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13. ABSTRACT (Maximum 200 words) The goal of this program is to obtain fundamental understanding that will lead to design of catalysts or catalyst systems for C-H bond activation that can function in direct organic fuel cells, and that are based upon molecular species, rather than metal surfaces. In studying C-H activation by platinum complexes, we have used the results of prior mechanistic studies to design complexes that effect C-H activation under milder conditions, and are working on incorporating these concepts into systems for catalytic alkane oxidation. In the area of metal oxo complexes, we have discovered a complex that efficiently oxidizes alcohols at significantly lower reduction potentials than previously observed, apparently by avoiding a undesirable high-energy one-electron mechanism. Our investigations are directed at extending this discovery to the design of catalysts that can operate at fuel-cell-relevant potentials. DTIC QUALITY INSPECTED 2				
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Statement of Problem Studied

The goal of this program was to obtain fundamental understanding that can lead to design of catalysts or catalyst systems for C-H bond activation that can function in direct organic fuel cells, and that are based upon molecular species, rather than metal surfaces. Low-temperature direct organic fuel cells using traditional solid metal electrodes, particularly with methanol as fuel, have been demonstrated, but only with performances far below those of H₂ fuel cells under similar conditions. There are several reasons for believing that soluble catalysts are a promising alternative. First, several discrete molecular complexes have been shown to be amazingly active for C-H bond cleavage, often even at very low (<0° C) temperatures. Second, molecular catalysts tend to be less susceptible to poisoning than metal surfaces. Third, an understanding of the detailed molecular mechanism of C-H activation is likely to be crucial for the rational design of good catalysts, and such mechanistic information is far easier to obtain for molecular catalysts than for surfaces. Two main lines of attack, consisting of basic mechanistic studies on two classes of complexes known to activate C-H bonds and to function under some fuel cell conditions, were selected as promising approaches towards validating and exploiting this concept. Our most important results for these two areas are summarized separately below.

Summary of Important Results

A. C-H ACTIVATION BY AQUEOUS PLATINUM COMPLEXES

The overall transformation shown in Eq. (1) is a (rare) example of an alkane oxidation that takes place under conditions that are both mild and potentially compatible with fuel cell operation. The crucial issue, about which little was known at the beginning of the project, is: how does the initial C-H bond activation take place? Such information would be central to a program of designing advanced catalysts for a fuel cell to run directly on hydrocarbons. It had been speculated that the activation proceeded via generation of an organoplatinum(II) complex, as shown in Eq. (2); and the majority of our studies were aimed at testing the validity of this speculation and determining how it might occur. Our main findings are summarized below. (References are to the list of publications at the end of this report.)

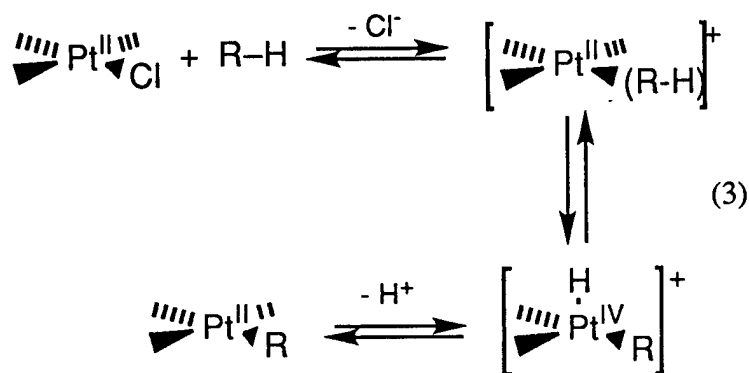


1. Preparation and study of $[\text{RPtCl}_3]^{2-}$.

We were able to prepare $[(\text{CH}_3)\text{PtCl}_3]^{2-}$ under special conditions, but it is stable only as a solid, and reacts too quickly in aqueous solution to be useful for extensive mechanistic study. We were able to demonstrate that it is oxidized by $[\text{PtCl}_6]^{2-}$ extremely rapidly, as required by the postulated overall mechanism for alkane oxidation (ref. 6).

2. Mechanism of C-H activation.

By utilizing amine- and phosphine substituted complexes as models for $[\text{RPtCl}_3]^{2-}$, and studying the protonolysis of Pt(II) alkyls (the microscopic reverse of Eq. (2)), we were able to get both direct and indirect evidence for the existence of two discrete intermediates along the pathway of Eq. (2), implicating the mechanism shown in Eq. (3) as responsible for C-H activation in these systems (refs. 1, 3).



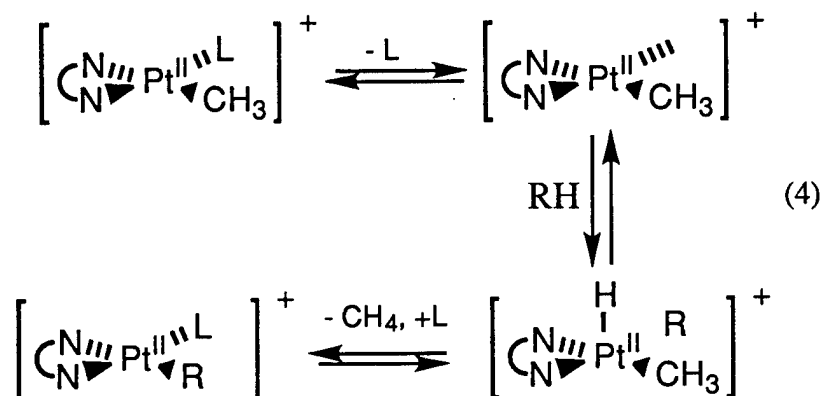
3. Ligand effects on C-H activation steps.

The ability of ligands to favor/disfavor the several individual steps required to accomplish C-H activation were probed in two ways: by examining the dependence of the rates of RH elimination and H/D exchange on the nature of the auxiliary ligands L in complexes of the form L_2PtRX (ref. 8); and by studying the effects of ligand variation on the formation and stability of dihydrogen adducts, $[\text{L}_2\text{PtX}(\text{H}_2)]^+$, which serve as models for the (RH) adduct shown as an intermediate in Eq. (3) (ref. 10).

4. Design of new C-H activating complexes.

By exploiting our mechanistic understanding, we were able to design Pt(II) complexes that activate C-H bonds to generate stable, isolable Pt alkyl complexes, as shown in Eq. (4), where the labile ligand L is pentafluoropyridine. The reaction shown takes place under milder conditions than the original aqueous chemistry. Future efforts will be directed towards incorporating this

new approach to increasing C-H activation activity into a system that can achieve overall alkane oxidation catalytically.



B. C-H ACTIVATION BY METAL OXO COMPLEXES

cis-(bpy)₂Ru(O)(OH₂)²⁺ (bpy = 2,2'-bipyridine) has been found to oxidize alcohols to the corresponding aldehydes or ketones. Although many Ru(IV)-oxo complexes will oxidize alcohols, most operate at relatively high redox potentials (> 1 V vs. NHE) and are not suitable as catalysts in fuel cells. These complexes typically oxidize alcohols via H-atom-transfer mechanisms. The 0.63-V Ru(IV/II) potential of *cis*-(bpy)₂Ru(O)(OH₂)²⁺ is too low for H-atom transfer to be viable.

The kinetics of these alcohol-oxidation reactions have been examined extensively during the course of this project. It has been found that the oxidation rate is not strongly sensitive to deuteration at the α-carbon atom (*k_H*/*k_D* = 1.2-1.5), but is quite sensitive to the solvent deuterium-isotope composition (*k_{H2O}*/*k_{D2O}* = 12-14). The data suggest that *cis*-(bpy)₂Ru(O)(OH₂)²⁺ oxidizes alcohols by an inner-sphere mechanism. The first step involves replacement of H₂O by ROH in the Ru inner coordination sphere. Oxidation of the coordinated alcohol is accomplished by hydride transfer from the α-carbon to the oxo ligand and deprotonation of the hydroxyl group.

The *cis*-(bpy)₂Ru(O)(OH₂)²⁺ complex has also been shown to oxidize a variety of amines, aldehydes, and ketones, including methylamine, *t*-butylamine, isopropylamine, pyridine, acetone and benzaldehyde. Preliminary kinetics investigations indicate that oxidations of amines are much faster than alcohol-oxidation reactions. Given that *t*-butylamine is one of the substrates, it is likely that the oxidation mechanism for amines differs from that for alcohols. It is possible that N-oxide formation is involved in these reactions.

Manuscripts Submitted or Published during the Performance Period:

1. "Formation and Reductive Elimination of a Hydridoalkylplatinum(IV) Intermediate upon Protonolysis of an Alkylplatinum(II) Complex." S. S. Stahl, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, **1995**, *117*, 9371-2.
2. "Photoinduced Oxidation of Microperoxidase-8: Generation of Ferryl and Cation-Radical Porphyrins." D. W. Low, J. R. Winkler and H. B. Gray, *J. Am. Chem. Soc.*, **1996**, *118*, 117-20.
3. "Exploring the Mechanism of Aqueous C-H Activation by Pt(II) through Model Chemistry: Evidence for Intermediacy of Alkylhydridoplatinum(IV) and Alkane σ -Adducts." S. S. Stahl, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, **1996**, *118*, 5961-76.
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5. "C-H Activation at Cationic Platinum(II) Centers." M. W. Holtcamp, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, **1997**, *119*, 848-9.
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7. "How Do Electronegative Substituents Make Metal Complexes Better Catalysts for the Oxidation of Hydrocarbons by Dioxygen?" A. Böttcher, E. R. Birnbaum, M. W. Day, H. B. Gray, M. W. Grinstaff and J. A. Labinger, *J. Mol. Catal.*, **1997**, *117*, 229-42.
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10. "Systematic Investigation of Factors Affecting the Stability of Dihydrogen Adducts of Platinum(II)." S. S. Stahl, J. A. Labinger and J. E. Bercaw, *Inorg. Chem.*, in press.

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