PCP Pincer Carbene Nickel and Palladium Complexes, and DMSO as Catalysts for Hydrosilylation and Reductive Functionalization of CO_2

A series of pincer carbene nickel and palladium complexes were synthesized and their catalytic activities were explored in the hydrosilylation of carbonyls and nitroarenes and reductive functionalization of CO_2. Two new pro-carbene PCP pincer ligands, 1,3-bis(diphenylphosphanylmethyl)imidazolidine (**L1**) and 1,3-bis(di-tert-butylphosphanylmethyl)imidazolidine (**L2**), were synthesized by a single-step process. Metalation with [$NiCl_2$(DME)] and $PdCl_2$(COD) in the presence of KPF_6 afforded pincer carbene complexes [(^{R}PCP)MCl]PF_6 (R = Ph and ^{t}Bu, M = Ni(II) and Pd(II)), respectively. Interestingly, an amine-nitrogen coordinated [(^{tBu}PNP)PdCl]PF_6 complex was also isolated. In addition, corresponding thiolate [(^{Ph}PCP)Ni(SPh)$_2$], [(^{R}PCP)M(SPh)]PF_6 and hydride [(^{tBu}PCP)M(H)]PF_6 complexes were synthesized and characterized. Out of nickel complexes, [(^{Ph}PCP)Ni(SPh)$_2$] showed better catalytic activity in the hydrosilylation of aldehydes, ketones and nitroarenes to give primary alcohols, secondary alcohols and aromatic amines, respectively, in high yields. Control experiments suggested the formation of the reactive nickel silyl intermediate in the hydrosilylation process.

Carbon dioxide (CO_2) is a renewable C1 source for the synthesis of valuable compounds. In this regard, [(^{tBu}PCP)M(SPh)]PF_6 complexes were found to be efficient catalysts for the hydroboration of CO_2 with 9-BBN to selectively give methoxyborane in excellent yields under mild conditions. The [(^{tBu}PCP)Ni(SPh)]PF_6 complex achieved a TON over 7000, while the [(^{tBu}PCP)Pd(SPh)]PF_6 reached a TON over 25000. A combined proposed mechanism based on control experiments indicates that the thiolate complexes form reactive adducts, exhibit two pathways for the methoxyborane formation, and hence, outperform the hydrides.

Organocatalysts are generally inexpensive, environmentally benign and more stable to air and moisture compared to organometallic catalysts. Dimethyl sulfoxide (DMSO), a readily available bulk chemical and a weak base, was investigated as a catalyst in the hydroboration of CO_2 with 9-BBN. When DMSO was used as a solvent, formoxyborane was selectively formed. Conversely, when DMSO was used in a catalytic amount, methoxyborane was selectively obtained under mild conditions. In both cases, DMSO first reacts with 9-BBN to form a reactive adduct in situ, through which these reduced products are formed. The adduct formation is supported by the structural characterization of the DMSO adduct of the formoxyborane, representing the first X-ray structure of its type. In addition, DMSO acts as a catalyst in the C-methylenation of indoles, affording bis(indolyl)methane derivatives in good yields. Mechanistic insights into both the CO_2 hydroboration and C-methylenation processes were proposed based on several control experiments.

The scope of the above catalytic process was further extended to the N-formylation and N-methylation of amines. Various primary and secondary amines were converted into their N-formylated and N-methylated derivatives in good to excellent yields. The N-methylation occurs at 25 °C. Interestingly, the reduction of CO_2 in the presence of carbazole and indole derivatives gave the N-hydroxymethylated products in good to excellent yields, representing the hitherto unknown direct conversion of CO_2 under mild conditions. Notably, novel C-N coupled products were isolated by the reaction of the N-hydroxymethylated products with indoles. For all these reactions, plausible mechanisms were proposed based on detailed control experiments.