Anodic Oxidation of Ethynylferrocene Derivatives in Homogeneous Solution and Following Anodic Deposition onto Glassy Carbon Electrodes

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Eight ferrocene derivatives linked by either an ether, amine, or phenylacetylene moiety to a terminal ethynyl group were covalently deposited on glassy carbon electrodes by anodic electrochemical methods. The lithio activation method, in which the terminal hydrogen of the ethynyl group is replaced by a lithium atom before anodic oxidation, was successfully employed in all cases. Direct oxidation of the unactivated ethynyl group also resulted in surface deposition. Surface coverages between 1 x 10^{-10} mol cm^{-2} and 14 x 10^{-10} mol cm^{-2} were achieved. Cyclic voltammetry scans of the modified electrodes in pure electrolytes differed depending on the size of the supporting electrolyte anion, as little as half the current being measured for a $[B(C_6F_5)_4]^-$ vs. $[PF_6]^-$ solution, suggesting differences in ion transport near the electrode surface. An ether-linked ethynylferrocenium ion (**5**$^+$) was isolated after electrolytic and chemical oxidation of **5** and characterized by X-Ray crystallography as its $[SbCl_6]^-$ salt.

1. Introduction

Recently it has been shown that radical-based electrografting processes are effective in preparing chemically modified electrodes to which molecules are covalently attached through an ethynyl group.[1-7] We have previously described an assortment of methods whereby metallocenes derivatized at a cyclopentadienyl ring with a terminal ethynyl group can be covalently attached to carbon surfaces.[1-4] The present paper augments that work by providing several new examples of glassy carbon (gc) electrodes that have been modified with ethynyl-attached ferrocene derivatives that differ in the number and types of bonds between the metal center and the ethynyl group. We also report on differences in the voltammetric behavior of the modified electrodes in different electrolyte media. Furthermore, we provide new information on the oxidation of ethynylferrocenes that better defines the conditions under which ethynylferrocenium radical cations are sufficiently long-lived in homogeneous solution to be easily characterized by spectroscopy and, in some cases, isolated as stable salts.

Two anodic deposition methods were employed for attachment of the ethynylferrocenes to gc. That involving oxidation of a ferrocene containing a lithium-activated ethynyl group was successfully employed for all the compounds in this study. In some cases, the so-called “direct oxidation” method was also utilized. In view of the fact that the advantages and disadvantages of these two methods have been previously detailed[4], only the basic ideas behind them will be reviewed here.

The lithio-activation method involves replacement of the hydrogen atom in R-C≡C-H by a lithium atom, followed by anodic oxidation of the R group (Eq 1). The anodic reaction results in the loss of lithium ion and formation of an ethynyl radical that is free to react with an atom on the electrode surface. In the present study, R contains the ferrocenyl moiety that is linked to the terminal ethynyl group.

$$(1)\quad R{-}C{\equiv}C{-}H \xrightarrow[\text{-BuH}]{\text{BuLi}} R{-}C{\equiv}C{-}Li \xrightarrow{-\,e^-} R{-}C{\equiv}C\bullet \;+\; Li^+$$

In the direct oxidation method, a potential is applied that is sufficient to oxidize the ethynyl (C≡C-H) group itself. Although the anodic chemistry of ethynyl groups is ordinarily complex, this method seeks to take advantage of the expected increase in the acidity of the ethynyl hydrogen, thereby facilitating a proton release that would provide the desired carbon-based radical. If R contains the more easily oxidized ferrocenyl group, the direct oxidation method requires oxidation of both R and the ethynyl group to provide the desired carbon-based radical (see Eq 2). In this method, the compound is initially deposited in the higher (ferrocenium) oxidation state, but is then reduced back to the lower (ferrocene) oxidation state when the applied potential is scanned negative.

$$(2)\quad R{-}C{\equiv}C{-}H \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} R^+{-}C{\equiv}C{-}H \xrightarrow{-\,e^-} R^+{-}C{\equiv}C\bullet \;+\; H^+$$

New directions and applications of anodic ethynyl deposition methods have already begun to appear. These include the depositions of a nickel cyclam complex that is an effective catalyst for CO_2 reduction, using the direct oxidation method[5], and several calixarenes anchored through multiple ethynyl groups, using the lithio activation method.[6] Both Sheridan *et al*[4] and Jouikov and Simonet[7] have shown that the direct oxidation method may be successful even when the leaving group of a terminal ethynyl moiety is $SiMe_3^+$. We note also that roughly a monolayer of an ethynylferrocene derivative has been bonded to graphitic carbon surfaces by a 400° C heat treatment.[8]

2. Results and Discussion

The eight ethynylferrocene derivatives discussed in this paper are shown in Scheme 1. After their oxidative behavior was characterized in a homogeneous solution of dichloromethane containing either 0.1 M $[NBu_4][PF_6]$ or 0.05 M $[NBu_4][B(C_6F_5)_4]$, one of two different anodic processes was carried out in order to deposit them onto glassy carbon surfaces. Although in some cases the "direct" oxidation of the ethynyl group was employed, oxidation of the lithium acetylide compound was more generally utilized. For the latter, the compound was treated with *n*-BuLi in THF, inducing deprotonation of the alkyne and replacement of the terminal hydrogen atom with a lithium atom. The resulting lithium acetylide was then anodized at the ferrocene potential, resulting in a strongly-attached molecular deposit in which the terminal ethynyl carbon atom is assumed to be covalently bonded to the electrode surface.

The anodic deposition processes of compounds **1**, **4**, and **5** have already been partially described[1,2,4]. The present paper offers additional examples of ethynyl-attached ferrocene derivatives and provides new information on how the electrolyte medium may affect both the surface deposition process and the voltammetry of the surface-bound species. In addition, we show that the one-electron oxidation products of non-activated ethynylferrocenes have significant longevity under bulk electrolysis conditions, and that the corresponding ferrocenium monocations may be isolated in some cases.

The $E_{1/2}$ potentials for the ferrocenyl-based oxidations of both the homogeneous and surface-bound compounds in dichloromethane/0.1 M $[NBu_4][PF_6]$ are given in Table 1. For each compound, the homogeneous oxidation was diffusion-controlled and quasi-Nernstian in character.

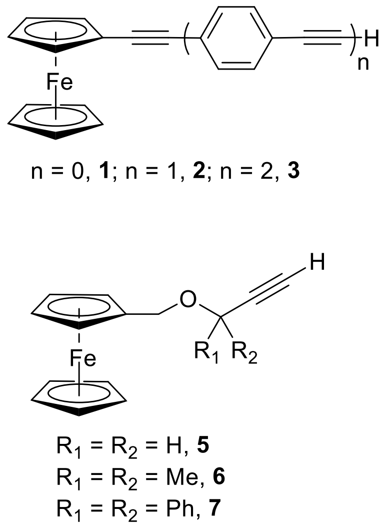

Figure 1. The compounds reported in this study.

Table 1. Oxidation potentials vs ferrocene of ethynylferrocenes in dichloromethane/0.1 M $[NBu_4][PF_6]$, either in homogeneous solution ($E_{1/2}$ (soln)) or deposited on a glassy carbon electrode ($E_{1/2}$ (gce)).

Compound	$E_{1/2}$ (soln)	$E_{1/2}$ (gce)	Compound	$E_{1/2}$ (soln)	$E_{1/2}$ (gce)
1	0.11	0.11	**5**	-0.01	-0.02
2	0.09	0.08	**6**	-0.05	-0.07
3	0.08	0.06	**7**	-0.02	-0.03
4	-0.03	-0.04	**8**	-0.01	-0.06

I) Ethynylferrocene and phenylethynylferrocenes, **1**-**3**

The one-electron oxidation of ethynylferrocene, **1**, is known to be chemically reversible on the CV time scale.[9-13] On a longer time scale, however, it had been previously reported that the lifetime of **1**$^+$ is much less than that generally observed for non-H-terminated ethynylferrocenes, and it was postulated that **1**$^+$ quickly dimerizes with loss of H-atoms to form the butadiyne compound Fc-C_4-Fc (Fc = ferrocenyl).[10] In our hands, although we were not able isolate pure salts of **1**$^+$, bulk anodic electrolysis of **1** in either dichloromethane or THF containing 0.1 M $[NBu_4][PF_6]$ showed that **1**$^+$ is stable (long-lived) when generated this way. Thus, cathodic back-electrolysis of **1**$^+$ (n_{app} = 1 e^-) regenerated the neutral starting material in 90-98% yield, as quantified by comparison of CV scans obtained at various points in the experimental sequence (see Figure 2). The nearly quantitative reversibility of this reaction allowed for an estimate of the diffusion coefficient of **1**$^+$ under these conditions, based on the comparative CV currents measured for **1** and **1**$^+$. Assuming a diffusion coefficient for neutral **1** equal to that of ferrocene (2.2×10^{-5} cm^{2}s^{-1})[14], the ratio of the peak currents (cathodic for **1**$^+$; anodic for **1**) gave a D_o value for **1**$^+$ of 1.3×10^{-5} cm^{2}s^{-1} in dichloromethane.

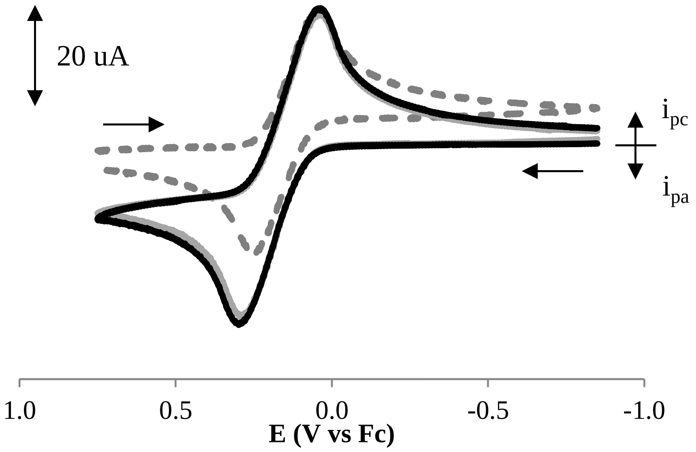

Figure 2. CV scans of 5 mM **1** in THF/0.1M [Bu_4N][PF_6]; 2 mm GCE, ν = 0.2 V/s, prior to electrolysis (black), after -1.42 C passed (n_{app} = 1.0) (gray ---), after re-electrolysis of 1.4 C (gray)

Attempts to isolate pure salts of **1**$^+$ through a chemical oxidation procedure were unsuccessful. When **1** was treated with an equivalent of the strongly oxidizing thianthrene cation [$C_{12}H_8S_2$]$^+$, presented as either the [$SbCl_6$]$^-$ or [$B(C_6F_5)_4$]$^-$ salt, solids were isolated (see Experimental section). An IR spectrum of the **1**[$SbCl_6$] sample showed that the C≡CH stretching frequency, $\nu_{C\equiv CH}$, had increased from 2106 cm^{-1} in **1** to 2120 cm^{-1} in **1**$^+$. However, CV scans of this sample showed reversible oxidation waves for one or two minor but unidentified side-products. Similar chemical oxidations of the ether-linked ethynylferrocene **5** were more successful in providing pure samples of the singly-oxidized product, and these results are given in section II.

Chemical modification of glassy carbon electrodes by surface-bound **1** through oxidation of the lithiated alkyne Fc-C≡CLi, **1-Li**, worked as previously described[1,4]. Analogous deposition of the phenylethynylferrocenes **2** and **3** was similarly carried out by oxidation of the lithium acetylides Fc-C≡C-(C_6H_4-C≡C)$_n$-Li (n = 1, **2-Li**; n = 2, **3-Li**). As demonstrated in Figure 3 for **3-Li**, CV scans of homogeneous solutions containing either **2-Li** or **3-Li** have a single, somewhat broadened, anodic wave displaying partial chemical reversibility. Its features are an overlay of the irreversible oxidation of the lithiated

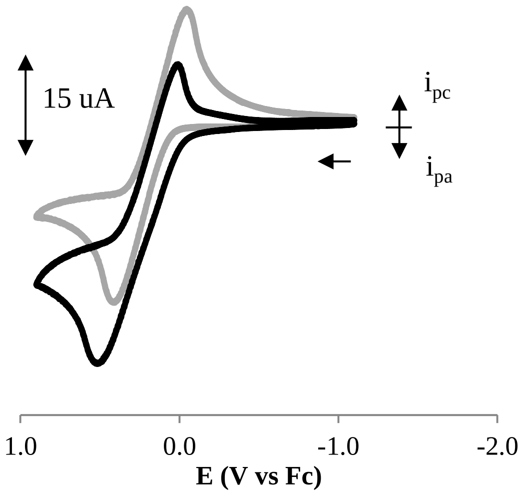

Figure 3. CV scans in THF/0.1 M [NBu_4][PF_6] at 2 mm gce, 0.2 V s^{-1}: gray line, 5.5 mM **3**; black line: same solution after addition of n-BuLi, giving solution of *ca* 5 mM **3-Li**.

species and the reversible oxidation of the unactivated parent species, e.g., **3-Li** and **3**, respectively. The latter is formed as a follow-up product of the oxidation of the lithiated species, as discussed earlier[4]. The fact that only one anodic wave is seen for either **2-Li** or **3-Li** means that the difference between E_{pa} for the lithiated species and $E_{1/2}$ for the parent species is very small, probably less than 30 mV. This is in contrast to **1-Li**, the E_{pa} of which is about 260 mV negative of the $E_{1/2}$ of **1**. The electronic effect of Li-for-H replacement on the ferrocenyl oxidation potential is clearly diminished in **2** and **3** owing to the more remote placement of the terminal ethynyl group in those compounds. CV scans from -0.5 V to 1 V (at 0.2 V s^{-1}) gave gc electrodes containing strongly-bound **2** or **3**, an example of which is shown in Figure 4. The amount of surface coverage increased with the number of deposition scans, reaching levels as high as

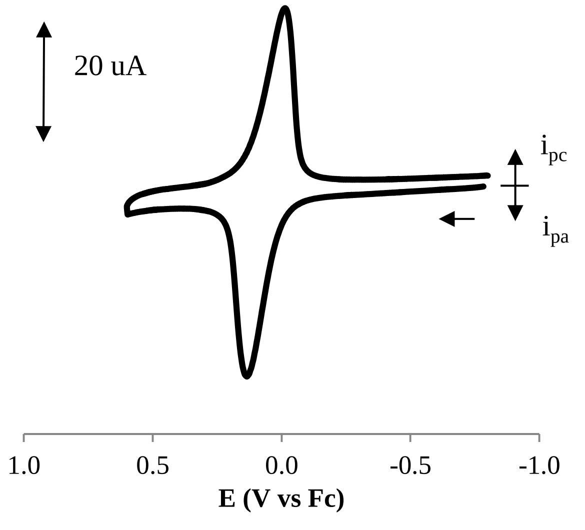

Figure 4. CV scan in dichloromethane/0.1 M [NBu_4][PF_6], 0.5 V s^{-1}, of a gc electrode modified by ten deposition scans of a solution containing **2-Li**.

2.7×10^{-9} mol cm^{-2} after ten scans. The relationship of surface coverage and wave shape to the number of CV deposition scans is given in Table 2 for compounds **1**-**3**. It is interesting to see that for single scans, after which the surface coverage is roughly that of a monolayer, the peak width of **1** (202 mV) was much greater than that of **2** (97 mV). This may be a consequence of increased electrostatic interactions arising from the tighter packing of **1** than is possible when there is a rotationally-flexible phenyl group in the compound, as there is in **2**. We assume that the deeper layers formed upon multiple anodic scans involve attack, and subsequent bonding, of a new ethynyl-based radical on an already surface-bound species.

Table 2. Degree of surface coverage on glassy carbon electrodes for three ethynylferrocene derivatives as a function of the number of CV scans of solutions nominally containing 4 mM of the lithiated compound in THF/0.1 M NBu$_4$][PF$_6$]. Scan was taken to 1 V vs ferrocene at 0.2 V s^{-1}. FWHM = full width at half-maximum for the anodic feature of the surface-bound species.

Analyte	**1**, coverage (mol cm^{-2})	**1**, FWHM (mV)	**2**, coverage (mol cm^{-2})	**2**, FWHM (mV)	**3**, coverage (mol cm^{-2})	**3**, FWHM (mV)
1 scan	5.8×10^{-10}	202	5.8×10^{-10}	97	4.0×10^{-10}	153
5 scans	8.5×10^{-10}	182	19×10^{-10}	106	8.1×10^{-10}	179
10 scans	15×10^{-10}	199	27×10^{-10}	119	14×10^{-10}	204

Comparison was also made of the scan-stability (i.e., repeatability) of the modified electrodes subjected to continuous CV scans in pure electrolyte solution containing [NBu$_4$][PF$_6$]. Those modified by **2** or **3** degraded at almost an order-of-magnitude faster rate than those containing **1**. Thus, after about 100 CV scans, there were losses of about 50% and 80% of the currents for electrodes containing surface-bound **2** and **3**, respectively.

II. Ether-linked ethynylferrocenes, **4**-**7**

The homogeneous electrochemistry of the ether-linked ethynylferrocenes, **4**-**7**, was straightforward in that they exhibited quasi-Nernstian one-electron oxidations. Given our desire to more completely characterize an ethynylferrocenium ion, we pursued the isolation of a pure sample of the monocation of compound **5**. Anodic bulk electrolysis of **5**, followed by back-reduction of **5**$^+$, was carried out to confirm the stability of the monocation **5**$^+$. A chemical oxidation was then carried out separately, wherein a dichloromethane solution of **5** was treated with [$C_{12}H_8S_2$][SbCl$_6$] and left overnight at -10° C, providing bright blue X-ray quality crystals of **5**[SbCl$_6$]. Perhaps the most relevant aspect of the molecular structure determined by X-ray analysis (Figure 5) is that the acetylenic C≡C bond length of 1.186 Å is essentially unchanged from that reported[15] for neutral **5**, and close to that reported for the ethynyldecamethylferrocenium ion.[13] We note also that the -C≡CH stretching frequency measured for **5**$^+$ was within experimental error of that of **5** (2121 cm^{-1} vs 2117 cm^{-1}, respectively). The essentially unchanged bond length and stretching frequency of the C≡C bond observed when **5** is oxidized indicates that the electronic interaction between the iron center and the ethynyl group is significantly weaker in **5** than it is in **1**. Recall that in the latter, the value of $\nu_{C\equiv CH}$ increased by 14 cm^{-1} in going from **1** to **1**$^+$.

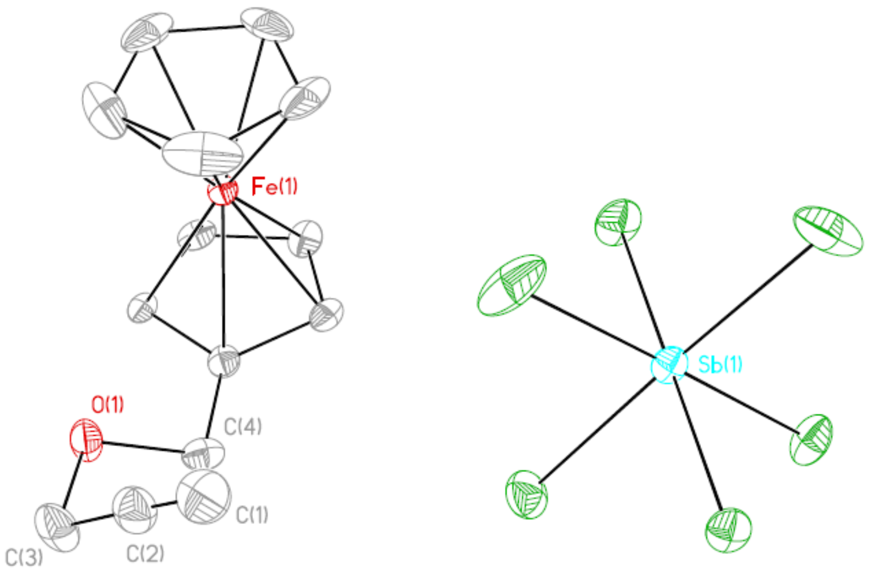

Figure 5. Molecular structure of 5[$SbCl_6$] with thermal ellipsoids drawn at 30%

Compounds **5**-**7** were all successfully deposited onto glassy carbon electrodes using the lithium-activation method (results for **4** have been described in a previous paper).[4] We were interested in seeing if the deposition process might be affected by steric factors arising from the nature of R_1 and R_2 in compounds **5**-**7**. As summarized in Table 3, the extent of surface coverage obtained from identical numbers of deposition scans did, in fact, decrease in the order $R_1 = R_2 = H > Me > Ph$. Comparative CVs for electrodes modified by **5**, **6** and **7** after ten deposition scans are shown in Figure 6.

Table 3. Surface coverages of ferrocenyl ethynylethers deposited onto gce as a function of the number of CV scans taken for the oxidation of the matching lithioacetylide in THF.

Number of CV deposition scans	Coverage (mol cm^{-2}) **5** ($R_1 = R_2 = H$)	Coverage (mol cm^{-2}) **6** ($R_1 = R_2 = Me$)	Coverage (mol cm^{-2}) **7** ($R_1 = R_2 = Ph$)
1	1.46×10^{-10}	1.26×10^{-10}	0.93×10^{-10}
5	5.14×10^{-10}	4.63×10^{-10}	1.32×10^{-10}
10	9.50×10^{-10}	4.96×10^{-10}	2.21×10^{-10}

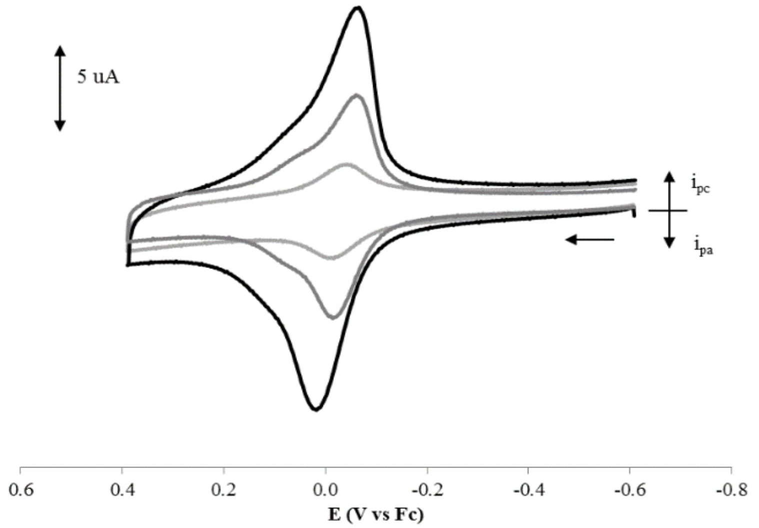

Figure 6. CV scans (0.5 V s^{-1}) taken in dichloromethane/0.1 M [NBu_4][PF_6] on 2 mm gc electrodes that had been modified by **5** (black), **6** (dark gray) or **7** (light gray). In each case, the electrodes had been modified by ten CV scans of the lithio-activated compounds in THF/0.1 M [NBu_4][PF_6]. The small shoulders for **5** and **6** are of unknown origin and did not appear in all deposition experiments.

III. Amine-linked ethynylferrocene, 8

The homogeneous anodic behavior of the amine-linked ethynylferrocene **8** is illustrated by the two sets of CV scans shown in Figure 7 [note that this solution contained a small amount of decamethylferrocene, which is responsible for the smaller feature near -0.5 V]. The scan exhibited in the bottom of Figure 7, reversed at 0.5 V, shows the reversible ferrocenyl oxidation ($E_{1/2}$ = -0.01 V). That exhibited at the top, reversed at 1 V, shows a second peak, this one resulting from oxidation of the amine group. Consistent with previous studies of amine oxidations in nonaqueous solvents[16-18], it is irreversible, E_{pa} = 0.83 V (ν = 0.4 V s^{-1}) and, under these conditions, may be expected to abstract an H-atom from solvent or trace moisture to give the corresponding ammonium salt **8-H**$^+$.[19-21]Since the ferrocenyl-based redox couple for **8-H**$^+$ is expected to appear at potential that is more positive than that of **8**, the reversible wave for the follow-up product appearing at $E_{1/2}$ = 0.15 V (dashed line in Figure 7) is assigned to the couple [**8-H**$^+$]$^{0/+}$. This assignment was confirmed by the observation that addition of an equivalent of HCl to the THF solution of **8** shifted the reversible wave from -0.01 V to 0.15 V. Subsequent addition of NaOH shifted the wave back to the original value of -0.01 V.

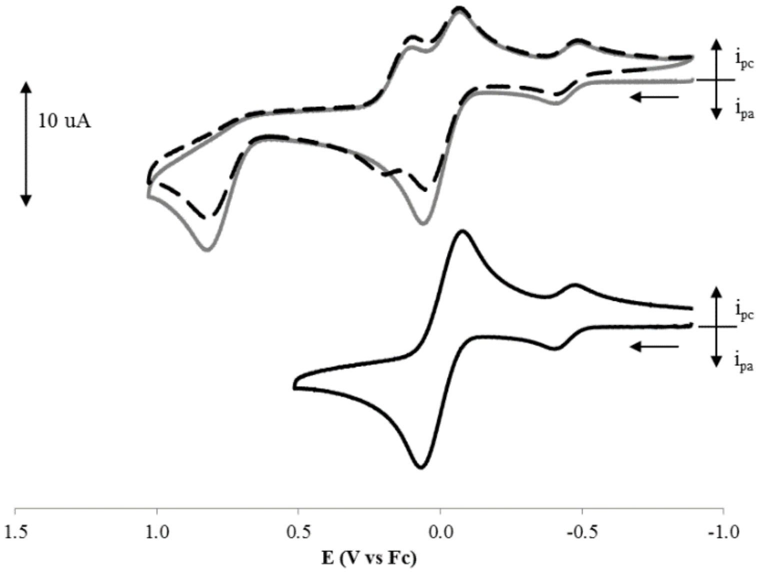

Figure 7. CV scans (0.4 V s^{-1}) of 1 mM **8** in THF/0.1 M $[NBu_4][PF_6]$ at 2 mm gce. Bottom: single scan between -0.9 V and 0.5 V. Top: two consecutive scans between -0.9 V and 1 V. The small waves near -0.5 V are due to decamethylferrocene present in the solution.

Relevant to the possible surface deposition of **8** is the anodic behavior observed for the lithium acetylide species **8-Li**. Similar to the behavior of the ether-linked analogue **4-Li**, oxidation of **8-Li** is only slightly negative of the oxidation of **8**. Thus, addition of n-BuLi to a solution of **8** results in a barely discernable pre-wave, as shown in Figure 8. As **8-Li** is oxidized in scans to 0.5 V, compound **8** is efficiently deposited on the electrode surface (see Figure 9).

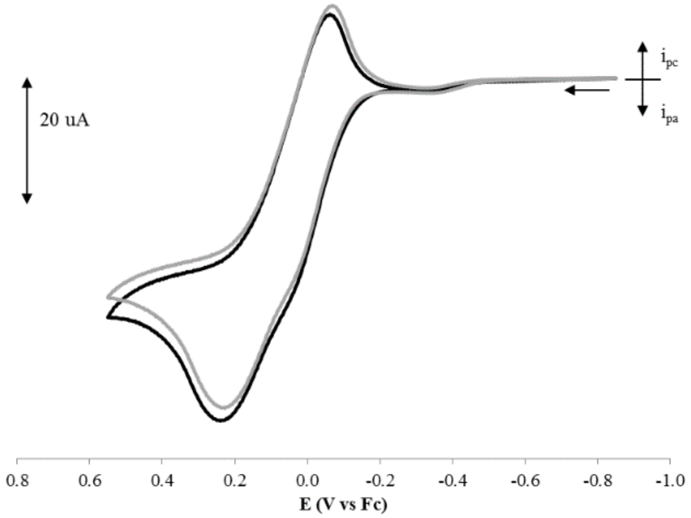

Figure 8. Two consecutive CV scans (0.1 V s^{-1}) of nominally 4 mM solution of **8-Li** in THF/0.1 M $[NBu_4][PF_6]$ at 0°C. Black: first scan; gray: second scan.

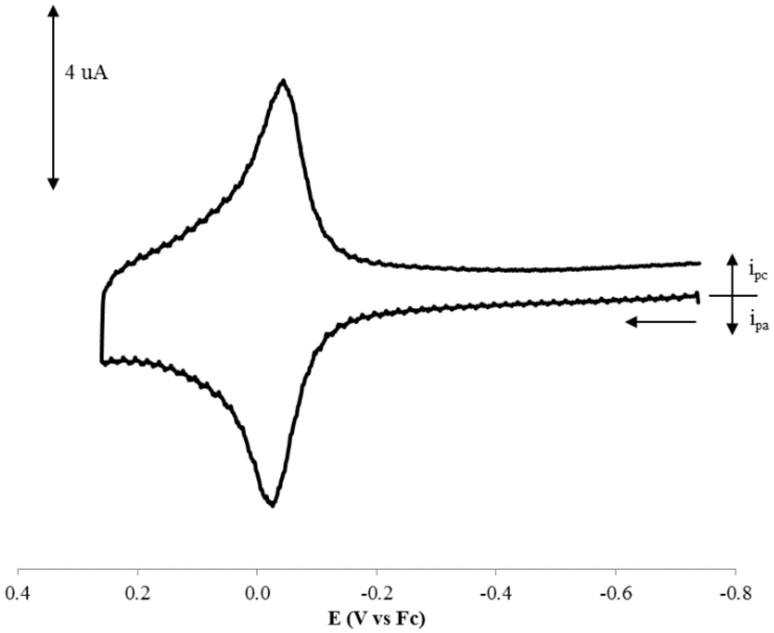

Figure 9. CV scan (0.4 V s^{-1}) in dichloromethane/0.1 M $[NBu_4][PF_6]$ of a 2 mm gce modified with **8**.

The acid/base chemistry of **8** was unchanged for the surface-deposited compound. In a pure solution of dichloromethane/0.1 M $[NBu_4][PF_6]$, repeated additions of HCl and NaOH simply moved the reversible couple for the surface-bound species back and forth between -0.01 V (for **8**) and 0.15 V (for **8-H$^+$**).

IV. Effects of supporting electrolyte anion

The lithio-activated anodic deposition process worked well when the THF solution contained either 0.1 M $[NBu_4][PF_6]$ or 0.05 M $[NBu_4][B(C_6F_5)_4]$ as the supporting electrolyte. When the resulting modified electrodes were probed by CV scans in pure electrolytes, however, differences were observed depending on whether the electrolyte anion was $[PF_6]^-$ or $[B(C_6F_5)_4]^-$. A representative comparison is shown in Figure 10 for surface-deposited **1**, wherein the waves obtained in $[B(C_6F_5)_4]^-$ are both broader (full width at half maximum = 320 mV, compared to 180 mV for $[PF_6]^-$) and smaller. Regarding the latter, integrations gave surface coverages of 5.0 x 10^{-10} mol cm^{-2} for the $[PF_6]^-$ scan and only 53% of this value (2.7 x 10^{-10} mol cm^{-2}) for the $[B(C_6F_5)_4]^-$ scan. The differential in currents was less dramatic for more heavily layered electrodes, being 80 % for an electrode having about ten times the amount of surface coverage (4.8 x 10^{-9} cm^2 s^{-1} in the $[PF_6]^-$ scan). Comparable diminishments of modified electrode currents were observed for all the ferrocenyl systems studied. We noted similar effects for smaller vs larger electrolyte anions in the voltammetry of carbon electrodes modified by attachment of bis(fulvalene)diiron (BFD) through an ethynyl group[22]. In the ethynyl-BFD case, the differences in the measured peak widths and surface currents became larger in the second oxidation process (in which the dication was formed), but were already observable in the first oxidation process. We ascribed this “large anion” effect on the surface currents to mixed diffusion near the electrode surface, in which diffusion of the anion must involve a transport process encumbered by steric effects. An analogous model has been proposed to account for similar reduced currents in polyviologen films[23].

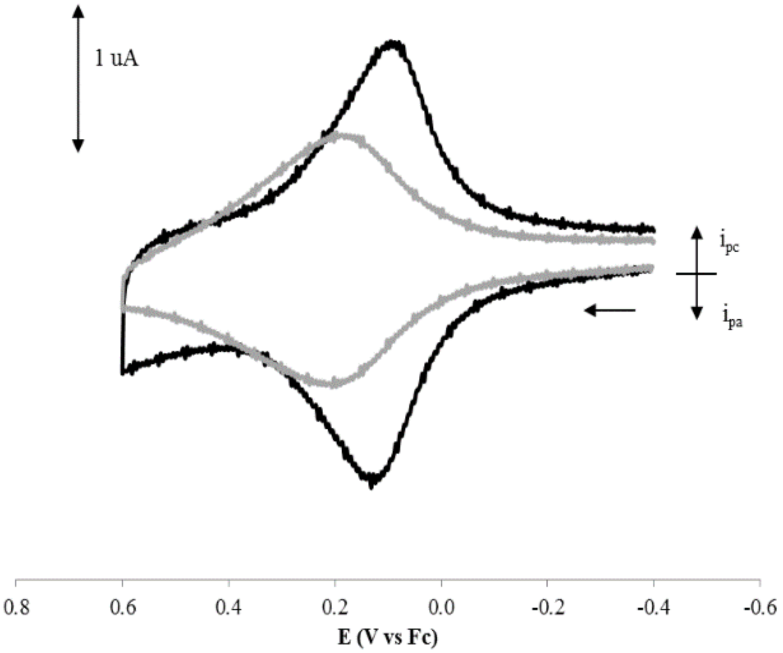

Figure 10. CV scans (ν = 0.5 V s^{-1}) in dichloromethane of a 1 mm glassy carbon electrode modified with **1** but recorded in two different supporting electrolytes: black, 0.1 M $[NBu_4][PF_6]$; gray, 0.05 M $[NBu_4][B(C_6F_5)_4]$.

One also notes that the $E_{1/2}$ potential is more positive (by 90 mV) when the electrolyte anion is $[B(C_6F_5)_4]^-$, which is consistent with comparative values for **1** in homogeneous solution (60 mV positive shift of $E_{1/2}$) and the general trends of larger anion electrolytes in solvents of lower polarity[21]. Smaller positive shifts in $E_{1/2}$ (30 mV for surface-bound 1; 0 mV in homogeneous solution) were measured when the scans were recorded in the more highly polar solvent nitromethane (ε = 36), in which ion-pairing effects are less important.

A somewhat surprising result was observed when the effect of the electrolyte anion on the scan-stability of the modified electrodes was probed. Compared to scans in a $[PF_6]^-$ solution, those taken in a $[B(C_6F_5)_4]^-$ solution showed about twice as fast a loss of surface waves, the opposite of what might have been anticipated, given the known general tendency of the $[B(C_6F_5)_4]^-$ anion to stabilize organometallic cation radicals[24]. In the present case, we suppose that tighter ion-pairing of the smaller $[PF_6]^-$ anion with oxidized ferrocenyl centers may protect them from follow-up reactions with adventitious nucleophiles such as trace water.

3. Conclusions

A number of new examples are reported in which ferrocenes containing terminal ethynyl groups have been strongly (most likely covalently) bonded to glassy carbon electrodes by anodic reactions in nonaqueous solvents containing $[NBu_4][PF_6]$ or $[NBu_4][B(C_6F_5)_4]$ as the supporting electrolyte. Either direct oxidation of the ethynyl group of the compound in dichloromethane, or oxidation of the ferrocenyl moiety of a compound that had been activated by lithiation of its ethynyl group in THF, proved successful in obtaining surface-modified carbon electrodes. Multiple deposition layers can be produced by repeated CV scans of the ferrocenyl compound's oxidation. Bulk electrolysis experiments and isolation of **5**[$SbCl_6$] provided insight into the stability of ethynyl-containing ferrocenium complexes and confirmed that further activation of the ethynyl-hydrogen bond is necessary for deposition to the electrode.

Both the direct oxidation method and the lithio-activation method were successfully employed for deposition of compounds **1**-**7**. However, the former was not suitable for compound **8** owing to the fact that the chemically irreversible oxidation of its tertiary amine group occurs at a potential less positive than that of its ethynyl group. In that case, the lithio-activation anodic method, which does not require direct oxidation of the ethynyl group of R-C≡CLi, was successfully employed. Acid-base chemistry for the amine in **8** was observed resulting in shifts in the redox potential between the amine and ammonium forms of both the homogeneous and surface-bound species.

A key factor in the efficacy of the lithio-activation method is that oxidation of R in R-C≡CLi must be accompanied by a sufficient transfer of positive charge to the ethynyl group to induce the loss of Li^+ and formation of the desired ethynyl radical. This mechanistic understanding suggests that if R is electronically removed from the ethynyl group, the increased positive charge in the latter resulting from the oxidation of R may be insufficient to trigger the loss of lithium ion. An important outcome of the present work is the observation that lithium ion expulsion occurs readily even when the redox center R (the ferrocenyl moiety in this case) is separated from the ethynyl group by two phenylethynyl moieties or three sigma bonds. Further work is necessary to how see much further a sigma-bonded bridge between R and C≡CLi may be extended before the anodic oxidation of R fails to free up Li^+ from the ethynyl group.

Experimental Section

General

Reactions and procedures were carried out under nitrogen, employing either Schlenk conditions or a Vacuum Atmospheres drybox. THF was dried either by treating it for at least 48 h with activated type 3 Å molecular sieve or by passing it through an alumina-based solvent system under argon. Compounds **1**-**8** were prepared as previously described[1,4,25] 1.6 M *n*-BuLi in hexanes was purchased from Acros or Aldrich and used as received. Details of the general conditions and approaches for this work are available in previous papers[1,4]. [NBu_4][$B(C_6F_5)_4$] was prepared as described earlier[26] and recrystallized from dichloromethane/diethyl ether. The $[SbCl_6]^-$ and $[B(C_6F_5)_4]^-$ salts of the thianthrene cation ($[C_{12}H_{18}S_2]^+$) were prepared as previously described.[27-29]

Electrochemistry

Voltammetry was carried out in cells having a separate reference electrode compartment in which an AgCl-coated silver wire was immersed in the same electrolyte used in the working/auxiliary compartments of the cell. At an appropriate point in the experiment, a small amount of decamethylferrocene (FcH^*) was inserted into the working compartment, allowing determination of the potential of $[FcH^*]^{0/+}$ vs Ag/AgCl in that cell. The analyte potentials thus measured vs FcH^* were converted to potentials vs ferrocene$^{0/+}$ by addition of 0.56 V in THF/0.1 M[NBu_4][PF_6] or 0.61 V in dichloromethane having either 0.1 M [NBu_4][PF_6] or 0.05 M [NBu_4][$B(C_6F_5)_4$] as the supporting electrolyte. All potentials in this paper are reported vs ferrocene, as recommended previously.[30-32]

Glassy carbon electrodes (Bioanalytical systems) were sequentially polished with Bühler diamond paste, washed with acetone, sonicated, and vacuum dried in the drybox antechamber before use. A PARC Model 273A potentiostat, linked to a personal computer that employed home-made software, was employed for voltammetry and electrolysis experiments. Bulk electrolysis experiments were carried out using a standard three-compartment "H-type" cell, using a Pt basket as the working electrode. When electrografting was to be carried out using the lithio activation method, particular attention was paid to the use of stringently dried glassware which had been heated overnight or longer at 110° C.

The *ex situ* lithio activation method[4] was carried out at 0° C. A 1 mL THF solution containing 100 μmol (*ca* 20 mg) of the ethynylferrocene derivative was prepared. To this was added approximately 1.1 equiv of *n*-BuLi taken from a 0.1 M stock solution prepared by addition of the commercial hexanes solution to THF. After allowing the lithiation reaction to proceed for 1 min, a sample was transferred to the working compartment of the electrochemical cell containing THF/0.1 M $[NBu_4][PF_6]$ at 0° C. This produced a nominal concentration of 4 mM of the lithiated ethynylferrocenyl derivative. Anodic oxidation of the lithio-activated compound at a gc electrode resulted in grafting of the compound onto the electrode surface. The electrode was then removed from solution, sonicated, and washed first with acetone and then with dichloromethane before putting it into a solution containing only solvent (THF or dichloromethane) and supporting electrolyte ($[NBu_4][PF_6]$ or $[NBu_4][B(C_6F_5)_4]$) for voltammetric characterization of the modified electrode.

The homogeneous bulk electrolysis experiments were carried out at ambient temperatures on 5-6 mM solutions of the unactivated ethynylferrocene derivative in either THF or dichloromethane. The applied potential of the large Pt basket working electrode was initially 0.4 V, sufficient to oxidize the ferrocene center but not the ethynyl group. The electrolysis was discontinued when the anodic current was less than 2% of the original value (typically after 20-30 min). After recording the voltammetry of the electrolyzed solution, the applied potential of the Pt basket was set at -0.6 V, sufficient to reduce the oxidation product back to the neutral starting material.

Chemical Oxidations

The chemical oxidations of compounds **1** and **5** were carried out with equimolar amounts of the thianthrene cation. The latter has a potential of approximately 0.86 V vs ferrocene,[31] sufficient to oxidize the ethynylferrocenes to the corresponding ethynylferrocenium cations. To 20 mg (78 μmol) of **5** in 1 mL dichloromethane was added 43 mg (78 μmol) of $[\text{thianthrene}][SbCl_6]$. To the resulting blue solution was added 5 mL hexanes, which caused precipitation of the desired salt in essentially quantitative yield. The solid was washed with hexanes and left to stand overnight at -10° C in dichloromethane, in which it had only limited solubility. In the morning, bright blue crystals had formed which were suitable for X-ray analysis. Similar oxidations were carried out on **1** by either $[\text{thianthrene}][SbCl_6]$ or $[\text{thianthrene}][B(C_6F_5)_4]$, resulting in isolation of salts of $\mathbf{1}^+$ that were contaminated with one or more minor side products (see Results and Discussion).

X-Ray Analysis

Three references (# 33-35) reserved for this section

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Conflict of Interest

The authors declare no conflict of interest.

Appendix: Supplementary data

13 pages describing the crystal data for [**5**][$SbCl_6$].

Keywords: electrochemical deposition; ferrocene; ethynyl group; electrolytes; large anions

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