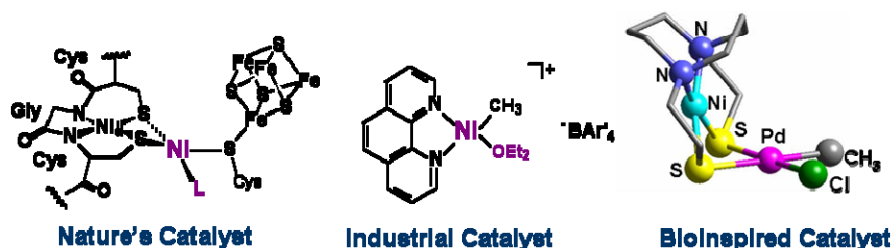


Bioinspired Metallodithiolate Ligands To facilitate C-C Coupling Reactions at Palladium

Marilyn V. Rampersad and Marcetta Y. Darensbourg

Department of Chemistry, Texas A&M University

Although enzyme active sites are surrounded by important secondary protein coordination sphere interactions, the structural features to the molecular active site frequently compare well with synthetic catalysts currently exploited by the chemical industry. The most recent and remarkable example is the acetyl-coA synthase which possesses a NiN_2S_2 unit as a “bidentate ligand” coordinated to a second nickel that mediates the assembly of a thioester in a C-C coupling reaction involving a CH_3^+ , CO and a $^-\text{SCoA}$ units.¹ This reaction observed in nature is consistent with classical organometallic chemistry utilizing diposphine or diimine ligands on nickel in CO/ CH_3 migratory insertion reactions (Scheme 1).^{2,3} Reactivity studies with heterobimetallic complexes consisting of a Pd(II) metal center and a synthetic metallodithiolate ligand facilitate CO addition followed by alkyl migration on a $d^8 \text{M}^{2+}$ similar to the acetyl-coA synthase enzyme.⁴ Preliminary studies on the mechanism of reactivity in comparison to traditional ligands⁴ will be presented. The significance in relation to the role of the Ni(CysGlyCys) ligand observed in acetyl-coA synthase will be discussed.



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