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Anodic oxidation of organometallic sandwich complexes using $[Al(OC(CF_3)_3)_4]^-$ or $[AsF_6]^-$ as the supporting electrolyte anion

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Dedicated to Russell Hughes, in appreciation of both his friendship and his contributions to organometallic chemistry.

ABSTRACT

Anodic voltammetry and electrolysis of the metallocenes ferrocene, ruthenocene, and nickelocene have been studied in dichloromethane containing two different fluorine-containing anions in the supporting electrolyte. The perfluoroalkoxyaluminate anion $[Al(OC(CF_3)_3)_4]^-$ has very low nucleophilicity, as shown by its inertness towards the strong electrophile $[RuCp_2]^+$ and by computation of its electrostatic potential in comparison to other frequently used electrolyte anions. The low ion-pairing ability of this anion was shown by the large spread in $E_{1/2}$ potentials ($\Delta E_{1/2} = 769$ mV) for the two one-electron oxidations of bis(fulvalene)dinickel. The hexafluoroarsenate anion $[AsF_6]^-$, on the other hand, reacts rapidly with the ruthenocenium ion and is much more strongly ion-pairing towards oxidized bis(fulvalene)dinickel ($\Delta E_{1/2} = 492$ mV). In terms of applications of these two anions to the anodic oxidation of organometallic sandwich complexes, the behavior of $[Al(OC(CF_3)_3)_4]^-$ is similar to that of other weakly-coordinating anions such as $[B(C_6F_5)_4]^-$, whereas that of $[AsF_6]^-$ is similar to the more traditional electrolyte anions such as $[PF_6]^-$ and $[BF_4]^-$. Additionally, the synthesis and crystal structure of $[Cp_2Fe][Al(OC(CF_3)_3)_4]$ are reported.

1. Introduction

Supporting electrolytes containing weakly-coordinating anions (WCAs) have proven to be superior to more traditional electrolyte anions such as $[BF_4]^-$ or $[PF_6]^-$ for the stabilization of reactive organometallic radical cations [1]. Among the WCAs used for organometallic electrochemistry, the fluoro-substituted aryl borates $[B(C_6F_5)_4]^-$ (TFAB) and $[B(C_6H_3(CF_3)_2)_4]^-$ (BArF$_{24}$) have garnered the greatest attention [1–3]. It is desirable, however, to expand the number of electrochemically-suitable WCAs in order to provide a larger "tool box" from which anions might be chosen for particular molecular applications.

Certain aspects of the electrochemical behavior of weakly-coordinating perfluorinated alkoxyaluminates $[Al(OR^F)_4]^-$ [4,5], have been published. Conductivities have been reported for their lithium [6] and tetraalkylammonium [7] salts, and it has been established that the anions are quite resistive to anodic oxidation [6,7]. A number of very reactive organic or inorganic cations have been stabilized and isolated as their $[Al(OC(CF_3)_3)_4]^-$ salts, including simple $[CX_3]^+$ carbenium ions (X = Cl, Br, I) [8], oxidants like $[NO]^+$ and $[NO_2]^+$ [9], electrophilic E–X cations (E = P, As, X = halogen) [10], and strong cationic Brønstead acids [11]. Moreover, this family of anions promotes the solubility and dissociation of compounds that are normally difficult to dissolve and prone to formation of strong ion pairs, e.g., silver (I) and copper (I) complexes in lower polarity solvents [12]. Imidazolium salts of these anions are ionic liquids at modest temperatures [13]. To our knowledge, however, fluoroalkoxyaluminate anions have not been evaluated for their efficacy in supporting electrolytes for molecular electrochemistry. This paper reports voltammetry and electrolysis experiments using the commercially available [14] $[NBu_4][Al(OC(CF_3)_3)_4]$ as the supporting electrolyte, and ferrocene, ruthenocene, and nickelocene, MCp_2 (M = Fe, Ru, Ni, respectively; Cp = η^5-C_5H_5) being the test compounds.

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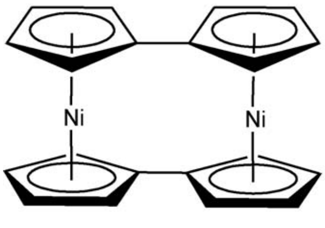
We also provide data involving the hexafluoroarsenate anion $[AsF_6]^-$, on the same metallocenes. Interest in this anion derives in part from the report that the anodic oxidation of C_{60} is chemically reversible in $CH_2Cl_2/[NBu_4][AsF_6]$, with even the trication $[C_{60}]^{3+}$ being detected by low-temperature cyclic voltammetry (CV) [15,16]. Owing to the fact that the oxidation of $[AsF_6]^-$ is very difficult, its anodic "window" is extended to more positive values than those of TFAB or $BArF_{24}$, and, as it turns out $[Al(OC(CF_3)_3)_4]^-$. This property could be of value in probing more difficult to oxidize organometallic systems. The metallocene complexes provide suitable tests of the nucleophilicity of $[AsF_6]^-$ towards organometallic radical cations as well as the solubilites of their salts in lower polarity solvents. The question of the ion-pairing strengths of $[Al(OC(CF_3)_3)_4]^-$ (anion structure shown below) and $[AsF_6]^-$, both relative to each other and to the fluoro-substituted aryl borate anions, were also probed through measurement of the separation of the two oxidative $E_{1/2}$ potentials of bis(fulvalene)dinickel, **1** [17,18].



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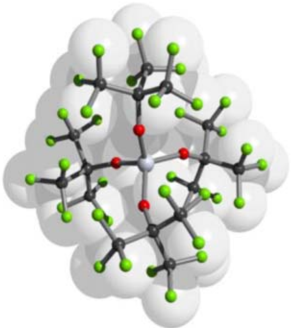

2. Results

2.1. Structure of $[Cp_2Fe][Al(OC(CF_3)_3)_4]$

In accordance with electrochemical experiments which showed the oxidation of ferrocene to be chemically reversible in fluoroalkoxyaluminate-based electrolytes (*vide infra*), the ferrocenium aluminate salt was easily isolated and structurally characterized. This compound may directly be prepared by chemical oxidation of ferrocene with the silver salt $Ag[Al(OC(CF_3)_3)_4]$ in o-$F_2C_6H_4$ solution; the crystalline material was analyzed by single crystal X-ray diffraction, leading to the molecular structure shown in Fig. 1.

$[Cp_2Fe][Al(OC(CF_3)_3)_4]$ consists of almost undisturbed, non-interacting ferrocenium cations and $[Al(OC(CF_3)_3)_4]^-$ anions, with structural parameters in the usual range.

2.2. Electrochemistry using $[NBu_4][Al(OC(CF_3)_3)_4]$

Tetraalkylammonium salts of fluorinated alkoxyaluminates have fairly high conductance values in lower polarity solvents [7], roughly comparable to those found for the equivalent TFAB salts [19]. A saturated solution (40 mM) of $[NBu_4][Al(OC(CF_3)_3)_4]$ in CH_2Cl_2 allows the recording of cyclic voltammetry (CV) scans with acceptable [19] ohmic errors. For example, a ΔE_p value [20] of 85 mV was measured for the ferrocene/ferrocenium couple under routine CV conditions (1 mM ferrocene, scan rate of 0.2 V s^{-1}, 2 mm glassy carbon electrode). The "window" available in CH_2Cl_2/0.04 M $[NBu_4][Al(OC(CF_3)_3)_4]$ was approximately 1.7 V *vs.* FcH in the positive direction and −2.4 V in the negative direction.

A good test for the nucleophilicity of an anion is in how it affects the anodic reaction of ruthenocene. As originally reported by Hill et al., a reversible one-electron oxidation is seen for this compound only in the absence of nucleophilic anions [2]. Subsequent work

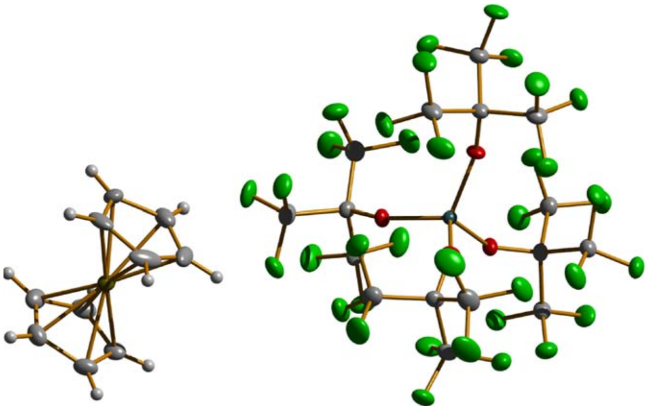

Fig. 1. Molecular structure of the asymmetric unit of the crystal structure of $[Cp_2Fe][Al(OC(CF_3)_3)_4]$ showing 50% thermal ellipsoids. Selected bond lengths [Å]: Al–O = 1.726(2)–1.731(2); C–O = 1.348(3)–1.357(3); C–F = 1.326(3)–1.350(3); Fe–C = 2.083(3)–2.097(3).

confirmed this observation, demonstrating that addition of minute amounts of $[PF_6]^-$ to a solution of $RuCp_2$ in CH_2Cl_2/0.05 M $[NBu_4][TFAB]$ resulted in rapid decomposition of the ruthenocenium cation and conversion of the oxidation of ruthenocene to a multi-electron process [21,22]. The anodic behavior of ruthenocene in CH_2Cl_2/0.04 M $[NBu_4][Al(OC(CF_3)_3)_4]$ mimics that observed in TFAB-based electrolytes. Its quasi-Nernstian [23] one-electron oxidation ($E_{1/2}$ = 0.57 V *vs.* FcH) is almost completely reversible at room temperature. There was also a small, broad, cathodic peak at approximately −0.2 V which was better presented when the electrode potential was held positive of the ruthenocene oxidation potential for 5 s before scanning back in the negative direction (see Fig. 2; this scan sequence allows the electrode products to reach a near steady-state concentration). This new cathodic feature is in the right range for reduction of the metal-metal bonded dimer dication $[Ru_2Cp_4]^{2+}$, which has been previously described in depth [21,22]. A diffusion coefficient of 2.1×10^{-5} cm^2 s^{-1} was measured for $RuCp_2$ using chronoamperometry. Bulk anodic electrolysis at 273 K confirmed the one-electron stoichiometry of the oxidation process and resulted in precipitation of an electrolysis product, presumably the dimer dication [22] $[Ru_2Cp_4][Al(OC(CF_3)_3)_4]_2$. Addition of decamethylferrocene to the solution reduced the dimer dication back to ruthenocene, regenerating about half of the original concentration of the metallocene. A second (unassigned) product was observed that had a partially chemically reversible oxidation at $E_{1/2}$ = 1.62 V, along with a small wave for the biruthenocene side product $[Ru_2Cp_2(\mu\text{-}C_{10}H_8)]$ ($E_{1/2}$ = 0.22 V) that

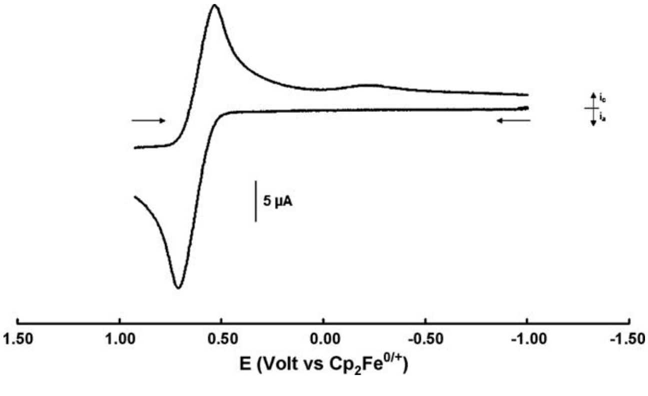

Fig. 2. Cyclic voltammogram of 1.1 mM $RuCp_2$ in CH_2Cl_2/0.04 M $[NBu_4][Al(OC(CF_3)_3)_4]$, scan rate 0.5 V s^{-1}. The potential sweep was stopped for 5 s at E_{appl} = 0.95 V to generate more of the follow-up product seen by its small cathodic wave at about −0.2 V.