
Hydrogen Storage Materials with Binding Intermediate Between Physisorption and Chemisorption

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a future energy source and modeling the structure and function of hydrogenases. New iron complexes are being synthesized that may be useful catalysts here and for syntheses of deuterated organics such as acetone- d_6 via isotopic exchange. A key component is the design of new ligands L that can stabilize 16-electron cationic complexes and promote catalytic reactions. The role of oxidation state and ancillary ligands in the binding and oxidative addition of small molecules to 16e complexes such as $M(\text{CO})_3(\text{PR}_3)_2$ (M= group 6) is a key factor for study also. Complexes with new multifunctional cationic phosphonium ligands are also being studied and will be tested for promoting catalytic conversions of organic compounds.

Objectives

The main purpose of the work is to study chemical binding and splitting of sigma bonds (H-H, C-H, etc) on transition metal complexes to provide groundwork for the design of new systems and catalysts for hydrogen production and storage as well as chemical conversions of other energy-relevant molecules. The work involves synthesis and characterization of new electrophilic transition metal complexes and dihydrogen complexes, particularly for heterolytic splitting and formation of H_2 on transition metal centers. This is highly relevant to, for example, biomimetic production of hydrogen as a future energy source. The role of oxidation state and ancillary ligands in the binding and oxidative addition of small molecules to 16e complexes such as $M(\text{CO})_3(\text{PR}_3)_2$ (M= group 6) is a key factor for study.

Technical Barriers

There are few technical barriers for progress, and these lie in the area of optimizing metal-ligand design for catalytic applications and the stability of the organometallic complexes to for example air.

Abstract

The main purpose of the work is to study chemical binding and splitting of sigma -bonds (H-H, C-H, etc) on transition metal complexes to provide groundwork for the design of new systems and catalysts for hydrogen production and storage as well as chemical conversions of other energy-relevant molecules. The work involves synthesis and characterization of new electrophilic transition metal complexes and dihydrogen complexes, particularly for heterolytic splitting and formation of H_2 on transition metal centers. This is highly relevant to, for example, biomimetic production of hydrogen as

Progress Report

Approach

- Electrophilic cationic metal complexes, particularly first-row metals such as iron, are being designed to coordinate and activate sigma bonds, e.g. H-H in dihydrogen, towards heterolytic cleavage. A key component is the design of new ligands L that can stabilize 16e⁻ cationic complexes and promote catalytic reactions. Complexes with new multifunctional cationic phosphonium ligands are being studied and will be tested for promoting catalytic conversions of organic compounds.
- We are examining the synthesis and characterization of organometallic sigma-bond complexes in non-coordinating solvents, e.g. ionic liquid media, to determine if binding and activation of weak ligands such as molecular hydrogen to highly electrophilic metal centers is favorable.
- Experimental and theoretical comparisons of thermodynamic and kinetic aspects of oxidative addition of molecules such as RE-ER (E = S, Se, Te) to $M(\text{CO})_3(\text{PR}_3)_2$ complexes to examine the role of oxidation state and ancillary ligands in metal complex induced reactions (collaborative work with Hoff, Fujita, Muckerman).

Results

- Research in collaboration with Carl Hoff and others on thermodynamic and kinetic aspects of the binding and oxidative addition of molecules such as RE-ER (E = S, Se, Te) to $M(\text{CO})_3(\text{PR}_3)_2$ complexes has been carried out. Two papers have been published and several others are being submitted involving both experimental and theoretical

(Muckerman, Schleyer) investigations of agostic interactions and small molecule activation (e.g. ethylene, diazo compounds) on group 6 complexes. Crystallographic structure determinations have been performed at LANL by Brian Scott. Key findings include energetics and mechanisms of oxidative addition and C-H binding/activation important in catalytic processes.

- Research relating to conversion of organic compounds from biomass such as glycerol to alcohols for fuel use was carried out by Marcel Schlaf (Univ. of Guelph) on a 5-month sabbatical. Reactions of glycerol catalyzed by electrophilic metal and non-metal compounds such as acids gave a multitude of organic products, and progress was made towards understanding methods to improve the catalysis to give more selective conversions.
- Further synthesis, characterization, and investigation of phosphonium complexes and reactivity patterns were carried out: (1) demonstration of bifunctional activation of H₂ by a Rh phosphonium complex Rh-PN₂ to obtain a Rh-PHN₂ product, (2) activation of C-O and C-N bonds in allylic substrates including efficient catalyzed cyclodimerization of N-allylaniline, (3) combined experiment/theory investigation of analogies between phosphonium ligands and CO or NO ligands in novel nickel complexes, and (4) preparation of the first chelating bis(phosphonium) ligands that should have applications in electrophilic homogeneous catalysis.
- Several invited articles were published, including chapters on H₂ and sigma-bond complexes in the multi-volume compendium *Comprehensive Organometallic Chemistry III* and the book, *Handbook of Hydrogen Transfer*. A very visible Perspective article on reversible H₂ splitting was published in *Science* in November. Two invited review articles on activation of hydrogen, including enzymatic systems, have been submitted to other prestigious journals (*PNAS* and *Chem. Rev.*). [see *Publications section*]

Future Directions

- Electrophilic complexes for coordination and heterolytic activation of X-H sigma bonds will be synthesized. We plan to study such complexes experimentally and theoretically as catalysts for new types of *isodesmic reactions*, e.g. transfer of OH functionality between hydrocarbons: R[CH(OH)]_nR + nR'H -> nR'OH + R[CH₂]_nR. Organic compounds from biomass such as glycerol have too much hydroxyl functionality and perhaps OH can be transferred to methane, which has no functional groups, to form methanol. This may solve two

needs simultaneously: conversion of natural gas to liquid fuels and utilization of biomass to make polymers, fuels, etc.

- Protonation of homoleptic anionic polyhydrides such as [FeH₆]⁴⁻ with acids with low-coordinating anions will be examined at low temperature in order to determine if dihydrogen complexes will be stable. Formation of neutral species with labile H₂ such as FeH₂(H₂)_n are possible also, and vibrational spectroscopy will be an important tool for characterization, e.g. hydride versus H₂ ligands. Novel media and conditions such as ionic liquids and high pressures would be employed for these and related studies that could involve C-H bond activation. Prof. Donald Linn will be joining us this summer for a 2-month sabbatical doing research on this and also metal polyhydrides as nanoparticle precursors.
- Ligand binding and activation on the unsaturated group 6 complexes M(CO)₅(PR₃)₂ will continue to be studied experimentally and theoretically in collaboration with Hoff, Fujita, and Muckerman.
- We will continue to investigate heterolytic splitting of H₂ gas on cationic metal-H₂ complexes in relation to hydrogen production schemes and modeling the structure and function of hydrogenases. New iron complexes are being synthesized that may also be useful for syntheses of deuterated organics such as acetone-*d*₆ via isotopic exchange. Acidic metal-H₂ complexes including simple aquo complexes such as [M(H₂O)₆][BF₄]₂ (M= Fe, Ru) that could undergo ligand displacement and exchange with D₂ gas will be examined as catalysts here.
- Reactivity of metal phosphonium complexes, including that for the first chelating examples, novel bifunctional reactivity with hydrogen and hydrocarbons, and applications in electrophilic catalysis will be studied.

Publications

1. "The Extraordinary Dynamic Behavior and Reactivity of Dihydrogen and Hydride in the Coordination Sphere of Transition Metals," G.J. Kubas, in *Handbook of Hydrogen Transfer*, R.L. Schowen (Ed.), Vol 1: *Physical and Chemical Aspects of Hydrogen Transfer*, J.T. Hynes, J.T.; Limbach, H.H. (eds); Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006. p. 603. [invited book chapter]
2. "Breaking The H₂ Marriage And Reuniting the Couple," Kubas, G. J. *Science*, 2006. 314,1096-1097. [invited Perspectives article]
3. "Dihydrogen and Other Sigma Bond Complexes," G. J. Kubas, *Comprehensive Organometallic Chemistry III*, R.H. Crabtree and D.M.P. Mingos, eds., Vol. 1, pp. 671-698, Elsevier: Oxford, 2006. [invited book chapter]

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4. “Fundamentals of Hydrogen Binding to Transition Metals in Coordination and Organometallic Compounds,” G. J. Kubas, *Chem. Rev.*, accepted for October, 2007, publication date. [invited]
 5. “Metal-Dihydrogen Complexes. Prototypes for The Coordination Chemistry of Saturated Molecules,” G. J. Kubas, *Proc. Natl. Acad. Sci. (PNAS)*, in press. [invited Perspectives-style article]