

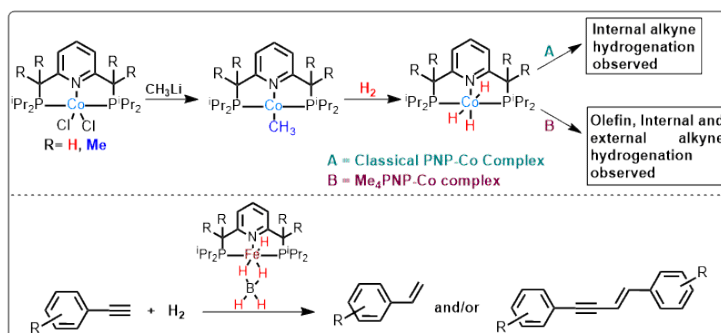
Bulky and non-bulky PNP complexes with earth abundant metals and their hydrogenation reactivity

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Precious transition metal complexes with PNP-pincer ligand backbone have exhibited substantial catalytic activity in a variety of hydrogenation and dehydrogenation reactions. Recent efforts are being made on the substitution of precious transition metals with cheaper, first row transition metals.¹

In this regard, cobalt and iron complexes with pincer ligands came up as potential solution for catalyzing the hydrogenation of alkenes, alkynes, ketones, aldehydes, and imines, etc. in presence of molecular hydrogen.² We



have previously developed a novel bulky PNP ligand, in which metal-ligand cooperation is disabled by methylation of the CH_2 arms, leading to unusual reactivity with Ni complexes.³ Herein, we report Co and Fe complexes with tetramethylated and classical PNP ligands and compare their reactivity in hydrogenation of alkenes and alkynes. We found that cobalt pincer complexes supported by the bulky tetramethylated PNP ligand $\text{Me}_4\text{PNP}^{\text{R}}$ ($\text{R} = ^i\text{Pr}$) are highly reactive towards H_2 and show catalytic activity in hydrogenation of alkenes and alkynes.⁴ The studies of the model systems show that in the case of Co(I) methyl complex as a precatalyst, the hydrogenation reactivity occurs via a sequence of two-electron oxidative addition and reductive elimination steps. This led to the development of catalytic protocol for alkene and alkyne hydrogenation. Finally, we will also discuss and compare the reactivity of Fe complexes with classical and tetramethylated PNP ligands in alkyne hydrogenation.

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