuBr]_2$ dimer (1). The identity of species 1 was determined using proton nuclear magnetic resonance spectroscopy (^1H NMR), which measures how the protons of a molecule are affected while in a magnetic field and can be used to identify a compound. Structural features of (1) were clarified using X-ray crystallography, which showed tetrahedral copper centers and bridging bromide ligands. X-ray crystallography allowed us to model a 3-D structure of a molecule by measuring the diffractions of an X-ray beam. Bond lengths measured from this structure were consistent with similar reported copper (I) structures.

Treating $[(^{Mes}DAB^{Me})CuBr]_2$ with benzylpotassium generates a rare copper (I) benzyl species, $(^{Mes}DAB^{Me})CuCH_2Ph$. Both $[(^{Mes}DAB^{Me})CuBr]_2$ and $(^{Mes}DAB^{Me})CuCH_2Ph$ serve as important precursors to copper hydrides. These complexes will be tested with many different kinds of reagents so that we may attempt to install a hydride onto the copper center.

In the future, the complexes resulting from these experiments can potentially be used to replace existing industrial catalysts with a safer and less expensive alternative, or to develop new catalysts for future industrial use.

Research advisor Suzanne Bart writes: "Nathan has worked diligently to start a new area of research for our group involving the synthesis of low-valent copper species that are only stable in the absence of air and moisture. Results from his work will help generate very active copper hydrides that have applications in organic and inorganic chemistry."



The reaction of $^{Mes}DAB^{Me}$ with CuBr is identified with a color change from bright yellow to a burnt red. The structure of this product was elucidated with X-ray crystallography, which produced the ball-and-stick model shown.

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