JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

An Anodic Method for Covalent Attachment of Molecules to Electrodes through an Ethynyl Linkage

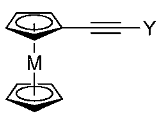
Matthew V. Sheridan, Kevin Lam, and William E. Geiger*

Department of Chemistry, University of Vermont, Burlington, Vermont 05405, United States

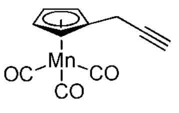
Supporting Information

ABSTRACT: Electroactive organometallic molecules have been covalently attached to electrode surfaces through an ethynyl linkage. The process takes advantage of ethynyl-based radicals generated by anodic oxidation of a lithio-activated terminal ethynyl group. Electrophores containing redox-active ferrocene, cymantrene, or cobaltocenium moieties have been deposited at the one-to-three monolayer level. Both metal-based and ligand-based chemical reactions have been carried out on the surface-modified systems.

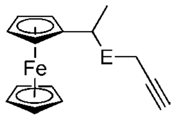
There is intense interest in broadening the families of electroactive molecular tags ("electrophores") which can be covalently attached to metal surfaces.[1] Attachment of an electrophore via an alkynyl linkage is particularly attractive owing to the structural rigidity of a −C≡C− moiety and its facility for efficient electron transfer.[2] The literature on electrografting from alkyne precursors is sparse. Halocarbon-substituted alkynes have been deposited on glassy carbon electrodes,[3] and the anodic reactions of ethynyl Grignards at surface-hydrogenated silicon have been reported to result in polymer layers having mostly single and double C−C bonds.[4] A wide-ranging electrochemical method for the covalent grafting of directly alkynyl-linked electrophores to surfaces has not been described. We now report such a method, which is based on the anodic oxidation of molecules having a lithio-activated ethynyl group generated by standard (*n*-BuLi in THF) *in situ* lithiation of a terminal ethyne. Among the electroactive organometallic moieties successfully deposited at the one-to-several monolayer level are those derived from ferrocene, cobaltocenium ion, and MnCp(CO)$_3$ (cymantrene, Cp = η^5-C$_5$H$_5$). Alkynyl-substituted amines and ethers have also been successfully deposited, indicating the molecular versatility of an activated alkyne approach. The ethynyl precursors for the electrografting reactions are shown below as compounds **1** and **3**−**6**. Strongly bound modified surfaces have been prepared using a number of different types of carbon and precious metal electrodes.



M = Fe, Y = H, **1**
M = Fe, Y = Li, **2**
M = Co$^+$, Y = H, **3**



4



E = N-^{n}Bu, **5**
E = O, **6**

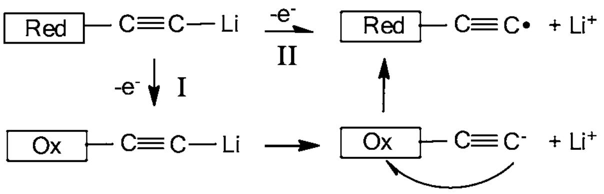
A terminal alkyne group, RC≡CH, has relatively high acidity, allowing for facile generation of its lithio derivative, RC≡CLi, under mild conditions. The deposition method involves anodic oxidation of RC≡CLi, which is expected to produce an alkynyl radical owing to rapid loss of lithium ion from the radical cation (eq 1), followed by reaction of the

$$\text{RC}{\equiv}\text{C-Li} - e^- \rightarrow [\text{RC}{\equiv}\text{C-Li}]^+ \rightarrow \text{RC}{\equiv}\text{C}\bullet + \text{Li}^+ \qquad (1)$$

$$\text{R}-\text{C}{\equiv}\text{C}\bullet + \boxed{\text{electrode}} \longrightarrow \text{R}-\text{C}{\equiv}\text{C}-\boxed{\text{electrode}} \qquad (2)$$

radical with an atom of the electrode (eq 2). In principle, the oxidation may occur either at R or at the alkynyl group, depending on the relative oxidizability of the two moieties (Scheme 1). In compounds **1**, **5**, and **6**, oxidation of R is clearly the more facile process (path **I** in the scheme), the potential for ferrocene being much lower than that usually encountered for an alkyne.[5] In these cases, production of the alkynyl radical is likely to occur through an internal electron-transfer (ET) process, with the electrophore acting as an ET mediator, analogous to the approach employed by Hernández-Muñoz et al. for the oxidatively promoted loss of CO$_2$ from ferrocenyl carboxylates.[6] In the case of compound **3**, the more facile oxidation is likely to occur directly at the ethynyl group (path II in Scheme 1) owing to the very high potential required to oxidize the cobaltocenium ion.[5,7] Both approaches have been used to produce modified electrodes.

Scheme 1



Attachment of an ethynylferrocenyl moiety to a glassy carbon electrode (GCE) follows path I. To an ∼100 mM solution of ethynylferrocene (**1**) in THF was added an equimolar amount of dilute (0.1 M) *n*-BuLi in THF to produce Fc-C≡CLi (**2**),[8] where Fc = FeCp(η^5-C$_5$H$_4$). After being stirred for only 1 min at 0 °C, a portion of the "lithio solution" sufficient to make a nominal 4 mM concentration of **2** was transferred to an electrochemical cell containing 0.1 M [NBu$_4$][PF$_6$] in THF, at which point cyclic voltammetry (CV) scans showed two major

Received: December 19, 2012
Published: February 5, 2013

dx.doi.org/10.1021/ja312405h | J. Am. Chem. Soc. 2013, 135, 2939−2942

anodic waves (gray insert of Figure 1). The irreversible first wave (A, $E_{pa} = -0.10$ V vs FcH)[9] is assigned to the oxidation of lithioethynylferrocene, with wave B ($E_{1/2}$ = 0.13 V) being assigned to oxidation of the parent, **1**.[10] If a CV scan at 0.1 V/s was carried out through wave A alone, followed by transfer of the electrode to a fresh dichloromethane/0.1 M $[NBu_4][PF_6]$ solution, evidence of monolayer-level coverage was obtained. Higher coverage levels (up to about three monolayers) were obtained by scanning through both waves A and B (typically, three times). However, it is important to note that no deposition was obtained when scanning through the oxidation of solutions of pure **1**, thus confirming the critical role of lithio activation of the ethynyl group. The electrode modifications are highly repeatable and their CV behavior in a pure electrolyte solution (Figure 1) is stereotypical[11] of a surface-confined reversible couple: peak currents are proportional to scan rate, and there are only small differences in the E_{pa} and E_{pc} values, the k^{o} value being 15 s^{-1}.[12] The $E_{1/2}$ value of 0.18 V vs FcH is consistent with the one-electron oxidation of an ethynyl ferrocene.[13] Little if any loss of current is seen in multiple scans, and the voltammetric performance did not degrade after storage of the modified GCE for several weeks under ambient conditions. Estimates of surface coverage (Γ) were obtained by integration of the CV waves. Based on comparison with the value of $\Gamma = 4.5 \times 10^{-10}$ mol/cm^2 calculated for an idealized ferrocene monolayer,[14] surface coverages of 1−3 monolayers are typically obtained.[15] Similar high-quality surface-confined waves were also obtained on edge and basalplane pyrolytic graphite, platinum, and gold electrodes.

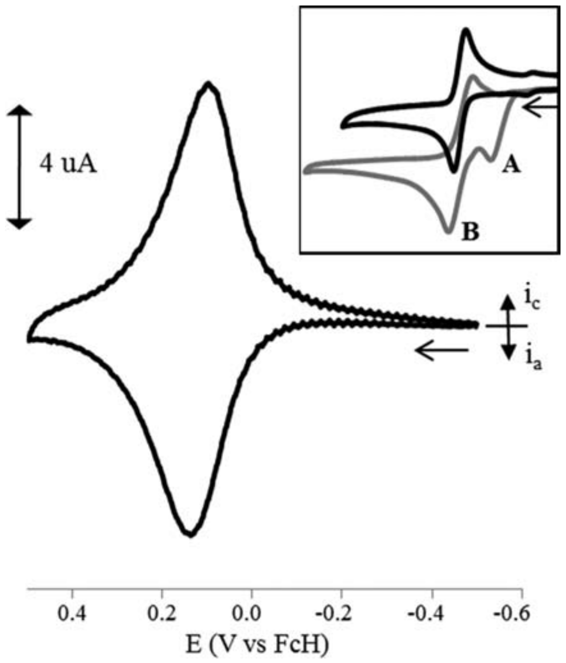


Figure 1. Background-subtracted CV of a GCE modified by **2** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$, scan rate 0.4 V/s, $\Gamma = 12.3 \times 10^{-10}$ mol/cm^2. The insert shows CVs in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ (scan rate 0.1 V/s) of gray line, 4 mM **2**; black line, 4 mM **1** and small amount of decamethylferrocene.

Ethynylferrocene-modified electrodes produced to date do not exhibit significant "blockage" toward electron-transfer to redox-active solution analytes (see CV for decamethylferrocene at an ethynylferrocene-modified GCE, Figure S1).

The question of whether this electrografting approach is restricted to alkynyl groups directly bonded to cyclopentadienyl rings was addressed by employing the lithio activation method to the amine **5** and the ether **6**. In the case of **5** a nominal monolayer was obtained after three CV scans of the lithio solution ($\Gamma = 3.7 \times 10^{-10}$ mol/cm^2) and multilayer coverage[16] has been obtained for **6** ($\Gamma = 33 \times 10^{-10}$ mol/cm^2). Surface-bound ligand reactivity was observed for electrodes modified by **5**, for which the ferrocenyl potential was either $E_{1/2}$ = 0.13 or −0.06 V, depending on whether the electrode had been dipped in acid or base,[17] respectively (see Figure 2 and Scheme 2). The positive shift of the ferrocenyl potential for the acid-treated derivative has been verified by independent study of both **5** and the ammonium salt, **5**-H$^+$, in homogeneous solution. This potential shift results from the electronic influence of the nitrogen atom on the oxidation at the iron center in **5**. The protonated amine is more electron deficient, resulting in a more positive oxidation potential.

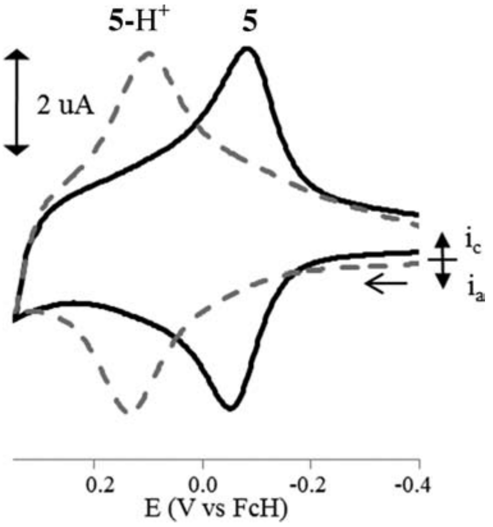
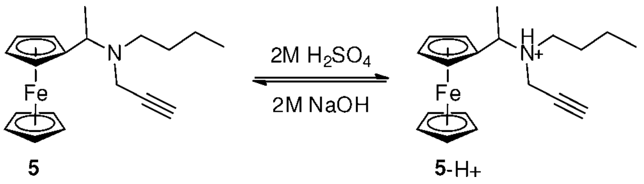


Figure 2. CV of modified GCEs in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ (scan rate 0.4 V/s). Solid line: electrode modified by amine **5**; dashed line: modified electrode after treatment with 2 M H_2SO_4, now containing **5**-H$^+$. The original solid line is regenerated after treatment of the **5**-H$^+$ electrode with 2 M NaOH.

Scheme 2



Metal-based chemical reactions have also been carried out on the organometallic-modified surfaces. Electrodes which had been modified by propargyl cymantrene (**4**) contain an anodic peak in pure CH_2Cl_2/0.05 M $[NBu_4][PF_6]$ at the potential (E_{pa} = 0.76 V) expected for a cymantrene derivative.[18] It is well known that, compared to their 18-electron counterparts, 17-electron metal carbonyl complexes have a greatly increased propensity for substitution of one or more COs by an electron-donating ligand.[19] To test this effect in the surface-bound manganese tricarbonyl system **4**, the modified electrode was scanned anodically in an electrolyte solution containing

$P(OMe)_3$ (Figure S2). A single scan past the oxidation of **4** resulted in loss of most of the cymantrene wave and introduction of reversible waves for follow-up products at $E_{1/2}$ = 0.41 and −0.18 V. The new waves (see square wave voltammogram in Figure 3, taken in pure electrolyte solution) are assigned to monosubstituted **7** and disubstituted **8**, respectively (see Scheme 3). Comparisons of the ligand substitution reactions with those observed in homogeneous solution[20] and at a directly cyclopentadienyl-bonded manganese tricarbonyl electrode[21] are underway.

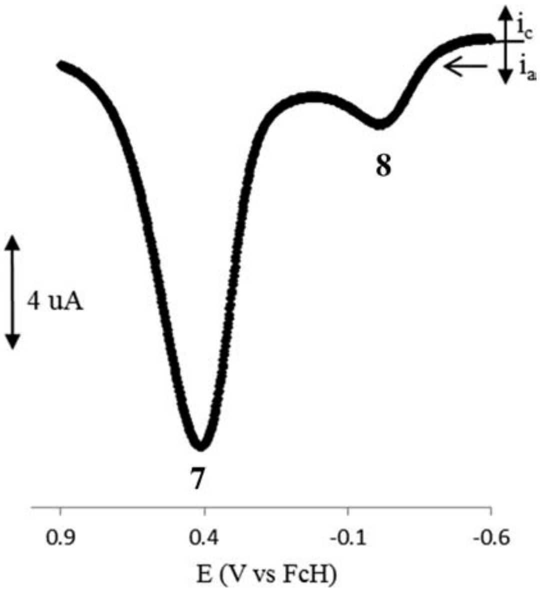
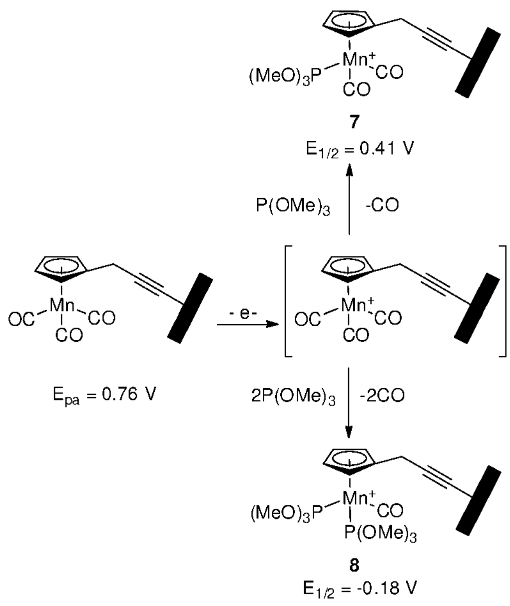


Figure 3. Square-wave voltammogram (200 Hz) of modified GCE in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$.

Scheme 3



Finally, we report a deposition ascribed to direct oxidation of the lithio-activated ethynyl moiety (path II in Scheme 1). A lithio solution of the ethynylcobaltocenium ion, **3**, which is not easily oxidizable at the metal center,[7] has complex anodic features in the range of −0.2 to 1.2 V (Figure S3). Scanning to 1.2 V resulted in an electrode with a surface wave at ($E_{1/2}$ = −1.31 V vs FcH, Figure 4) that is consistent with the one-electron reduction of ethynylcobaltocenium to ethynylcobaltocene.[22,23]

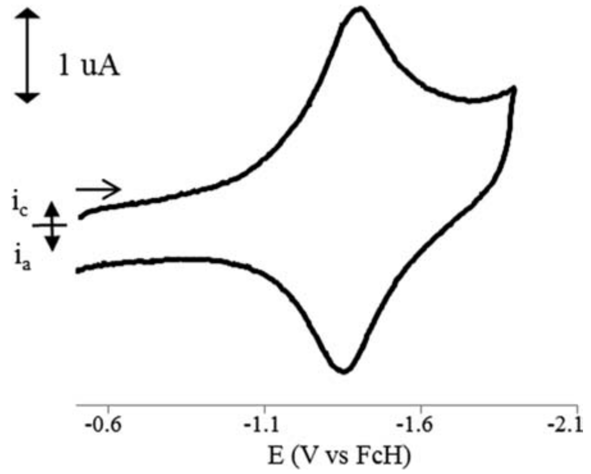


Figure 4. CV of a GCE modified with **3** in THF/0.1 M $[NBu_4][PF_6]$, scan rate 0.4 V/s.

In summary, a route to covalently modified electrodes is described based on the method of anodic oxidation of lithio-activated[24] ethynyl groups. Organometallic electrophores varying in transition metal, ligand composition, and charge have been attached at the one-to-several monolayer level to a number of different electrode surfaces. The surface-bound molecules undergo either metal-based or ligand-based reactions which mimic the homogeneous reactions of their parent molecules. Although the grafting process has conceptual analogies in other radical-based electrode modification procedures, including the aryldiazonium reduction[1,25] and carboxylate oxidation[6] procedures, an ethynyl-based method offers the unprecedented advantage of molecule-to-electrode bonding through a structurally rigid π linkage. Future work will concentrate on developing the surface chemistry of the organometallic-modified electrodes and in expanding the attachment method to include strictly organic electrophores.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for the electrode modifications, a table of potentials relevant to this work, sample cyclic voltammograms, and the preparation of new compounds **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

william.geiger@uvm.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE -0808909 and -1212339).

REFERENCES

(1) Bélanger, D.; Pinson, J. *Chem. Soc. Rev.* **2011**, *40*, 3995.

(2) For leading references, see: (a) Gendron, F.; Burgun, A.; Skelton, B. W.; White, A. H.; Roisnel, T.; Bruce, M. I.; Halet, J.-F.; Lapinte, C.; Costaus, K. *Organometallics* **2012**, *31*, 6796. (b) Roberts, H. N.; Brown, N. J.; Edge, R.; Fitzgerald, E. C.; Ta, Y. T.; Collison, D.; Low, P. J.; Whiteley, M. W. *Organometallics* **2012**, *31*, 6322. (c) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2006**, *106*, PR1. (d) Low, P. J. *Dalton Trans.* **2005**, 2821. (e) Ren, T. *Organometallics* **2005**, *24*, 4854.

(3) (a) Vase, K. H.; Holm, H.; Pedersen, S. U.; Daasbjberg, K. *Langmuir* **2005**, *21*, 8085. (b) Weissmann, M.; Baranton, S.; Coutanceau, C. *Langmuir* **2010**, *26*, 15002.

(4) Fellah, S.; Amiar, A.; Ozanam, F.; Chazalviel, J.-N.; Vigneron, J.; Etcheberry, A.; Stchakovsky, M. *J. Phys. Chem. B* **2007**, *111*, 1310.

(5) The oxidation potentials of alkynes are typically 1 V vs ferrocene or higher. See: (a) Fu, Y.; Liu, L.; Yu, H.-Z.; Wang, Y.-M.; Guo, Q.-X. *J. Am. Chem. Soc.* **2005**, *127*, 7227. (b) Katz, M.; Wendt, H. *Electrochim. Acta* **1976**, *21*, 215. (c) Bauer, R.; Wendt, H. *J. Electroanal. Chem.* **1977**, *80*, 395.

(6) Hernández-Muñoz, L. S.; González-Fuentes, M. A.; Díaz-Sánchez, B. R.; Fragoso-Soriano, R.; Vázquez-López, C.; González, F. J. *Electrochim. Acta* **2012**, *63*, 287.

(7) The Co(III) metal center is not further oxidized until 2.6 V vs FcH. See: Bard, A. J.; Garcia, E.; Kukharenko, S.; Strelets, V. V. *Inorg. Chem.* **1993**, *32*, 3258.

(8) Yuan, Z.; Taylor, N. J.; Marder, T. B.; Williams, I. D.; Cheng, L.-T. *J. Organomet. Chem.* **1993**, *449*, 27.

(9) Ag/AgCl was used as the experimental reference electrode, with decamethylferrocene (FcH*) being the in situ reference owing to its oxidation potential being well negative of the potentials of the lithioethynyl analytes. Conversion to the IUPAC-recommended ferrocene potential was made by subtraction of 0.45 V from the FcH* potential.

(10) Compound **1** is likely formed in the electrochemical reaction layer owing to follow-up reactions of the radical Fc-C≡C$^\bullet$ with solvent. It may also be present owing to incomplete lithiation of **1**.

(11) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley & Sons: New York, 2001; pp 589−592.

(12) Laviron, E. *J. Electroanal. Chem.* **1979**, *101*, 19.

(13) Štěpnička, P.; Trojan, L.; Kubišta, J.; Ludvík, J. *J. Organomet. Chem.* **2001**, *637−639*, 291.

(14) Seo, K.; Jeon, I. C.; Yoo, D. J. *Langmuir* **2004**, *20*, 4147.

(15) The relationship of surface coverage to electrolysis conditions, which has been intensely studied[1] for other radical attachment methods, will be discussed in due course. In brief, deeper coverage is obtained with an increased number of CV scans, a higher concentration of the lithiated alkynyl complex, or more positive potential scans.

(16) Of the systems studied to date, **6** shows the greatest tendency to form deeper layers, depending on electrolysis conditions (Figure S4). The coverage given here was the result of 10 CV scans.

(17) Postmodification, the electrode was washed with acetone and dichloromethane, sonicated in dichloromethane for 5 min, and rewashed with both solvents. After it was quickly dipped into an acid or base solution, the electrode was washed with distilled water and acetone before being placed in a pure electrolyte solution.

(18) Laws, D. R.; Chong, D.; Nash, K.; Rheingold, A. L.; Geiger, W. E. *J. Am. Chem. Soc.* **2008**, *130*, 9859.

(19) (a) Basolo, F. *New J. Chem.* **1994**, *18*, 19. (b) Geiger, W. E. *Organometallics* **2007**, *26*, 5738, see especially pp 5756−5759.

(20) (a) Atwood, C. G.; Bitterwolf, T. E.; Geiger, W. E. *J. Electroanal. Chem.* **1995**, *397*, 279. (b) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

(21) Laws, D.; Sheats, J.; Rheingold, A.; Geiger, W. E. *Langmuir* **2010**, *26*, 15010.

(22) Separate measurements give $E_{1/2}$ of the reduction of **3** in THF/[NBu$_4$][PF$_6$]solution as −1.18 V.

(23) With limiting Γ values of about 1.9×10^{-10} mol cm^2, the surface coverage for **3** is only about half the amount calculated for a neutral alkynyl-linked metallocene monolayer. However, the location of the $[PF_6]^-$ counterion is not taken into account in this model.

(24) Organolithio solutions generally contain a number of concentration-and counterion-dependent equilibrating systems, including Li−C bonded species, ion pairs, aggregates, and solvates. See: (a) Reich, H. J. *J. Org. Chem.* **2012**, *77*, 5471. (b) Bauer, W. In *Lithium Chemistry*; Sapse, A.-M., von Raugé Schleyer, P. Eds.; John Wiley & Sons: New York, 1995; pp125−172. The effects of changes in supporting electrolytes on the deposition processes are being probed.

(25) Delamar, M.; Hitmi, R.; Pinson, J.; Savèant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 5883.