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Synthesis and Reactivity of Modified Electrodes Derived from $TiCl_4$ and Other Early-Transition-Metal Complexes

Stanton Ching,* Elie A. Tabet, Raymond C. Dudek, and Joseph P. Magiera

Department of Chemistry, Connecticut College, New London, Connecticut 06320

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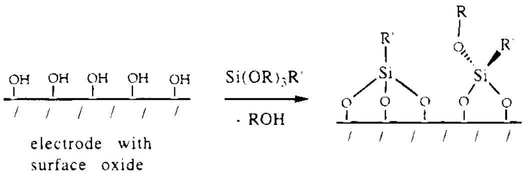
Glassy carbon (GC) and Pt electrodes have been derivatized with $TiCl_4$ and other early-transition-metal complexes in reactions analogous to those of moisture-sensitive silanes. The modified electrodes have been characterized by cyclic voltammetry and scanning Auger microscopy. The electrode surfaces are proposed to have a thin multilayer coating of metal oxide which supports a metal oxychloride overlayer. Reactions of electrodes with $TiCl_4$ result in complete surface coverage, whereas treatment with other early-transition-metal halides yields partial coverage. The surface films of supported metal complexes are not electroactive and apparently do not influence the electrochemistry of soluble redox probes such as ferrocene and TCNQ. Reactivity of $TiCl_4$-treated electrodes has been explored with reagents containing hydroxyl and thiol groups. Exposure to moisture causes rapid hydrolysis of surface Ti−Cl bonds. Treatment with alcohols is believed to give surface Ti alkoxides. Reaction with (hydroxymethyl)ferrocene produces a modified surface with supported electroactive ferrocene moieties. Reaction with 6-ferrocenylhexanethiol generates electrodes having pendant ferrocenes anchored by Ti thiolate bonds. Attempts to derivatize electrodes with various other organometallic titanium complexes result in either no reaction or formation of surface-confined species that are unstable to cyclic voltammetric analysis. Overall, the characteristics of modified electrodes derived from $TiCl_4$ are very similar to those of silane-modified electrodes. However, $TiCl_4$-modified electrodes appear more amenable to subsequent to reactions with molecules containing thiol functionality.

Introduction

Direct reactions of molecular reagents with surface functional groups are established methods of generating chemically modified electrodes.[1−5] This approach has been used in the design and construction of a wide variety of electrode systems, many of which have assisted in fundamental studies of electron transfer. Modified electrodes have also been prepared for potential applications in microelectronics and electrocatalysis. Numerous synthetic strategies have been devised for direct reactions of molecular species with electrodes. One of the most prominent is the reaction of a moisture-sensitive silane with a hydroxylated electrode surface (eq 1A). This general procedure provides access to a wide variety of systems due to the considerable diversity of organosilane chemistry. An analogous method of surface modification employs hydrolytically unstable early-transition-metal complexes to generate supported metal species (eq 1B). This approach is mainly used to derivatize solid oxide surfaces of heterogeneous catalysts.[6−9] Surprisingly, readily hydrolyzed transition metal complexes have not been exploited for introducing metal centers onto electrode surfaces. Indeed, prior to our initial communication of electrode modification with $TiCl_4$,[10] there was only one other reported system prepared by this strategy.[11] The system described in the literature was generated by using chromium carboxylic acid complexes to modify tin oxide electrodes.[11] The chromium centers were proposed to be directly bonded to the surface as well as cross-linked through bridging hydroxyl ligands.



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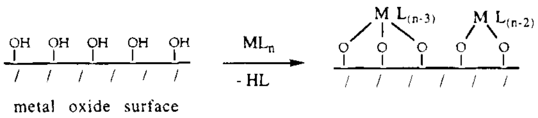

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We have several motivations for wanting to study modified electrodes with supported early-transition-

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metal complexes. First, we have a general interest in creating new modified electrode systems. Reactions of silanes on electrode surfaces have been thoroughly investigated, but analogous chemistry with early-transition-metal complexes has not been explored. The variety of transition-metal complexes with hydrolytically unstable metal−ligand bonds offers a potentially large pool of precursors for new modified electrode systems. Second, early-transition-metal species can act as Lewis acids on surfaces and may therefore promote unique electrochemical reactions. Supported silanes, by contrast, do not function as Lewis acids. Third, early-transition-metal species on electrodes are potentially active sites for electrocatalysis. Supported electropositive metals and metal complexes have been shown to be effective promoters in heterogeneous catalysis, but their influence in electrocatalytic processes is unknown.

This paper focuses on the synthesis and reactivity of glassy carbon and platinum electrodes having supported early transition metal halides. Particular attention is given to electrodes modified with $TiCl_4$. We establish for the first time that the general reactions developed for anchoring silanes to electrode surfaces are also applicable to hydrolytically unstable early-transition-metal halides. Cyclic voltammetry and Auger electron spectroscopy have been the principal methods of characterization. Preliminary results have been communicated.[10]

Experimental Section

Methods and Materials. All manipulations were carried out under a prepurified N_2 atmosphere using standard Schlenk line and syringe techniques[13] or in a Braun MB-150-M glovebox. Reagent-grade solvents were distilled from appropriate drying agents[14] and stored under N_2 prior to use. $TiCl_4$ (Aldrich) was used without further purification and stored under N_2 as a 10% solution in hexane. (Hydroxymethyl)ferrocene (HMFc), $CpTiCl_3$, Cp_2TiCl_2, $Ti(OEt)_4$, $NbCl_5$, $TaCl_5$, and WCl_6 (Strem) were used as received. $ZrCl_4$ (Strem) was sublimed prior to use. $TiCl_3(OC_6H_5)$,[15] $TiCl_2(OC_6H_5)_2$,[16] and 6-ferrocenylhexanethiol[17] were prepared according to published procedures. The $[Bu_4N][PF_6]$ supporting electrolyte was prepared from $[Bu_4N]Br$ and HPF_6 using a procedure analogous to that of $[Bu_4N][BF_4]$.[18]

Instruments and Equipment. Cyclic voltammograms were recorded with either a Bioanalytical Systems CV-1B potentiostat coupled with a Yokogawa 3025 $X-Y$ recorder or a Bioanalytical Systems CV-50W computer driven potentiostat. Glassy carbon (GC) electrodes were fabricated either from Teflon-shrouded 4.0-mm disks mounted on brass rods or from 2.0-mm rods sealed in Teflon tubing. Pt electrodes were fabricated either from Teflon-shrouded 4.0-mm disks mounted on brass rods or from 1.5-mm wires sealed in Teflon tubing. The GC (V 25 grade) and Pt (99.95%) were obtained from Atomergic Chemetals and Johnson Matthey, respectively. Final polishing of GC and Pt electrodes was carried out with 1 μm alumina powder and 1 μm diamond paste (Buehler), respectively. The polished electrodes were thoroughly rinsed and sonicated with distilled deionized water. Electrochemistry was typically carried out using 0.1 M $[Bu_4N][PF_6]$ in CH_3CN with a Pt wire auxiliary electrode and either a Ag wire quasi-reference electrode or a $Ag/AgNO_3$ reference electrode.

Auger electron spectroscopy was performed with a Perkin-Elmer PHI 610 scanning Auger microprobe. Analyses were carried out on 10−15 spots that were spaced at 60−100 μm intervals. The spot size was 1 μm. Control experiments with untreated electrodes gave no evidence of contamination due to residual halide or transition metal species. Air-sensitive samples were handled with a Perkin-Elmer Model 04−100A vacuum transfer vessel.

Electrode Pretreatment. Glassy carbon electrodes were pretreated to optimize surface hydroxyl groups. The method used was a variation of the one employed by Kuwana and coworkers.[19] Polished GC electrodes were baked in air at 70 °C for a minimum of 12 h. The electrodes were then exposed to a slurry of $LiAlH_4$ in Et_2O at room temperature for 3 h. Surfaces were cleaned by rinsing twice with 1 M HNO_3 followed by thorough rinsing with distilled deionized water. Platinum electrodes were pretreated by standard anodization in 1 M H_2SO_4.[20] Both GC and Pt electrodes were dried under vacuum for at least 1 h prior to use.

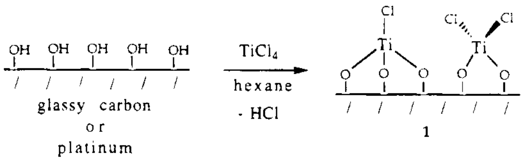
Electrode Treatment with Metal Halides. Pretreated GC and Pt electrodes received similar handling in surface modification reactions with early-transition-metal halides. Reactions with $TiCl_4$ were carried out using 10% hexane solutions for 1 h. Reactions with $ZrCl_4$ were carried out using stirred slurries of CH_3CN for 3 h. Reactions with $TaCl_5$ and WCl_6 were carried out using stirred slurries of either toluene or CH_3CN for 3 h. Reactions with $NbCl_5$ were carried out using a stirred slurry of toluene for 1 h or a stirred slurry of CH_3CN for 3 h. Modified electrodes were rinsed thoroughly with fresh solvent after each reaction.

Metal Halide-Treated Electrodes + HMFc. GC and Pt electrodes with supported metal halides were treated identically in reactions with HMFc. An electrode previously derivatized with a metal halide was exposed to a stirred 50 mM solution of HMFc in toluene for 3 h. The electrode was rinsed thoroughly with toluene and soaked in CH_3CN for a minimum of 15 h prior to electrochemical analysis.

$TiCl_4$-Treated Electrodes + 6-Ferrocenylhexanethiol. A GC or Pt electrode previously derivatized with $TiCl_4$ was exposed to 2−3 mL of a stirred 5 mM solution of 6-ferrocenylhexanethiol in toluene for 24 h. The electrode was rinsed thoroughly with toluene and CH_3CN and then soaked for a minimum of 15 h in CH_3CN prior to electrochemical analysis.

Results and Discussion

$TiCl_4$-Modified Electrodes. $TiCl_4$ reacts readily with hydroxyl groups on glassy carbon (GC) and Pt electrodes to generate the supported titanium oxychloride species, **1**, shown idealized in eq 2. The reaction



(2)

is carried out in hexane solution under a dry, nitrogen atmosphere. The resulting modified surface was analyzed by cyclic voltammetry and found to be nonelectroactive within the potential window of a CH_3CN/0.1 M $[Bu_4N]PF_6$ solution (Figure 1A). In the early stages of this research, a significant increase in capacitive current starting near −1.0 V vs Ag wire was often observed. However, further experience suggested that

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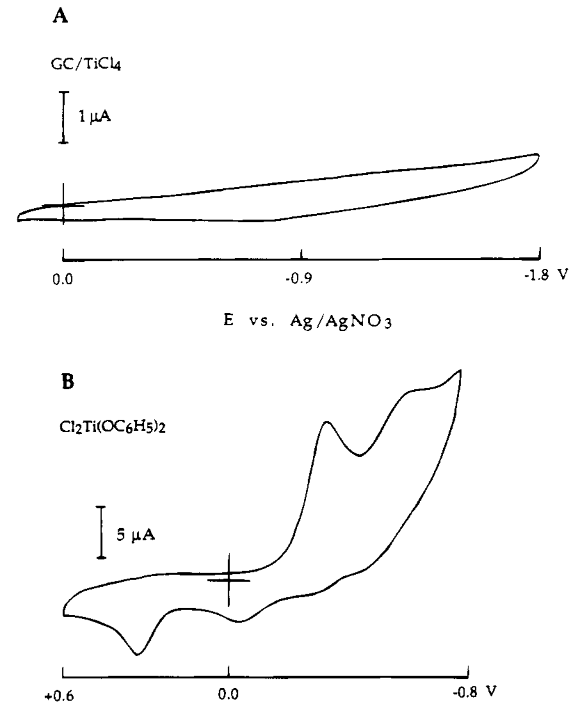

Figure 1. (A) Cyclic voltammogram of a GC electrode modified with $TiCl_4$ (**1**). (B) Cyclic voltammogram of 2 mM $Cl_2Ti(OC_6H_5)_2$ using a GC electrode. The electrolyte solution is CH_3CN with 0.1 M $[Bu_4N][PF_6]$. The scan rate is 100 mV/s. The scan was started at 0.0 V and initiated in the negative direction.

this phenomenon was caused by significant amounts of TiO_2 forming from inadvertent hydrolysis of $TiCl_4$. Cyclic voltammograms obtained with TiO_2 electrodes in CH_3CN were reported with similar background currents.[21]

Though there is no discernible electroactivity from modified electrodes of **1**, scanning Auger microprobe measurements clearly establish that both Ti and Cl are present on the surface. The Ti:Cl ratios typically favor Ti and fall in the range of 4:1 to 1:1. Much lower Ti:Cl ratios on the order of 1:2 have been obtained for systems prepared from reactions of gaseous $TiCl_4$ with silica particles.[22] In such systems, much higher temperatures were used for drying the solid support and carrying out the reaction. The data presented here suggest that small amounts of titanium oxide multilayers have formed on the electrode. Oxide coatings may come about through scavenging reactions with small amounts of residual water or surface oxide species. Such reactions can generate TiO_2 and/or titanium oxychloride oligomers. The multilayer coatings are not surprising for a reactive system such as this. Similar observations have been well documented for electrodes modified with silanes.[20,23] Lateral profile analyses using 10−15 evenly spaced, 1 μm spots at 60−100 μm intervals show little variation in elemental composition and provide good evidence for homogeneous surface coverage.

The electrochemistry of molecular complexes such as $TiCl_3(OC_6H_5)$ and $TiCl_2(OC_6H_5)_2$ were investigated as possible models of titanium oxychloride species on GC. However, these complexes undergo a series of reduction and oxidation processes as shown by the cyclic voltammogram of $TiCl_2(OC_6H_5)_2$ (Figure 1B). Apparently the Ti complexes are inappropriate models for **1** since the titanium oxychloride species undoubtedly resides on the titanium oxide multilayer and is not directly attached to the GC surface.

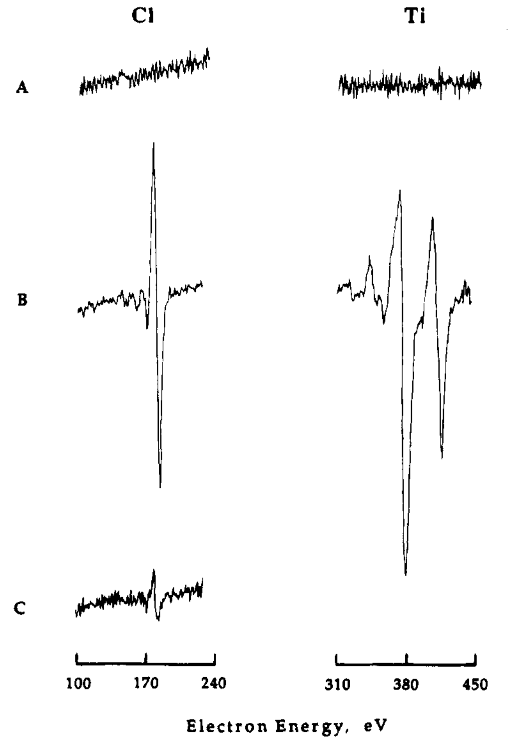

Figure 2. Auger electron spectra for Cl and Ti LMM signals on glassy carbon electrodes. Units for the vertical axis are d*N*(*E*)/d*E*. (A) Unmodified GC. (B) GC treated with $TiCl_4$. (C) GC treated with $TiCl_4$ then exposed to air for 15 min. The Ti LMM signal for (B) and (C) are essentially the same.

The Ti−Cl bonds of **1** rapidly hydrolyze upon exposure to air and moisture. Auger analysis reveals a large decrease in surface chlorine concentration whereas the concentration of titanium is essentially unchanged (Figure 2). The titanium oxide/titanium oxychloride coatings apparently do not have a significant affect on the electrochemistry of standard redox probes. Cyclic voltammograms of ferrocene or TCNQ obtained with GC or Pt electrodes of **1** exhibit little or no distortion relative to unmodified electrodes. Similar results are also obtained with electrodes of **1** that have been hydrolyzed. Such observations support the Auger data which indicate that multilayer titanium oxide coatings are thin. Though the electrochemical and Auger results do not exclude the possibility of pinholes in the modified surface, reactions of **1** with long-chain alcohols suggest that this is not the case. Irreversible electrochemistry is observed for both ferrocene (Figure 3) and TCNQ after electrodes of **1** were exposed to 10% solutions of octanol or decanol in hexane for 24 h. It is believed that these reactions generate surface $Ti{-}O{-}(CH_2)_nCH_3$ groups that hinder the approach of diffusing redox probes and/or charge-compensating electrolyte ions. These results would not be expected for a modified surface with large exposed regions of bare electrode. Very similar results have been reported for blocking experiments with redox probes in propylene carbonate using dodecanethiolate

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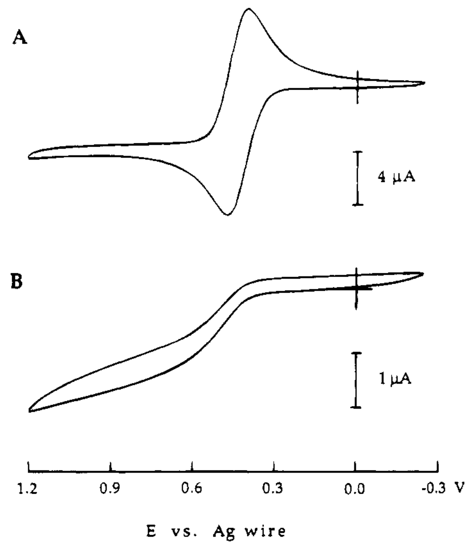
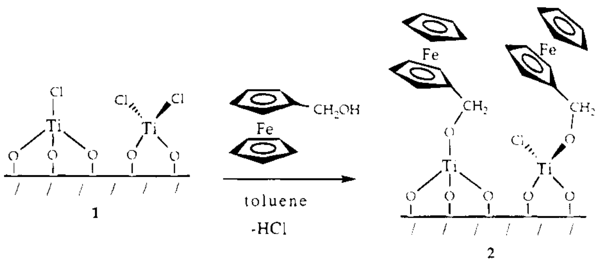


Figure 3. Cyclic voltammograms of 2 mM ferrocene in CH_3CN with 0.1 M $[Bu_4N][PF_6]$. (A) $TiCl_4$-treated GC electrode. (B) $TiCl_4$-treated GC electrode reacted with decanol. The scan rate is 100 mV/s.

self-assembled monolayers on gold.[24] Long-chain alkanethiolates on gold electrodes are also extremely effective in blocking electron transfer at aqueous interfaces.[25] Voltammograms of ferrocene and TCNQ, exemplified in Figure 3B, are also consistent with radial diffusion of these probe molecules through microscopic pinholes which might range from a few tens of microns to near molecular dimensions. However, given the monolayer coverage calculated for pendant ferrocenes on these electrodes, it seems unlikely that such pinholes are abundant. Furthermore, an abundance of pinholes with sufficiently close spacing is expected to result in overlapping radial diffusion profiles and therefore produce voltammograms that have linear diffusion characteristics.

$TiCl_4$-Modified Electrodes and (Hydroxymethyl)ferrocene. To provide an electroactive probe of titanium oxychloride-coated GC and Pt electrodes, (hydroxymethyl)ferrocene (HMFc) was reacted with **1** to generate the idealized modified surface **2** (eq 3). Cyclic voltammetry of **2** in CH_3CN solution containing only $[Bu_4N]PF_6$ supporting electrolyte is indicative of a surface-confined ferrocene moiety (Figure 4). Electrodes of **2** also produce voltammetric peaks with appropriate shape and scan rate dependence.[1,4] The peak potential of the HMFc surface wave is +0.16 V vs $Ag/AgNO_3$ for both GC and Pt. This is 60 mV positive of the +0.10 V measured for freely diffusing HMFc. The positive shift in redox potential is consistent with the attachment of the methoxyferrocene group to an electron-withdrawing Ti(IV) metal center. Peak separation (ΔE_p) measured for the modified electrodes is typically less than ΔE_p for freely diffusing ferrocene in the same solution, but greater than the theoretical value of 0 mV. Peak width at half-height is also greater than ideal, with values typically in the vicinity of 200 mV compared to 91 mV from theory. Peak broadening is likely caused by small differences in local Ti bonding sites which is manifested in numerous, unresolved voltammetric peaks with similar $E^{\circ\prime}$ for the HMFc moiety. Interactions between neighboring redox centers might also contribute to peak broadening.[26] Surface coverage (Γ) was obtained by coulometric analysis of the HMFc surface wave and were not corrected for surface roughness. Coverage generally falls in the range $(2-4) \times 10^{-10}$ mol/cm^2, which is reasonable for monolayers of tethered ferrocenes.[20,27,28] Larger values of Γ up to 8×10^{-10} mol/cm^2 have also been measured, indicating occasional multilayer coverage of HMFc moieties.



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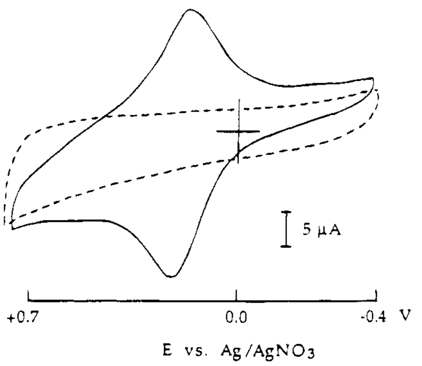

Figure 4. Cyclic voltammogram of a $TiCl_4$-treated GC electrode reacted with HMFc (**2**). The electrolyte solution is CH_3CN with 0.1 M $[Bu_4N][PF_6]$. The scan rate is 100 mV/s. The dashed line represents an underivatized GC electrode.

Auger measurements provided surface elemental analyses of Ti, Cl, and Fe for several GC and Pt electrodes of **2**. Elemental ratios on the surface were generally on the order of 2–4(Ti):1(Cl):1(Fe) after factoring in differences in elemental sensitivities. Electrode surface homogeneity was confirmed to 1 μm resolution by lateral profile measurements. The Cl:Fe ratios varied somewhat from sample to sample, but not to the extent that the Ti:Cl and Ti:Fe ratios varied. The detection of Cl suggests incomplete reaction between HMFc and Ti–Cl bonds of the surface. Unreacted Ti–Cl bonds may reflect restricted steric access of HMFc to all Ti–Cl sites on the surface. The relatively high Ti concentration on the surface can be attributed to TiO_2 and/or oligomeric titanium oxychloride films as noted previously for electrodes of **1**.

Modified surfaces of **2** are stable to prolonged soaking in CH_3CN, THF, and CH_2Cl_2 for at least a month if kept

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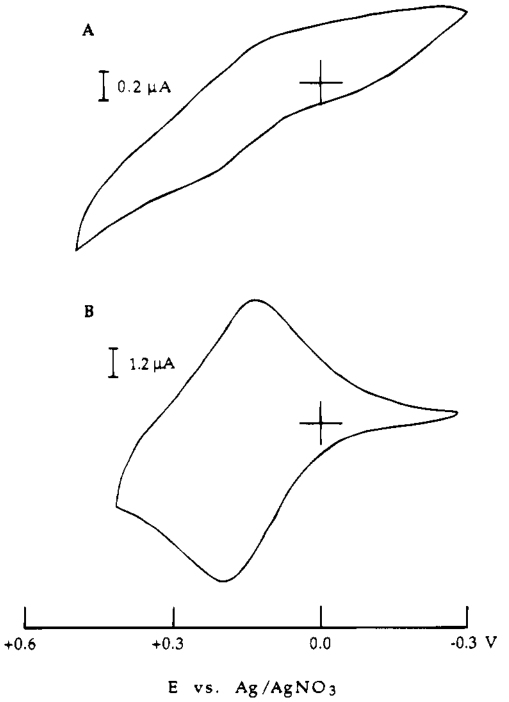

Figure 5. Cyclic voltammograms of **2** in CH_3CN with 0.1 M $[Bu_4N][PF_6]$ after 15-min exposure to air. (A) GC electrode of **2**. (B) GC electrode of **2** after treatment with MeOH. The scan rate is 100 mV/s.

under inert atmosphere. Periodic CV scans offer little or no evidence for changes in the HMFc surface wave. However, when electrodes of **2** are exposed to air for 10−15 min, the wave is either severely distorted or absent altogether. Degradation of the modified surface is believed to originate from hydrolysis of the remaining Ti−Cl bonds on the electrode. This reaction, in turn, has a destabilizing effect on the surface-confined HMFc groups. Sensitivity to air may be reduced by reacting **2** with methanol (Figure 5). It is believed that this reaction converts reactive surface Ti−Cl groups into less reactive $Ti-OCH_3$ functionality. Auger analysis supports this contention as surfaces of **2** treated with methanol show considerable loss of chlorine. These results indicate that Ti−Cl bonds in **2** are accessible to small molecules such as water and methanol whereas a complex such as HMFc is too large to reach all the reactive sites. This supports the earlier proposal that steric congestion is responsible for unreacted Ti−Cl bonds in **2**. The accessibility of Ti−Cl bonds in these reactions also provides further evidence that titanium oxychloride moieties are mostly at the surface of the titanium oxide multilayers instead of being randomly dispersed throughout the bulk of the multilayer films.

Continuous cycling through the surface wave between +0.6 and −0.4 V at 100 mV/s causes rapid loss of electroactivity from the HMFc moiety (Figure 6). Slower degradation has generally been observed for ferrocene derivatives in silane-modified Pt electrodes.[20] Auger analyses of electrodes of **2** taken before and after prolonged cycling shows a decrease in the Fe:Ti ratio. These results suggest that degradation of the modified electrode originates from instability in the HMFc moiety or its linkage to Ti centers on the surface. Similar instability has been reported for ferrocene derivatives attached to silane tethers on Pt.[20] The degradation may be related to observations of ferrocene decomposition during oxidation in CH_3CN,[29] though in this system Fe decomposition products do not concentrate at the electrode.

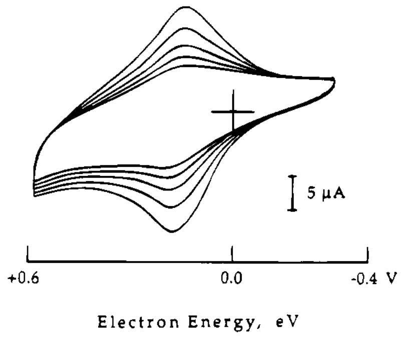

Figure 6. Degradation of the surface-confined HMFc wave for a GC electrode of **2** in CH_3CN with 0.1 M $[Bu_4N][PF_6]$. The scan rate is 100 mV/s. The waves represent scans 10, 20, 30, 40, and 50 in order of decreasing current.

Several control reactions were performed to assess the potential for interference from HMFc adsorption on electrodes of **2**. Derivatization reactions were carried out with deliberate omission of $TiCl_4$. HMFc was also dip-coated and drop-coated from toluene solutions onto pretreated GC and Pt electrodes without prior reaction with $TiCl_4$. Electrodes previously reacted with $TiCl_4$ were exposed to ferrocene instead of HMFc. Finally, $TiCl_4$-reacted electrodes were hydrolyzed prior to reaction with HMFc. In all cases, cyclic voltammetry revealed surface waves that were either absent or insignificantly small after electrodes were allowed to soak in CH_3CN for 24 h.

$TiCl_4$-Modified Electrodes and 6-Ferrocenylhexanethiol. Although alkanethiolate derivatives have been extensively studied in self-assembled monolayers on gold electrode,[24,25,30,31] they are not widely applicable in surface reactions with organosilanes. Derivatization of $TiCl_4$-treated electrodes with thiols would therefore establish chemistry in these systems that is not known for the analogous silane-modified electrodes. Precedent for the surface reactions comes from titanium thiolate molecular complexes, which are commonly synthesized from organotitanium halides and organic thiols.[32] Exposure of GC or Pt electrodes of **1** to toluene solutions of 6-ferrocenylhexanethiol for 24 h generates a modified surface that is proposed to have the idealized structure **3** shown in eq 4. Cyclic voltammograms of GC and Pt electrodes of **3** have the same general appearance (Figure 7A). Values of Γ were determined in the range $(2-5) \times 10^{-10}$ mol/cm^2.

Control reactions using unmodified GC or hydrolyzed GC electrodes of **1** gave only minor indications of adsorption as surface waves were weak and highly distorted. Control experiments with bare Pt electrodes indicated strong adsorption as cyclic voltammograms were very similar to those obtained from Pt electrodes of **3**. However, additional control reactions carried out

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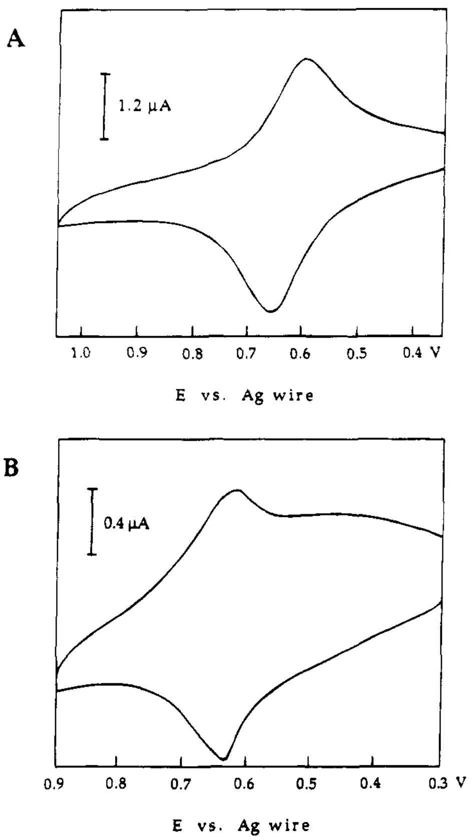
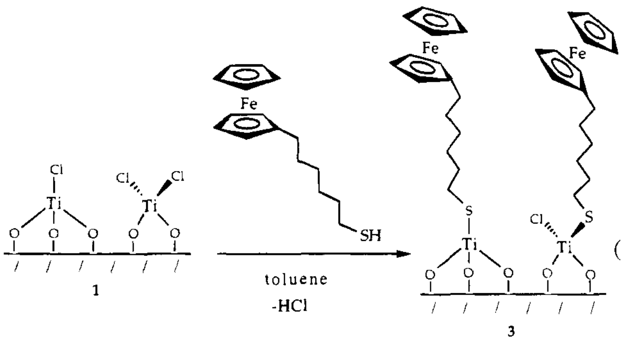


Figure 7. Cyclic voltammograms of modified Pt electrodes reacted with 6-ferrocenylhexanethiol. (A) Initial treatment with $TiCl_4$. (B) Initial treatment with $SiCl_4$. The electrolyte solution is CH_3CN with 0.1 M $[Bu_4N][PF_6]$. The scan rate is 100 mV/s.



(4)

with 6-ferrocenylhexanethiol and hydrolyzed Pt electrodes of **1** or with $SiCl_4$-treated Pt electrodes yielded modified surfaces showing much weaker voltammetric waves (Figure 7B). Weak adsorption of 6-ferrocenylhexanethiol on hydrolyzed Pt electrodes of **1** seem to confirm the presence of pinholes in films on $TiCl_4$-treated Pt electrodes, as discussed previously for blocking experiments. Adsorption may occur through small imperfections in the surface coating which allow the thiol to access small areas of underlying Pt. Control reactions with $SiCl_4$-treated Pt electrodes were carried out on the premise that $SiCl_4$ and $TiCl_4$ react similarly with Pt, but surface Ti–Cl bonds are more reactive with thiols. Submonolayer coverage of ferrocenylalkanethiols on $SiCl_4$-treated Pt was recently confirmed.[33] The voltammograms shown in Figure 7 indicate that $TiCl_4$-treated electrodes are superior substrates for covalent attachment of thiols compared to analogous treatment with standard silanes. However, it must be noted that $Co(CO)_4$ derivatives of chlorosilanes have been shown to be excellent precursors for well-defined electroactive monolayer films.[34]

Reactions with Other Ti Complexes. Unlike reactions involving alkoxysilanes, GC and Pt electrodes apparently do not undergo significant modification when exposed to hexane solutions containing $Ti(OEt)_4$. Auger analyses of electrodes after 1 h reactions detected only small amounts of surface titanium. Electrodes treated with $Ti(OEt)_4$ could not be further derivatized with HMFc. Reactions of Cp_2TiCl_2 and $CpTiCl_3$ were also explored with GC and Pt electrodes. No reaction was observed for Cp_2TiCl_2 in dichloromethane at room temperature. Reactions in acetonitrile and nitromethane at temperatures up to 70 °C were likewise unsuccessful. Glassy carbon electrodes could be modified with $CpTiCl_3$ in nitromethane at 70 °C, but subsequent cyclic voltammetric analysis induced irreversible reduction near −1.8 V (vs Ag wire) which caused stripping of the surface-confined species. It has been proposed that $CpTiCl_3$ reacts with metal oxides such as alumina by loss of only one Ti–Cl bond and thus generates surface-confined $\{CpTiCl_2{-}O{-}\}$ moieties.[35] If such a complex exists on GC, it is not stable to electrochemical reduction and is lost through chemical irreversibility. Though not the case here, electrochemically induced stripping of supported complexes can be utilized to promote electrode modification.[34]

Modified Electrodes with Other Early-Transition-Metal Halides. The electrode modification reaction with $TiCl_4$ has been extended to other hydrolytically unstable early transition metal chlorides such as $ZrCl_4$, $NbCl_5$, $TaCl_5$, and WCl_6. These complexes react with GC and Pt electrodes in CH_3CN and/or toluene slurries to give modified surfaces that are apparently analogous to **1**. The reactions in CH_3CN occur through solvent-coordinated metal halides. In toluene, color changes indicate the formation of charge-transfer complexes. It is unlikely, however, that solvent interactions disturb the general nature of the surface reaction. Just as with $TiCl_4$-treated electrodes, the modified electrodes generated from $ZrCl_4$, $NbCl_5$, $TaCl_5$, and WCl_6 are not inherently electroactive and all react with air. These modified surfaces were characterized by Auger analyses and electrochemical measurements after subsequent surface reactions.

Although the reactant complexes have a varying number of chloride ligands, Auger experiments were unable to distinguish differences in metal:Cl ratios for the modified surfaces. In all cases, metal concentrations were favored by up to a factor of 3 and lateral profiles indicated homogeneous coverage. Though the surface analyses are consistent with multilayer metal oxide coatings, comparison of metal and chlorine signals to oxygen and carbon signals indicate that the metal and chlorine concentrations are much lower compared to $TiCl_4$-treated electrodes of **1**. The electrode surface concentrations determined from Auger analyses showed

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significant fluctuation for different electrodes, but on average the values were about one-third relative to electrodes of **1**. These results indicate that while multilayers are evenly dispersed across the electrode, most of the surface remains unmodified. In support of this view, electrodes subsequently treated with 10% solutions of decanol in hexane for 24 h were unable to block soluble redox probes such as ferrocene and TCNQ. Cyclic voltammograms of these molecules in CH_3CN clearly showed reversible characteristics. Slightly larger peak currents were observed for untreated electrodes, suggesting that the modified areas provided partial blocking. Reactions of the electrodes with HMFc were apparently successful, but surface waves were broad and peak currents were weak. Calculated surface coverage was in the range $(0.5-1.0) \times 10^{-10}$ mol/cm^2, which is a fraction of what was determined for electrodes of **1**. Peak potentials for surface-confined HMFc showed little variation from electrodes treated with metal chlorides and were the same for GC and Pt:$TiCl_4$ (+0.16 V), $ZrCl_4$ (+0.16 V), $NbCl_5$ (+0.16 V), $TaCl_5$ (+0.15 V), WCl_6 (+0.13 V), vs Ag/$AgNO_3$. Peak broadening was similar in these systems as it was for $TiCl_4$/HMFc-modified electrodes. This can be accounted for by small, localized differences in how the ferrocene moiety is attached to the electrode. However, if interactions between neighboring ferrocenes are responsible for broadening, then the submonolayer electrode coverage might be described in terms of highly concentrated regions of surface modification with adjacent regions of barren electrode. The level of inhomogeneity would also have to be unresolvable by the 1 μm spot size of scanning Auger experiments. Submonolayer coverage resulting from dilute and isolated ferrocene groups would be expected to give narrow voltammetric peaks. Modified electrodes were also prepared from analogous early-transition-metal bromides. However these reactions were found to be inferior to those using metal chlorides.

Summary

We have demonstrated that glassy carbon and Pt electrodes can be derivatized with early-transition-metal halides in reactions that are analogous to those of moisture-sensitive silanes. Modified electrodes are coated with a thin multilayer of metal oxide having metal oxychloride species supported at the surface interface. Reactions with $TiCl_4$ generate full coverage of the electrode surface whereas reactions with other early-transition-metal halides result in partial coverage. The modified electrodes are not electroactive, but redox probes may be attached using subsequent reactions of metal−chlorine bonds on the surface. Electrodes modified with $TiCl_4$ are found to react with molecules bearing hydroxyl and thiol functional groups. Other organometallic titanium complexes either do not react with electrodes or the supported species are unstable to electrochemical analysis. Modified electrodes derived from $TiCl_4$ offer no immediate advantage over silane-modified electrodes except that surface Ti−Cl functionality are more amenable to subsequent reactions with thiol compounds. Given the air-sensitive nature of the $TiCl_4$-modified electrodes, is unlikely that $TiCl_4$ will supplant silanes as covalent links to electrodes, unless unique Ti surface chemistry is discovered. We are currently investigating other methods of supporting early-transition-metal complexes on electrodes.

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