Transition metal adduct formations with small molecules such as carbon dioxide and carbon monoxide are drawing much attention due to their importance in developing synthetic catalysts. This attention has been in part motivated by a desire to study species possessing uncommon metal-to-carbon multiple bond(s) such as carbene and carbyne via partial or complete group transfer. In this presentation, a particular study of such species will be presented to show their respective roles in small-molecule transformations that include, carbon dioxide transformation for modeling ACS/CODH active site chemistry and carbon monoxide conversion as a key step for Fisher-Tropsch synthesis. To test the validity of hypotheses concerning nickel’s crucial roles in the reversible C-O and C-C bond formation at a single metal center, synthetic model systems are needed. Such systems can test the chemical compatibility of nickel with various proposed intermediates, and their reactivity patterns. In this presentation, a particular study with low-valent metal complexes will be presented to show their respective roles in small-molecule transformations. Synthesis and characterization of a four coordinate (PEP)M-L scaffold (M = Ni, Co or Cu; E = N, P or Si) where the L site is occupied by ligands such as N2, CO, CO2 and COOR will be described. The systems with a (PNP)Ni scaffold accommodating terminally bound CO in the three formal oxidation states (nickel(0), +1, and +2) and their reactivity toward electrophiles will be illustrated. A series of CO2 adducts and analogous species have been generated revealing unique binding character to a nickel center. Regarding the geometry and reactivity relationship, tetrahedral and square planar nickel species will be discussed. In fact, unanticipated metal-ligand cooperation employing a (PPP)Ni scaffold will be presented in which reversible methoxy group transfer occurs between a phosphide moiety of the ligand and the nickel ion.