

Pyridinol Based CNC Pincer Catalysts for Carbon Dioxide Reduction: The Big Impact of One Small Remote Group

The first examples of a CNC pincer ligands with a central pyridinol derived ring were recently reported. The differences in catalytic reactivity between CNC ligands with a central pyridine ring vs. a pyridinol derived ring are substantial and highly active and robust catalysts have been synthesized and studied. In these pincer ligands, the 4-substituent can be OMe, OH, or O⁻ and these latter two options allow for altered catalyst properties as a function of proton concentration. Catalytic studies have used ruthenium(II), nickel(II), and other transition metals. We have made metal complexes that can be protonated or deprotonated reversibly *in situ* to switch on or off the photocatalytic performance towards CO reduction. Furthermore, the methoxy group on the pyridine ring offers unique catalysis advantages not seen with the unsubstituted analog. Our best catalysts offer selective CO formation, >300 turnover cycles, and a 40 h lifetime. Highly active self-sensitized catalysts have recently been developed. Steric and electronic ligand effects are being studied with these catalysts by experimental and computational methods.