low values for e^2qQ/h reported for the two deuterides studied are reasonably consistent with the present results.

Using the magnitude of the splitting observed in the upper spectrum of Figure 1, 8.8 kHz, in eq 1, it is possible to calculate the Mn–D distance. We assume that the field gradient tensors on Mn and D are colinear. Since this is necessarily the case in the isolated molecule, and since there is very little distortion in the crystals, it appears a very safe assumption. The fact that the asymmetry parameter is approximately zero for D, and very nearly so for ^{55}Mn is additional indication that the field gradient tensors are aligned along the Mn–D axis. The calculated value for the Mn–D distance from the observed splitting is 1.61 Å with an uncertainty of about 0.01 Å, in excellent agreement with the diffraction result.[4]

The SEDOR experiment, first performed at zero or very low magnetic field by Emshwiller, Hahn, and Kaplan,[12] has received little attention. Ragle and coworkers have employed it in essentially the same manner we have to obtain several D quadrupole coupling constant data, using ^{35}Cl spin echoes as the indicator nuclear channel.[13-15] The present results, however, are the only ones of which we are aware in which a clearly defined dipolar splitting has been seen. It is apparent from this example, that application of the SEDOR technique to other hydride complexes of the transition metals has the potential for yielding interesting information about M–D bonds. In addition to observing terminal M–D bonding in species such as $DRe(CO)_5$, $DCr(CO)_5^-$, $DCo(CO)_4$, and $HCo[P(C_6H_5)_3]_3N_2$, the technique may be very useful in more precisely defining the nature of bridge bonding situations, as in $H_3Mn_3(CO)_{12}$, $H_3Re_3(CO)_{13}$, $HRe_3(CO)_{14}$, and many others.

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A Chiral Electrode

Sir:

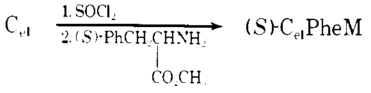
Although electrode surfaces can be altered by adsorption it would be of interest to more drastically and permanently modify the surface by covalently binding molecules to it. If a method for securely anchoring such molecules could be found, advantage could be taken of the molecular structure to build surfaces with unique and widely varying properties. Indeed, the attached molecules could be used in the sense of chemical reagents to perform reactions in tandem with the electron transfer processes characteristic of chemically inert electrodes. In the present case a chiral electrode surface was synthesized and used to perform an asymmetric reduction.

Heating graphite in air produces acidic surface oxides, some of which have been chemically characterized as carboxylic acids.[1] Our initial approach was to bind optically active amino acids to these sites via amide bonds, thereby providing a stable, chiral interfacial region for electrochemical reactions.

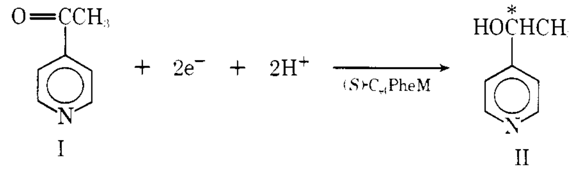
Spectroscopic grade graphite rods (4 in × 0.25 in., density = 0.65 g/cm^3) were baked in air at 160° for 36 hr. This introduced acidic groups which could be titrated with base.[1,2] Modification of these oxidized electrodes was accomplished by first treating them with thionyl chloride in dry benzene for 24 hr. This was followed by reaction with 1 g of (*S*)-(−)-phenylalanine methyl ester ((*S*)-(−)-PheM) in 50 ml of methylene chloride. Crystals of phenylalanine methyl ester hydrochloride formed in the solution indicating that reaction between the amino acid and acid chloride was successful. After 24 hr the electrodes were removed, and then soaked in 100 ml of 0.5 *M* acetate buffer for 4 hr. These modified electrodes, (*S*)-C_{el}PheM, were indistinguishable by eye or sweep voltammetry (−0.5 to −1.5 V, acetate buffer, sweep rate 5 mV/sec) from the unmodified version.

The reduction of 4-acetylpyridine was chosen for initial study. This ketone reduces at relatively positive potentials[3] and the expected product, alcohol(II), has been characterized.[4] All reductions were performed under N_2 at −1.05 V vs. SCE in a three-compartment cell, and the catholyte was 100 ml of 0.5 *M* acetate buffer, 100 ml ethanol. When the (*S*)-C_{el}PheM was used as a cathode, addition of I (0.5 ml, 4.5 mmol) caused an increase in current from 8 to 32.5 mA. The current decayed to 19 mA after a period of 320 min (1.10 faraday/mol). The catholyte was then reduced to 40 ml volume on a rotary evaporator. This was made basic (pH 10) with solid Na_2CO_3 and extracted with three 50-ml portions of ether. The combined extracts were washed with saturated NaCl solution and dried over anhydrous calcium sulfate. The solution was filtered and evaporated to give a clear, water white oil. The oil (0.5 g) was analyzed by NMR and showed only I and II in the ratio 48:52. GLC collection of the product at 107° from an SE-30 column resulted in a colorless oil (45 mg) identified by comparison with an authentic sample of II. The electrolysis product had $\alpha_{OBS} = -0.325$, $[\alpha]^{20}D$ −7.22 (c = 3, $CHCl_3$). Reinjection on the GLC gave only one peak. Recollection gave an identical specific rotation.

Reduction of I to II on an electrode treated with $SOCl_2$ in benzene followed by buffer acetate soaking proceeded very similarly. The yields of II were again high, but it was optically inactive.



$$C_{el} \xrightarrow[2.\,(S)\text{-}PhCH_2\underset{\displaystyle CO_2CH_3}{\underset{|}{C}}HNH_2]{1.\,SOCl_2} (S)\text{-}C_{el}PheM$$

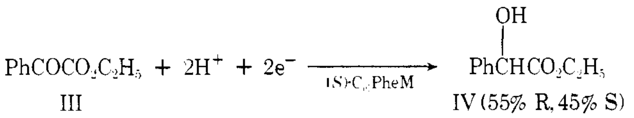


The absolute configuration and specific rotation of II have been reported.[4] However, both we and others[5] have demonstrated that the reported rotation is too low and a reliable[6] absolute rotation is not available.

It was established that this electrode could be used again (isolated II, $[\alpha]^{20}\text{D}$ −4.2°) and that an electrode with the *R* configuration could be synthesized. This (*R*)-C_{el}PheM produced II, $[\alpha]^{20}\text{D}$ +6.1. A further control experiment was then undertaken. It is known that optically active alkaloids in solution can lead to asymmetric induction.[7] Indeed, it has been shown that reduction of 4-acetylpyridine on a mercury electrode in the presence of alkaloids gives optically active II.[5] We, therefore, reduced I on an untreated graphite electrode in the presence of 0.015 *M* (*S*)-PheM. Although catalytic hydrogen evolution was noted from the amino acid, this was suppressed by addition of I and alcohol II was produced as the major product. After GLC purification this alcohol had a rotation $\alpha_{OBS} = -0.015$. A second trial gave $\alpha_{OBS} = +0.025$.

It is concluded that no asymmetric induction occurred and the origin of the activity from (*S*)-C_{el}PheM reductions is, on the surface, not from material cleaved and in solution. The state of the amino acid during reduction is not known. In particular the ester moiety is susceptible to reaction and may not be intact.

The reduction of ethyl phenylglyoxylate (III) on this chiral electrode was also performed. Using the above procedure and (*S*)-C_{el}PheM the alcohol IV was formed in 94% yield at −1.05 V. It was purified by GLC, characterized spectrally, and had $[\alpha]^{20}\text{D}$ −12.5° (*c* = 0.8, $CHCl_3$). Pure IV was prepared from optically pure (+)-mandelic acid and found to have a rotation of +128.4° (*c* = 1.2, $CHCl_3$). The observed asymmetric induction corresponds, therefore, to an optical purity of 9.7%.



$$\underset{\text{III}}{PhCOCO_2C_2H_5} + 2H^+ + 2e^- \xrightarrow[(S)\text{-}C_{el}PheM]{} \underset{\text{IV (55\% R, 45\% S)}}{PhCH(OH)CO_2C_2H_5}$$

The above results demonstrate the principle of covalently modified electrodes. The particular examples are easily and inexpensively prepared, and it would seem that such modified electrodes would have substantial applications in preparative and analytical electrochemistry and in energy conversion. In essence, one can combine the selectivity of chemical processes with the catalytic nature of an electrode for electron transfer processes to perform selective, catalytic redox processes.

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Stereoselective Bifunctional Catalysis of the Dedeuteration of Cyclopentanone-*2,2,5,5-d$_4$*[1]

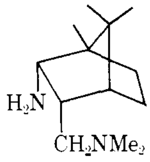
Sir:

Certain monoprotonated primary-tertiary diamines have been found to catalyze the dedeuteration of acetone-d_6 and isobutyraldehyde[2] via formation of an iminium ion, which is dedeuterated internally by attack of the tertiary amino group. We have now found marked stereoselectivity in such catalysis.

Dedeuteration of cyclopentanone-*2,2,5,5-d$_4$* in the presence of perchloric acid or monofunctional bases follows Scheme I, in which the rate is proportional to the number of deuterium atoms present.[3] The sample kinetic plot in Figure 1 could be used for any such catalyst if the log *t* scale were renumbered to apply to the appropriate *k* value. In the presence of monoprotonated (1*R*,2*S*,3*R*,4*R*)-3-dimethylaminomethyl-1,7,7-trimethyl-2-norbornanamine (**1**),[4] however, two of the deuterium atoms exchange faster than the other two. This is explained by Scheme II, where k_d and k_l are rate constants, per deuterium atom, for removal of the two different types of deuterium atoms attached to the prochiral α carbon atoms of the ketone. Equations for the fraction of ketone present as D4, D3, etc., as a function of k_d, k_l, and the time were obtained by application of the operator method[5] and neglect of the D0, D1, and D2 present in the starting material, which was about 91% D4 and 8% D3. The results obtained in a run using **1** and the corresponding theoretical curves based on these equations are shown in Figure 2. The results are consistent with Scheme II and not with Scheme I, which demands that the D1 concentration reach a maximum before eight half-lives for the disappearance of D4 (rather than >100 D4 half-lives, as observed).

Scheme I

$$\text{D4} \xrightarrow{4k} \text{D3} \xrightarrow{3k} \text{D2} \xrightarrow{2k} \text{D1} \underset{}{\overset{k}{\rightleftharpoons}} \text{D0}$$



1

Scheme II

$$\begin{tikzcd}
\text{D4} \arrow[r, "2k_d"] \arrow[d, "2k_l"'] & d\text{-D3} \arrow[r, "k_d"] \arrow[d, "2k_l"'] & d\text{-D2} \arrow[d, "2k_l"'] \\
l\text{-D3} \arrow[r, "2k_d"] \arrow[d, "k_l"'] & \text{i-D2} \arrow[r, "k_d"] \arrow[d, "k_l"'] & d\text{-D1} \arrow[d, shift right, "k_l"'] \\
l\text{-D2} \arrow[r, "2k_d"] & l\text{-D1} \arrow[r, shift left, "k_d"] & \text{D0} \arrow[l, shift left] \arrow[u, shift right]
\end{tikzcd}$$

A partly dedeuterated sample containing about 68% D2, 17% D1, and 13% D3 showed at 277 nm the largest absolute rotation (Figure 3) we are aware of for a compound whose optical activity is wholly an isotope effect. This rotation was shown to arise from the ketone rather than an impurity by the observation of racemization in the presence of 3-dimethylaminopropionitrile at a rate corresponding to a primary kinetic isotope effect (k_H/k_D) of 3.4. Application of the octant rule[6,7] in its simplest form to the positive Cotton effect in the vicinity of the uv absorption maximum of the ketone (noting the larger atomic polarizability of protium