

Ligand Flexibility in Surface-Inspired Cluster Chemistry

Neil C. Tomson

University of Pennsylvania

<http://tomsongroup.chem.upenn.edu/>

Metallic surfaces perform many chemical transformations that hold promise for the future energy economy, including N₂ reduction, NH₃ oxidation, and alkane synthesis, but surfaces are difficult to tune, limiting chemists' ability to improve their efficiencies. Molecular cluster complexes inspired by surface chemistry have been studied for decades as a way to capitalize on the advantages of metallic surfaces while avoiding the scaling relationships that govern their activities. Progress in this area has been hampered, however, by the lack of ligand architectures able to provide an appropriate degree of geometric and electronic flexibility to the cluster core.

This talk will describe our use of macrocyclic, multi-nucleating ligands that have been designed to bind small metal clusters (2-4 metal atoms) in a way that mimics M–M bonding. Doing so allows for both facile electron redistribution within the cluster-ligand assembly and a high density of thermally accessible electronic states. These ligands have the added advantage of providing the geometric flexibility needed for stabilizing a range of surface-relevant species. Examples include diiron dinitrogen complexes that exist in a geometry reminiscent of the side-on binding of N₂ to the Mittasch catalyst, a diiron-supported *sp*-hybridized bridging nitride that converts into an *sp*³-hybridized bridging amide following hydrogen atom transfer, and the first (putative) dicobalt bridging nitride – a highly reactive species that mimics aspects of surface nitrides that develop during NH₃ oxidation in the Ostwald Process. Particular attention will be paid to the electronic structures of the electrophilic diiron and dicobalt bridging nitrides, which appear to exhibit sub-valent oxidation states.