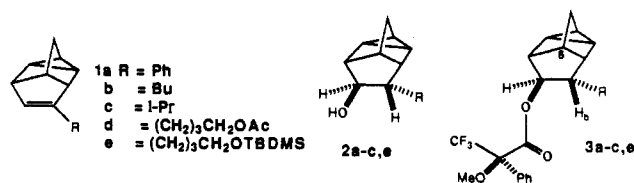the ee's were confirmed by integration of the NMR shifts of the diastereotopic protons formed upon complexation with Ag-(FOD)/Eu(hfbc)₃.[16]

In **3a**, the benzylic proton, H_b, in the diastereomers was clearly resolved at 200 MHz. Integration of the resonances appearing at 3.40 and 3.29 ppm provided a measure of the diastereomeric excess, which then gave the ee.[15a] The absolute stereochemistry of the cycloadducts can be assigned by using the method first described by Mosher.[15b,17] In the extended conformations depicted in **3a** and *enant*-**3a**, or their corresponding Newmann projections, the proton syn to the phenyl ring, H_b, is further upfield in **3a** due to through-space interaction with Ph_a. The assignment of the absolute stereochemistry was confirmed by X-ray crystallography.[18] *S,S*-Chiraphos gives the cycloadduct with the absolute
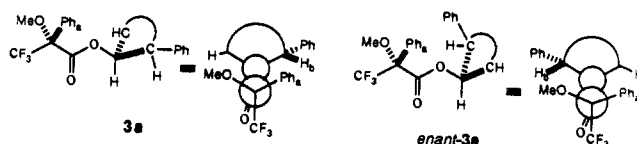
stereochemistry as depicted in **1a**, while *R*-prophos gives *enant*-**1a** as the predominant product. The ratios of diastereomers for **3b**, **3c**, and **3e** were easily measured by integration of the H_6 resonances, which were well-resolved at 400 MHz, at ca. 2.05 and ca. 2.15 ppm for the two diastereomeric esters.[19] The absolute stereochemistry of these derivatives was assumed by analogy to be the same as that determined for **3a** since the downfield resonance (for H_6) was the major signal observed in **3a** as well as in the other adducts prepared with *S,S*-chiraphos.

The effects of temperature, solvent, amount of catalyst, and acetylene structure on the enantioselectivity were examined (Table I). The ee of **1a**, using *S,S*-chiraphos, improved as the temperature was decreased, entries 1 and 2. Reaction at <20 °C gave little cycloadduct. Hexyne and norbornadiene gave **1d** in high chemical and optical yield in the presence of 2 mol % of catalyst at ca. 30 °C, entry 4, which rose to 91% ee when less catalyst was used, entry 5. Since the reaction is quite exothermic, this increase in ee is presumably a result of maintaining the internal reaction temperature closer to the optimum value of ca. 27 °C. The amount of catalyst used was varied as a means of obtaining optimal ee's. There is a trade-off between high chemical yields that tend to occur with higher amounts of catalyst and high ee's that arise from lower reaction temperatures. *R*-Prophos gave the enantiomeric adduct with good levels of selectivity. We noted a decrease in the ee in a coupling between NBD and hexyne with THF as solvent; this may be due to complexation of the solvent oxygen, entries 5 and 7. Increasing steric bulk near the acetylene also results in lower selectivity or no reaction. For example, cycloaddition between norbornadiene and 3-methylbutyne in benzene gave **1c** in high chemical yield but relatively low ee, 36%. In this

instance the use of *R*-prophos was marginally more effective than *S,S*-chiraphos.

An acetylene bearing a remote oxygen also reacted with high enantioselectivity. However, we have found the choice of protecting group and solvent to be critical variables, entries 10–12. A side-chain oxygen which is capable of intramolecular coordination to the cobalt, entry 11, disrupts the complexation of the phosphine, NBD, and acetylene, which appears to be required for highly selective reactions. This effect was overcome through the use of a protecting group bearing a more remote oxygen, entry 10, or by carrying out the reaction in THF, which competes for a coordination site and displaces the OTBDMS group (entries 5 and 7 vs 11 and 12). In these reactions 4 mol % of catalyst was used so as to obtain reasonable yields and reactions times.

From these data we conclude that the structure of the active complex is similar to that first proposed by Lyons[11a,b] in which the chelating phosphine, norbornadiene, and acetylene are simultaneously coordinated to the cobalt. The methyl(s) in the connecting chain of the chiral phosphine ligand control the orientation of the phenyl rings, which in turn determines the position of the acetylene R group so as to minimize nonbonding interactions. Similar arguments have been used to explain enantioselectivity observed in other systems with *S,S*-chiraphos.[20]

In conclusion, we have demonstrated for the first time that a highly enantioselective cobalt-catalyzed homo Diels–Alder reaction can be performed with chiral phosphines.

Supplementary Material Available: General experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the prepared compounds (9 pages). Ordering information is given on any current masthead page.

(16) (a) Wenzel, T. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1982,** *104,* 382. (b) Offermann, W.; Mannschreck, A. *Org. Magn. Reson.* **1984,** *22,* 355.

(17) For the use of *O*-methylmandelate esters see: ref 15b and: (a) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986,** *51,* 2370. (b) Roy, B.; Deslongchamps, P. *Can. J. Chem.* **1985,** *63,* 651.

(18) The crystal used for the structure determination was obtained by crystallization of a diastereomeric mixture of **3a** and *enant*-**3a** from pentane. *enant*-**3a** crystallized selectively as colorless needles. ¹H NMR showed that the crystals had the sense of induction that is predominant from reactions with *R*-prophos. Details of the structure will be reported by Dr. Alan Lough.

(19) The values were consistent with those obtained from the ¹⁹F spectrum. The upfield peak was the major signal in the ¹⁹F spectrum for samples prepared with *S,S*-chiraphos.

(20) Yamamoto, A. *Organotransition Metal Chemistry: Fundamental Concepts and Applications;* Wiley-Interscience: New York, 1986; p 368.

Selective Hydroxylation of Methyl Groups by Platinum Salts in Aqueous Medium. Direct Conversion of Ethanol to Ethylene Glycol

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Many intriguing examples of the activation of C–H bonds in alkanes by transition-metal complexes, often under remarkably mild conditions, have appeared in the last few years.[1] However, major barriers to development of a practical alkane conversion process remain. In particular, most systems studied are incompatible with O_2, the most desirable co-reagent to obtain a thermodynamically favored, economically viable catalytic reaction. Also, potential products (alcohols, alkenes, etc.) are often more reactive than the starting alkanes, which limits achievable yields. The latter is especially problematical when a hydrogen atom abstraction route is involved, as with P-450 and models thereof.

(1) (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes;* D. Reidel: Dordrecht, 1984. (b) Crabtree, R. H. *Chem. Rev.* **1985,** *85,* 245. (c) Hill, C. L., Ed. *Activation and Functionalization of Alkanes;* Wiley-Interscience: New York, 1989.
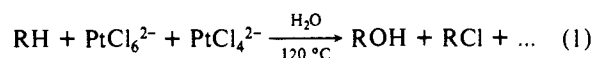
Shilov's Pt^{II}–Pt^{IV} system (eq 1)[2] appears attractive in that the

$$RH + PtCl_6^{2-} + PtCl_4^{2-} \xrightarrow[120\,°C]{H_2O} ROH + RCl + ... \quad (1)$$

species involved will tolerate O_2, although catalytic oxidation has not yet been achieved; nor is much known about detailed mechanism or selectivity. In an attempt to further delineate the mechanism we have examined oxidation of *water-soluble* model substrates and report here unexpected findings of selectivity.

p-Toluenesulfonic acid (**1**) is oxidized by the Pt^{II}–Pt^{IV} system according to eq 2, with *sequential* formation of alcohol **2** and aldehyde **3**.[3] No products resulting from reaction at aromatic ring positions could be detected by NMR. Solutions appear to remain homogeneous during the first few hours of the reaction, although eventual deposition of platinum metal was observed in all cases.[4]
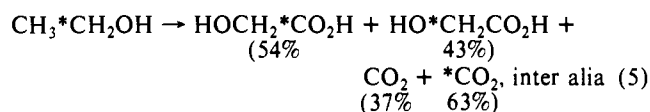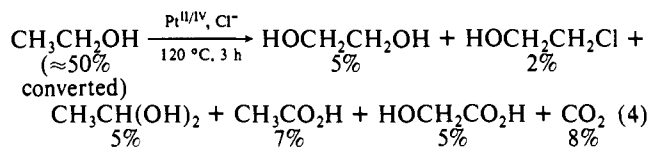
$$p\text{-}HO_3SC_6H_4CH_3 \xrightarrow[H_2O,\ 80-120\ °C,\ 6\ h]{Pt^{IV}/Pt^{II},\ Cl^-} \underset{\mathbf{2}}{ArCH_2OH} \rightarrow \underset{\mathbf{3}}{ArCHO}$$
$$\underset{\mathbf{1}}{\phantom{p\text{-}HO_3SC_6H_4CH_3}}$$
$$(2)$$
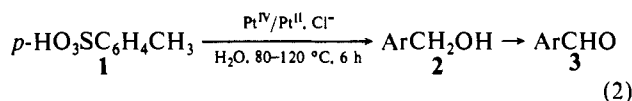
While neither the progress of the reaction over time nor the dependence on $[Pt^{II}]$ or $[Pt^{IV}]$ could be fit to any simple rate law,[5] from the *initial* rate of product appearance it appears that (i) reaction rates correlate much more strongly with $[Pt^{II}]$ than $[Pt^{IV}]$ (Pt^{IV} may even be omitted and the oxidation still proceeds; in this case precipitation of Pt metal begins immediately) and (ii) oxidation of **2** to **3** proceeds about 2/3 as rapidly as that of **1** to **2**,[6] while oxidation of **3** is much slower still.[7] Substantial oxidation occurs at the β position of the ethyl analogue of **1** (eq 3),[8] indicating that benzylic activation is not required for these reactions.

$$^-O_3SC_6H_4CH_2CH_3 \rightarrow$$
$$\mathbf{4}$$
$$ArCH_2CH_2OH + ArCH(OH)CH_3 + \text{ring oxidation} \quad (3)$$

These selectivity patterns are clearly incompatible with a radical mechanism. The fact that CH_3 can be *more* reactive than CH_2OH suggests the possibility that an alcohol might be oxidized to a glycol instead of, or in addition to, the expected[9] aldehyde. Indeed, when

ethanol is substituted for **1** in reaction 2, up to 5% ethylene glycol is produced, along with additional products are shown in eq 3.[10] When $^{12}CH_3^{13}CH_2OH$ is used as substrate, the glycolic acid produced is labeled nearly equally in the two positions (eq 5), demonstrating that it arises mostly (>90%) via oxidation of ethylene glycol rather than hydroxylation of acetic acid. The CO_2 shows an excess of ^{13}C, suggesting that around 40% comes from oxidative decarboxylation of acetic acid and 60% from ethylene glycol, presumably via oxalic acid.

$$CH_3CH_2OH \xrightarrow[120\,°C,\ 3\ h]{Pt^{II/IV},\ Cl^-} HOCH_2CH_2OH + HOCH_2CH_2Cl +$$
$$\underset{\substack{(\approx50\% \\ \text{converted})}}{} \underset{5\%}{} \underset{2\%}{}$$
$$CH_3CH(OH)_2 + CH_3CO_2H + HOCH_2CO_2H + CO_2 \quad (4)$$
$$\underset{5\%}{} \underset{7\%}{} \underset{5\%}{} \underset{8\%}{}$$

$$CH_3{}^*CH_2OH \rightarrow HOCH_2{}^*CO_2H + HO^*CH_2CO_2H +$$
$$\underset{(54\%}{\phantom{CH_3{}^*CH_2OH}} \underset{43\%)}{}$$
$$CO_2 + {}^*CO_2,\ \text{inter alia} \quad (5)$$
$$\underset{(37\%}{} \underset{63\%)}{\phantom{{}^*CO_2}}$$

From these labeling studies it appears that roughly *equal* amounts of products deriving from attack at the methyl and hydroxymethyl groups of ethanol are formed. This result is striking: *any* direct conversion of ethanol to ethylene glycol appears to be unprecedented in the literature. Even higher selectivity for oxidation at the methyl group is found for 1-propanol: at 25% conversion, selectivities are 48% to 1,3-propanediol and 30% to 3-chloro-1-propanol.

Remarkable selectivity for attack at C–H has been recently reported in oxidative additions of alcohols and epoxides to reactive metal centers.[11] We propose that selectivity, in the latter as well as the present system, is determined by the initial M–H–C interaction and is probably mainly of steric origin. Although the oxidations demonstrated here are not catalytic, the selectivity is not outstanding, and the rates are too low for practical application, the specificity for methyl group hydroxylation coupled with the stability toward oxidizing conditions suggests considerable potential for further development.

Note Added in Proof. Ethylene glycol is also obtained on heating Zeise's salt, $[PtCl_3(C_2H_4)]^-$, with Pt^{IV}; however, the rate is much too slow for Zeise's salt to be an intermediate in eq 4.

(2) Reference 1a, pp 163–182; ref 1c, pp 3–11. Related chemistry has also been found for Pd^{2+}: Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* **1987**, *109*, 8109.

(3) Reactions were carried out in D_2O solution (initial concentrations 0.2–0.4 M **1**, 0.2–0.4 M Na_2PtCl_6, and 0.02–0.05 M Na_2PtCl_4) in sealed NMR tubes, which were heated in an inverted position to avoid interference from Pt metal particles or mirrors. Products were identified and quantitated by NMR; compound **2** was independently synthesized by literature methods (Hubbuch, A.; Bindewald, R.; Fohles, J.; Nuithani, V. K.; Zuhn, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 394). In a typical experiment 31% of **1** was converted, with selectivities to **2** and **3** (based on converted **1**) of 80% and 20%, respectively, and overall mass balance (relative to a weighed amount of an NMR reference added at the end of the reaction) 102%. At the higher $Pt^{IV}/1$ ratios, formation of some R–Cl products is observed as well.

(4) This raises the question of possible heterogeneous activation. Addition of metallic mercury (Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855) does *not* completely suppress oxidation; there is some decrease in rate, attributable to the fact that Hg^0 reduces both Pt^{II} and Pt^{IV}. Other observations also support a homogeneous mechanism.

(5) This is not unexpected, as the solution contains a *mixture* of species $(PtCl_n(H_2O)_{4-n}^{(2-n)+}; PtCl_n(H_2O)_{6-n}^{(4-n)+})$ whose relative concentrations (along with $[Cl^-]$) are continually changing as reaction proceeds.

(6) The relative reactivities of **1** and **2** are obtained both from the initial rates with use of each as substrate and by fitting data for reaction 2 to a simple kinetic model, although for the latter it was necessary (in the absence of any reliable rate law) to ignore the (probably) complex dependence on [Pt]. Similarly, an Eyring plot of initial rate data collected from 80 to 122 °C gives $\Delta H^* = 26$ kcal mol^{-1}, $\Delta S^* = 11$ eu; but without a rate law the significance of these parameters is unclear.

(7) Conversion of **3** is inferred from the appearance of additional weak NMR signals in the aromatic region toward the end of reaction 2; these have not been assigned, but they do *not* correspond to the expected *p*-$HO_3SC_6H_4$-CO_2H that was independently synthesized: Smiles, S.; Harrison, D. C. *J. Chem. Soc.* **1922**, *21*, 2023.

(8) Under the same conditions as above,[3] with 30% conversion of **4**, selectivities are 24% β, 35% α, and 30% ring oxidation; mass balance is 97%. Oxidation of **4** in the conjugate acid form gives a product whose NMR suggests a coordinated styrene derivative, presumably resulting from acid-catalyzed dehydration of the alcohol products of eq 3.

(9) Stern, E. W. In *Transition Metals in Homogeneous Catalysis*; Schrauzer, G. N., Ed.; Dekker: New York, 1971; pp 107–8.

(10) Conditions are the same as in eq 2, except that acid (e.g., 1 equiv of HCl/Pt^{IV}) must be added to stabilize the system against early precipitation of Pt metal. Two-carbon products were identified by ^1H and ^{13}C NMR, using un-, mono- and di-^{13}C-labeled ethanol; all shifts, J_{CH} and J_{CC} values, agree with literature data (including acetaldehyde, which in aqueous solution exhibits ^{13}C signals characteristic of the hydrate: Chastrette, F.; Bracoud, C.; Chastrette, M.; Mattioda, G.; Christidis, Y. *Bull. Soc. Chim. Fr.* **1985**, 66). The presence and amount of ethylene glycol was further verified by gas chromatography. CO_2 was quantified by Toepler pump transfer to a volumetric bulb and thence to a cell for infrared spectroscopic identification; the expected frequency shift is found when ^{13}C-labeled ethanol is oxidized, confirming the origin of the CO_2. About 65% of the consumed ethanol is accounted for in eq 4; a number of signals in the ^1H and ^{13}C NMR spectra (mostly weak) remain to be assigned. Peaks for several products show evidence for partial H/D exchange. Complete spectral details will be reported in a full paper.

(11) For example, ethylene oxide preferentially adds a C–H bond to Rh rather than opening the strained C–O bond (which does occur at higher temperatures (Wu, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7628); similarly, with *tert*-butyl alcohol Ir inserts into a C–H, not an O–H, bond (Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704).