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Most of the work described follows on from our prior transfer hydrogenation work [1] or else applications of catalysts prepared for that study that subsequently also proved useful in collaborative work. The grant expired on 11-30-14, but we obtained a no-cost extension to complete some of the projects that remained unfinished. The funds are now exhausted. The renewal proposal document also contains a report of activities in the grant period.

Mild, Reversible Reaction of Ir(III) Amido Complexes with CO_2. [2] In collaboration with the Maseras theory and Hazari inorganic groups, we looked into the reactivity of CO_2 with some of our prior DOE-catalysis compounds. Unlike some other Ir(III) hydrides, a cyclometalated aminopyridine complex does not insert CO_2 into the Ir-H bond. Instead it reacts with CO_2 to form a carbamato species by insertion into the Ir-N bond. To compare the insertion of CO_2 into the Ir-N bond of the cyclometalated species, a family of compounds were prepared. The rate of CO_2 insertion is faster for the more nucleophilic amides. DFT studies suggest that the mechanism of insertion involves initial nucleophilic attack of the nitrogen lone pair of the amide on CO_2 to form an N-bound carbamato complex, followed by rearrangement to the O-bound species. The CO_2 insertion into the PPh_3 complex is reversible in the presence of H_2.

Amorphous Ir Water-Oxidation Electrocatalysts from Soluble Precursors [3] In collaboration with the Brudvig biophysical and D'Souza physical groups we looked at the energy related topic of water oxidation (WO) where complexes originally synthesized for our DOE catalysis project proved useful for WO. We find that an extremely active, low overpotential, robust heterogeneous catalyst that operates at neutral pH can be electrodeposited from soluble organometallic precursors, $Cp^*Ir(OH_2)_3]SO_4$ **1** and $CpIr(OH_2)_3]SO_4$, **2**. The catalyst films appear as blue layers on the anode when sufficiently thick, and most closely resemble hydrous iridium(III,IV) oxide by voltammetry. The deposition rate and cyclic voltammetric response of the electrodeposited material depend on whether the precursor complex is **1** or **2**, and do not match, in either case, iridium oxide anodes prepared from non-organometallic precursors. From electrochemical quartz crystal nanobalance (EQCN) studies, we found differences in the rate of electrodeposition of catalyst layers from the two half-sandwich precursors; however, the resulting layers operated as water-oxidizing anodes with indistinguishable overpotentials and H/D isotope effects. Furthermore, using the mass data collected by EQCN and not otherwise available, we show that the electrodeposited materials are excellent catalysts for the water-oxidation reaction, showing maximum turnover frequencies >0.5 mol O_2 per mol Ir per sec. We see quantitative conversion of current to product dioxygen. Importantly, these anodes maintain their high activity and robustness at very low Ir loadings (45 cents per sq. ft loading). Our organometallic precursors contrast with preformed iridium oxide nanoparticles, which form an unstable electrodeposited material that is not stably adherent to the anode surface at even moderately oxidizing potentials.

<u>Resolving Heterogeneity Problems and Impurity Artifacts in Operationally Homogeneous Transition Metal Catalysts</u>. [4] This is a central problem in homogeneous catalysis and the methods suggested in this review have attracted continued attention from the catalysis community, resulting in 123 citations to this paper in the relatively short time it has been available.

<u>Cp*Ir Precatalysts for Selective C-H Hydroxylation via Direct O Atom Insertion</u>. [5] Complexes prepared for our DOE catalysis studies also proved useful in a collaboration with the Eisenstein theory group and CCHF EFRC. In this work, we found that a series of Cp*Ir complexes are active precatalysts in C-H oxidation of cis-decalin, cyclooctane, 1-acetyl-pyrrolidine, tetrahydrofurans, and γ-lactones. Moderate to high yields were achieved, and surprisingly, high selectivity for mono-oxidation of cyclooctane to cyclooctanone was observed. Kinetic isotope effect data in the C-H oxidation of ethylbenezene to acetophenone yield $k_H/k_D = 15.4 \pm 0.8$ at 23°C and 17.8 ±1.2 at 0°C, are consistent with C-H oxidation being the rate-limiting step with a significant tunneling contribution. The nature of the active species was investigated by TEM, UV-vis; microfiltration, and control experiments. DFT calculations showed that the C-H oxidation of cis-decalin by Cp*Ir(ppy)(Cl) (ppy = o-phenylpyridine) follows a direct O atom insertion mechanism on the singlet potential energy surface, rather than the radical rebound route that would be seen for the triplet, in good agreement with the retention of stereochemistry observed in this reaction.

<u>Characterization of an activated Ir water splitting catalyst using IR photodissociation of H_2 tagged ions</u>. [6] In collaboration with the Johnson physical chemistry group, we reported the vibrational predissociation spectra of two related organometallic half-sandwich Ir species recently reported by us as activated intermediates in homogenous water oxidation. These compounds are extracted from solution into a cryogenic photofragmentation mass spectrometer and "tagged'' with weakly bound H_2 molecules that do not significantly perturb the intrinsic structures of the ions. The resulting spectra display very sharp (~5 cm^{-1}), well-resolved bands that provide a stringent test for electronic structure calculations, and are accurately recovered by harmonic predictions for the bare species. The spectra reveal subtle distortions of the ligand structure when acetonitrile is directly coordinated with the metal center.

<u>Synthesis and computational studies of Mg-terpy complexes</u>. [6] In collaboration with the Hazari inorganic, Batista theory and Brudvig biophysical groups, a wide variety of substituted terpyridines were shown to react with Grignard reagents to give a variety of Mg alkyls of potential interest in CO_2 reduction chemistry.

<u>Aqueous electrochemistry of a water-soluble Mn phthalocyanine</u>. [7] In collaboration with the Brudvig biophysical group, a variety of MnPc complexes,

considered potential candidates for oxidation catalysis, were prepared and studied by the title method. This was a paper in which we looked for useful catalytic activity from a cheap metal, manganese. This is a problematic case because as soon as highly labile Mn(II) is formed in a catalytic cycle, the complex generally falls apart. Phthalocyanines are an exceptional case in which the Mn(II) state is stable, however no useful catalytic properties were identified but we were able to publish an article on the electrochemical properties. There was a long delay before publication because work of greater importance came up for study. [The heterogeneous systems studied by by coauthor JFH were supported under the DOE catalysis grant.]

Electron-Rich biphenyl-2,2'-diyl Complexes.[8] This work was an attempt to load the Group 9 metals with so many strong donor ligands that they would form a stable M(IV) complex potentially suitable for oxidation catalysis. Only Ir proved satisfactory but electrochemistry showed that the Ir(IV) state was only a transient and the complex has not so far shown any useful catalytic properties.

Transfer Hydrogenation & Reductive Amination. The transfer hydrogenation activity of the title complex in [9] suggested that the alkoxide must be very basic. In this paper, we confirmed this proposal by finding a particularly strong, symmetrical hydrogen bond formed with the alkoxide. Although we do not have a n-diffraction structure, we collaborated with the Eisenstein group to use her computational crystallography approach to confirm the symmetrical nature of the hydrogen bond. The results in [10] proved to be an extremely successful approach in that we adapted the prior DOE transfer hydrogenation catalyst to reductive amination, a new class of transformation for metal catalysis.

Distinguishing Homogeneous from Heterogeneous Catalysis.[11] This review proved to be popular with readers, being cited 122 times already.

Redox-Active Ligands in Catalysis.[11] This is a strategy that we think may be useful for making cheap metals behave like precious metals in the sense of being able to undergo 2e redox processes.

Outer Sphere Catalysis. This review [13] covers a second possible approach for making cheap metals behave like precious metals and was written in collaboration with Odile Eisenstein, Montpellier.

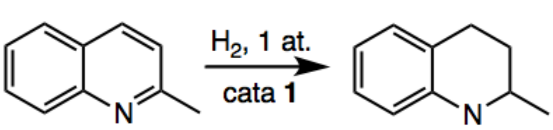
Abnormal N-heterocyclic Carbene Ligands. This review [14] was written to propose a way of thinking about NHCs that is still a minority viewpoint.

The Stability of Organometallic Ligands in Oxidation Catalysis. The title topic arose because of the author's attempts to introduce ligands suitable for making cheap metals behave as precious metals.

Synthetic contributions to collaborative projects. Numerous papers involve using compounds originally made for DOE catalysis studies but which subsequently proved useful for other projects carried out by others in the group. We omit these here to save space and because they have been reported in the annual reports.

Textbook. The sixth edition of my textbook, *The Organometallic Chemistry of the Transition Metals,* embodying many of the principles developed under DOE support, has now been published.

Outer Sphere N-Heterocycle hydrogenation. Arenes have been difficult substrates for homogeneous hydrogenation, but, as mentioned above, we found that they are susceptible to reduction by an outer sphere, two step mechanism in which a M-(H_2) complex first transfers H^+ to the N atom, followed by H^- transfer to an adjacent carbon of a now-activated C=N bond, thus selectively reducing the heterocyclic ring under suprisingly mild conditions (Eq. 1, 1 atm H_2; 25-40°). Isomerization permits C=C reduction at the 3,4 position of the heterocyclic ring.



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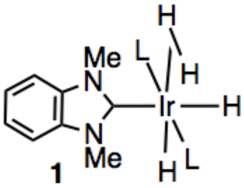

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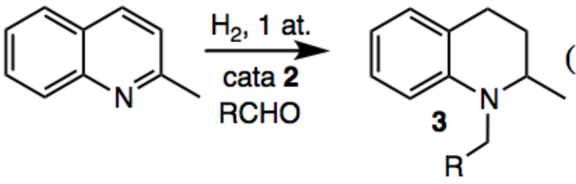

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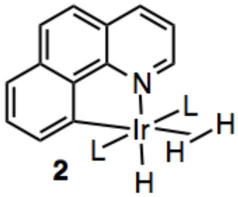

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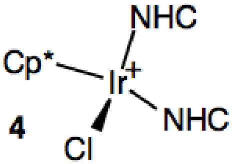
In an extension of this work, we have found [17] a tandem hydrogenation-reductive alkylation of quinaldine with a variety of aldehydes (Eq. 2) to give products of type **3**. A striking feature of these pathways is that no change of oxidation state occurs at the metal, in principle allowing 1st row metals to act in this way, but our search for such activity has so far been without success in spite of some effort; we do not yet understand the difficulty unless it is that H_2 complexes are rather rare for the base metals.

Transfer hydrogenation (TH): The most striking results have come from work with catalysts **4-6**. These are much more active than any of a wide range of similar complexes and the bis-NHC arrangement seems key. Surprisingly, the Cp* is lost from **4** to provide the active species, apparently a solvated $\{Ir(NHC)_2H_2\}^+$ cation.[18,19][7,9] Precursors **5-6** seem to give the same highly active catalyst. Detailed study eliminates nanoparticles as active species.



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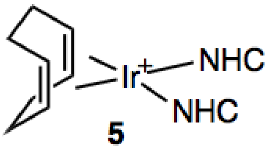

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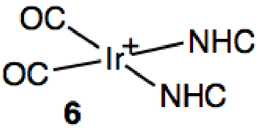

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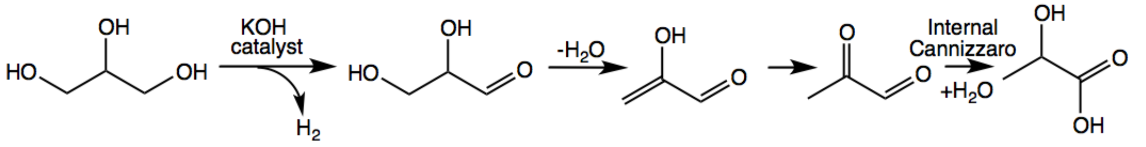
Oxidative conversions: Beyond simple TH, all these catalysts are also active for dehydrogenation-hydrolysis of alcohols such as of aqueous MeOH to H_2 and CO_2. [20] This is of potential interest as a method of H_2 storage in a transportable liquid. As applied to glycerol, this pathway gives H_2 and lactic acid (Eq. 3), [21] thus coproducing useful products from a potential future biodiesel byproduct. The advantage of our catalyst is that it operates on neat glycerol, not just dilute solutions, needs much lower temperatures and has much higher selectivity (95%) than prior catalysts. The metal catalyzed step is the dehydrogenation—the rest is classic, base-catalyzed, atom-economic organic chemistry. In very recent work [22] we find that sorbitol converts to lactic acid under similar conditions, a very unusual C_6 to C_3 conversion. All these transformations are energy-related because they relate to biofuel processing and hydrogen storage in organic materials.



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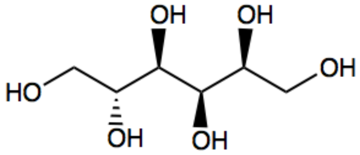

Sorbitol

In unpublished work in collaboration with Nilay Hazari in the post-grant hiatus period, we have an Fe complex that is highly active for the glycerol conversion. A catalyst deactivation review is also recently published [23].

High Impact. Our papers as a whole, largely funded by DOE continue to be highly cited; our *h* factor is now 94.

Papers published in 2011-15.

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[3] Blakemore, JD; Schley, ND; Kushner-Lenhoff, MN; Winter, AM; D'Souza, F; Crabtree, RH; Brudvig, GW., *Inorg. Chem.,* 51, 2012, 7749-7763. [The Crabtree DOE-catalysis grant permitted the discovery and synthesis of the catalyst precursors.]

[4] Crabtree, RH., *Chem. Rev.*, 112, 2012, 1536-1554. [The problem arose in attempts by the PI to tackle mechanistic problems in the DOE catalysis program.]

[5] Zhou, M; Balcells, D; Parent, AR; Crabtree, RH; Eisenstein, O., *ACS Catalysis,* 2, 2012, 208-218. [The Crabtree DOE-catalysis grant permitted the discovery and synthesis of the catalyst precursors.]

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[9] Schley ND, Halbert S, Raynaud C, Eisenstein O, Crabtree RH, Symmetrical Hydrogen Bonds in Iridium(III) Alkoxides with Relevance to Outer Sphere Hydrogen Transfer, Inorg. Chem., 2012, 51, 12313. [No other Crabtree grant acknowledged]

[10] Manas MG, Graeupner J, Allen LJ, Dobereiner GE, Rippy K, Hazari N, Crabtree RH, Hydrogenation of Quinaldine and Benzylic Aldehydes both Separately and Combined in a Tandem Hydrogenation-Reductive Alkylation of Quinaldine by Aldehydes with Iridium Benzoquinoline Catalysts, Organometallics, 2013, 32, 4501. [This was mainly supported by the DOE catalysis grant but product analysis by coauthor LJA was carried out under a different aegis because she was an expert in this area.]

[11] Crabtree RH, Resolving Heterogeneity Problems and Impurity Artefacts in Operationally Homogeneous Transition Metal Catalysts, Chem Rev., 2012, 112, 1536–1554. [This review, being relevant to all the DOE supported projects, cites all the Crabtree grants]

[12] Luca OR, Crabtree, RH, Redox active ligands in catalysis, Chem. Soc. Rev., 2013, 42, 1440 – 1459 (Invited for Werner Special Issue) [This review, being relevant to all the DOE supported projects, cites all the Crabtree grants]

[13] Eisenstein O, Crabtree RH, Outer Sphere Hydrogenation Catalysis, New J Chem, 2013, 37, 21-27 (Invited Focus article).

[14] Crabtree RH, Abnormal, Mesoionic and Remote N-Heterocyclic Carbene Complexes, Coord. Chem. Rev., 2013, 257, 755-766. [No other Crabtree grant acknowledged]

[15] Crabtree, RH, The Stability of Organometallic Ligands in Oxidation Catalysis, J. Organometal. Chem., 2014, 751, 174-180. [Invited review for 50th anniversary issue.] [No other Crabtree grant acknowledged]

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17. Manas MG, Graeupner J, Allen LJ, Dobereiner GE, Rippy K, Hazari N, Crabtree RH, Hydrogenation of Quinaldine and Benzylic Aldehydes both Separately and Combined in a Tandem Hydrogenation-Reductive Alkylation of Quinaldine by Aldehydes with Iridium Benzoquinoline Catalysts, *Organometallics*, 2013, 32, 4501-6. [Funded almost exclusively by DOE catalysis but the product analysis was carried out by an organic expert member of our group under a different aegis]

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22. Manas MG, Campos J, Sharninghausen LS, Lin E, Crabtree RH, Selective Catalytic Oxidation of Sugar Alcohols to Lactic acid, Green Chem, 2015, 17, 594-600. [DOE catalysis is the only funding agency]

23. Crabtree, R. H. Deactivation in Homogeneous Transition Metal Catalysis: Causes, Avoidance and Cure. *Chem. Rev.,* **2015***, 105,* 127. [This review, being relevant to two DOE supported projects, cites them both, including the DOE catalysis grant]