Table IV. Concentration Dependence of the Fluorescence Decay Parameters for the Complex of *trans*-L with Mg^{2+}

$[L] \times 10^5$, M	$[Mg^{2+}] \times 10^3$, M	τ_1, ps $\pm 10\%$	A_1, %	τ_2, ps $\pm 10\%$	A_2, %
4.2		138	100		
0.05	0.6	34	97	410	3
0.22	0.6	36	93	375	7
0.55	0.6	38	91	354	9
1.0	0.6	35	90	365	10
2.2	0.6	34	89	360	11
3.2	0.6	38	88	360	12
4.2	0.6	49	85	365	15
1.6	3.8	45	93	460	7
1.6	38	25	100		
1.6	270	21	100		

effect could be that trans complex aggregation occurs only for the zwitterionic dye. Thus, the reported stability constants are apparent constants.

The hypothesis of trans complex aggregation finds additional support in the time-resolved fluorescence experiments. In Table III are presented fluorescence decay parameters for *trans*-L and its complexes with Mg^{2+}, Ca^{2+}, and Ba^{2+}. Upon excitation at 355 nm by a 8-ps laser pulse, emission was detected at wavelengths above 480 nm. The decay of the free ligand is purely monoexponential with a lifetime of 137 ps, in good agreement with the value of 150 ps calculated from the fluorescence quantum yield and the radiative lifetime estimated from the absorption spectrum. The fluorescence decays of the trans complexes, however, are biexponential with a fast component lifetime τ_1 of about 25 ps and the slower component lifetime τ_2 in the subnanosecond region. The variation of τ_1 upon changing the complexed metal from Mg^{2+} through Ba^{2+} is within experimental error. (Note that the total instrument response function is ca. 70 ps fwhm). However, τ_1 for the Ba^{2+} complex was reproducibly larger than that for Mg^{2+} complex, in agreement with the relationship between the corresponding fluorescence quantum yields. The contribution of the slower component is decreased, and τ_2 increased in the series from Mg^{2+} to Ba^{2+}, correlating again with increased cation size. The faster component can thus be attributed to monomer ligand complex fluorescence, and the slower component to aggregate fluorescence.

At high metal cation concentrations (above 10^{-2} M), only the faster component is observed (Table IV). This is readily ascribed to aggregate decomposition deriving from association of the sulfonate group with an additional metal cation. With increasing ligand concentration at a fixed cation concentration (an intermediate value of 6×10^{-4} M was taken in order to provide complete ligand complexation, but not to cause aggregate decomposition), the contribution of the slower component is also increased, Table IV. The lifetimes of both components remain unchanged upon varying the complex concentration, within experimental error. An attempt to fit these data to a simple scheme including only the equilibrium between the monomers and dimers depicted in Figure 5 failed, thus indicating that more complex equilibria are involved. Nonetheless, aggregation influences the π-system only weakly. In fact, the observed absorption spectra of the free trans complexes were almost independent of concentration.

Summary

The complexation of a zwitterionic crown ether styryl dye with divalent alkaline-earth cations is dramatically shifted by geometric photoisomerization. The enhanced stability of the cis ligand complex is attributed to the interaction of the crowned cation with an anionic sulfonate group. Aggregation in dilute solutions of the trans complex derives from a strong interaction between the sulfonate group in one complex and the crowned cation in another.

Acknowledgment. Those portions of this work conducted in Austin were supported by the U.S. National Science Foundation and the Robert A. Welch Foundation. We thank Dr. S. J. Atherton for assistance in the single-photon counting experiments which were performed at the Center for Fast Kinetics Research, which is jointly supported by the Biomedical Research Technology Program of the Division of Research Resources of the National Institute of Health (RR00886) and by the University of Texas at Austin.

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(19) Ushakov, E. N.; Stanislavsky, O. B. Unpublished results.

C–H Activation in Aqueous Medium. The Diverse Roles of Platinum(II) and Metallic Platinum in the Catalytic and Stoichiometric Oxidative Functionalization of Organic Substrates Including Alkanes

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Abstract: The oxidation of ethers, alcohols, esters, and light alkanes (ethane, propane) by K_2PtCl_4 and Pt/O_2 in aqueous medium has been studied. Results appear to indicate that unactivated C–H bonds were attacked and oxidized by Pt(II) whereas C–H bonds α to an oxygen were activated and catalytically oxidized by metallic Pt in the presence of O_2. For example, Pt(II) was found to oxidize ethane selectively to the alcohols, ethanol, and ethylene glycol. In the presence of metallic Pt and O_2, further oxidation of the alcohol functionality occurred to generate the corresponding carboxylic acids. Thus, with proper choice of the C–H activating system, it was possible to oxidize substrates with a fairly high degree of selectivity with respect to the oxidation level, as well as the particular C–H bond that was functionalized. With respect to the latter, because of the "chelate effect", the selective activation and oxidation by Pt(II) of C–H bonds suitably distant from a coordinating oxygen was achieved. For ethers, the order of reactivity was α-C–H < β-C–H < γ-C–H.

The selective, oxidative functionalization (preferably catalytic) of hydrocarbons, especially alkanes, through a C–H activation step is one of the most challenging chemical problems, in addition to being of great practical importance. There are *three* critical issues that need to be addressed in the design of a successful procedure. The first, of course, is the requirement of a facile C–H cleavage step. The other two equally important factors that need to be considered involve selectivity: selectivity with respect to the

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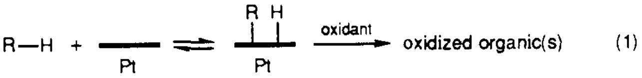
degree of oxidation, as well as selectivity with regard to the particular C–H bond that is functionalized.

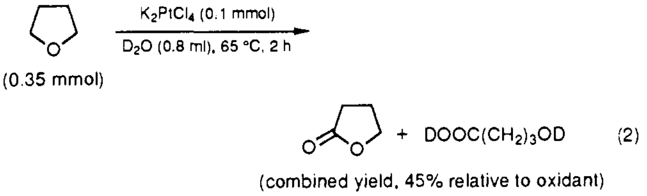
In recent years, several groups have demonstrated that platinum(II) salts can activate and oxidize the C–H bonds of a number of organic substrates.[1,2] This system is particularly attractive because the reactions proceed under mild conditions in water, and because of its compatibility with dioxygen, which is the most desirable ultimate oxidant. The key C–H activation step has generally been assumed to occur in solution at an electrophilic Pt(II) center.[1,2a] Herein, we provide evidence that strongly suggests that depending on the nature of the C–H bond the activation step may take place either at a Pt(II) center or on metallic Pt that is formed in situ. In the latter case, the role of the Pt(II) ion is primarily to oxidize the resultant surface-bound hydrocarbyl groups (eq 1). Indeed, in this case, the Pt(II) ion can be replaced



by other oxidants including O_2. Furthermore, since Pt(II) and metallic Pt exhibit very different selectivities with respect to C–H activation, it is possible to design systems that will oxidize organic substrates, including simple alkanes, with a fairly high degree of selectivity with respect to the degree of oxidation, as well as to the particular C–H bond that is functionalized.

Results and Discussion

Oxidation of Ethers. The starting point for our investigation was the Pt(II) oxidation of ethers—a class of substrates that has not been hitherto examined. As summarized in eqs 2 and 3, the oxidation proceeded in aqueous solutions with the simultaneous deposition of Pt metal. In eq 2, γ-hydroxybutyric acid was formed by in situ hydrolysis of γ-butyrolactone (metallic Pt appeared to promote this hydrolysis). The noteworthy feature of eq 3 was the formation of glycolic acid together with a smaller amount of ethylene glycol (and chloroacetic acid). The reaction involves the oxidation of the remote methyl group, and the formation of these products from diethyl ether is unprecented although the analogous oxidation of the methyl group of ethanol has been recently reported.[2a] A separate experiment indicated that acetic acid can be further oxidized to glycolic acid under the reaction conditions[2b] but at a rate slower than that observed for eq 3. Thus, the majority of glycolic acid in eq 3 was not derived from acetic acid. The apparently lower yield observed at higher reaction temperature was due to further oxidation of glycolic acid, eventually to CO_2 and water.



(combined yield, 45% relative to oxidant)

$$CH_3CH_2OCH_2CH_3 \xrightarrow[D_2O\ (0.7\ ml),\ 110\ ^\circ C,\ 48\ h]{K_2PtCl_4\ (0.1\ mmol)} DOCH_2CH_2OD + DOCH_2COOD + CH_3COOD$$

(0.25 mmol)

(ratio, 1:5:1; combined yield, 9.1% relative to oxidant)

$$\xrightarrow[D_2O\ (0.7\ ml),\ 90\ ^\circ C,\ 48\ h]{K_2PtCl_4\ (0.1\ mmol)} DOCH_2CH_2OD + DOCH_2COOD + ClCH_2COOD + CH_3COOD$$

(ratio, 1:2:1.5:2; combined yield, 20.1% relative to oxidant)

(3)

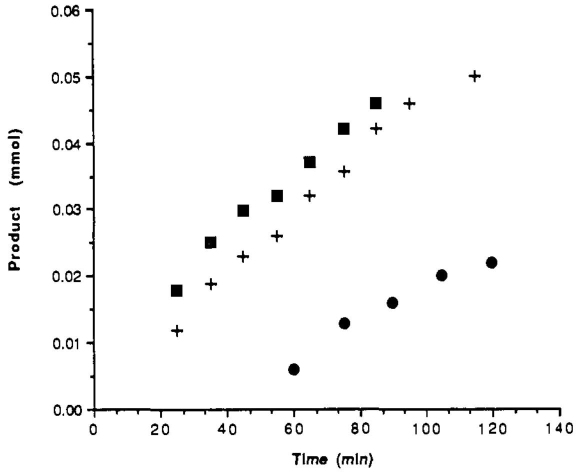
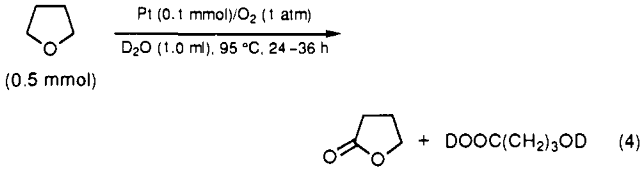


Figure 1. Yield of products (γ-butyrolactone + γ-hydroxybutyric acid) from tetrahydrofuran versus time. Conditions: 60 °C, D_2O (0.8 mL), K_2PtCl_4 (0.1 mmol) (●); with added Pt metal (0.1 mmol) (+); with added Pd metal (0.1 mmol) (■).

A study of the kinetics of the oxidation of tetrahydrofuran (THF) revealed the presence of an induction period (Figure 1). *This induction period was eliminated and the rate was enhanced upon the addition of either metallic Pt or Pd* (Figure 1). Hence, we hypothesize that the key C–H activation step was occurring on metallic Pt or Pd rather than in solution at a Pt(II) center (eq 1). Under this scenario, the role of the Pt(II) ion is simply to oxidize the surface-bound hydrocarbyl groups. Indeed, K_2PtCl_4 could be replaced by other oxidants such as O_2. Thus, as shown below, it was possible to catalytically oxidize THF and diethyl ether by O_2 in water in the presence of metallic Pt (eqs 4 and 5).



(96% conversion)

$$\underset{(0.4\ mmol)}{CH_3CH_2OCH_2CH_3} \xrightarrow[D_2O\ (1.0\ ml),\ 95\ ^\circ C,\ 48-60\ h]{Pt\ (0.1\ mmol)/O_2\ (1\ atm)} \underset{(96\%\ conversion)}{CH_3COOD} \quad (5)$$

In either case, the catalyst could be recovered and used repeatedly. Note that similar oxidation of cyclic ethers by Pt metal and O_2 has been reported previously.[3]

The catalytic conversion of diethyl ether to acetic acid appears to involve ethyl acetate as an intermediate. This latter compound was observed in significant yields (up to 8% relative to starting ether) when the reaction was carried out for shorter time periods. Additionally, ethyl acetate was converted smoothly to acetic acid in water in the presence of Pt metal and O_2 (eq 6).

$$CH_3CH_2OCH_2CH_3 \xrightarrow[D_2O,\ 95 ^\circ C]{Pt/O_2} CH_3COOCH_2CH_3 \xrightarrow[D_2O,\ 95\ ^\circ C]{Pt/O_2} [CH_3COOCOCH_3] \xrightarrow{D_2O} 2CH_3COOD \quad (6)$$

Typically, 0.2 mmol of ethyl acetate was quantitatively oxidized to form acetic acid as the sole organic product in 48 h, in the presence of 0.1 mmol of Pt. Under identical conditions ethanol was catalytically oxidized,[4] first to acetaldehyde (and its hydrate), and finally to acetic acid. Note that, analogous to our observations

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[1] (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Dordrecht, 1984; Chapter V. (b) Shilov, A. E. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989; p 1.

[2] (a) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 5658. (b) Kao, L.-C.; Sen, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1242.

[3] The catalytic oxidation of cyclic ethers, including THF, by metallic Pt and O_2: Heyns, K.; Buchholz, H. *Chem. Ber.* **1976**, *109*, 3707.

[4] Recent reference on catalytic oxidation of alcohols by metallic Pt and O_2: Nicoletti, J. W.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 759.

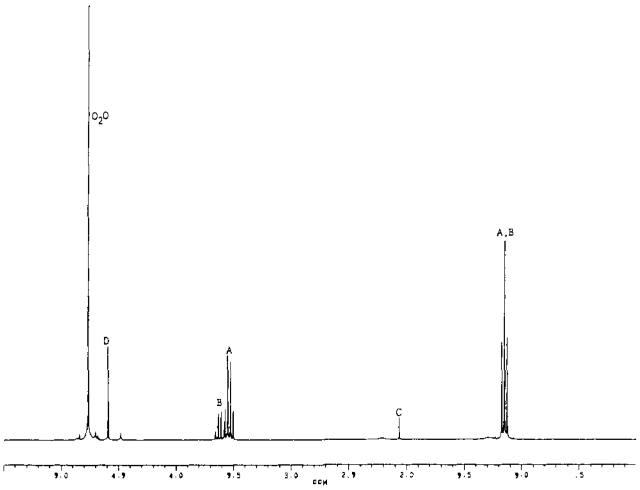
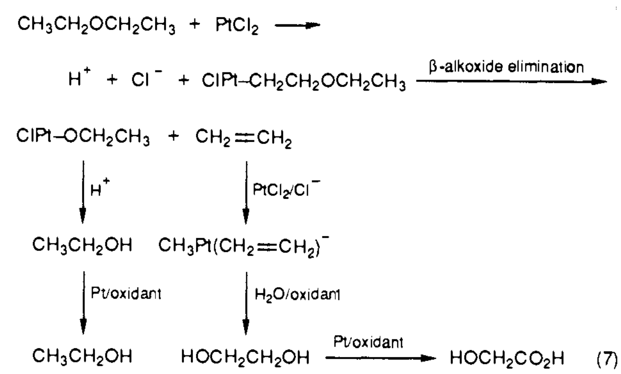


Figure 2. ^{1}H-NMR spectrum observed under the following reaction conditions: diethyl ether (0.1 mmol), K_2PtCl_4 (0.1 mmol), D_2O (0.5 mL), 90 °C, 2 h. (A) $CH_3CH_2OCH_2CH_3$, (B) CH_3CH_2OH, (C) CH_3CO_2H, (D) $PtCl_3(CH_2{:}CH_2)^-$.

with ethers, Bocarsly has reported that the oxidation of ethanol by Pt(II) is also catalyzed by metallic platinum.[5]

A *key* difference in the oxidation of diethyl ether in the presence and absence of Pt(II) was that in the latter case diethyl ether was converted solely to acetic acid (eq 5) rather than a mixture of ethylene glycol, glycolic acid, and acetic acid (as well as chloroacetic acid) as shown in eq 3. One possibility is that the products other than acetic acid arose through an oxidation step involving Pt(II) rather than metallic Pt. A careful examination of the reaction products after the reaction of Pt(II) with diethyl ether was allowed to proceed at a lower temperature and for a shorter time period indicated that the primary products were $PtCl_3(CH_2{:}CH_2)^-$[6] and ethanol in approximately equal amounts (together with a small amount of acetic acid) (Figure 2). A rational mechanism that explains the formation of these products involves an attack on one of the remote methyl groups by Pt(II) followed by β-alkoxy elimination from the resultant Pt-alkyl species (eq 7). β-Hydroxy elimination from a Cr(III)-alkyl complex has been reported recently.[7] An alternative mechanism would involve C–O bond cleavage by Pt(II) followed by β-hydrogen abstraction from the resultant Pt–ethyl species. We currently favor the former mechanism for the following reasons. As described in the following section and in previous work, the Pt(II) ion is capable of attacking unactivated C–H bonds of methyl groups (of ethane, for example). The olefin complex, $PtCl_3(CH_3CH{:}CH_2)^-$,[8] was observed as an intermediate in the oxidation of diisopropyl ether but *not* di-*n*-propyl ether. This can be rationalized on the basis of eq 7 since, assuming initial attack on a methyl group, a β-alkoxy–Pt species will be formed from the former substrate but not from the latter. On the other hand, the second mechanism, involving initial C–O activation, should not only lead to the olefin complex starting from either substrate but should also be more facile with di-*n*-propyl ether for steric reasons. The formation of $PtCl_3(CH_2{:}CH_2)^-$ from ethyl ethers during oxidation by Pt(II) is quite general since the substrates $CH_3CH_2O(CH_2CH_2O)_nCH_2CH_3$ (n = 1, 2) both generated this species as an intermediate. On the other hand, the olefin complex was not generated from the compounds $CH_3O(CH_2CH_2O)_nCH_3$ (n = 1–4). Finally, it is conceivable that hydrolysis of ethyl ethers led to ethanol as the primary product and that $PtCl_3(CH_2{:}CH_2)^-$ arose through the reaction of Pt(II) with ethanol. However, we consistently failed to generate the olefin complex through this route using the experimental conditions that were employed for the ether reactions. The formation of $PtCl_3(CH_2{:}CH_2)^-$ from K_2PtCl_4 and *pure* ethanol has been reported[9] and did, indeed, occur in our hands.



(7)

The ethylene glycol (and glycolic and chloroacetic acids), formed by the oxidation of diethyl ether with Pt(II) (eq 3), appears to arise from the observed intermediate olefin complex, $PtCl_3(CH_2{:}CH_2)^-$. Using Zeise's salt,[6] $K[PtCl_3(CH_2{:}CH_2)]$, as a model, we found that the addition of an oxidant, such as Pt(IV), Pt(II), or H_2O_2, resulted in its conversion to ethylene glycol. Chloroethanol and acetic acid respectively were observed as additional products when Pt(IV) and Pt(II) were used as oxidants. Under different reaction conditions, the formation of chloroethanol from $PtCl_3(CH_2{:}CH_2)^-$ has also been reported.[10] Ethylene glycol and its precursor $PtCl_3(CH_2{:}CH_2)^-$ were also observed when K_2PtCl_6 was added to K_2PtCl_4 during the reaction of the latter with diethyl ether (K_2PtCl_6 was found to be unreactive toward diethyl ether). The function of K_2PtCl_6 was to act as an oxidant and prevent the precipitation of metallic Pt.[2] However, in the absence of added Pt(IV) salt, the formation of metallic Pt invariably occurred and the latter then catalyzed the oxidation of the alcohols to the corresponding carboxylic acids as illustrated in eq 8. Thus, eq 7 summarizes the overall reaction of diethyl ether with K_2PtCl_4 in water.

$$\underset{(0.09\ \text{mmol})}{HOCH_2CH_2OH} \xrightarrow[D_2O\ (1.0\ \text{mL}),\ 90\ °C,\ 48\ \text{h}]{Pt\ (0.075\ \text{mmol})/O_2\ (1\ \text{atm})} \underset{(90\%\ \text{conversion})}{DOCH_2COOD} \qquad (8)$$

Our observations relating to the oxidation of ethers show the diverse roles of Pt(II) and metallic Pt in the activation of substrate C–H bonds. The most significant aspect of our observations is that *unactivated C–H bonds were attacked by Pt(II) (and took place in the absence of metallic Pt) whereas C–H bonds α to an oxygen were activated by metallic Pt (and this occurred even in the absence of Pt(II))*. It is particularly curious that Pt(II) will attack unactivated C–H bonds but not C–H bonds α to an oxygen. A possible explanation for this reactivity pattern is illustrated in Scheme I. Assuming initial coordination of the oxygen atom, the activation of an α-C–H bond would result in the formation of a highly strained three-membered-ring intermediate, while β-C–H activation would give an intermediate with a less strained four-membered ring. Such a scenario would lead to the prediction that γ-C–H activation would be even more favorable because of the intermediacy of a five-membered ring. Indeed, the *only* product initially observed in the reaction of di-*n*-propyl ether with Pt(II) was 1,3-dihydroxy propane; *no* product derived from β-C–H activation was detected. The mechanism also nicely explains the observation of Labinger and Bercaw[2a] that the reaction of *n*-propanol with a combination of Pt(II) and Pt(IV) resulted in oxidation at the γ-carbon but not at the β-carbon. Also, we had earlier reported a very similar "chelate effect" in Pt(II) catalyzed selective remote oxidation of unactivated C–H bonds in aliphatic carboxylic acids.[2b]

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[5] Cameron, R. E.; Bocarsly, A. B. *Inorg. Chem.* **1986**, *25*, 2910.

[6] The NMR spectra were identical to that of Zeise's salt, $K[PtCl_3(CH_2{:}CH_2)]$, prepared independently: Chatt, J.; Searle, M. L. *Inorg. Synth.* **1957**, *5*, 210.

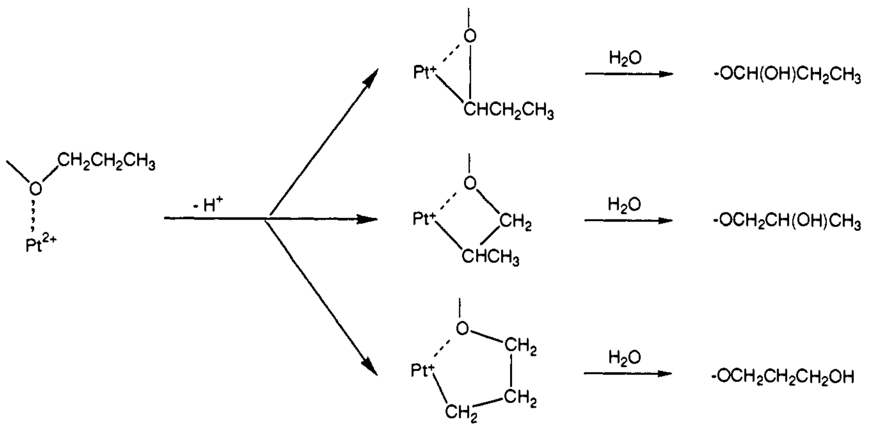
[7] Cohen, H.; Feldman, A.; Ish-Shalom, R.; Meyerstein, D. *J. Am. Chem. Soc.* **1991**, *113*, 5292.

[8] The NMR spectrum was identical to that observed for $K[PtCl_3(CH_3CH{:}CH_2)]$, prepared independently from K_2PtCl_4 and C_3H_8: Hartley, F. R., *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; p 370.

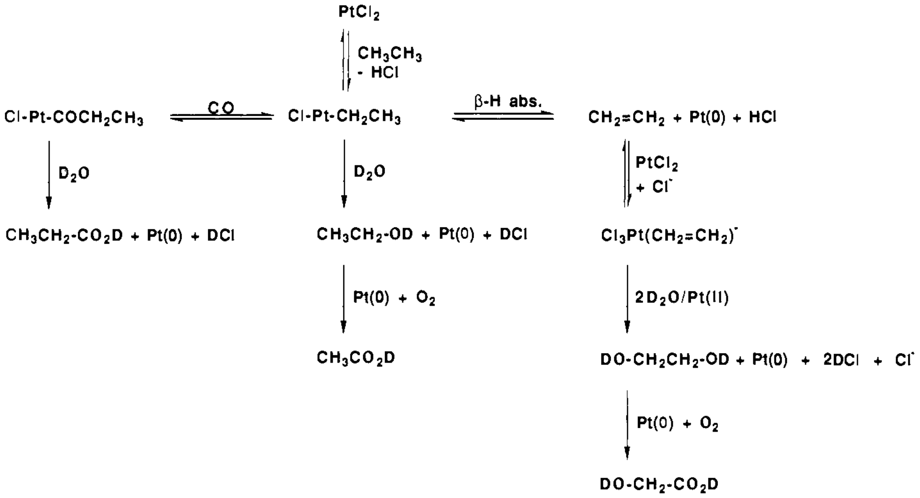
[9] Hartley, F. R. *Inorg. Chim. Acta* **1971**, *5*, 197.

[10] Halpern, J.; Jewsbury, R. A. *J. Organomet. Chem.* **1979**, *181*, 223.

Scheme I



Scheme II



Oxidation of Alkanes. In this section we describe how the complementary roles played by Pt(II) and metallic Pt in the activation of substrate C–H bonds can be exploited to achieve the selective oxidation of alkanes. Specifically, we report the first example of direct conversion of ethane to acetic and glycolic acids, under mild conditions[11] (eq 9). Under appropriate conditions,

$$C_2H_6 + O_2 \xrightarrow[D_2O,\ 108\text{–}134\ ^\circ\mathrm{C}]{PtCl_4^{2-} + \text{Pt black}} CH_3CO_2D + DOCH_2CO_2D \qquad (9)$$

hydroxycarbonylation of ethane to propionic acid was also achieved. Additionally, the oxidation procedure is general since it appears that higher alkanes may be oxidized through a similar mechanism. The system employed consists of a homogeneous (Pt(II) and a heterogeneous (metallic Pt) component. The initial C–H activation occurs at the Pt(II) center culminating in the formation of ethanol and ethylene glycol. The role of the metallic Pt is to catalyze the subsequent oxidation of these alcohols to the corresponding carboxylic acids.

Equation 10 shows the typical reaction conditions. On allowing

$$\begin{aligned} &C_2H_6\ (36.2\%)/O_2\ (4.2\%)/Ar\ (59.6\%)\ [\text{total pressure} = \\ &500\ \text{psi}] \xrightarrow[D_2O,\ 122\ ^\circ\mathrm{C},\ 68\ \mathrm{h}]{K_2PtCl_4/Pt\ (0.1\ \text{mmol each})} \underset{(0.084\ \text{mmol})}{CH_3CO_2D} + \underset{(0.032\ \text{mmol})}{DOCH_2CO_2D} \end{aligned} \qquad (10)$$

the reaction to proceed for a longer time period, the yield of acetic acid increased while that of glycolic acid decreased, presumably due to its further oxidation, eventually to CO_2. Since the conversion of ethane to acetic acid and glycolic acid represents $6e^-$ and $8e^-$ oxidations, respectively, the overall transformation represented a net 0.76 mmol electron oxidation.

The following observations pertain to the mechanism of the above oxidation (Scheme II). *The Pt(II) ion was primarily responsible for the initial C–H activation step, since little or no reaction was observed in its absence.* The electrophilic displacement step leading to the formation of a Pt-alkyl species, as depicted in Scheme II, is similar to that postulated earlier.[1,12] A Pt–CH_2CH_3 species appears to be an intermediate since a significant quantity of $CH_3CH_2CO_2D$ was formed (approximately 15–20% relative to CH_3CO_2D at 30 psi CO) when CO was added to the system. As shown in Scheme II, the carboxylic acid may form by the reaction of D_2O with a Pt–$COCH_2CH_3$ species, formed in turn by CO insertion into the Pt–CH_2CH_3 bond. This sequence of steps is observed in many catalytic reactions, such as the hydrocarboxylation of olefins.[13] A second observation that implicated the intermediacy of a Pt–CH_2CH_3 species was the appearance of a resonance ascribable to $PtCl_3(CH_2{:}CH_2)^-$ [6] in the ^{1}H-NMR spectra of the reaction mixtures. This latter species was presumably formed by β-H abstraction from Pt–CH_2CH_3 followed by scavenging of the released $CH_2{:}CH_2$ by a Pt(II) ion. Note that $PtCl_3(CH_2{:}CH_2)^-$ was also observed in the reaction of C_2H_6 with $PtCl_4^{2-}$ *even in the absence of* O_2. Also, no reaction was observed between C_2H_6 with K_2PtCl_6 under these conditions. Clearly, Pt(IV) that might be present as an impurity or formed in situ by the oxidation of Pt(II) was *not* responsible for the C–H activation step.

The *primary* oxidized organics formed were ethanol and ethylene glycol. These could be detected in reactions carried out

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(11) Preliminary report: Sen, A.; Lin, M. *J. Chem. Soc., Chem. Commun.* **1992**, 508.

(12) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421.

(13) Mullen, A. In *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; p 243.

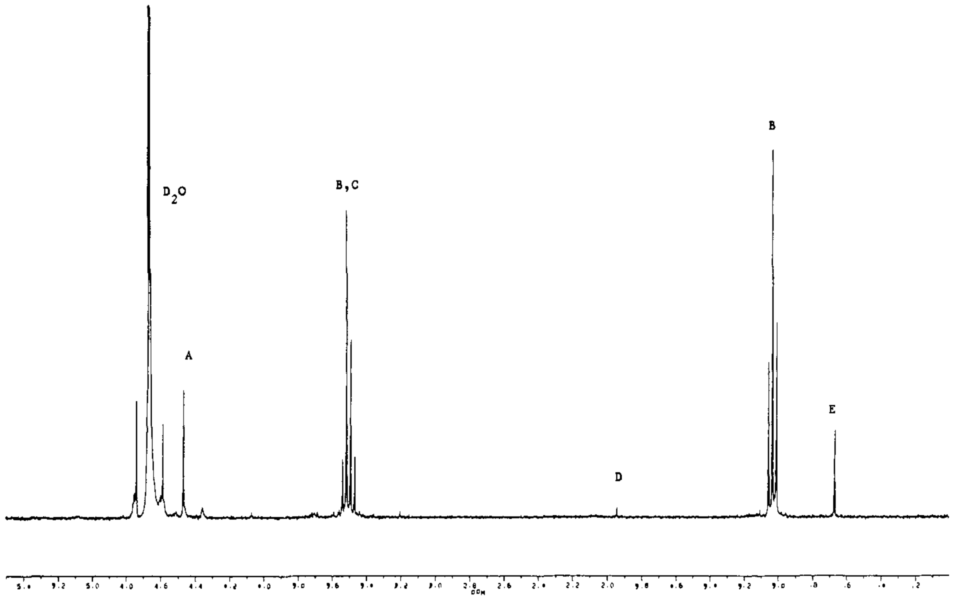

Figure 3. ^{1}H-NMR spectrum observed under the following reaction conditions: C_2H_6 (450 psi), O_2 (100 psi), K_2PtCl_4 (0.05 mmol), K_2PtCl_6 (0.05 mmol), D_2O (4 mL), 105 °C, 20 h. (A) $PtCl_3(CH_2{:}CH_2)^-$, (B) CH_3CH_2OD, (C) $DOCH_2CH_2OD$, (D) CH_3COOD, (E) C_2H_6.

at lower temperatures and for shorter time periods (eq 11). The ethanol was presumably formed by attack of D_2O on Pt–CH_2CH_3.

$$C_2H_6\ (36.2\%)/O_2\ (4.2\%)/\text{Ar}\ (59.6\%)\ [\text{total pressure} = 500\ \text{psi}] \xrightarrow[D_2O,\ 108\ ^\circ C,\ 19\ h]{K_2PtCl_4/Pt\ (0.1\ \text{mmol each})} \underset{(0.004\ \text{mmol})}{CH_3CH_2OD} + \underset{(0.002\ \text{mmol})}{CH_3CO_2D} + \underset{(0.002\ \text{mmol})}{DOCH_2CH_2OD} + \underset{(0.0017\ \text{mmol})}{DOCH_2CO_2D} \quad (11)$$

In order to find out whether this was a viable step, a Pt(IV)–CH_2CH_3 species was generated by the reaction of $PtCl_4^{2-}$ with C_2H_5I.[14] This species was found to react with D_2O at 25 °C over a period of several hours to form C_2H_5OD. Although this may not be an exact model since the oxidation state of the metal was different, it does lend support for the hydrolysis step. The formation of an alcohol by the hydrolysis of a Pt–alkyl bond is curious since it indicates a Pt–C bond polarity that is *opposite* of that normally observed for metal–alkyls (metal–alkyls generally yield alkane and metal–hydroxide upon hydrolysis). As before, ethylene glycol was formed by the oxidative hydrolysis of $PtCl_3(CH_2{:}CH_2)^-$ (see section on ethers).

The ultimate products, acetic acid and glycolic acid, were formed by Pt metal catalyzed oxidation of the corresponding alcohols by O_2. As discussed in the section on ethers, metallic platinum is able to catalyze the oxidation of alcohols to the corresponding acids in the presence of an oxidant, such as O_2 or even Pt(II). Consistent with this scenario was the observation that *only* ethanol and ethylene glycol (together with $PtCl_3(CH_2{:}CH_2)^-$) were formed when K_2PtCl_6 was added to K_2PtCl_4 during the reaction of the latter with C_2H_6 and O_2 (Figure 3). Note that a separate experiment indicated that K_2PtCl_6 was unreactive toward ethane. The function of K_2PtCl_6 was to act as an oxidant and prevent the reduction of Pt(II) to metallic Pt[2], thus making the ethane to alcohol transformation truly catalytic in Pt(II), as has been observed previously for the remote C–H oxidation in aliphatic carboxylic acids.[2b] Monitoring the reaction by ^{195}Pt-NMR spectroscopy indicated that as expected the concentration of K_2PtCl_6 decreased with time. In the absence of added Pt(IV) salt, however, the alcohol to acid oxidation step could not be stopped by excluding Pt(0) from the initial reaction mixture since Pt(0) was formed during the conversion of ethane to ethanol and ethylene glycol by Pt(II). Hence acetic acid and glycolic acid were the ultimate products even in the absence of externally added metallic Pt. The advantage of adding O_2 to the reaction mixture was that it replaced Pt(II) as the oxidant in the Pt metal catalyzed oxidation of alcohols. As a result, the role of the Pt(II) ion remained confined to the initial oxidation of ethane to the two alcohols. On this basis, assuming no reoxidation of the reduced Pt(II), the total yield of the products should not exceed 100% relative to the Pt(II) originally present in the system. As eq 10 indicates, yields of up to 116% relative to Pt(II) were observed thereby indicating *some* Pt(0) to Pt(II) reoxidation under the reaction conditions. Note that since the Pt(II) ion was no longer consumed in the alcohol to acid oxidation step, the overall effect of the addition of O_2 was that a greater yield of oxidized organic products was obtained from ethane. Consistent with this scenario was the observation that the reduction of Pt(II) to Pt(0) was very much slower in the presence of O_2.

Finally, the reaction of propane with $PtCl_4^{2-}$ under conditions similar to that described above gave $PtCl_3(CH_3CH{:}CH_2)^-$ along with 1- and 2-propanol and acetone (Figure 4). Thus, in principle, it should be possible to oxidize higher alkanes through a procedure analogous to that used for ethane.

Conclusion

We have demonstrated the facile catalytic and stoichiometric activation and subsequent oxidation of C–H bonds of organic substrates including alkanes in water under relatively mild conditions. The most significant aspect of this chemistry is that *unactivated C–H bonds were attacked by Pt(II) (and took place in the absence of metallic Pt) whereas C–H bonds α to an oxygen were activated by metallic Pt (an this occurred even in the absence of Pt(II))*. Thus, with proper choice of the C–H activating system, it was possible to oxidize substrates with a fairly high degree of selectivity with respect to the oxidation level, as well as the particular C–H bond that is functionalized. For example, in the absence of metallic Pt, the oxidation of a substrate C–H bond by Pt(II) stopped at the alcohol stage; further oxidation occurred only in the presence of metallic Pt. Also, because of the "chelate effect", it was possible to carry out the selective activation by Pt(II) of C–H bonds suitably distant from a coordinating oxygen. For ethers, the order of reactivity was α-C–H < β-C–H < γ-C–H. An analogous "chelate effect" has also been observed in the Pt(II)-catalyzed selective hydroxylation of remote C–H bonds in aliphatic carboxylic acids.[2b] In this case, the order of reactivity was α-C–H $\ll$ β-C–H < γ-C–H $\geq$ δ-C–H $\approx$ ϵ-C–H. Note that,

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[14] A similar procedure has been reported: (a) Kusch, L. A.; Lavrushko, V. V.; Misharin, Yu. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729. (b) Zamashchikov, V. V.; Kitaigorodskii, A. N.; Litvinenko, S. L.; Rudakov, E. S.; Uzhik, O. N.; Shilov, A. E. *Bull. Acad. Sci. USSR* **1985**, *34*, 1582. (c) Zamashchikov, V. V.; Rudakov, E. S.; Mitchenko, S. A.; Nizova, G. V.; Kitaigorodskii, A. N.; Shul'pin, G. B. *Bull. Acad. Sci. USSR* **1986**, *35*, 175. (d) Zamashchikov, V. V.; Rudakov, E. S.; Garkusha-Bozhko, V. S.; Mitchenko, S. A.; Litvinenko, S. L.; Chuprina, V. S. *Soviet J. Coord. Chem.* **1986**, *12*, 474.

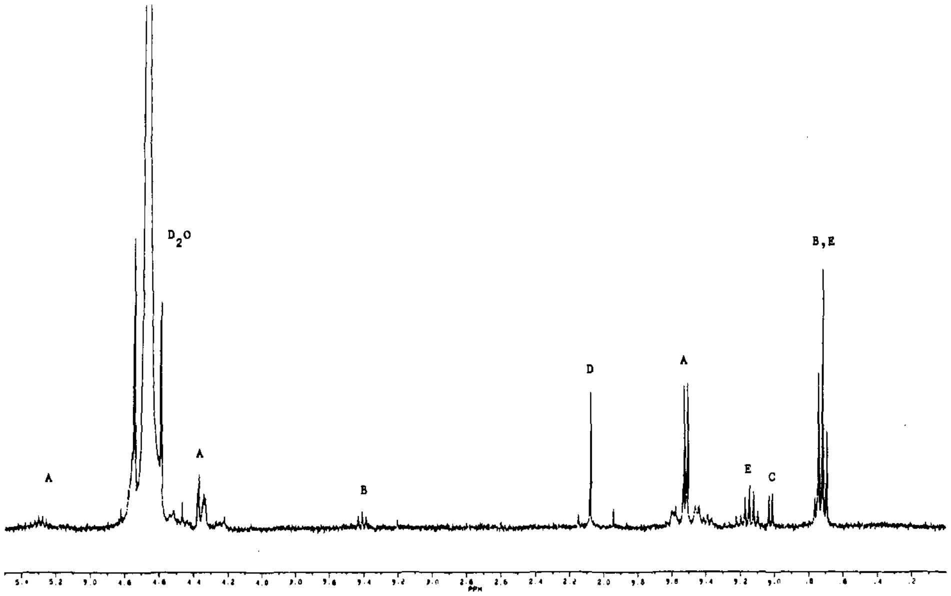

Figure 4. ^{1}H-NMR spectrum observed under the following reaction conditions: 35% C_3H_8, 4% O_2, and 61% Ar (total pressure 220 psi), K_2PtCl_4 (0.12 mmol), D_2O (4 mL), 110 °C, 2 h. (A) $PtCl_3(CH_2{:}CHCH_3)^-$, (B) $CH_3CH_2CH_2OD$, (C) $CH_3CH(OD)CH_3$, (D) CH_3COCH_3, (E) C_3H_8.

both for ethers and aliphatic carboxylic acids, the Pt(II) ion did not discriminate between primary, secondary, and tertiary C–H bonds; the chelate effect was *all* that was important. These observations open up the possibility of carrying out oxidations (such as hydroxylation) of highly flexible linear and branched alkyl chains with unprecedented regioselectivity. Finally, the direct oxidative dehydrogenation of ethane and propane to the corresponding olefins in homogeneous media is unprecedented (dehydrogenations under photochemical[15] and transfer hydrogenation[16] conditions are, however, known).

Experimental Section

General. All of the operations were carried out in air. All organic reagents were purchased from commercial sources and used as received. The gas mixtures of methane, ethane, or propane with oxygen and argon were purchased from Matheson Co. K_2PtCl_4, K_2PtCl_6, Na_2PtCl_6, and platinum black were obtained from Johnson Matthey, Inc. and used as received. Zeise's salt, $K[PtCl_3(CH_2CH_2)]$, was prepared according to the literature procedure.[6] Reaction products were identified by their ^{1}H-NMR spectra recorded on a Brucker AM 300 FT-NMR spectrometer using tetramethylsilane or solvent resonance at the appropriate frequency as an internal standard. Vapor-phase chromatograms were obtained on a Varian 3700 gas chromatograph equipped with a flame ionization detector and a Supelco 6 × $^1/_8$ in. carbowax column. Integration was done on a Shimadzu CR501 Chromatopac integrator. The mass spectra were recorded on a Kratos MS9/50 mass spectrometer.

Oxidation of Ethers, Alcohols, and Esters. 1. K_2PtCl_4 + THF. K_2PtCl_4 (41.5 mg, 0.1 mmol) was dissolved in 0.8 mL of D_2O in a 5-mm NMR tube sealed with a rubber septum. THF (28 μL, 0.35 mmol) was added to the solution with a microsyringe. The NMR tube was heated at 65 °C in an oil bath for 2 h and shaken frequently so that the platinum formed as a fine powder. At this time the solution was almost colorless. The tube was then cooled to room temperature for half an hour and platinum black settled out. A sealed capillary tube loaded with 1 μL of DMSO in 60 μL of D_2O was put into the NMR tube as an integration standard. The proton intensity of DMSO had been assigned by comparison with a 0.01 M solution of THF or CH_3CO_2H in D_2O. The ^{1}H NMR spectrum indicated that the sole organic products were γ-butyrolactone [δ, ppm: 4.27 (2 H, t, J_{H-H} = 7.0 Hz), 2.42 (2 H, t, J_{H-H} = 7.7 Hz), 2.13 (2 H, m)] (0.011 mmol) and $DOCH_2CH_2CH_2COOD$ (δ, ppm: 3.42 (2 H, t, J_{H-H} = 6.7 Hz), 2.06 (2 H, t, J_{H-H} = 7.5 Hz), 1.62 (2 H, m)] (0.009 mmol). The combined yield was 45% relative to oxidant.

2. Kinetics of Oxidation of THF. A procedure similar to that described above was followed. Five 5-mm NMR tubes, each containing 0.8 mL of 0.125 M K_2PtCl_4 and 0.44 M THF in D_2O, were heated at 60 °C for 60, 75, 90, 105, and 120 min, respectively. When the tubes were cooled in an ice–water bath for 30 min the platinum black settled out and left a clear, colorless solution. A sealed capillary tube containing a standard amount of DMSO in D_2O was put into the NMR tube. The integration of peak intensity of the ^{1}H NMR spectra indicated the yields of the oxidation products as shown in Figure 1. Similar experiments were also performed with NMR tubes containing either 19.5 mg of platinum black (NMR recorded after 25, 35, 45, 55, 65, 75, 85, 95, and 120 min) or 10.6 mg of palladium black (NMR recorded after 25, 35, 45, 55, 65, 75, 85 min).

3. K_2PtCl_4 + Diethyl Ether. A procedure similar to that used for THF oxidation was used.

(a) A 5-mm NMR tube containing diethyl ether (2.7 μL, 0.025 mmol) and K_2PtCl_4 (41.5 mg, 0.1 mmol) in 0.7 mL of D_2O was heated at 110 °C for 48 h. The ^{1}H-NMR spectrum indicated that the only organic products were CH_3COOD [δ, ppm: 1.95 (s)] (4.7 × 10^{-4} mmol), $DOCH_2CH_2OD$ [δ, ppm: 3.55 (s)] (6.9 × 10^{-4} mmol), and $DOCH_2COOD$ [δ, ppm: 4.12 (s)] (2.5 × 10^{-3} mmol). The combined yield was 9.1% relative to oxidant.

(b) When the same reaction was run at 90 °C for 48 h, the ^{1}H-NMR spectrum indicated that the organic products were CH_3COOD (2.9 × 10^{-3} mmol), $DOCH_2CH_2OD$ (1.3 × 10^{-3} mmol), $DOCH_2COOD$ (2.4 × 10^{-3} mmol), and $ClCH_2COOD$ [δ, ppm: 4.17 (s)] (1.9 × 10^{-3} mmol). The combined yield was 20.1% relative to oxidant.

(c) Diethyl ether (10.5 μL, 0.1 mmol) was added to a 5-mm NMR tube containing K_2PtCl_4 (41.5 mg, 0.1 mmol) in 0.5 mL of D_2O. After the solution was heated at 90 °C for 2 h, the ^{1}H-NMR spectrum indicated that the products were $K[PtCl_3(CH_2{:}CH_2)]$ [δ, ppm: 4.60 (s, J_{Pt-H} = 66 Hz)] (23.3%), CH_3COOD [δ, ppm: 2.06 (s)] (5.4%), and CH_3CH_2OD [δ, ppm: 3.63 (2 H, q, J_{H-H} = 7.2 Hz), 1.15 (2 H, t, J_{H-H} = 7.2 Hz)] (25.4%). The spectrum is shown in Figure 2.

4. K_2PtCl_4 + Acetic Acid. Acetic acid (2.9 mL, 0.05 mmol) was added to a 5-mm NMR tube containing K_2PtCl_4 (41.5 mg, 0.1 mmol) in 0.7 mL of D_2O. After the solution was heated at 110 °C for 48 h, the ^{1}H-NMR spectrum indicated the presence of the following: $DOCH_2COOD$ (0.013 mmol, 26%) and CH_3COOD (0.030 mmol, 60%).

5. Na_2PtCl_6 + Diethyl Ether. Diethyl ether (10.5 μL, 0.1 mmol) was added to a 5-mm NMR tube containing $Na_2PtCl_6{\cdot}4H_2O$ (26.3 mg, 0.05 mmol) in 0.6 mL of D_2O. After the solution was heated at 95 °C for 72 h, the ^{1}H-NMR spectrum indicated that diethyl ether was the only species in the solution.

6. K_2PtCl_4/K_2PtCl_6 + Di-*n*-propyl Ether. Di-*n*-propyl ether (70 μL, 0.5 mmol) was added to a 5-mm NMR tube containing K_2PtCl_4 (20.8 mg, 0.05 mmol) and K_2PtCl_6 (24.3 mg, 0.05 mmol) in 0.6 mL of D_2O (K_2PtCl_6 was not completely soluble). After the solution was heated at 95 °C for 72 h, the ^{1}H NMR spectrum indicated that the sole organic products were $CH_3CH_2CH_2OD$ [δ, ppm: 3.52 (2 H, t, J_{H-H} = 6.6 Hz), 1.50 (2 H, m), 0.84 (3 H, t, J_{H-H} = 7.5 Hz)] and $DOCH_2CH_2CH_2OD$ [δ, ppm: 3.63 (4 H, t, J_{H-H} = 6.6 Hz), 1.75 (2 H, m)], along with trace amounts of $CH_3CH_2CO_2D$ [δ, ppm: 2.45 (2 H, q, J_{H-H} = 7.6 Hz), 1.05 (3 H, t, J_{H-H} = 7.6 Hz)], CH_3CO_2D, and HCO_2D.

7. K_2PtCl_4/K_2PtCl_6 + Diisopropyl Ether. Diisopropyl ether (10 μL, 0.071 mmol) was added to a 5-mm NMR tube containing K_2PtCl_4 (20.8

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mg, 0.05 mmol) and K_2PtCl_6 (24.3 mg, 0.05 mmol) in 0.6 mL of D_2O. After the solution was heated at 95 °C for 2 days, the ^{1}H-NMR spectrum indicated that the sole organic products were CH_3COCH_3 and $K[PtCl_3(CH_2{:}CHCH_3)]$ [δ, ppm: 5.33 (1 H, m, J_{Pt-H} = 68.6 Hz), 4.39 (1 H, d, J_{H-H} = 8.9 Hz, J_{Pt-H} = 71.0 Hz), 4.38 (1 H, d, J_{H-H} = 12.7 Hz, J_{Pt-H} = 64.6 Hz), 1.55 (3 H, d, J_{H-H} = 6.2 Hz, J_{Pt-H} = 40.4 Hz)].

8. Pt-Catalyzed Oxidation of THF. Pt black (19.5 mg, 0.1 mmol) was stirred in 1.0 mL of D_2O in a 5-mL pear-shaped flask sealed with a rubber septum. THF (40.5 μL, 0.5 mmol) was added through a microsyringe. After the solution was heated in an oil bath at 95 °C for 24–36 h under 1 atm of O_2, the flask was cooled in an ice–water bath and then left at room temperature for 30 min, while Pt black settled out. Finally, 0.6 mL of solution was taken for the ^{1}H-NMR spectrum which indicated the sole organic products were γ-butyrolactone and $DOCH_2CH_2CH_2COOD$ (96.0% combined yield relative to THF).

9. Pt-Catalyzed Oxidation of Diethyl Ether. Diethyl ether (21 μL, 0.2 mmol) was added to 1.0 mL of D_2O containing 19.5 mg (0.1 mmol) of platinum black. After the solution was heated at 95 °C under 1 atm of O_2 for 48–60 h, the ^{1}H-NMR spectrum indicated that the only organic compound was CH_3CO_2D (95.5% yield relative to ether).

When an identical solution was heated at 110 °C under 1 atm of O_2 for 14 h, the ^{1}H NMR spectrum indicated that the only organic species present were CH_3CO_2D (78.7%), $CH_3CO_2CH_2CH_3$ [δ, ppm: 3.96 (2 H, q, J_{H-H} = 7 Hz), 1.10 (3 H, t, J_{H-H} = 7 Hz), 1.95 (3 H, s)] (8.2%) and $CH_3CH_3OCH_2CH_3$ (13.1%).

10. Pt-Catalyzed Oxidation of Ethyl Acetate. $CH_3CO_2CH_2CH_3$ (20 μL 0.2 mmol) was added to 1.0 mL of D_2O containing 19.5 mg of platinum black. After the solution was heated at 95 °C under 1 atm of O_2 for 48 h, ^{1}H-NMR indicated that the only organic compound was CH_3CO_2H.

11. K_2PtCl_4 + $CH_3CH_2OCH_2CH_2OCH_2CH_3$ under O_2. K_2PtCl_4 (188 mg, 0.46 mmol) was dissolved in D_2O (6 mL) and O_2 was bubbled through it for 3–5 min. The solution was sealed in a reaction tube and ethylene glycol diethyl ether (65 μL, 0.46 mmol) added through a microsyringe. The contents were heated between 80 and 90 °C for 1 h. The ^{1}H-NMR spectra indicated that the sole products were $K[PtCl_3(CH_2{:}CH_2)]$, CH_3CHO, CH_3CO_2D [δ 1.98, s], and $OCHCH_2OCH_2CH_3$ [δ, ppm: 9.79 (1 H, t, J_{H-H} = 4.6 Hz), 4.45 (2 H, d, J_{H-H} = 4.6 Hz)].

12. K_2PtCl_4 + $CH_3CH_2(OCH_2CH_2)_2OCH_2CH_3$. The same procedure as given in 11 was used. After 2 h, the ^{1}H-NMR spectrum indicated that the major products were $K[PtCl_3(CH_2{:}CH_2)]$ and CH_3CO_2H.

13. K_2PtCl_4 + $CH_3O(CH_2CH_2O)_4CH_3$. A procedure similar to that described in 11 was used. $CH_3O(CH_2CH_2O)_4CH_3$ (51 μL, 0.23 mmol) was added to a solution of K_2PtCl_4 (94 mg, 0.23 mmol) in 6 mL of D_2O. After the solution was heated at 80 °C for 30 min, the platinum metal settled out. The ^{1}H-NMR spectrum indicated that the major product was $OCHCH_2OR$ [δ, ppm: 9.79 (1 H, t, J_{H-H} = 4.6 Hz), 4.45 (2 H, d, J_{H-H} = 4.6 Hz)].

14. Pt-Catalyzed Oxidation of Ethanol. CH_3CH_2OH (5.0 μL, 0.086 mmol) was added to 1.0 mL of D_2O containing 14.5 mg of platinum black. After the solution was heated at 95 °C under 1 atm of O_2 for 24 h, the ^{1}H NMR spectrum indicated that the only organic compound was CH_3COOD (yield 95.0% relative to CH_3CH_2OH).

15. Pt-Catalyzed Oxidation of Ethylene Glycol. A procedure similar to that described in 14 was used. $HOCH_2CH_2OH$ (5.0 μL, 0.090 mmol) was added to 1.0 mL of D_2O containing 14.5 mg of platinum black. After the solution was heated at 95 °C under 1 atm of O_2 for 48 h, the ^{1}H NMR spectrum indicated that the sole organic species present were $DOCH_2COOD$ [δ, ppm: 4.05 (s)] (90.0%) and $DOCH_2CH_2OD$ (10%).

Oxidation of Zeise's Salts,[6] $K[PtCl_3(CH_2{:}CH_2)]$. 1. $K[PtCl_3(CH_2{:}CH_2)]$ + Na_2PtCl_6. $K[PtCl_3(CH_2{:}CH_2)]$ (23.4 mg, 0.064 mmol) and $Na_2PtCl_6{\cdot}4H_2O$ (42.3 mg, 0.080 mmol) were dissolved in 0.6 mL of D_2O in a 5-mm NMR tube. The solution was heated at 75 °C for 3 h. The ^{1}H-NMR spectrum indicated that the sole organic products were $DOCH_2CH_2OD$ [δ, ppm: 3.55 (s)] (55%) and $ClCH_2CH_2OD$ [(δ, ppm: 3.82 (2 H, t, J_{H-H} = 6.3 Hz), 3.65 (2 H, t, J_{H-H} = 6.3 Hz)] (45%).

2. $K[PtCl_3(CH_2{:}CH_2)]$ + K_2PtCl_4. $K[PtCl_3(CH_2{:}CH_2)]$ (8.2 mg, 0.022 mmol) and K_2PtCl_4 (13.6 mg, 0.032 mmol) were dissolved in 0.8 mL of D_2O. After the solution was heated at 85 °C for 3 h, the ^{1}H-NMR spectrum indicated that the sole organic products were $DOCH_2CH_2OD$ (45.0%) and CH_3CO_2D (55.0%).

3. $K[PtCl_3(CH_2{:}CH_2)]$ + Na_2O_2 + DCl. Two drops of DCl (20% in D_2O) were added to a solution of Na_2O_2 (3 mg, 0.032 mmol) and $K[PtCl_3(CH_2{:}CH_2)]$ (8.0 mg, 0.022 mmol) in 0.7 mL of D_2O in a 5-mm NMR tube so that the pH of the solution was less than 1. After the solution was heated at 95 °C for 2 h, the ^{1}H NMR spectrum indicated that the only organic product was $DOCH_2CH_2OD$.

Oxidation of Alkanes. 1. K_2PtCl_4/Pt + $CH_3CH_3/O_2/Ar$. K_2PtCl_4 (41.5 mg, 0.1 mmol) was dissolved in 5 mL of D_2O in a glass container equipped with a magnetic stirring bar. After the K_2PtCl_4 was completely dissolved, Pt black (19.5 mg, 0.1 mmol) was added to the solution. The glass container was then placed in a high-pressure bomb which was sealed and pressurized to 500 psi with a mixture of $CH_3CH_3/O_2/Ar$ (ratio 36.2/4.2/59.6). Afterwards, the apparatus was placed in a 120–125 °C oil bath and the contents allowed to stir for 3–5 days. The bomb was then removed from the oil bath and cooled in an ice–water bath. The gases were vented and the reaction vessel opened. The glass container was taken out of the bomb and allowed to sit at room temperature for 30 min. When the Pt black had completely settled out, 0.8 mL of the solution was taken out for ^{1}H-NMR and GC analysis which indicated that the sole organic products were CH_3COOD and $DOCH_2COOD$. The yields of the product are shown below:

	yield (mmol)	
time (h)	CH_3CO_2D	$DOCH_2CO_2D$
68	0.084	0.032
109	0.100	0.020

2. K_2PtCl_4 + $CH_3CH_3/O_2/Ar$ + CO. K_2PtCl_4 (41.5 mg, 0.1 mmol) was dissolved in 5.0 mL of D_2O in a glass container. The glass container was placed in a high-pressure bomb which was then sealed. Afterwards the bomb was first pressurized to 200 psi with the $CH_3CH_3/O_2/Ar$ mixture, the pressurized to 230 psi with CO, and finally pressurized to 500 psi with the $CH_3CH_3/O_2/Ar$ mixture so that the partial pressure of CO was 30 psi. The remaining procedure was the same as reaction 1. After being heated at 100 °C for 24 h, the solution was analyzed by ^{1}H-NMR spectroscopy which indicated that the organic products were CH_3CO_2D, $CH_3CH_2CO_2D$ [δ, ppm: 2.45 (2 H, q, J_{H-H} = 7.5 Hz), 1.20 (3 H, t, J_{H-H} = 7.5 Hz)] and $DOCH_2CH_2OD$. The ratio of CH_3CO_2D to $CH_3CH_2CO_2D$ was approximately 5 to 1.

3. K_2PtCl_4/K_2PtCl_6 + CH_3CH_3/O_2. K_2PtCl_4 (20.8 mg, 0.05 mmol) and K_2PtCl_6 (24.3 mg, 0.05 mmol) were dissolved in 4 mL of D_2O in a glass container (K_2PtCl_6 was not completely soluble in D_2O). The glass container was placed in a high-pressure bomb which was then sealed. The bomb was purged and pressurized to 100 psi with O_2 and then pressurized with CH_3CH_3 to 550 psi. The ratio of CH_3CH_3 to O_2 was below the explosion limit.[17] The contents were stirred at 105 °C for 2 h following which ^{1}H-NMR spectrum indicated that the products were $K[PtCl_3(CH_2{:}CH_2)]$, CH_3CH_2OD, $DOCH_2CH_2OD$, and a trace of CH_3COOD (Figure 3).

4. K_2PtCl_6 + CH_3CH_3. K_2PtCl_6 (48.6 mg, 0.1 mmol) was dissolved in 5 mL of D_2O in a glass container. The glass container was placed in a high-pressure bomb which was then sealed and pressurized to 550 psi with CH_3CH_3. After the contents were heated at 100 °C for 24 h, the ^{1}H-NMR spectrum indicated that the only organic species present was CH_3CH_3.

5. K_2PtCl_4 + $CH_3CH_2CH_3/O_2/Ar$. A similar procedure as in 1 was employed. K_2PtCl_4 (50 mg, 0.12 mmol) was dissolved in 4 mL of D_2O in a glass container. The glass container was placed in a high-pressure bomb which was then pressurized with 220 psi of the gas mixture $C_3H_8/O_2/Ar$ (35.2/4.0/60.8). The contents were stirred at 110 °C for 2 h. The ^{1}H-NMR spectrum indicated the products in the solution were $K[PtCl(CH_2{:}CHCH_3)]$ [δ, ppm: 5.33 (1 H, m, J_{Pt-H} = 68.6 Hz), 4.39 (1 H, d, J_{H-H} = 8.9 Hz, J_{Pt-H} = 71.0 Hz), 4.38 (1 H, d, J_{H-H} = 12.7 Hz, J_{Pt-H} = 64.6 Hz), 1.55 (3 H, d, J_{H-H} = 6.2 Hz, J_{Pt-H} = 40.4 Hz)], $CH_3CH_2CH_2OD$ [δ, ppm: 3.52 (2 H, t, J_{H-H} = 6.6 Hz), 1.50 (2 H, m), 0.84 (3 H, t, J_{H-H} = 7.5 Hz)], $CH_3CH(OD)CH_3$ [δ, ppm: 3.85 (1, H, 7-plet, J_{H-H} = 7.6 Hz), 1.11 (6 H, d, J_{H-H} = 7.6 Hz)], and CH_3COCH_3 (Figure 4).

Synthesis of $K[PtCl_3(CH_2{:}CHCH_3)]$.[8] An aqueous solution of K_2PtCl_4 (142 mg in 2.0 mL) sealed in a high-pressure vessel and pressurized with 150 psi of propylene was stirred at room temperature for 36 h. The solvent was removed under vacuum. A yellowish solid remained and its ^{1}H NMR spectrum contained the following peaks (δ, ppm): 5.33 (1 H, m, J_{Pt-H} = 68.6 Hz), 4.39 (1 H, d, J_{H-H} = 8.9 Hz, J_{Pt-H} = 71.0 Hz), 4.38 (1 H, d, J_{H-H} = 12.7 Hz, J_{Pt-H} = 64.6 Hz), 1.55 (3 H, d, J_{H-H} = 6.2 Hz, J_{Pt-H} = 40.4 Hz).

K_2PtCl_4 + ICH_2CH_3. K_2PtCl_4 (41.5 mg, 0.1 mmol) was dissolved in 0.8 mL of D_2O in a 5-mm NMR tube sealed with a rubber septum. ICH_2CH_3 (8 μL, 0.1 mmol) was added to the solution through a microsyringe. The contents were allowed to stay at room temperature for 8 h. The ^{1}H-NMR spectra indicated the following: $K_2[PtCl_5(CH_2CH_3)]$ [δ ppm: 3.96 (2 H, q, J_{H-H} = 7.2 Hz, J_{Pt-H} = 86 Hz), 0.43 (3 H, t, J_{H-H} = 7.2 Hz)] and CH_3CH_2OD.

After the solution was allowed to stand in the NMR tube for 2 days, the ^{1}H-NMR spectrum indicated that the only species remaining was CH_3CH_2OH.

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For a comparison reaction, 8 mL of ICH_2CH_3 (0.1 mmol) was added to 0.8 mL of D_2O in a 5-mm NMR tube. After the solution was allowed to stand at room temperature for 2 days, the ^1H-NMR spectra indicated that ICH_2CH_3 was the only species in the solution.

Acknowledgment. This research was funded by grants from the National Science Foundation (CHE-8906587) and the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295). We thank Johnson Matthey, Inc. for a generous loan of platinum salts.

Registry No. THF, 109-99-9; K_2PtCl_4, 10025-99-7; Pt, 7440-06-4; O_2, 7782-44-7; $DO(CH_2)_3CO_2D$, 141981-61-5; CH_3COOD, 758-12-3; $DO(CH_2)_2OD$, 2219-52-5; $K[PtCl_3(CH_2{=}CH_2)]$, 12012-50-9; Na_2PtCl_6, 16923-58-3; K_2PtCl_6, 16921-30-5; $CH_3(CH_2)_2OD$, 4712-36-1; $DO(CH_2)_3OD$, 58161-12-9; $CH_3CH_2CO_2D$, 21388-62-5; HCO_2D, 925-94-0; CH_3COCH_3, 67-64-1; $K[PtCl_3(CH_2{=}CHCH_3)]$, 12075-59-1; $CH_3CO_2CH_2CH_3$, 141-78-6; $CH_3CH_2OCH_2CH_2OCH_2CH_3$, 629-14-1; CH_3CHO, 75-07-0; $OCHCH_2OCH_2CH_3$, 22056-82-2; $CH_3CH_2(OCH_2CH_2)_2OCH_2CH_3$, 112-36-7; $CH_3O(CH_2CH_2O)_4CH_3$, 143-24-8; $OCHCH_2O(CH_2CH_2O)_3CH_3$, 141981-62-6; CH_3CH_2OH, 64-17-5; $HOCH_2CH_2OH$, 107-21-1; $DOCH_2COOD$, 81278-02-6; $ClCH_2COOD$, 1837-59-8; CH_3CH_2OD, 925-93-9; $Cl(CH_2)_2OD$, 14848-86-3; CO, 630-08-0; $CH_3CH(OD)CH_3$, 3979-51-9; ICH_2CH_3, 75-03-6; $K_2[PtCl_5(CH_2CH_3)]$, 141981-63-7; H_2O, 7732-18-5; ethane, 74-84-0; propane, 74-98-6; γ-butyrolactone, 96-48-0; diethyl ether, 60-29-7; acetic acid, 64-19-7; di-*n*-propyl ether, 111-43-3; diisopropyl ether, 108-20-3; propylene, 115-07-1.

Homogeneous Catalysis: A Ruthenium-Based Lewis-Acid Catalyst for the Diels–Alder Reaction

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Abstract: In order to circumvent some of the inherent drawbacks of using traditional Lewis acids to catalyze the Diels–Alder and other Lewis-acid-promoted reactions, a ruthenium-based catalyst has been devised. The readily prepared catalyst is *trans*-$[Ru(salen)(NO)(H_2O)]SbF_6$, where salen is the *N,N′*-bis(salicylidene)ethylenediamine dianion ligand. It has been fully characterized; it is stable to oxygen and can be handled under normal laboratory conditions. At 1 mol % loadings, the catalyst accelerates Diels–Alder reactions by many orders of magnitude over the corresponding thermal reaction. In many cases, accelerations of $>10^5$ are observed. The catalysis proceeds even in the presence of water. Slight product inhibition is observed, but the catalyst will continue to turn over substrates indefinitely. The binding of the Diels–Alder adduct of methacrolein and isoprene with the catalyst has been examined. Binding of the dienophile is stronger than that of the adduct. It is found that binding of the dienophile is endoergic, exchange of the aquo ligand is rapid and reversible, and a competitive equilibrium exists between the aquo species and the dienophile adduct. Overall, the catalyst is a mild Lewis acid which promotes Diels–Alder reactions of aldehyde and ketone dienophiles but not of α,β-unsaturated esters. Its mild Lewis-acid characteristics, however, serve to suppress polymerization even with sensitive substrates.

The classical Diels–Alder reactions involving, among others, α,β-unsaturated aldehydes, ketones, and 1,3-dienes are known to be promoted by Brønsted[1] and Lewis acids.[2] Moreover, the Lewis-acid-induced transformations always lead to higher stereoselectivities than do the corresponding thermal reactions. The most commonly used Lewis acids are the lighter halides of tervalent boron and tetravalent titanium and tin. For reasons which we discuss presently, these species are generally employed in stoichiometric or greater proportions. Even when the Lewis acids are used at catalytic levels, the loadings are generally high, of the order of 20 mol %. Many of these catalytic species have been modified by incorporation of chiral ligands. Although these modifications lead to less active Lewis acids, they are capable of engaging in enantioselective transformations. Remarkably high enantiomeric excesses have been obtained, generally at low temperatures, for the classical and hetero Diels–Alder reactions.[3] As a practical matter, these successes represent important achievements but attempts to understand the mechanisms of catalysis and selectivity present a formidable challenge because of the complexity of the chemical behavior of these modified Lewis acids. Consequently, the design of these modified chiral catalysts is largely dependent on intuition and on untested suppositions about the origins of the selection. It is for these reasons that we have searched for less complicated Lewis-acid systems. This is the first in a series of papers which attempts to circumvent the intrinsic problems associated with the use of classical Lewis acids for enantioselective catalysis. We describe a Lewis–acid catalyst derived from a transition metal which has many unique characteristics, including its potential rational modification into an asymmetric catalyst.

General Considerations

The traditional Lewis acids, BX_3, AlX_3, TiX_4, and SnX_4, have a number of undesirable or inconvenient characteristics. Among these is, first, their extreme sensitivity to water, which is one of the reasons that they are generally employed at high catalytic loadings. Second, binding between traditional Lewis acids and the oxygen atoms of the dienophile and of the product is generally thermodynamically strong, and in some cases exchange may be

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