CBC SEMINAR ANNOUNCEMENT

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Coordination Chemistry of 1st-row Transition Metal Pincer Complexes

Transition metal adduct formations with small molecules such as N₂, H₂, CO and CO₂ are drawing much attention due to their importance in developing synthetic catalysts for various industrial processes. The chemistry is based on pincer complexes with attention to the uniqueness of the coordination geometry (square-planar or pseudotetrahedral), which is crucial in allowing for particular reactivity toward small molecules. In our laboratory, a series of pincer complexes with low-valent 1st row transition metals are currently under investigation. Synthesis and characterization of four coordinate (PEP)M-L complexes (E = N or P and M = Co, Ni) will be described, where the L site is occupied by various ligands such as NHR₂, N₂, COx and COOR. Regarding the geometry and reactivity relationship, a (PPP)M scaffold reveals the interconversion between square planar and tetrahedral geometry, in which reversible alkoxy group transfer occurs between a phosphide moiety of a PPP ligand and a nickel ion via unanticipated metal-ligand cooperation. This unusual group transfer reaction is tightly coupled with metal’s local geometry and its 0/II redox couple. In fact, a central phosphide moiety of a PPP ligand acts as a single electron donor to form a P radical revealing the metal-ligand cooperativity involving a single electron exchange between Ni and P. By employing such cooperativity, nitrene group transfer was successfully accomplished to generate a dimeric nickel(0)-CO species along with mesitylamine and mesityl isocyanate. In contrast, a (PNP)M scaffold presents unusual reactivity occurring at the structurally rigidified nickel center. Unique open-shell reactivity of a T-shaped nickel(I) metalloradical supported by a rigidified acridane-based pincer ligand will be discussed. Having a sterically exposed half-filled dₓ₂₋ᵧ₂ orbital, this three-coordinate Ni¹ species reveals unique open-shell reactivity including the homolytic cleavage of various σ-bonds, such as H-H, N-N, and C-C.

Date: 17th December 2018 (Monday)
Time: 11:00am – 12:30pm
Venue: SPMS Research & Graduate Studies Office Conference Room
Host: Assistant Professor Soo Han Sen