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Coordination Chemistry of the Pincer Complexes of Co, Ni, Cu

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Transition metal adduct formations with small molecules such as dinitrogen, carbon monoxide and carbon dioxide are drawing much attention due to their importance in developing synthetic catalysts for various industrial chemical processes. This attention has been in part motivated by a desire to study species possessing uncommon metal-to-ligand multiple bond(s) such as metal-nitrene and carbene/carbyne via partial or complete group transfer. In our laboratory, a series of such species are currently under investigation to show their respective roles in small-molecule transformations that include the CO_x and NO_x (x = 1 – 3) transformations for modeling ACS/CODH active site chemistry and biological denitrification processes, respectively. Such fundamental study will contribute to develop synthetic catalytic systems for industrial applications such as hydroformylation, Fisher-Tropsch and Haber-Bosch processes. In this presentation, a particular study with low-valent 1st row mid to late transition metal complexes will be discussed. Synthesis and characterization of a four coordinate (PEP)M-L scaffold (M = Co, Ni or Cu; E = N, P or Si), where the L site is occupied by various ligands such as NHR₂, NO_x, N₂, CO_x and COOR will be described. Regarding the geometry and reactivity relationship, tetrahedral and square planar metal complexes were studied. In fact, unanticipated metal-ligand cooperation employing a (PPP)M scaffold was investigated from our laboratory, in which reversible methoxy group transfer occurs between a phosphide moiety of a PEP ligand and a nickel ion. This unusual group transfer reaction is tightly coupled with metal's local geometry and its oxidation state. This chemistry can be further applied to the catalytic conversion of various small molecules utilizing several pincer systems.

本講演は、大学院総合化学院『化学研究先端講義／総合化学特別研究第二』の一部として認定されています。

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