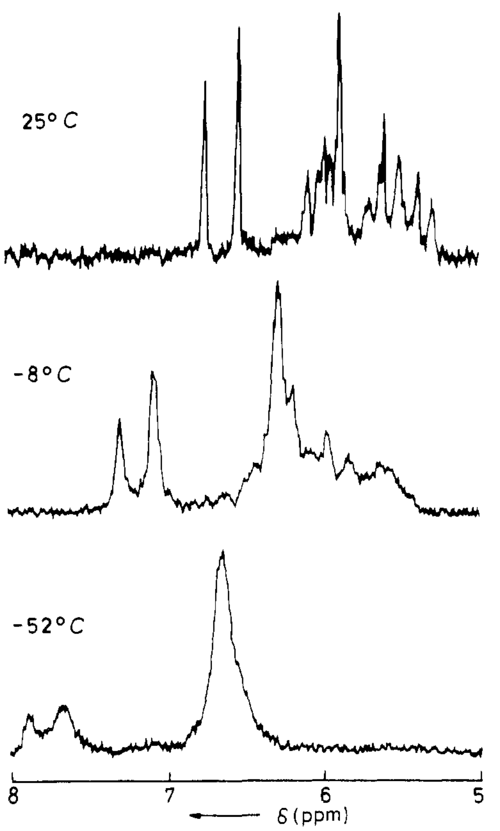
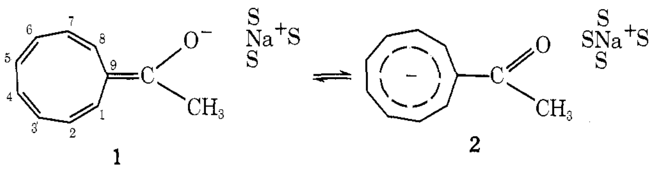


Figure 1. ^{1}H NMR spectral characteristics of the equilibrium $1 \rightleftharpoons 2$ in THF at 25, −8, and −52 °C. Chemical shifts are in parts per million from Me_4Si.



S = THF

perature from 25 to −52 °C. **1** and **2** are prepared from 9-acetyl-*cis,cis,cis,cis*-cyclonona-1,3,5,7-tetraene and sodium bis(trimethylsilyl)amide or sodium hydride in THF. Figure 1 shows the ^{1}H NMR spectrum at *25 °C* (δ_{rel} (Me_4Si internal standard) 5.25–6.10 (m, H^2–H^7), 6.62 (d, H^1 and H^8, J = 12.5 Hz),[3] which resembles closely the spectra of the corresponding Li^+ salt in THF and the silyl enol ether in $CDCl_3$.[4] This and the facile transformation ($\tau_{1/2}$ at 50 °C, 25 min) into the dihydroindene valence isomer[4] support the fulvenoid structure **1**. The spectrum at −52 °C (δ_{rel} 6.31–6.88 (m, H^2–H^7), 7.78 (br d, H^1 and H^8)) on the other hand, is essentially the same as the spectrum of the aromatic K^+ salt in THF.[4] Thus, at −52 °C the aromatic ion pair **2** is the preferred one. *Between 25 and −52 °C* (as, e.g., at −8 °C) one observes spectra with weighted average values. Therefore, one can estimate a rate constant $k \geq 330\ s^{-1}$ for the exchange $1 \rightleftharpoons 2$, corresponding to $\Delta G^{\ddagger}(-52\ °C) \leq 10.2$ kcal mol^{-1}.

The temperature dependence and the differences in the structures of the species **1** and **2** are in agreement with known properties of anion-Na^+ and solvent-Na^+ interactions.[1,2,5] At 25 °C, the enolate oxygen is closely bound to Na^+ to give **1**, most likely a contact ion pair.[2] It is only at lower temperatures that the donor abilities of the THF oxygen[6] enable it to compete successfully for a near-neighbor site[5] at Na^+ to form **2** ($\Delta H°$ = −6.9 kcal mol^{-1}; $\Delta S°$ = −30 eu), supposedly a solvent separated ion pair.[7] This is in accord with the ^{1}H NMR observation that only **2** is formed in 1,2-dimethoxyethane.

In summary, we have demonstrated that the concentration of the aromatic anion **2** can be a *function of temperature* owing to ion-pair effects. Furthermore, the system **1**–**2** is a very simple and sensitive probe for the study of solvent-M^+ interactions.

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Facile Attachment of Transition Metal Complexes to Graphite Electrodes Coated with Polymeric Ligands. Observation and Control of Metal–Ligand Coordination among Reactants Confined to Electrode Surfaces

Sir:

Intense recent research on the modification of electrode surfaces by chemical treatments[1] has included several instances in which polymeric materials were attached to electrodes[2–5] or appear to be formed during the attachment procedures.[6,7] Electrochemical responses from attached polymers containing ferrocene centers[2,5–7] have been observed, but electrochemical monitoring of the binding of metal ions to an attached polymeric ligand has not previously been reported. We have found conditions under which polymers containing functional groups that are good ligands for metal ions can be quickly and strongly attached to graphite electrode surfaces. The resulting surfaces extract metal complexes from solution by coordination and the oxidation and reduction of the attached complex can be readilly observed and controlled electrochemically.

In this report we describe representative examples in which ruthenium complexes are attached to graphite electrodes coated with polyvinylpyridine (PVP) or polyacrylonitrile. The simplicity and speed of the polymer attachment and metalation procedures, the longevity of the resulting electroactive coatings, and the availability of a large variety of polymeric ligands indicate that the same general method may be used to prepare electrode surfaces that will accept almost any desired metal cation. The obvious potential that such electrode surfaces hold for exploitation in electrocatalytic cycles supplied much of the incentive for the present investigation.

Pyrolytic graphite disks with the graphite basal planes exposed were sealed into glass tubing with heat-shrinkable polyolefin tubing and electrical contact was made to the rear

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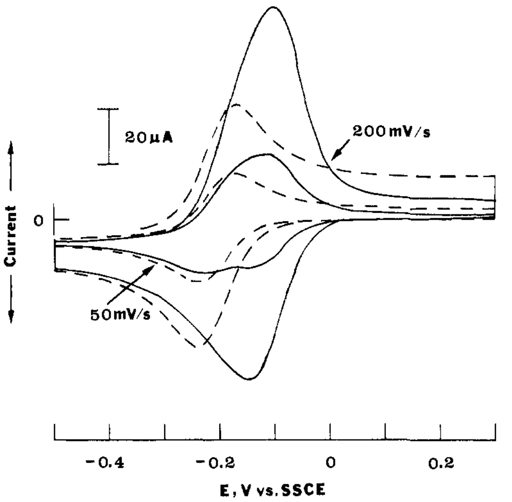

Figure 1. Cyclic voltammograms at basal plan pyrolytic graphite electrodes for a 1.0 mM Ru(III)EDTA solution: (- - -) uncoated electrode; (—) PVP-coated electrode. Scan rates: 50 and 200 mV s^{-1}. Supporting electrolyte: 0.2 M CF_3COONa at pH 3.2. Reference electrode: sodium chloride saturated calomel electrode (SSCE).

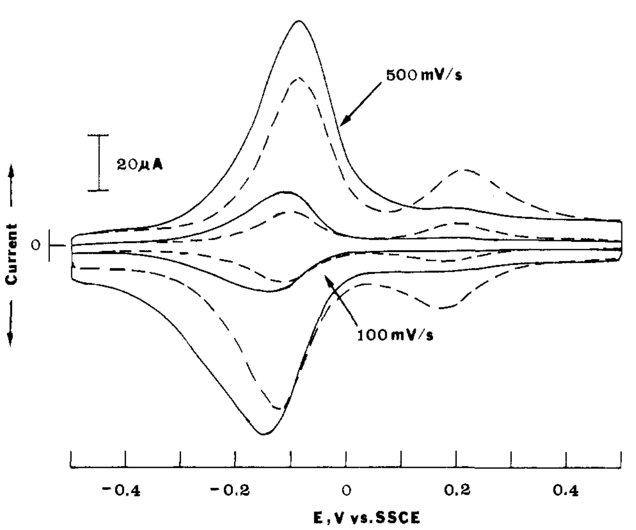

Figure 2. Steady-state cyclic voltammograms for Ru(III)EDTA bound to a PVP-coated graphite electrode in the absence of unattached complex. The coated electrode was immersed in a 1 mM Ru(III)EDTA solution for 15 min, washed with water, and transferred to a 0.2 M CF_3COONa at pH 3.2 where the voltammograms were recorded with scan rates of 100 and 500 mV s^{-1}: (—) after 30 min; (- - -) after 3.5 h.

face of the disk. A fresh surface was produced by cleaving the disk in air with a scalpel and the polymer was applied by immersing the disk for 15 min in a 0.5% solution of poly(4-vinylpyridine) in methanol. After copious washing with methanol and water, the electrode was placed in an aqueous solution of the EDTA complex of Ru(III) where cyclic voltammograms were recorded. Figure 1 compares the resulting voltammograms with those obtained in the same solution with an uncoated electrode.

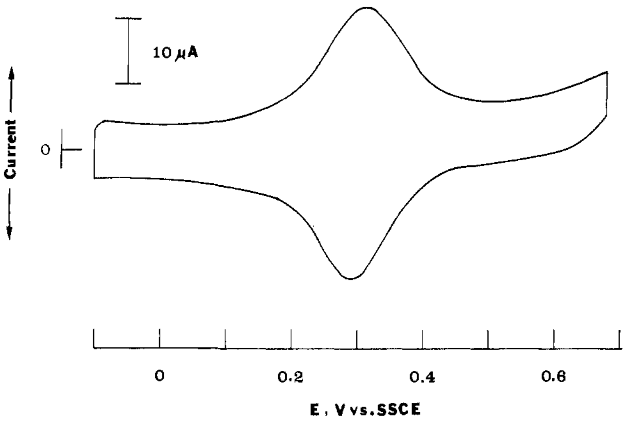

Figure 3. Steady-state cyclic voltammogram for the pyrolytic graphite electrode surface obtained by dip coating from a 0.35% solution of polyacrylonitrile in dimethyl sulfoxide, followed by washing and exposure to an aqueous solution containing 2 mM $Ru(NH_3)_5OH_2^{2+}$ for 30 min. The resulting electrode was washed with water and transfered to 0.2 M CF_3COONa at pH 3.2 where the voltammogram was recorded with a scan rate of 200 mV s^{-1}.

The rapid binding[9,10] of the Ru(III)EDTA complex to the PVP-coated electrode surface is revealed by the greater area of the voltammogram obtained with the coated electrode along with the presence of the double wave in the cathodic half of the cycle caused by the differences in the potential and symmetry[11] of the voltammograms for the attached and unattached reactant. When the electrode was washed thoroughly with water and transferred to a solution containing only supporting electrolyte, the voltammograms in Figure 2 were obtained. They exhibit the symmetrical shape and linear dependence of peak current on scan rate that are characteristic of an attached reactant.[11] The area under the voltammograms corresponds to 4–5 × 10^{-9} mol cm^{-2} of attached Ru–EDTA. This amounts to ~50 times more complex than could be accommodated in a monolayer. Even greater quantities of the complex can be attached by prolonging the time that the coated electrode is soaked in the Ru–EDTA solution, but the additional complex leaves the surface much more quickly than the initially attached complex.

The peak potential of the prominent wave in the initial voltammogram in Figure 2 matches the formal potential of the pyridine complex of Ru(III)EDTA.[12] The transformation of the initial voltammogram containing a single wave into the voltammogram with two waves (the dashed curves in Figure 2) occurs gradually if the electrode is maintained at a potential where the ruthenium is in its reduced state. The transformation is essentially complete after ~3 h at pH 3.2. A similar transformation occurs in the voltammogram for the reduced complex in homogenous solution at pH 7 in the presence of a fivefold excess of pyridine. The more positive formal potential of the second wave, which falls within 30 mV of that for the second wave that develops with the PVP-coated electrode, clearly signals the coordination of a second pyridine molecule to the Ru(II) center. We therefore believe that the second wave in Figure 2 corresponds to Ru–EDTA complexes that form cross-links between two pyridine residues in the polymer coating. Such cross-linked structures have been reported for a variety of transition metal PVP complexes.[13] The total area under the two voltammetric waves decreased very little during the development of the second wave which indicates that the species responsible for the wave is formed without major loss of ruthenium from the surface. Even after 4 h, <10% of the Ru–EDTA was lost from the electrode surface so long as its potential was maintained at values which maintained the Ru in oxidation state +2. If the potential is maintained at values where the Ru is in the +3 oxidation state, no second wave develops and the quantity of Ru–EDTA attached decreases more rapidly (e.g., two thirds is lost in 2 h). However, the depleted surface can be restored to its initial state by reimmersion in a Ru(III)EDTA solution showing that the PVP coating remains intact. These results demonstrate that both the lifetime and the coordination of the attached complex can be observed and controlled by appropriate manipulation of the potential of coated electrodes.

PVP-coated electrodes also react with $Ru(NH_3)_5OH_2^{2+}$ to produce an attached complex. In addition, both $Ru(NH_3)_5OH_2^{2+}$ and Ru(III)EDTA undergo attachment reactions with electrodes that are dip coated with polyacrylonitrile from dimethyl sulfoxide. The cyclic voltammogram for the attached pentaamine polyacrylonitrile complex, Figure 3, has an average peak potential that is shifted by almost 500 mV from that of the aquopentaamine complex to which the coated electrode was exposed. It falls very close to the reported formal potential of the corresponding acetonitrile complex measured in homogeneous solution.[14]

The nature of the surface chemistry which is responsible for the strong, long-lived attachment of the polymeric ligands to graphite surfaces has thus far been examined only cursorily. It was determined that pyrolytic graphite with edge planes exposed to the coating solutions could also be coated with PVP, but the resulting voltammograms for attached Ru(III)EDTA were more distorted and contained a larger number of smaller waves. This suggests that the presence of extensive oxygen functionality on the graphite may lead to less uniform environment within the polymer coatings. Platinum electrodes are also susceptible to dip coating by PVP, but the resulting films accept much smaller quantities of Ru-EDTA. Additional exploratory experiments are underway in these laboratories to extend the range of polymers, attachable metal complexes, and electrode materials that can be combined to yield electrode surfaces with catalytic and analytical utility.

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Rhenium Formyl and Carboxy Complexes Derived from the $(C_5H_5)Re(CO)_2(NO)^+$ Cation: Models for the Fischer–Tropsch and Water Gas Shift Reactions

Sir:

The conversion of coal into liquid fuels and petrochemicals is currently dependent upon the heterogeneous catalysis of the oxidation of CO in the water gas shift reaction 1[1] and of the reduction of CO as in the Fischer–Tropsch reaction 2.[2] The development of homogeneous analogues for both the catalysts and proposed intermediates involved in reactions 1 and 2 is the primary goal of much current research.[3,4]

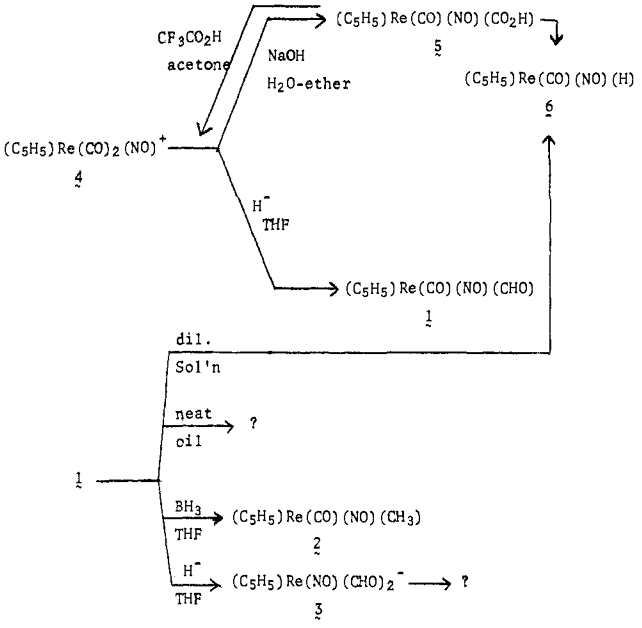
$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (1)$$

$$CO + H_2 \longrightarrow C_nH_{2n+2},\ C_nH_{2n+2}O_n,\ \text{etc.} \qquad (2)$$

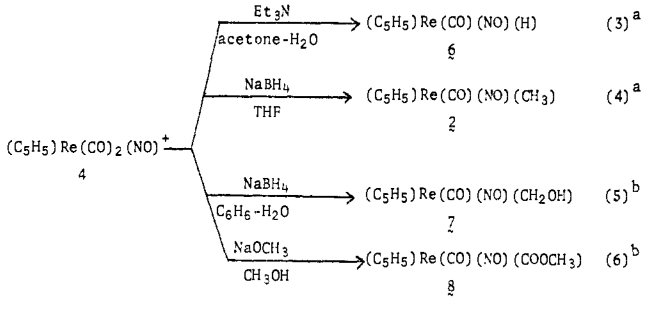
We,[4k] and others,[4e,5a,b] have recently reported the reduction of metal carbonyl compounds by borohydride reducing agents to give anionic metal formyl complexes which are models for initial intermediates in CO reduction.[2] The moderate kinetic stability observed for these anionic metal formyl compounds may be related to the delocalization of negative charge onto the formyl oxygen atom. We have now initiated studies of neutral metal formyl complexes to see if these compounds might also be stable. Previously, only two partially characterized neutral metal formyl complexes have been reported. $Os(Cl)(CO)_2(PPh_3)_2(CHO)$[5c] and $Ru(H)(Et_2O)(PPh_3)_3(CHO)$.[5d] Neutral formyl compounds were also desired for studies of the further reduction of metal formyl complexes since they should be more susceptible to reduction than anionic complexes.

We report here the synthesis and characterization of a neutral metal formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ (**1**), together with its subsequent reduction with borane to give $(C_5H_5)Re(CO)(NO)(CH_3)$ (**2**) and with lithium triethylborohydride to give the first diformyl metal complex $(C_5H_5)Re(NO)(CHO)_2^-$ (**3**) (Scheme I). In addition, we have reinvestigated the chemistry of $(C_5H_5)Re(CO)_2(NO)^+$ (**4**) (Scheme II)[6,7] and have prepared the new carboxy metal complex $(C_5H_5)Re(CO)(NO)(CO_2H)$ (**5**) which is an intermediate in the reaction of cation **4** with water to give

Scheme I. New Chemistry of the $(C_5H_5)Re(CO)_2(NO)^+$ Cation



Scheme II. Previously Reported Chemistry of the $(C_5H_5)Re(CO)_2(NO)^+$ Cation



[a] Reference 6. [b] Reference 7.

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