DOE/EPSCoR Progress Final Report

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Title: Synthetic and Thermodynamic Investigations of Ancillary Ligand Influence on Catalytic Organometallic Systems

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Progress

During the grant period we have been involved in synthesizing and experimentally determining solution enthalpy values associated with partially fluorinated ligands. This has lead to the publication of manuscripts dealing with synthetic, calorimetric and catalytic behavior of partially fluorinated ligands. The collaboration with Los Alamos researchers has lead to the publication of catalytic results in sc CO₂ which have proven very interesting. Furthermore, we have also examined ligands that behave as phosphine mimics. The N-heterocyclic carbenes have been explored as alternatives for tertiary phosphines and have resulted in the design and construction of efficient palladium and nickel system capable of performing C-C and C-N cross coupling reactions. The initial studies in this areas were made possible by exploratory work conducted under the DOE/EPSCoR grant. Relevant publications are listed below. Exploration of these area are ongoing.

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Enhanced Regioselectivity of Rhodium-Catalysed Alkene Hydroboration in Supercritical Carbon Dioxide. (Chem. Comm, 2000, 347-348)

In this contribution we have shown that catalysed alkene hydroboration proceeds in supercritical carbon dioxide with several rhodium phosphine complexes bearing tunable fluorinated ligands. The catalysis shows higher regioselectivity relative to tetrahydrofuran or perfluoromethylcyclohexane. We have demonstrated that catalysed alkene hydroboration can proceed in supercritical carbon dioxide without any difficulty from B-H reactivity with the solvent. Regiocontrol can be achieved using tunable ligands of the form R_2PR_f and R_2POR_f . Catalysis in this medium can complement fluororous phase approaches.

Synthetic and Thermochemical Studies of Fluorinated Tertiary Phosphine Ligands R_2PR_f [$R = Cy, Ph, ^iPr$; $R_f = CH_2CH_2(CF_2)_5CF_3$] in an Organoiron System. (Inorg. Chim. Acta, 2000, 300-302, 987-991)

The fluorinated phosphine ligands $[PR_2R_f]$ ($R = Cy$ (2); iPr , (3); Ph , (4); $R_f = CH_2CH_2(CF_2)_5CF_3$) react with $Fe(CO)_3(BDA)$ (1) ($BDA = (C_6H_5)CH=CHC(O)CH_3$, benzylideneacetone) to yield the corresponding $Fe(CO)_3(PR_2R_f)_2$ ($R = Cy$, (5) iPr , (6) Ph , (7)) complexes. Infrared studies on the carbonyl complexes and solution calorimetry studies of the reaction of 1 with 2, 3 and 4 have been performed to quantify the donor strength of this series of ligands. As previously observed with electron-poor/ π accepting N-pyrrolyl phosphines and fluoroalkoxy "pigtail" phosphorus ligands, two isomers were detected in PPh_2R_f adducts indicating that similar electronic effects are apparent in this systems. However in the $(PR_2R_f)_2Fe(CO)_3$ ($R = ^iPr, Cy$) systems only the axial/equatorial complexes are formed despite the steric bulk of the iPr and Cy substituents.

Catalytic Dehalogenation of Aryl Halides Mediated by a Palladium/Imidazolium Salt System. (Organometallics, 2001, 20, 3607-3613)

Dehalogenation of unreactive aryl chloride, species also present in contaminated ground samples in the form of polychlorinated aromatics such as PCB's can be converted to innocent arenas in the presence of these palladium/NHC complexes.

Preparation and Activity of Polymer-Supported Ruthenium Olefin Metathesis Catalysts. (*Organometallics*. 2002, 21, 671-679)

Olefin metathesis catalyst attached to solid supports have been examined. Issues of recyclability and catalytic activity were examined. These supported versions of the ruthenium-based systems show great promise.

How to Insulate a Reactive Site from a Perfluoroalkyl Group: Photoelectron Spectroscopy, Calorimetric and Computational Studies of Long-Range Electronic effects in Fluorous Phosphines $P((CH_2)_m(CF_2)_7CF_3)_3$. (*J. Am. Chem. Soc.* 2002, 124, 1516-1523)

The effects of ligand fluorination on metal-ligand binding in a catalytically relevant system were explored. The degree of insulation afforded by separating methylene units was quantified.

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