Special Chemistry Seminar

Wednesday, January 8, 2020 at 10:30am
Bent Room 209 Havemeyer

Managing Redox Equivalents in Small Molecule Activation, Group Transfer, and Catalysis

Presented by Joshua Buss, University of Wisconsin

Small molecules are central to biological energy cycles and represent promising building blocks for commodity chemicals and solar fuels. The valorization of these feedstocks through selective transformations, however, is often challenging to control and mechanistically complex. The reduction of CO₂ and CO to C₂ products, is a topical example and is central to closing an anthropogenic carbon cycle. A series of Mo complexes, bearing a conserved terphenyl diphosphine ligand scaffold, shed light on important mechanistic aspects of both CO reductive catenation and CO₂ reduction. Low temperature synthesis maps out the elementary steps by which C₁ oxygenates are reduced and coupled at a single metal site; spectroscopy, kinetics, and isotopic labeling provide key insights into reaction design elements to control mechanistic branching points. Contrasting this reductive chemistry, oxidation of Mo⁴⁺≡E complexes (E = N, P, C) can provide a route to productive E–E coupling. This process, germane to NH₃ and H₂O oxidation, is dictated by the degree of spin-delocalization and radical character at the terminally bound atom. The same fundamental principles of controlling single electron transfers can be applied to catalyst speciation. Mechanistic probes highlight the importance of kinetically tuned reductants in maintaining catalyst activity in Cu-catalyzed site-selective radical-relay C–H functionalization. These examples showcase that careful management of redox equivalents in both stoichiometric and catalytic reactions controls the selective (de)construction of chemical bonds, leveraging fundamental mechanistic understanding to achieve challenging transformations.

Hosted by Gerard Parkin