An Organometallic Electrode Based on Covalent Attachment of the Cobaltocenium Group to Carbon

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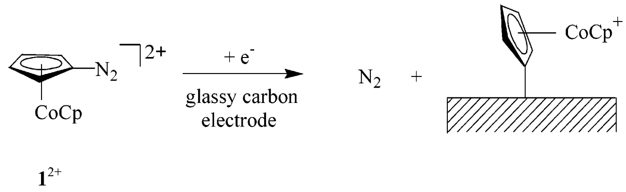
Summary: Electrochemical reduction of a cobaltocenium diazonium complex results in covalent attachment of the cobaltocenium ion to a glassy-carbon surface and formation of an "organometallic electrode".

Modification of surfaces with sites or layers containing organometallic groups is an emerging area of materials chemistry.[1] In many cases, it is desirable to attach the organometallic moiety to the surface more strongly than is possible through other modification strategies, such as the use of polymer films and weakly bound molecular tethers (e.g., thiols on gold).[2] This goal has been realized in the case of purely organic aryls on conducting surfaces by the radical process first described by Delemar et al.[3a] In this procedure, one-electron reduction of an aryldiazonium ion at a carbon electrode results in covalent attachment of the aryl group to the electrode.[3,4] It is generally believed that rapid loss of dinitrogen from the cathodically produced neutral radical (($C_6H_4R{-}N_2)^\bullet \rightarrow C_6H_4R^\bullet + N_2$) produces an aryl radical which attacks and bonds to carbon and perhaps to surface functional groups.[3,5] In an effort to extend this promising methodology to organometallic systems, we turned to complexes of the ubiquitous cyclopentadienyl (Cp) ligand, specifically with the goal of electrochemically generating an organometallic radical that would covalently attach to the electrode surface through the C_5H_4 ring. One restriction in this strategy is the scarcity of well-characterized cyclopentadienyl-diazotized precursors. This is attributable in part to the strong oxidizing power of the diazonium ion,[6] which could lead to unwanted reactions with oxidation-prone metal centers (e.g., Fe(II) in ferrocene).[7] The cobaltocenium ion avoids this impediment, owing to its already high Co(III) oxidation state. Sheats reported the in situ preparation of the diazotized cobaltocenium derivative $[CoCp(C_5H_4N_2)]^{2+}$ (**1**$^{2+}$) and the study of its coupling reactions with phenols.[8] Prompted by his earlier report, we sought to electrochemically reduce **1**$^{2+}$ by one electron, thereby producing the monocation radical $[CoCp(C_5H_4)]^{\bullet+}$, a certain fraction of which would form a carbon-to-surface bond with the electrode (Scheme 1).[9]

Scheme 1



The present communication reports the success of this approach in the radical attachment of a cobaltocenium group to a glassy-carbon electrode. The cyclopentadienyl-to-carbon attachment provides an entry into "organometallic electrodes" having electrophores which may be of utility in the development of catalysts[10] and electrochemical sensors.[11]

Treatment of a $[PF_6]^-$ salt of cobaltocenium amine, $[CoCp(C_5H_4NH_2)]^+$, by a standard diazotization process (273 K, 6 M H_2SO_4, 1 equiv of $NaNO_2$, 5 min, followed by addition of HBF_4) gave a modest yield of a yellow-brown solid that is analytically consistent with **1**$^{2+}$ containing a mixture of $[PF_6]^-$ and $[BF_4]^-$ counterions.[12] When fresh solutions of 2−5 mM **1**$^{2+}$ in CH_3CN con-

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[9] The radical $[CoCp(C_5H_4)]^{\bullet+}$ will also undergo traditional homogeneous reactions such as H atom abstraction from the medium and formation of the cobaltocenium ion in fluid solution. Specific adsorption (see: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001; pp 554ff) of **1**$^{2+}$ prior to the cathodic reduction is expected to increase the fraction of surface-bonded species.

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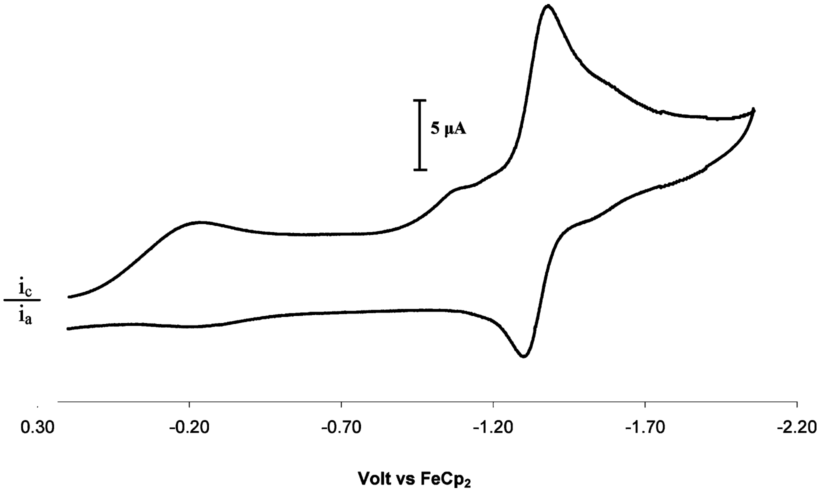

Figure 1. Cyclic voltammogram of 3 mM $\mathbf{1}^{2+}$ in CH_3CN/0.1 M $[NBu_4][BF_4]$ at a glassy-carbon electrode (2 mm diameter), with a scan rate of 0.2 V s^{-1}.

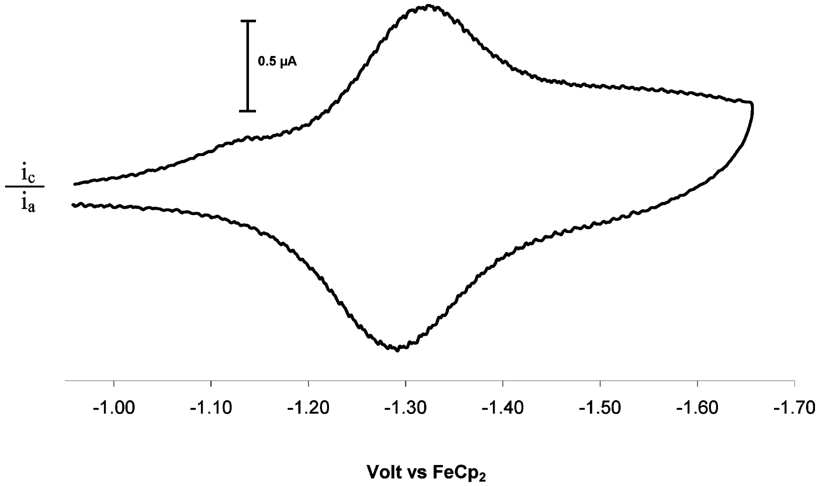

Figure 2. Cyclic voltammogram of a cobaltocenium-modified glassy-carbon electrode (2 mm diameter) in CH_3CN/0.1 M $[NBu_4][BF_4]$ with a scan rate of 0.1 V s^{-1}.

taining 0.1 M $[NBu_4][BF_4]$ were investigated by cyclic voltammetry (CV), a highly *ir*reversible reduction was observed at E_{pc} = ca. −0.25 V (all potentials vs ferrocene/ferrocenium)[13] and assigned to the reduction of the cyclopentadienyldiazonium ligand.[14] One or more apparently reversible features are also seen at ca. −1.3 V (see Figure 1), in the region expected for a cobaltocenium/cobaltocene couple.[15]

If, after an electrolysis potential of −0.7 V is applied for 10 min, the electrode is removed from solution, rinsed with acetonitrile, and transferred to a solution containing *only* solvent and supporting electrolyte, a chemically reversible pair of surface waves is observed at $E_{1/2}$ = −1.32 V, as expected[15] for a $[CoCp(C_5H_4R)]^{+/0}$ redox process (Figure 2). Repeated scans through this wave result in little, if any, change in current. A second cathodic peak, this one irreversible, at E_{pc} = −2.46 V is also observed and assigned to formation of the highly reactive[16] cobaltocene anion. Scanning through this second wave severely diminishes the surface waves at −1.32 V, apparently owing to a chemical follow-up reaction of the cobaltocene anion.

At a CV scan rate of 0.1 V s^{-1}, the cathodic and anodic peaks attributed to $[CoCp(C_5H_4R)]^{+/0}$ have a ΔE_p value of ca. 40 mV. Although a ΔE_p value of 0 V is expected for an idealized monolayer displaying Nernstian charge transfer,[17] the measured value is similar to those typically observed for surface-immobilized redox couples.[18] The cathodic wave has a linear dependence of peak current on CV scan rate, confirming that it arises from a surface-confined species. The small prewave shown in Figure 2 does not appear in all samples and may arise from a chemically distinct second surface site. It diminishes with successive scans.

The modified electrode does not appear to undergo a significant loss of surface material if it is washed with water or with organic solvents, and it retains most of its coverage even when subjected to extensive sonication

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(12) Anal. Found (Robertson Laboratories): C, 26.59; H, 1.64; N, 6.30; P, 5.72, S, 0.06. Calcd for $[CoCp(C_5H_4N_2)][BF_4][PF_6]$: C, 26.80; H, 2.03; N, 6.26; P, 6.92.

(13) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

(14) Reduction of the diazonium group in the well-studied ion $[C_6H_5\text{-}(4\text{-}NO_2)]^+$ occurs at an E_{pc} value of −0.20 V. The potential of +0.20 V vs SCE reported for $[C_6H_5(4\text{-}NO_2)]^+$ in ref 2b has been converted to the $[FeCp_2]^{0/+}$ reference value by the procedure given in ref 6.

(15) (a) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527. (b) Stojanovic, R. S.; Bond, A. M. *Anal. Chem.* **1993**, *65*, 56.

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in water. It is unchanged after being exposed to ambient air for several weeks. An electrochemically clean electrode may be regenerated by a traditional mechanical polishing of the surface.

The fact that the observed chemical and physical properties of the modified electrode are highly analogous to those reported for aryl-modified organic electrodes[3−5] is strong evidence that the cobaltocenium moiety is bound to the electrode predominantly through a cyclopentadienyl carbon-to-surface covalent bond. The idealized structure shown in Scheme 1 assumes a bent horizontal structure in which no H atom is closer than its van der Waals radius of 1.2 Å. On the basis of this geometry, the monolayer coverage is estimated as 3.8×10^{-10} mol cm^{-2}, a value that should be considered an upper limit, because it does not take into account the presently unknown position of the $[BF_4]^-$ counterion. The surface coverage was measured by integration of the cathodic portion of the CV curve as $[2.4(\pm 0.4)] \times 10^{-10}$ mol cm^{-2}, consistent with approximately monolayer coverage. In the case of organic aryl systems, prolonged electrolysis may give thicker layers,[4b,5a,19] an apparent consequence of attack on the surface-bound aryl group by another electrochemically generated aryl radical. We have, to date, found no evidence of multilayering in the cobaltocenium-modified electrode, but more detailed studies of this possibility are underway.

The cobaltocenium-modified electrode allows the detection of analytes in the bulk solution which are redox active at potentials higher than −1.3 V vs $[FeCp_2]^{+/0}$. The CV peak separations of nominally Nernstian analyte couples are slightly increased over the values observed at a nonmodified electrode, implying a somewhat slower charge-transfer rate for the analyte at the modified electrode. For example, ΔE_p is 120 mV at $v = 0.2$ V/s for solution ferrocene at the cobaltocenium-modified electrode (see the figure in the Supporting Information), compared with 65 mV or less at a normal polished glassy-carbon electrode. Similar charge-transfer rate effects, sometimes referred to as electrode "barrier properties", are commonly observed for solution analytes at different types of modified electrodes[5a,b,20,21] and can arise from a number of factors, including charge transfer through surface defect sites.[22] The origin of sluggish electron transfer in the present case will be more apparent when more is known about the layer structure (e.g., integrity of coverage) of the electrode.

In summary, we present evidence that cathodic one-electron reduction of the diazotized cobaltocenium derivative $[CoCp(C_5H_4N_2)]^{2+}$ produces a radical cation that binds covalently to carbon and possibly to other atoms[23] on a glassy-carbon electrode, thereby providing approximately monolayer coverage of a strongly bound cobaltocenium group. This appears to be the first example of direct covalent bonding of a cyclopentadienyl ring to an electrode surface and confirms that the electrochemically induced radical method is a viable route to attachment of cyclopentadienylmetal systems to conducting surfaces.[24] Owing to the strength of the cyclopentadienyl-to-surface bond (>100 kcal/mol assumed for the C−C bond), this electrode is much more robust[25] than modified electrodes and surfaces which depend on attachment through weaker chemical bonds (e.g., S−Au[2b,26]). On the basis of the aryl-radical analogy,[3−5] we expect that the cyclopentadienyl-radical attachment strategy will also be successful on other types of carbon surfaces (e.g. carbon nanotubes[3c]) as well as on certain families of metals.[4,5d] In addition to contributing to the area of metallocenyl-based sensors,[11] metal−cyclopentadienyl-derivatized surfaces may also prove useful in the broader area of catalysis.[10]

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Supporting Information Available: Figure giving the cyclic voltammogram of 1 mM ferrocene in acetonitrile/0.1 M $[NBu_4][PF_6]$ using a cobaltocenium-modified electrode, at a scan rate of 0.2 V s^{-1}. The material is available free of charge via the Internet at http://pubs.acs.org.

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