

- (13) IR, ν_{CO} , CH_2Cl_2 : 1700, 1671 cm^{-1} ; ^1H NMR, τ , CDCl_3 , 4.48 (s, 10 H), 4.59 (s, 10 H) at -50°C ; ^{13}C NMR, δ_c , CH_2Cl_2 , 235.6 dt ($J_{\text{Rh-C}} = 49$ Hz, $J_{\text{Rh-C}} = 35$ Hz) at -63°C . Compound 4 displays fluxionality below room temperature, in contrast to its cobalt analogue.¹⁴ The dynamic behavior of 4 will be discussed separately.
- (14) K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Organomet. Chem.*, **97**, 283 (1975).
- (15) The electron-impact mass spectrum of 1 is complex and shows evidence for $\text{Cp}_4\text{Rh}_4(\text{CO})_2^+$ (m/e 728), as previously reported.^{2a} In our hands (170 $^\circ\text{C}$, 70 eV) the intensity ratio (588/728) was ca. 3/1. We attribute the appearance of tetramer peaks to thermal decomposition of 1 in the probe (see footnote 11). In contrast, the field-desorption spectra of 1 and 4, with ionization at room temperature, show only the molecular ions for each compound.
- (16) Spectra were obtained on a Jeol Fx-60 spectrometer at 15.03 MHz, accumulating ca. 20 000 pulses for each spectrum. Solutions ($\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$ or $\text{CH}_2\text{Cl}_2/(\text{CD}_3)_2\text{CO}$) were saturated in 1 and ca. 0.015 M in $\text{Cr}(\text{acac})_3$.
- (17) A similar process has been suggested for carbonyl scrambling in $\text{Fe}_3(\text{CO})_{12}$ ^{18a} which apparently occurs with a very low activation barrier.^{18b} See also ref 6.
- (18) (a) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4155 (1974); (b) F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).
- (19) However, only one Cp resonance should be observed. Similar patterns of equilibration (incomplete for the carbonyls) should obtain for $\text{Cp}_3\text{Co}_3(\text{CO})_3$, which apparently adopts solution structures related to 2.²⁰
- (20) F. A. Cotton and J. D. Jamerson, *J. Am. Chem. Soc.*, **98**, 1273 (1976).

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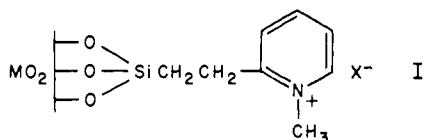
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Chemically Modified Electrodes. 3. SnO_2 and TiO_2 Electrodes Bearing an Electroactive Reagent

Sir:

In an emerging new approach to electrochemistry, the surfaces of carbon^{1,2} and tin oxide^{3,4} electrodes have been chemically modified with several covalently attached reagents. The electrode surfaces exhibit the reagents' properties, such as inducing chirality in electrochemical processes¹ and surface base protonation equilibria.^{2,3} We report here the first examples of chemically modified electrode surfaces which bear a covalently anchored⁵ electroactive reagent. Such chemically modified electrodes present opportunities for fundamentally new approaches to the study of electrochemical reactions and to the tailoring of electrode surfaces for specific electrocatalytic properties.

The electrode materials employed are F-doped SnO_2 films (~ 5000 Å, 5 Ω square) on glass,³ and TiO_2 films (est. 1000 Å) on titanium prepared by anodization (15% H_2SO_4 , 20% NaH_2PO_4 , 50 V) of polished titanium^{7,8} followed by heating in 10% H_2 (in N_2 , 400 $^\circ\text{C}$) for several hours.⁹ The surfaces of both electrodes were reacted with β -trichlorosilyl(2-ethyl)pyridine in benzene under anhydrous conditions¹⁰ and then with refluxing neat CH_3I . The surface molecule sought is



The silanization of SnO_2 electrodes has been demonstrated;³ chemical modification of TiO_2 electrode surfaces has not been previously reported. We will refer to the chemically modified electrodes I as $\text{TiO}_2/\text{py}(\text{CH}_3)^+$ and $\text{SnO}_2/\text{py}(\text{CH}_3)^+$.

Figure 1 shows N 1s ESCA spectra of various TiO_2 electrodes. Following silanization (curve B), pyridine N 1s appears at 400.0 eV. Methylation (curve D) produces a new band with binding energy (401.5 eV) quite close to that of N 1s in authentic methylpyridinium iodide (curve C). An analogous set of ESCA N 1s spectra is obtained for SnO_2 electrodes. The methylation reaction is not quantitative on either electrode ($\sim 50\%$ on TiO_2 , $\sim 70\%$ on SnO_2). ESCA spectra of the surface

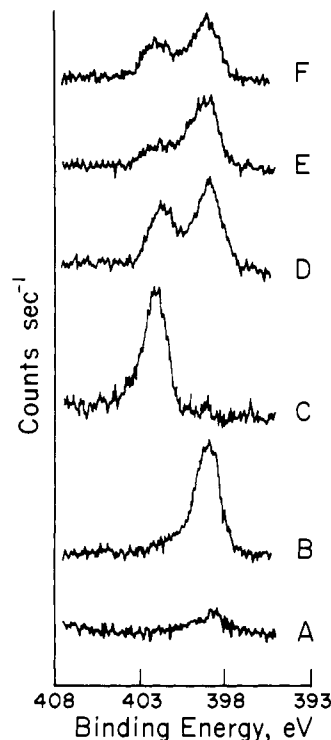


Figure 1. ESCA N 1s spectra of chemically modified TiO_2 electrodes. Binding energies are referenced to C 1s at 285 eV. Curve A is blank TiO_2 .

counterion X^- after exposure of the electrode to solutions of various anions (I^- , Br^- , Cl^- , ClO_4^- , BF_4^-) show that X^- is readily exchangeable. The ESCA results are consistent with the expectations of I above, except that the actual number of MOSi bonds is undetermined.

Alkylpyridinium ions are electroreducible¹² but have not been studied in CH_3CN solvent. The initial (one electron) reduction product is thought to undergo dimerization. Figure 2 illustrates cyclic voltammograms in CH_3CN of free $\text{py}(\text{CH}_3)^+$ and of the surface molecule I. On a Pt electrode (curve A) free $\text{py}(\text{CH}_3)^+$ shows an irreversible current peak -1.32 v vs. SCE and shows a reoxidation wave at -0.15 V. Exhaustive reduction (coulometric $n \approx 1$) of free $\text{py}(\text{CH}_3)^+$ enhances the -0.15 V wave; reoxidation of the product solution, presumably the mentioned dimer, regenerates $\sim 80\%$ of the original cation wave. On an unmodified TiO_2 film electrode (curve B), the irreversible free $\text{py}(\text{CH}_3)^+$ wave appears at -1.56 V. No reoxidation wave is seen, unsurprisingly, since its potential (on Pt) lies anodic of the flat band potential of the n-type TiO_2 semiconductor electrode.^{13,14}

A fresh $\text{TiO}_2/\text{py}(\text{CH}_3)^+$ electrode exhibits an irreversible reduction wave (curve C, Figure 2) at a potential (-1.35 ± 0.04 V) close to free $\text{py}(\text{CH}_3)^+$ on Pt. An immediate repeat scan yields a current envelope (curve D) identical with a background scan¹⁵ on an unmodified TiO_2 electrode. Potentiostating a reduced $\text{TiO}_2/\text{py}(\text{CH}_3)^+$ electrode at 0.0 V for a few minutes, however, regenerates reproducibly $\sim 30\%$ of the original surface wave as seen on the cathodic sweep, curve E. These results indicate that on TiO_2 the surface species I is indeed electroreducible, and that its reduction product remains bound to the electrode and can be reoxidized. ESCA data support this view. Curve E of Figure 1 shows that the 401.5 eV quaternary nitrogen band is substantially eliminated on a $\text{TiO}_2/\text{py}(\text{CH}_3)^+$ electrode reduced at -1.8 V. Curve F shows a $\text{TiO}_2/\text{py}(\text{CH}_3)^+$ electrode first reduced, then reoxidized at 0.0 V; the pyridinium N 1s band returns to an extent consistent with the electrochemistry. That the reoxidizable surface species is actually the 4,4' dimer of I is consistent with (but not proven

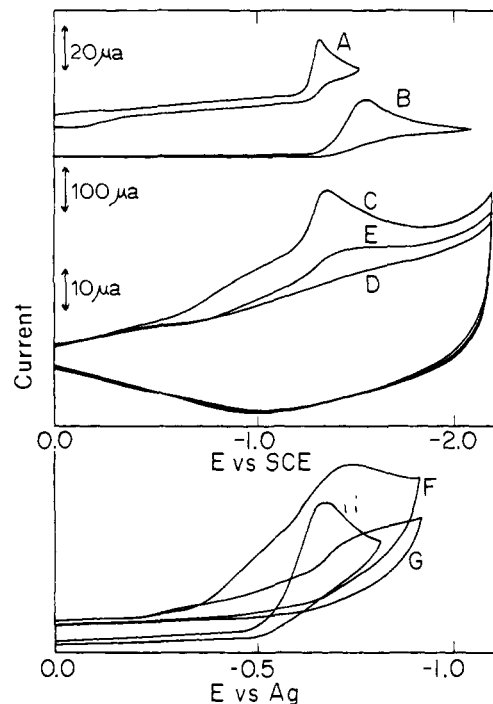


Figure 2. Cyclic voltammograms in 0.2 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$. Curves A,B (0.1 V/s) and H (0.05 V/s) are free $\text{py}(\text{CH}_3)^+$ on unmodified electrodes. Curves C-E (0.50 V/s) and F, G (0.050 V/s) are $\text{MO}_2/\text{py}(\text{CH}_3)^+$.

by) these data. Given its rectifying properties,^{13,14} the observed reoxidation reaction at TiO_2 may be somewhat unusual. We note, however, that the TiO_2 films used may be too thin for development of a full semiconductor space charge, that the reoxidation rate is quite slow, and that chemical modification as used here could introduce new surface states.

$\text{SnO}_2/\text{py}(\text{CH}_3)^+$ electrodes also exhibit a cathodic wave (curve F) ascribable to reduction of I. In this case, three-four repeat scans are required before the current falls to a steady background (curve G). The $\text{SnO}_2/\text{py}(\text{CH}_3)^+$ reduction peak is ~ 0.010 V negative of that for free $\text{py}(\text{CH}_3)^+$ (curve H) on unmodified SnO_2 . The ESCA N 1s spectrum of reduced $\text{SnO}_2/\text{py}(\text{CH}_3)^+$ confirms reduction of the quaternary nitrogen; the X^- counterion spectrum also disappears. Although oxidations are observed on these heavily doped SnO_2 electrodes,³ we have not observed reoxidation of a reduced $\text{SnO}_2/\text{py}(\text{CH}_3)^+$ electrode to regenerate the cathodic peak of curve F.

The surface population Γ of $\text{MO}_2/\text{py}(\text{CH}_3)^+$ centers is estimable from the charge passed in the cyclic voltammograms for their electrochemical reduction. The estimate is complicated somewhat by the broad background current enhancement¹⁶ which is observed on both electrodes and which vanishes after a reduction cycle. On $\text{TiO}_2/\text{py}(\text{CH}_3)^+$ assuming $n = 1$, $\Gamma = 2.0 \pm 0.2 \times 10^{-9}$ mol/cm² and 2.6×10^{-10} mol/cm² (average of five electrodes) based respectively on inclusion of, and correction for, this background. The corrected analysis on $\text{SnO}_2/\text{py}(\text{CH}_3)^+$ is 0.8×10^{-10} mol/cm². The corrected analysis is quite compatible with a molecular model estimate ($\sim 4 \times 10^{-10}$ mol/cm²) of monolayer coverage of $\text{py}(\text{CH}_3)^+$ on the MO_2 surfaces. Surface roughness (factor $< 2\times$ estimated by microscopic examination) and unmethylated surface pyridine are partially self-cancelling factors not included in this coverage estimate.

Electroactivity of I requires a steric "floppiness" of the electroactive center allowing a close approach to the electrode, as the connecting chain is electronically insulating. Neighbor-neighbor steric interferences could thus interfere with the electron transfer event. That I is shown in fact to be electro-

active, on two electrode materials, demonstrates that the strategy of immobilizing electron transfer sites on electrodes using flexible yet insulating molecular architecture can be successful. Other examples of electrochemically active chemically modified electrodes, and a more detailed analysis of the $\text{MO}_2/\text{py}(\text{R})^+$ electrodes, are subjects of continuing investigations.

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- (15) The unusual shape of this background is due to the high sweep rate and current sensitivity plus the electrode's semiconductor properties.
- (16) This background current is absent on some specimens and has been observed on modified electrodes bearing other electroactive groups.

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Synthesis of a Doubly Alkylated Binuclear Cobalt Carbonyl Complex. Generation of Acetone, a Process Involving the Formation of Two New Carbon-Carbon Bonds, in Its Thermal Decomposition

Sir:

The past few years have seen the development of several methods for carbon-carbon bond formation which employ mononuclear organometallic complexes as catalysts or stoichiometric reagents; recent mechanistic investigations have begun to elucidate the patterns by which these reagents operate.¹ The field of *binuclear* C-C bond forming processes is much less well-developed (despite the possible relevance of such processes to reactions promoted by clusters and heterogeneous catalysts²), partly because of the limited number of complexes available having alkyl groups bound to adjacent metal centers. In connection with this problem, we wish to report the preparation and thermal decomposition of a doubly alkylated binuclear complex (**2**). We find that this material decomposes under mild conditions in a reaction which forms *two* carbon-carbon bonds with surprising efficiency, and report preliminary data that provide an insight into the mechanism of this transformation.

The bistrisphenylphosphineiminium salt of bis-(η^5 -cyclo-