Metal-Ligand Cooperation as Key in Formation of Dearomatized Ni(II)-H Pincer Complexes and in their Reactivity Towards CO and CO_2.

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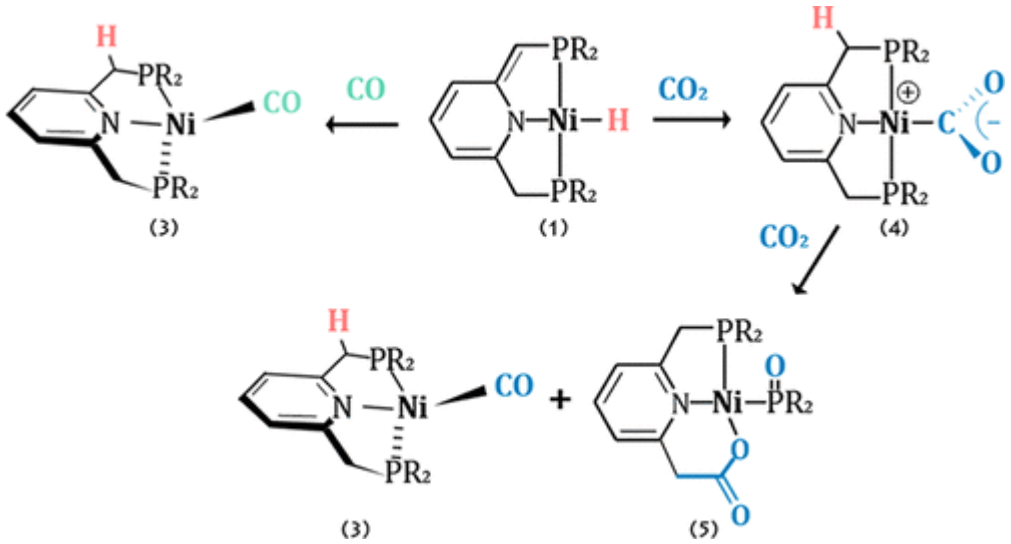
The unique synthesis and reactivity of [(^{R}PNP*)NiH] complexes, based on metal-ligand cooperation (MLC), is presented (^{R}PNP* = deprotonated PNP ligand, R = ^{i}Pr, ^{t}Bu). Unexpectedly, the dearomatized complexes were obtained by reduction of the dicationic complexes [(^{R}PNP)Ni(MeCN)])$(BF_4)_2$ with sodium amalgam, or by reaction of the free ligand with Ni(0)$(COD)_2$. The ^{i}Pr complex reacts with CO via MLC, to give a rare case of a distorted octahedral PNP-based pincer complex, the Ni(0) complex [(^{iPr}PNP)Ni(CO)]. The dearomatized complexes also react with CO_2 via MLC to form a rare example of η^1-binding of CO_2 to nickel, [(^{R}PNP)Ni-η^1-CO_2]. The ^{i}Pr analog of this complex is capable of CO_2 cleavage process involving C-O and C-P cleavage and C-C bond formation leading to the Ni-CO complex and to the new complex [($P^{i}Pr_2NC_2O_2$)Ni($P(O)^{i}Pr_2$)]..



1. **Metal–Ligand Cooperation as Key in Formation of Dearomatized NiII–H Pincer Complexes and in Their Reactivity toward CO and CO2** Dror Oren, Yael Diskin-Posner, Liat Avram, Moran Feller, and David Milstein *Organometallics* **2018** *37* (14), 2217-2221 DOI: 10.1021/acs.organomet.8b00160