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Electron-Transfer Activation of Thiophene

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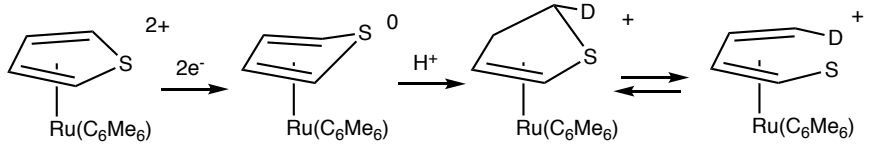
Abstract

The research supported by contract FG02-90ER14146 from the U.S. Department of Energy to Thomas B. Rauchfuss is summarized. Seven research themes are described. The work on thiophenes identified pathways for desulfurization that are initiated by electron transfer or hydrolysis. Using similar half-sandwich platforms, a large family of molecular cyanometallate cages were prepared. These cages exhibit host-guest behavior, with a notable affinity for cesium ions. A series of investigations made pioneering contributions to the understanding of the catalytic properties of the hydrogenase enzymes. Work on molecular metal sulfides focused on elucidating hydrogen activation pathways, relevant to the corresponding reactions that are invoked for metal sulfide heterogeneous catalysts. The theme of proton-activated catalysis was continued with the elucidation of the effects of Bronsted acids and oxidation on inducing H_2 activation by metal-amides. The proton-activation theme was shown to be a powerful vehicle for upgrading bio-derives substrates including sugars. The project concluded with emphasis on developing ligand platforms that facilitate the use of earth-abundant metals in homogeneous catalysis.

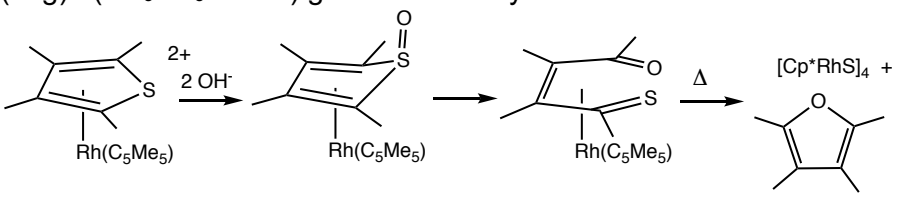
I. Electron Transfer and Hydrolytic Activation of Thiophenes

The most significant result of this research was the identification of metal-promoted pathways for cleaving C-S bonds in thiophenes. These results provide models for commercial hydrodesulfurization catalysis. Reduced thiophene complexes $(C_6Me_6)Ru(\eta^4\text{-}C_4R_4S)$ (R = Me or H) are readily protonated by the weak acid NH_4^+. Thus complexation to Ru(0) increases the basicity of thiophene by about 20 orders of magnitude. Protonation causes a change in the coordination of the heterocycle such that the sulfur becomes bound and the tetrahedral carbon detaches from the metal. The stereochemistry of the protonation is endo which suggests that it occurs initially at Ru followed by migration to carbon. The $C(sp^3)$-S distance in $[(C_6Me_6)Ru(C_4Me_2H_3S)]PF_6$ is quite long at 1.91 Å, vs. 1.71 Å in free thiophene. The unusual pK_a of $(C_6Me_6)Ru(C_4R_4S)$ vs. free C_4Me_4S is not due to a change in the site of protonation since tetramethylthiophene itself is also protonated at carbon.

The protonated complex of thiophene $(C_6Me_6)Ru(C_4H_5S)^+$ were found to reversibly undergo C-S scission to give a thiapentadienyl derivative. It was possible to separate the ring-opened isomer from the starting material by fractional crystallization. With these purified samples we were able to examine the approach to equilibrium from both directions. These measurements give K_{eq} (300 K) = 4.38. The rates of isomerization (k_1, k_{-1}) were both first order, as expected for simple unimolecular processes. The ring opening/closing processes are stereospecific as determined through studies on $(C_6Me_6)Ru(C_4H_4S\text{-}2\text{-}D)^+$. Decoupling and nOe measurements established the position of the deuterium. The fact that the C-S scission also occurs in the solid state highlights the relevance of these results to heterogeneous catalysis. The reaction was monitored by solid state ^{13}C NMR spectroscopy:

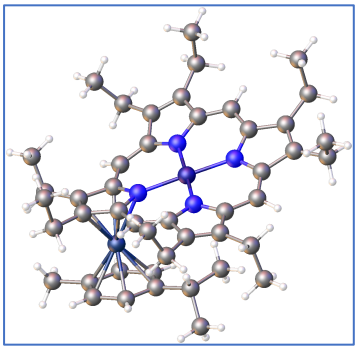


We discovered that metal-promoted base hydrolysis provides a means to desulfurization thiophenes. At high $[OH^-]$, dications convert to S-oxides, whose structures are analogous to those initially obtained by oxygenation of reduced thiophene complexes. In all cases S-oxides isomerize to the acylthiolates. For very stable S-oxides, such as $(C_5Me_5)Ir(C_4Me_4SO)$ and $(cymene)Os(C_4Me_4SO)$, the isomerization requires a two-step procedure beginning with protonation by NH_4^+. This generates the 2-hydroxy derivatives such as $(C_5Me_5)Rh(2\text{-}HOC_4Me_4S)^+$. Thermal fragmentation of acylthiolato complexes of the type $(ring)M(SC_3Me_3COMe)$ gives tetramethylfuran and metal sulfide clusters:



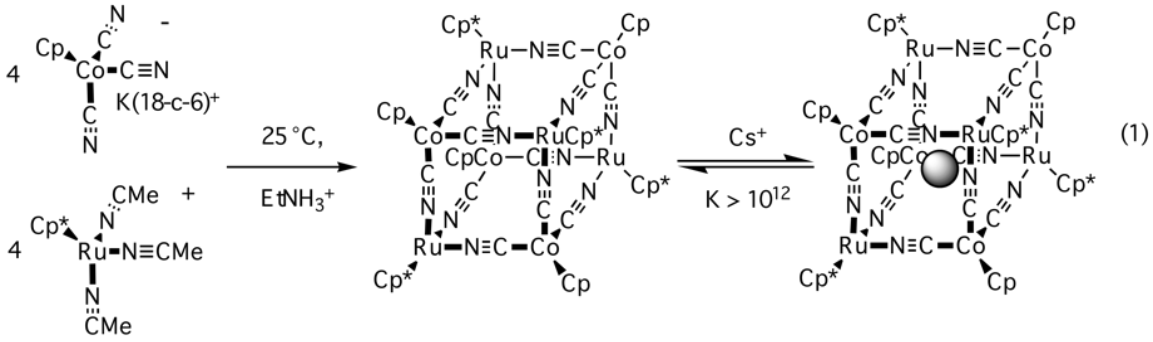
Dicationic pi-thiophene complexes were also found to react efficiently and reversibly with amines to give monocations resulting from the net addition of NRH^-. Using chiral amines, the first optically active pi-thiophene complex was resolved into its enantiomers.

We reported the first examples of complexes of metalloporphyrins as models for hydrodemetallation reactions (See image to right).



II. Cage Chemistry and Inclusion Compounds

We invented an area of coordination cages that exhibit high selectivity for Cs^+, a significant target for the Separations theme in BES. Reaction of $[CpCo(CN)_3]^-$ and $[Cp^*Ru(NCMe)_3]^+$ in the presence of Cs^+ gives $\{Cs[CpCo(CN)_3]_4[Cp^*Ru]_4\}^+$. In the presence of $EtNH_3^+$ the condensation of $PPN[CpCo(CN)_3]$ and $[Cp^*Ru(NCMe)_3]^+$ affords the neutral, empty box $\{[CpCo(CN)_3]_4[Cp^*Ru]_4\}$. Starting with $\{[CpCo(CN)_3]_4[Cp^*Ru]_4\}$ enabled relatively detailed studies of the ion-binding tendencies of the cages. Several ions insert: K^+, Rb^+, Tl^+, NH_4^+, $MeNH_3^+$, and $N_2H_5^+$. For the alkali metal cations, the rate of insertion is inversely related to size, except that Na^+ and Li^+ do not form complexes with the box. No di- or trivalent ion has been found to bind. Competitive binding studies of Cs^+ versus K^+ revealed $\{[CpCo(CN)_3]_4[Cp^*Ru]_4\}$ binds K^+ fast (kinetic product) but that over the course of days, Cs^+ displaces K^+:



Studies on the ammonium-containing box $\{NH_4\subset[CpCo(CN)_3]_4[Cp^*Ru]_4\}^+$ provided insights into the extent that the guest molecule is shielded from the bulk medium. MeCN solutions of this salt are unreactive toward D_2O and unaffected by the addition of strong bases. Using the rate constants from our kinetic analysis, we could estimate the binding affinity, K_f, for Cs^+ to be 10^{10}, probably the highest affinity known for a molecular Cs^+ complexant.

In addition to the $M_8(CN)_{12}$ boxes, we produced "defect boxes" containing three *terminal* cyanide ligands (CN_t). The three CN_t ligands in $\{[(C_5R_5)M(CN)_3]_4[Cp^*Rh]_3\}^{2+}$ (where $(C_5R_5)M$ = CpCo, Cp*Rh) are exo with three Cp* groups forming a lid over a bowl-shaped cavity (discussed below). In Cs^+- or NH_4^+-containing defect Co-Ru boxes, the orientation of the CN_t ligands is more complex (and interesting). Relevant to Cs^+ complexation are two key results: (i) neutral and anionic cages exhibit high affinities for the larger monocations, with a marked preference for Cs^+ and (ii) exchange rates for the *boxes* can be slow. These findings motivated the development of ionophilic defect boxes, specifically $\{NH_4\subset[Cp^*Rh(CN)_3]_4[Cp^*Ru]_3\}$. We propose that this defect box is a functional but soluble representation of the defective PB framework:

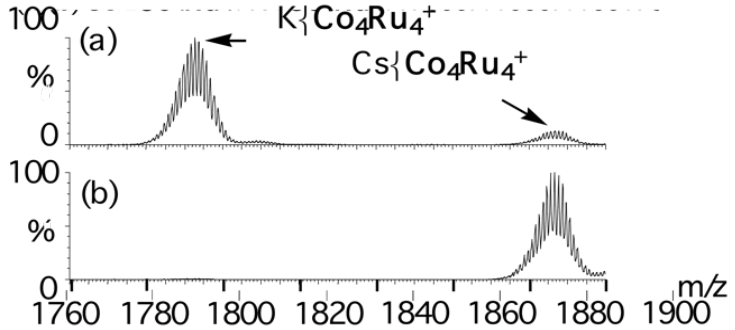
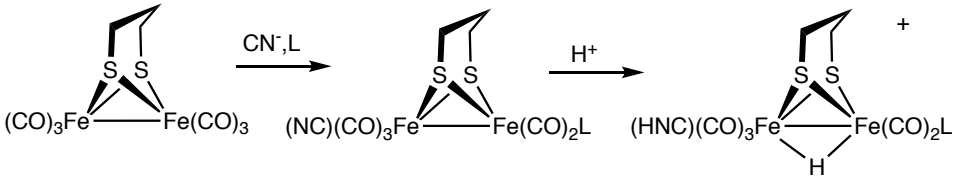


Figure. ESI-MS for 0.0057 M MeCN soln. of $\{[CpCo(CN)_3]_4[Cp^*Ru]_4\}$ upon treatment with 2 equiv each of K^+ and Cs^+ after 10 min. (a) and after seven days (b).

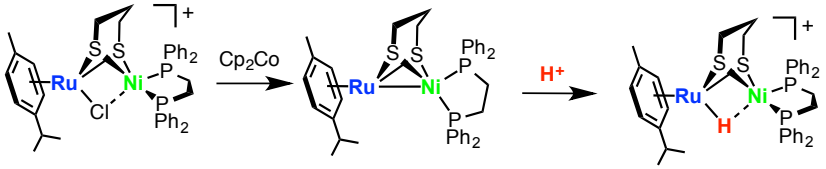
III. Fundamental Studies on Fe-CN-CO Ensembles Related to the Hydrogenase Enzymes

Our group crystallized complexes of the type $[Fe_2(SR)_2(CN)_2(CO)_4]^{2-}$ as the first synthetic models for the [FeFe]-hydrogenase active site. We also prepared the related phosphine derivative $[Fe_2(S_2C_3H_6)(CN)(PMe_3)(CO)_4]^-$, which was shown to be an excellent proton reduction catalyst and the first functional model for the [FeFe]-hydrogenases. Our observations indicated a mechanism for HER that begins with the formation and reduction of $[HFe_2(S_2C_3H_6)(CNH)(PMe_3)(CO)_4]^+$:

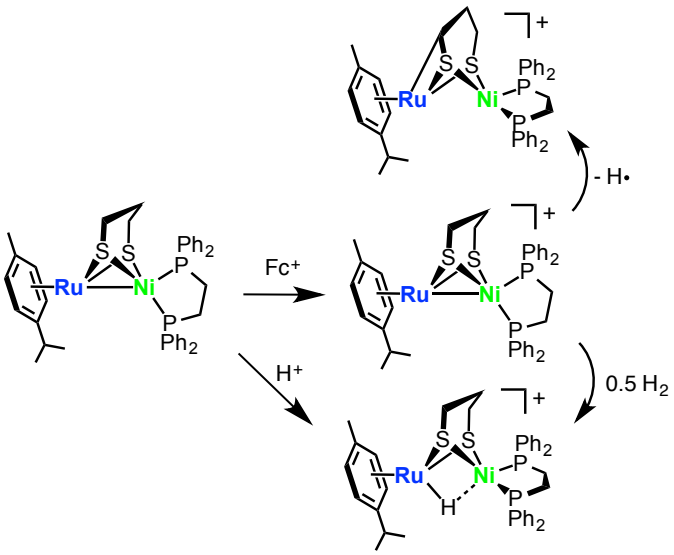


Protonation is followed by chemical reactions that are relatively fast on the voltammetric time scale. The electrochemistry is highly informative. Hydrogen gas was collected and identified; the faradaic yield was quantitative (i.e. all current was expended for production of H_2). Supporting mechanistic studies focused on the diphosphine $Fe_2(S_2C_3H_6)(CO)_4(PMe_3)_2$, which also easily protonates at the Fe-Fe bond. We probed the ligand-binding properties of Fe^{II} in diverse ligation environments to better understand the role of Fe centers in biocatalysis.

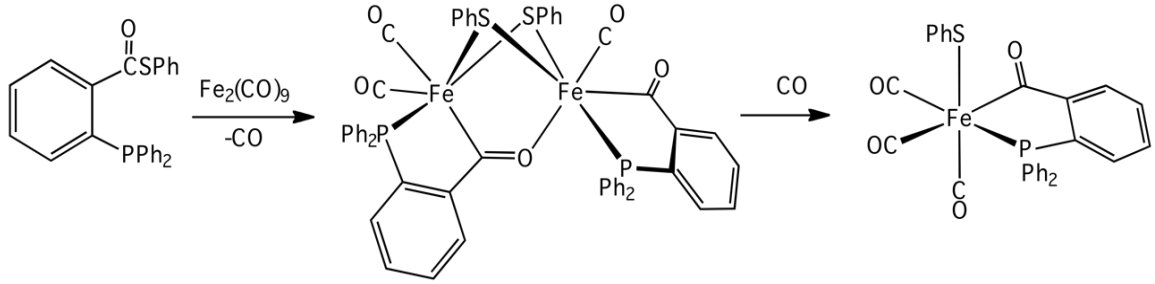
We pursued Ru analogues of these enzyme active sites. In terms of its Brønsted basicity, $[Ru_2(S_2C_3H_6)(CN)_2(CO)_4]^{2-}$ is >10 pK_a units greater than the analogous diiron compound. This high basicity means that the Ru_2 species is a poor catalyst for H_2 evolution because it is difficult to reduce. Hydrogen Activation by Ruthenium-Nickel Dithiolates. The work involved a new family of RuNi dithiolates featuring geometrically flexible Ni centers that enable both acid-base and redox chemistry, behavior which is characteristic of the hydrogenases. Treatment of Ni(pdt)(dppe) with $(cymene)_2Ru_2Cl_4$ affords the salt [(cymene)Ru(Cl)(pdt)Ni(diphos)]Cl (pdt = 1,3-propanedithiolate, diphos = various bidentate diphosphines). These species reduce by 2e to give neutral Ru-Ni species. Crystallographic characterization of these compounds revealed short Ru−Ni distance and tetrahedral Ni sites. Variable temperature NMR studies show that the Ni center is rigid. The reduced complexes are highly basic (pK_a^{PhCN} ~ 19), forming hydrides with unsymmetrical Ru−H···Ni interactions. Protonation causes the Ni center to convert from tetrahedral to square planar, demonstrating the flexibility of this site:



The mixed valence Ru(II)Ni(I) complex, a structural model for the Ni-L state of the [NiFe]-hydrogenases, was characterized crystallographically, spectroscopically, and in terms of its reactivity. Measurements indicate that these cations are described as Ru(II)-Ni(I). Correspondingly, the neutral precursor is best described as Ru(II)Ni(0). The fast electron self-exchange rate of 10^7 $M^{-1}s^{-1}$ between $[\mathbf{1}]^0$ and $[\mathbf{1}]^+$ confirms the minor reorganization associated with this redox, consistent with a Ni(0)/Ni(I) oxidation state change than a Ni(I)/Ni(II) couple. In solution, Ru(II)-Ni(I) slowly disproportionates to two diamagnetic derivatives, the hydride cation and the thioaldehyde $SCHCH_2CH_2S$ arising from C-H activation of the pdt backbone. The H-atom abstracting reagent TEMPO converts the Ni(I) species to the thioaldehyde:



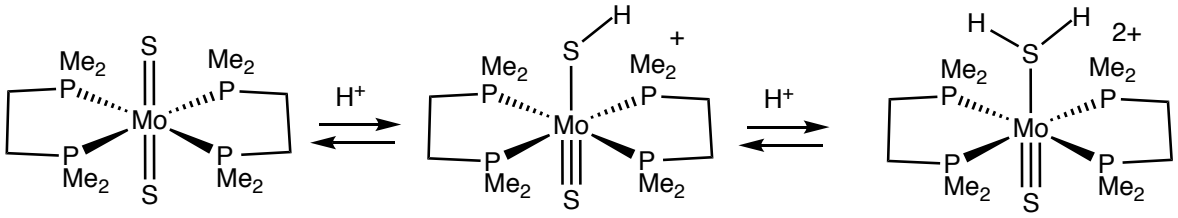
For first generation models of the "third hydrogenase", Hmd, we sought to simulate the coordination environment of the Fe center inhibited by CO. The coordination sphere consists of three CO's, thiolate, pyridine (simulated as phosphine), and acyl. To generate this environment, we investigated the oxidative addition of thioester-modified phosphines to Fe(0) reagents. Thioester-phosphines containing a variety of aryl and alkylthio substituents were prepared via carbodiimide coupling of thiols and diphenylphosphinobenzoic acid. Several of these phosphine thioesters were found to afford *di*iron(II) diacyl dithiolato derivatives. Thus, treatment of a hot THF suspension of $Fe_2(CO)_9$ with these thioesters gives diiron dithiolato complexes with the formula $Fe_2(SR)_2(CO)_3[Ph_2PC_6H_4C(O)]_2$:



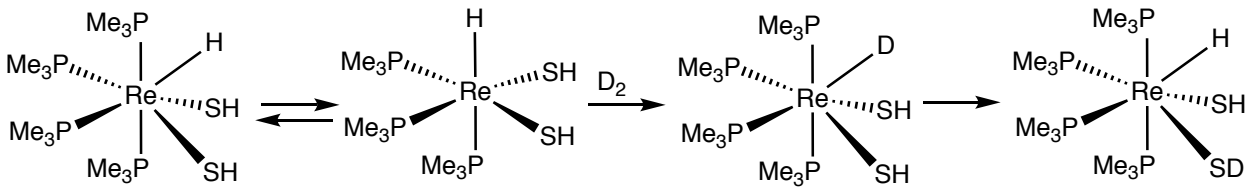
We were unable to prepare corresponding pyridine-Fe-thiolate derivatives from thioester-pyridines. The model complex $Fe(SPh)(Ph_2PC_6H_4CO)(CO)_3$ was obtained by medium pressure carbonylation of the diiron derivative. The structure of this monoiron derivative compares well with the structure of the C176A mutant of Hmd, which has been characterized at 2.15 Å resolution. In this mutant, one cysteinyl ligand is replaced by one thiolate of dithiothreitol, which also provides an alcohol ligand in the coordination site trans to the acyl.

IV. Acid-Base Chemistry of Mo, W, Re Sulfides

The acid-base reactivity of *trans*-$MS_2(dmpe)_2$, where M = Mo and W and dmpe = $Me_2PCH_2CH_2PMe_2$, was examined, guided by the idea that these species feature the Mo(IV) sulfide seen in HDS catalysts. These species arise via our discovery of the reaction $(NH_4)_2MS_4$ + 2.5 dmpe. They are highly basic at sulfur, undergoing protonation to give the stable salts $[MS(SH)(dmpe)_2]X$. The pK_a's of the Mo and W compounds are ca. 16 in MeCN solution. Protonation causes the M=S distances to diverge from 2.24 in *trans*-$MS_2(dmpe)_2$ to 2.06 and 2.57 Å in $[MS(SH)(dmpe)_2]^+$, i.e. from two "pure" double bonds to a triple and a single bond. ^1H and ^{31}P NMR studies for reveal the proton exchange in $[MS(SH)(dmpe)_2]X$ occurs on the NMR time-scale. In some salts, separate signals are observed for "top" and "down" PMe groups. Slow-proton exchange had not been observed in *any* metal sulfide.

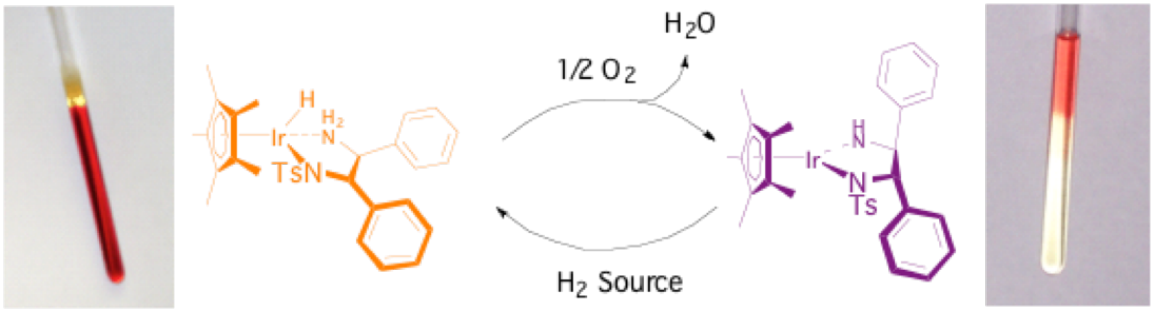


While sulfur is often described as a catalyst poison, many of nature's most remarkable enzymes feature metals embedded in a sulfur-rich coordination sphere. Inspired by this fact precedents, there is much interest in metal sulfides that interact with H_2. MeCN solutions of $[NEt_4][ReS_4]$ react with excess PMe_3 under an atmosphere of H_2S to give $[ReH(SH)_2(PMe_3)_4]$. The complex catalyzes the unusual reaction of $H_2S + PMe_3 \rightarrow SPMe_3 + H_2$. The kinetic lability of **1** is also indicated by its rapid reaction with CO to give *cis*-$ReSH(CO)_x(PMe_3)_{4-x}$, Treatment of **1** with dmpe ($Me_2PCH_2CH_2PMe_2$) gave $ReH(SH)_2(PMe_3)_2(dmpe)$, a unique example of a complex with nonequivalent S−H groups, and magnetization transfer experiments show that exchange between these S-bound H sites is slow. Solutions of **1** react with D_2 to rapidly give $ReD(SH)_2(PMe_3)_4$. Under the same conditions, the reaction of D_2 (1 atm) with the dmpe derivative is slow. We conclude that H/D exchange proceeds via the intermediate 16 e^- species $[ReH(SH)_2(PR_3)_3]$. Exchange of protons between the M−H and M−SH sites in **1** occurs over the course of several hours at room temperature. Solutions of **1** catalyze isotopic exchange between D_2 and H_2S to give HD and DHS. In contrast to the high reactivity of **1**, the corresponding trihydride $[ReH_3(PMe_3)_4]$ is kinetically inert. In other words, the usual view that sulfur poisons catalysts is clearly inappropriate in this case: the sulfide ligands are *enabling.* The catalytic properties of **1**result from its bifunctional nature with both protic (SH) and hydridic (ReH) sites that communicate by an intramolecular exchange process. Complex **1** uniquely undergoes H/D exchange at both S*H* and Re*H* with D_2. The importance of our results is that HDS catalysts use H_2, and it is exciting to see that the M−SH group is an electronically important spectator in the H_2 activation process. Compound **1** is a singular example of a $L_nM(H)(SH)$ compound where the hydride site undergoes exchange with D_2 at a faster rate than the SH site:



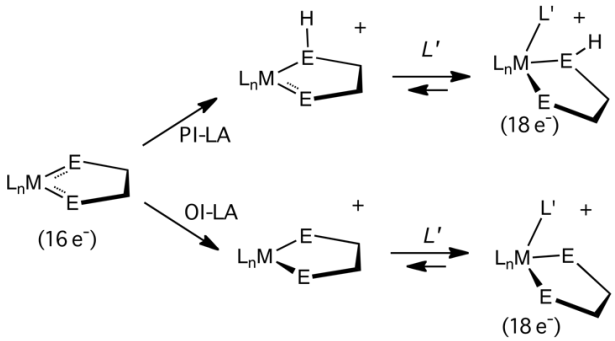
V. H_2- and O_2-Activation by Metal-Amido Complexes

We found that the amino-hydride complex Cp*IrH(TsDPEN) exhibits remarkable reactivity with O_2 resulting in the bis-amido complex, Cp*Ir(TsDPEN-H). We showed that the bis-amido complex can add hydrogen to form the amino-hydride complex in the presence of H^+. The addition of hydrogen and oxygen results in a catalytic cycle for the production of water. Through deuterium labeling studies we determined that the oxygen interacts directly with the iridium hydride bond which undergoes a further reaction with a second equivalent of the iridium hydride to give the bis-amido complex.



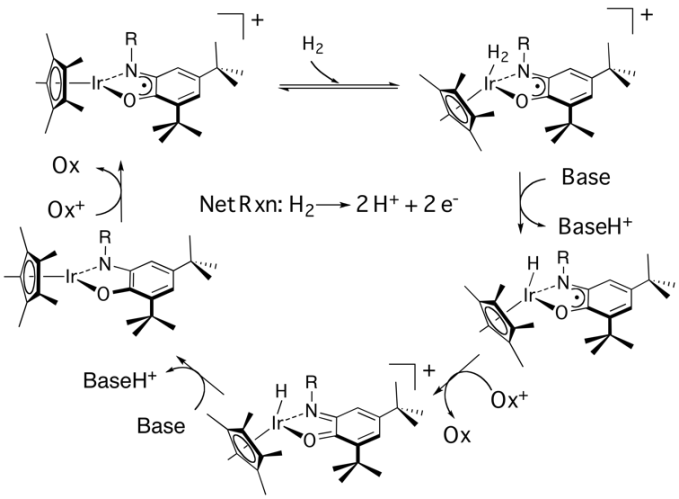
The insight from these studies on the reaction of H_2 + O_2 illustrates the connection between mechanistic organometallic chemistry and challenges associated with fuel cells.

Induced Lewis Acidity of Organoiridium Complexes. Two parallel reaction schemes were developed, termed protonation-induced Lewis acidity (PI-LA) and oxidation-induced Lewis acidity.



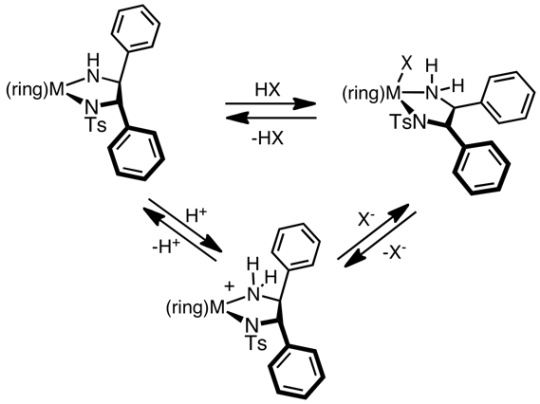
Scheme. General reactions for protonation-Induced Lewis Acidity (PI-LA) and oxidation-induced Lewis acidity (OI-LA).

OI-LA. Unsaturated organoiridium complexes with amidophenolate ligands were shown to undergo two 1e oxidations. Upon oxidation, the amidophenolate ligands acquires some quinoid character. Coulometry measurements indicate that H_2 is oxidized by the monocations, not the corresponding dications. Oxidation of H_2 is catalytic in the presence of a noncoordinating base at potentials required for the generation these cations.



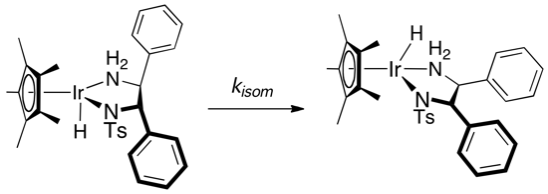
Scheme. Pathway for the oxidation of H_2 by iridium amidophenolate radical cations.

PI-LA. We showed that a third state of the TH catalysts arises by protonation of their "dehydro" state. The cation $[Cp^*Ir(TsDPEN)]^+$ is a soft Lewis acid with potentially distinctive properties. It is not poisoned by water or many related oxygenic ligands, a property that is key



Scheme. Three states of half-sandwich transfer hydrogenation catalysts.

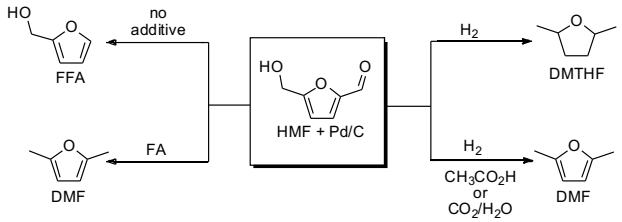
to its reactivity toward H_2 in polar media. It is interesting that protonation enhances the reactivity of these complexes toward H_2:



VI. Catalytic Conversions of Lignocellulosic Feedstocks

For hexose-based feedstocks, 5-hydroxymethylfurfural (HMF) is of central importance as it could simply be produced from sugars via dehydration. The imminent availability of cheap HMF places greater emphasis on its conversion to liquid fuels and chemicals. It can be deoxygenated to 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF) with further hydrogenation, which are both suitable fuel additives owing to their high energy density, volatility and solubility.

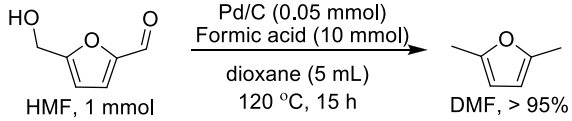
Focusing initially on Pd/C-catalyzed reactions, we found ways to guide catalysis in each



Scheme. Reaction of HMF catalyzed by Pd/C with and without additives. HMF: 5-hydroxymethylfurfural; FFA: furfuryl alcohol; DMF: dimethylfuran; FMF: 5-(formyloxymethyl)furfural; DMTHF: dimethyltetrahydrofuran.

of three separate pathways: decarbonylation, hydrogenolysis, or ring hydrogenation.

In the presence of formic acid (FA), the Pd/C-catalyzed decarbonylation was suppressed. Instead, 2,5-dimethylfuran (DMF) is produced as the near exclusive product. Such conversions entail both hydrogenation of the formyl group and hydrogenolysis of the hydroxymethyl groups, but the furan ring hydrogenation is inhibited.



Scheme. Conversion of HMF to DMF with Pd/C and FA.

Our studies implicate a beneficial role for formate ester intermediates, 2-(formoxymethyl)furfural (FMF) and 2,5-bis(formoxymethyl)furan (BFMF). Such species are efficiently generated by dissolving HMF and BHMF in FA (normal carboxylic acids, e.g. acetic acid, do not esterify so readily). For the FMF → DMF conversion 5-MF is an intermediate, indicating that RCH_2-OCHO hydrogenolysis is faster than RCHO hydrogenation. Under comparable conditions, we established the sequence HMF → BHMF → DMF, indicating that the formyl hydrogenation is faster than hydrogenolysis of the RCH_2-OH bond. In contrast to the high reactivity of formates, (acetoxymethyl)furfural is far less susceptible to hydrogenolysis. Experiments established the influence of FA on the Pd/C-catalyzed hydrogenation (using H_2) of furanic substrates. Whereas H_2-Pd/C converts HMF to tetrahydrofurans, FA and to some extent HOAc suppressed ring hydrogenation. Carbonic acid acts similarly, regardless of whether it is generated from hydration of CO_2 or hydrolysis of dimethyldicarbonate.

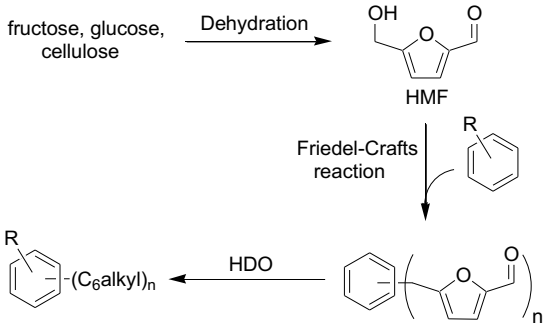
In this work, formic acid serves multiple roles: a mild source of hydrogen, a precursor to formate esters that are activated toward hydrogenolysis, and a catalyst moderator that suppresses decarbonylation and ring hydrogenation. Our results revealed the following relative rates for 2-furanyl substituents: hydrogenolysis of C-OC(O)H > hydrogenation of C=O> hydrogenolysis of C-OH bond.

In a novel approach to diesel precursors from sugars we developed ways for coupling C_5-C_6 precursors to diesel range MW and stripping functionality. Our approach involves the

Friedel-Crafts coupling between HMF and petrochemically derived arenes (from benzene-toluene-xylene or BTX stream):

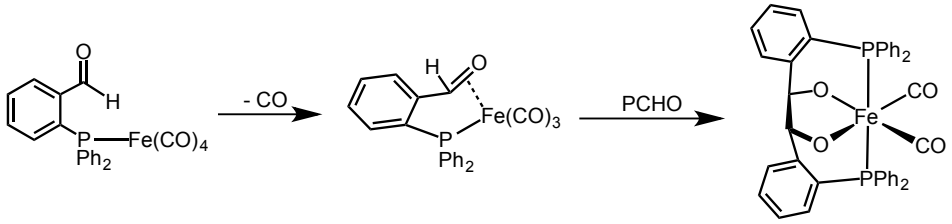
Our studies focused on reactions with mesitylene, which simplified product analysis since it gives only a single isomeric alkylated product. We obtained the coupled product, 5-(mesitylmethyl)furfural (MMF) in high yields (>90%) via the $FeCl_3$-catalyzed reaction of mesitylene and HMF in $MeNO_2$. Other arenes and non-oxygenated solvents also worked with high efficiency. $FeCl_3$ could be replaced by *p*-toluenesulfonic acid (*p*-TsOH). At 120 °C, FA promoted the same coupling almost quantitatively after 4 h. The alkylation proceeds via 5-(formyloxymethyl)furfural (FMF). Encouraged by the effectiveness of FA as a reactive solvent, we replaced HMF with fructose, obtaining MMF in yields up to 72% using FA.

Glucose and even cellulose are known to convert into 5-(chloromethyl)furfural (CMF) in high yield in a biphasic system of aqueous HCl and dichloroethane. We adapted this one-pot process using HCl, 1,2-dichloroethane, FA, and mesitylene to give MMF in 37% from cellulose. Our major finding is that formic acid functions effectively as both solvent and catalyst for reactions of fructose, glucose, and even cellulose. By replacing the reactive hydroxyl group with a stable aryl ring, the methodology also minimizes the formation of humins from HMF, which complicates conversions involving polysaccharides.

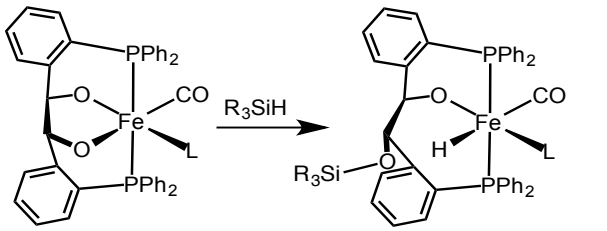


VII. Earth-Abundant Complexes Relevant to Catalysis

Development of catalytic platforms employing base metals was a main theme of this program. Of interest is how functionality on the ligands complement or enhance metal-centered reactivity. We prepared the complex $Fe(P_2O_2)(CO)_2$, a rare example of an 18e low-spin ferrous carbonyl. It arises via a pinacol-like coupling of two phosphine aldehyde ligands:

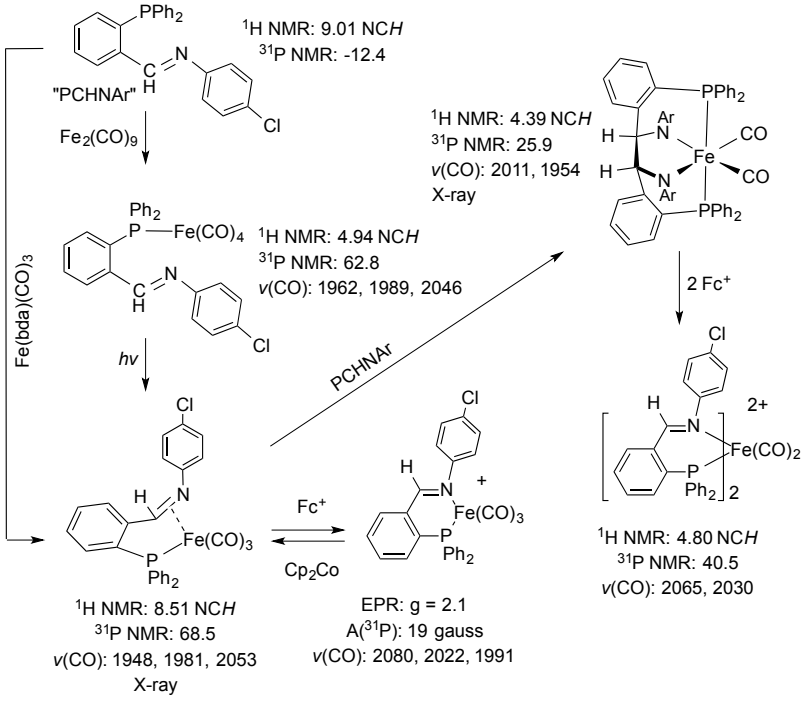


The coupling pathway was elucidated by isotopic labeling and replacement of the formyl group with an imine. The intermediate tetra- and tricarbonyls were characterized spectroscopically. The alkoxides are basic as evidenced by isolation of Lewis acid adducts.
$Fe(P_2O_2)(CO)_2$ reacts with Ph_2SiH_2 to give the O-silylated hydridoiron(II) complex that is relatively inert. The monocarbonyl derivatives $Fe(P_2O_2)(CO)(L)$ (L = NCMe, PMe_3, acetamide) catalyze the hydrosilylation of benzaldehyde, acetophenone, and styrene:



(precatalyst for hydrosilylation when L ≠ CO)

The phosphine-imine exhibit redox-switched hapticity of the imine, which is unprecedented. The redox-induced retro-azapinacol coupling of the diphosphine-diamide is also highly unusual.



Recognition

During the course of this contract, Professor Rauchfuss received the following national or international awards. This extensive recognition is a direct result of the research guided and supported by the Department of Energy:

1992 Guggenheim Fellowship
1997 Fellow, Japan Society for the Promotion of Science
1999 Humboldt Senior Scholar
2000 Fellow, Royal Society of Chemistry
2002 ACS Award in Inorganic Chemistry
2009 ACS Fellow (inaugural)
2014 Nyholm Medal, Royal Society of Chemistry
2018 ACS Award for Distinguished Service to Inorganic Chemistry

Publications Resulting from this Contract

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