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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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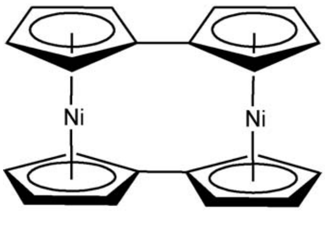
We also provide data involving the hexafluoroarsenate anion $[AsF_6]^-$, on the same metallocenes. Interest in this anion derives in part from the report that the anodic oxidation of C_{60} is chemically reversible in $CH_2Cl_2/[NBu_4][AsF_6]$, with even the trication $[C_{60}]^{3+}$ being detected by 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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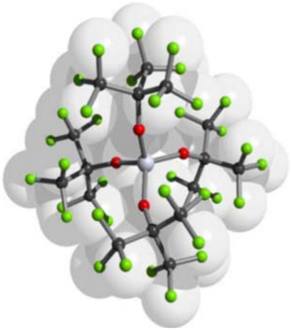

2. Results

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 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

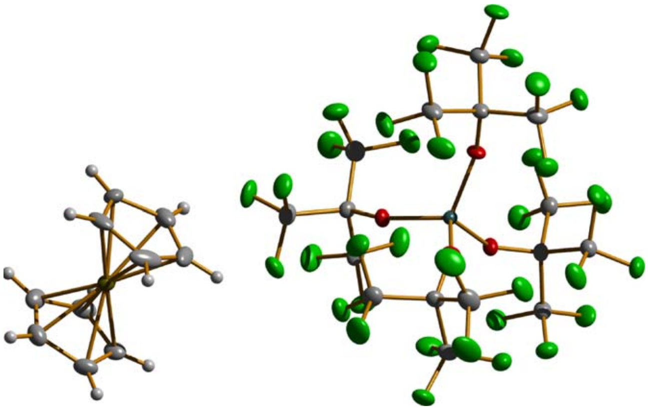

Fig. 1. Molecular structure of the asymmetric unit of the crystal structure of $[Cp_2Fe][Al(OC(CF_3)_3)_4]$ showing 50% thermal ellipsoids. Selected bond lengths [Å]: Al–O = 1.726(2)–1.731(2); C–O = 1.348(3)–1.357(3); C–F = 1.326(3)–1.350(3); Fe–C = 2.083(3)–2.097(3).

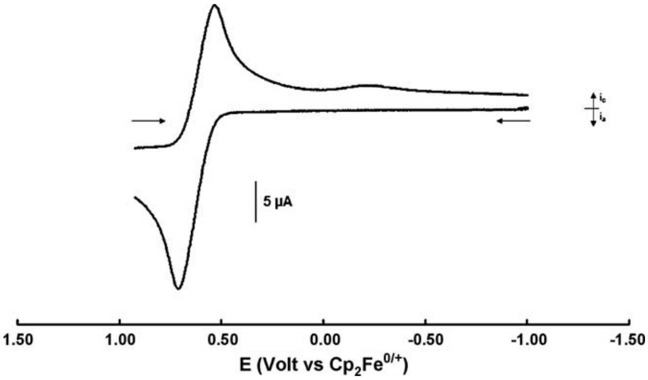

Fig. 2. Cyclic voltammogram of 1.1 mM $RuCp_2$ in CH_2Cl_2/0.04 M $[NBu_4][Al(OC(CF_3)_3)_4]$, scan rate 0.5 V s^{-1}. The potential sweep was stopped for 5 s at E_{appl} = 0.95 V to generate more of the follow-up product seen by its small cathodic wave at about −0.2 V.

had also been observed when the electrolysis of ruthenocene was carried out in TFAB-media [22].

Another metallocene anodic process which is quite medium-dependent is the second oxidation of nickelocene [24]. The neutral complex undergoes two successive one-electron oxidations (Eq. (1)) that are well-behaved and highly reversible only with non-donor

$$NiCp_2 \underset{E_{1/2}(1)}{\overset{-e^-}{\rightleftharpoons}} NiCp_2{}^{+} \underset{E_{1/2}(2)}{\overset{-e^-}{\rightleftharpoons}} NiCp_2{}^{2+} \qquad (1)$$

solvents and electrolyte anions that lend solubility to the nickelocene dication (e.g., CH_2Cl_2/[NBu_4][TFAB]). Dichloromethane was therefore chosen for the investigation of nickelocene in a $[Al(OC(CF_3)_3)_4]^-$-based electrolyte. Although a certain degree of chemical reversibility was seen in CV scans for the $NiCp_2{}^{+/2+}$ couple ($E_{1/2}(2)$ = 1.16 V), differential pulse voltammetry showed a highly diminished peak current for this process (see Fig. 3). This kind of behavior has been shown to be indicative of voltammetric complications in the $NiCp_2{}^{+/2+}$ process [24]. In the present case, in which the chemical reversibility argues against a fast follow-up reaction between $NiCp_2{}^{2+}$ and $[Al(OC(CF_3)_3)_4]^-$, it is likely that the nickelocene dication is strongly adsorbed on the electrode, an explanation supported by the fact that the working electrode had to be re-polished in between scans to avoid electrode "history" effects.

In terms of the thermodynamics of the two one-electron processes, the separation between them, $\Delta E_{1/2}$ (=$E_{1/2}(2) - E_{1/2}(1)$), of 1.59 V is even higher than the value of 1.52 V measured earlier for nickelocene in CH_2Cl_2/[NBu_4][TFAB] [24], indicating very weak ion-pairing of the perfluoroalkoxyaluminate anion with the nickelocenium dication. Additional comments about the ion-pairing tendency of $[Al(OC(CF_3)_3)_4]^-$ follow when considering the results obtained on bis(fulvalene)dinickel (*vide infra*).

2.3. Electrochemistry using [NBu_4][AsF_6]

Hexafluoroarsenate salts have found occasional application as a supporting electrolyte for a number of years, including use in liquid SO_2 anodic electrochemistry which involved the generation of reactive organic radical cations [25]. Bruno et al. showed that the nucleophilicity of $[AsF_6]^-$ is sufficiently low to allow at least transient generation of the trication $C_{60}{}^{3+}$ [15], and the actual isolation of the $[AsF_6]^-$ salt of the C_{60} dication has been reported [26]. As noted experimentally by Bruno et al., and confirmed calculationally [27], the hexafluoroarsenate anion has the advantage of offering a more positive electrochemical window compared to TFAB and $BArF_{24}$. However, the chemical properties of $[AsF_6]^-$ are generally quite similar to those of $[PF_6]^-$ [28], and complexes between Lewis-acidic metals and the $[AsF_6]^-$ moiety are well known [29]. Hence the nucleophilicity of $[AsF_6]^-$ towards reactive organometallic radical cations was still open to inquiry. A good test of this property was whether or not the highly electrophilic ruthenocenium ion [2,21,22] was stable in the presence of $[AsF_6]^-$. CV scans of $RuCp_2$ in CH_2Cl_2/0.1 M [NBu_4][AsF_6] gave a completely irreversible anodic wave (Fig. 4), of considerably greater than one-electron height (3–4 electrons by chronoamperometry), showing that $[RuCp_2]^+$ undergoes rapid attack by $[AsF_6]^-$.

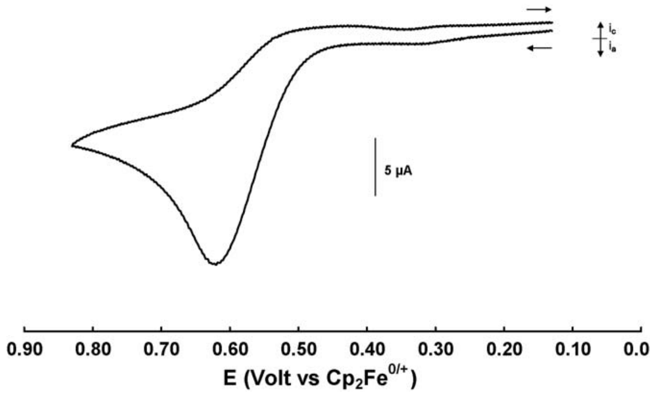

Fig. 4. Cyclic voltammogram of 1.0 mM $RuCp_2$ in CH_2Cl_2/1.0 M [NBu_4][AsF_6], scan rate 0.2 V s^{-1}.

The influence of $[AsF_6]^-$ on the oxidation of $NiCp_2$ was also probed. As shown in the dashed line of Fig. 5, the one-electron oxidation process $[NiCp_2]^{0/+}$ ($E_{1/2} = -0.43$ V *vs.* FcH) was well-behaved and reversible. Oxidation of nickelocene to the dication (E_{pa} *ca.* 0.6 V), however, gave every indication of severe adsorption of $[NiCp_2][AsF_6]_2$ onto the electrode, accompanied by a cathodic stripping wave at about −0.35 V. These scans are highly reminiscent of those seen for $[PF_6]^-$-based electrolytes in this solvent [24].

2.4. $\Delta E_{1/2}$ values for bis(fulvalene)dinickel$^{0/+/2+}$

Bis(fulvalene)dinickel, $Ni_2(\mu\text{-}C_{10}H_8)_2$ [30] has been used as a "standard" for probing the relative ion-pairing effects of anions in nonaqueous solutions by determining the separation in $E_{1/2}$ values of the two one-electron processes **1**/**1**$^+$ and **1**$^+$/**1**$^{2+}$ [17]. Investigation of the two anions considered in this paper $[Al(OC(CF_3)_3)_4]^-$

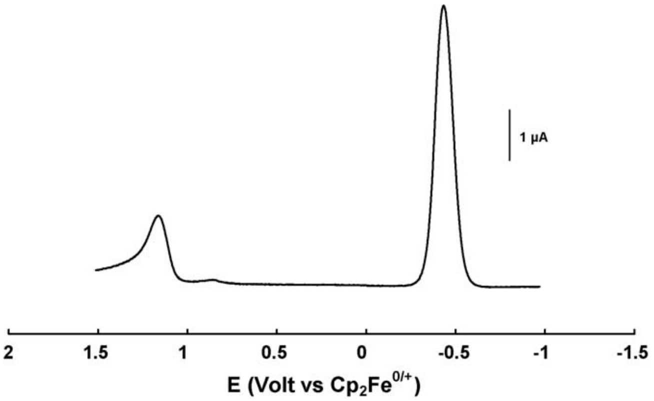

Fig. 3. Differential pulse voltammogram of 1.0 mM $NiCp_2$ in CH_2Cl_2/0.04 M [NBu_4][$Al(OC(CF_3)_3)_4$], pulse height 25 mV.

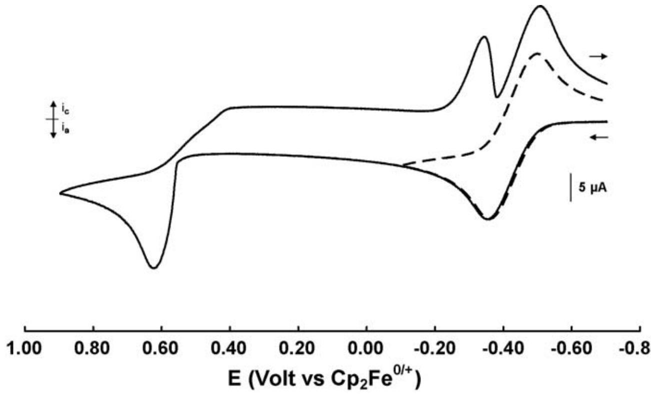

Fig. 5. Cyclic voltammogram of 1.3 mM $NiCp_2$ in CH_2Cl_2/1.0 M [NBu_4][AsF_6], scan rate 0.2 V s^{-1}. The dashed line switches the scan just positive of the first oxidation process.

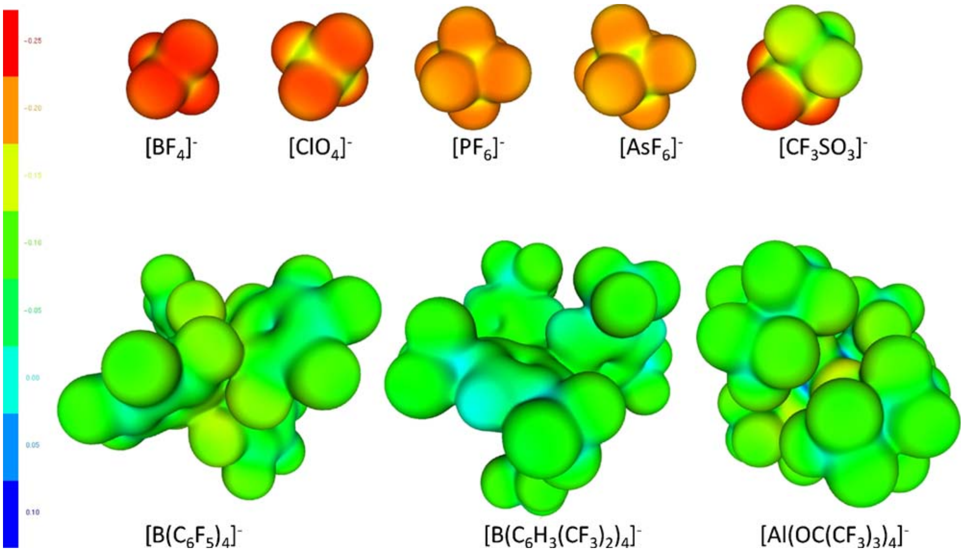

Fig. 6. Calculated electrostatic potentials, mapped on a 0.005 e^- $bohr^{-3}$ isosurface. The calculations were done using Turbomole (DFT-BP86/SV(P) full optimization including COSMO solvation model with epsilon = infinity).

and $[AsF_6]^-$, was straightforward, as there were no complications to the reversible one-electron processes observed by CV and by differential pulse voltammetry. $E_{1/2}$ potentials of −0.705 and 0.064 V, were measured, respectively, for the $\mathbf{1}/\mathbf{1}^+$ and $\mathbf{1}^+/\mathbf{1}^{2+}$ couples in CH_2Cl_2/0.04 M $[NBu_4][Al(OC(CF_3)_3)_4]$, and potentials of the corresponding couples in CH_2Cl_2/0.1 M $[NBu_4][AsF_6]$ were −0.731 and −0.239 V. The substantial difference in $\Delta E_{1/2}$ values (769 mV for $[Al(OC(CF_3)_3)_4]^-$ *vs.* 492 mV for $[AsF_6]^-$) is consistent with a greatly decreased ion-pairing interaction between the dication $\mathbf{1}^{2+}$ and the fluoroalkoxyaluminate anion. The ion-pairing of the oxidized forms of **1** with $[Al(OC(CF_3)_3)_4]^-$ is almost unchanged compared to TFAB ($\Delta E_{1/2}$ = 753 mV for 0.1 M $[NBu_4]$[TFAB] [17]), as is the ion-pairing of $[AsF_6]^-$ compared to $[PF_6]^-$ ($\Delta E_{1/2}$ = 480 mV for 0.1 M $[NBu_4]$[TFAB] [17]).

The conclusions with respect to ion-pairing are supported by the projection of the BP86/SV(P)-calculated electrostatic potentials of the traditional *vs.* weakly-coordinating anions. The pictorial image of the charge distributions in representative anions is shown in Fig. 6.

3. Conclusions

The $[NBu_4]^+$ salt of the weakly-coordinating anion $[Al(OC(CF_3)_3)_4]^-$ performs well as a supporting electrolyte anion in CH_2Cl_2. The anodic electrochemical behavior of representative metallocenes, MCp_2, M = Fe, Ru, Ni, mimics that observed previously for these complexes in TFAB- or $BArF_{24}$-containing media. It appears that electrode adsorption of cationic products may be more prevalent in CH_2Cl_2 when $[Al(OC(CF_3)_3)_4]^-$ is the electrolyte anion. The fluoroalkoxyaluminate anion does not appear to act as a nucleophile towards the ruthenocenium cation radical, and it undergoes only very weak ion-pairing with the bis(fulvalene)dinickel dication, befitting its broadly distributed negative charge (Fig. 6).

The hexafluoroarsenate anion $[AsF_6]^-$, on the other hand, mimics the behavior of the more commonly employed $[PF_6]^-$ anion towards organometallic cations. It is a strong nucleophile towards $[RuCp_2]^+$ and precipitates the nickelocenium dication onto a glassy carbon electrode, behavior previously seen for its congeneric phosphate counterpart. Its ion-pairing ability is also very similar to that of $[PF_6]^-$. Although $[AsF_6]^-$ clearly has some advantages over anions such as TFAB and $[Al(OC(CF_3)_3)_4]^-$ in terms of its positive potential window, its application to the anodic processes of organometallic complexes will most likely be limited by its chemical and physical similarity to other traditional [31] electrolyte anions.

4. Experimental

Electrochemical experiments were carried out under nitrogen in a drybox using dried and distilled solvents as previously described [32]. All potentials in this paper are referenced to ferrocene [33] and the working electrode was a 2 mm glassy carbon disk (Bioanalytical Systems) polished as necessary by standard procedures [32].

Crystalline $[Cp_2Fe][Al(OC(CF_3)_3)_4]$ was prepared in *o*-$C_6H_4F_2$ (5 cm^3) that was added to $Ag[Al(OC(CF_3)_3)_4]$ (0.117 g, 0.1 mmol) and Cp_2Fe (0.059 g, 0.5 mmol, 5 equiv.) under an atmosphere of dry argon. A dark blue solution with some dark precipitate was observed immediately after addition of the solvent. The mixture was stirred for 30 min before the solvent volume was reduced to give a concentrated, oily solution (*ca.* 0.5 cm^3). This was stored at 3 °C yielding purple/blue crystals of $[Cp_2Fe][Al(OC(CF_3)_3)_4]$ that were suitable for single crystal X-ray diffraction studies. Crystallographic details: Crystals were selected in Perfluoroetheroil (ABCR), and then mounted with a CRYOLOOP (Hampton Research) on a Rigaku R-Axis Spider diffractometer equipped with a Curved Image Plate detector. The frames were collected using Mo Kα-radiation (0.71073 Å) at T = 103(2) K (Oxford Cryostream 700). Cell refinement, data reduction, Lorentz, polarization and empirical absorption correction as well as integration were carried out with the CRYSTALCLEAR software utilizing the FSPROCESS routine. The structure was solved with the Patterson method (SHELXS97), and then refined stepwise by full-matrix least squares refinement on F^2 with SHELXL97. Empirical formula: $C_{26}H_{10}AlF_{36}FeO_4$, formula weight 1153.17; monoclinic, space group C2/c; a = 19.5587(5) Å; b = 19.4014(5) Å; c = 19.2831(5) Å; β = 96.788(2)°; volume 7266.0(3) $Å^3$; Z = 8, density (calculated) 2.108 Mg/m^3; absorption coefficient 0.662 mm^{-1}; crystal size 0.5 × 0.25 × 0.25 mm; theta range for data collection 1.48–27.48°; index ranges $-25 \leq h \leq 25$, $-23 \leq k \leq 25$, $-25 \leq l \leq 24$; reflections collected 33760; independent reflections 8317 [R_{int} = 0.0390]; completeness to theta = 27.48°: 99.7%; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 8317/62/651; goodness-of-fit on F^2: $S = 1.081$; R indices [for 6528 reflections with $I > 2\text{sigma}(I)$] R1 = 0.0461, wR2 = 0.0961; R indices (for all 8317 data): R1 = 0.0630, wR2 = 0.1017; largest diff. peak and hole: 0.371 and -0.343 eÅ^{-3}.

$[NBu_4][Al(OC(CF_3)_3)_4]$ [7] was prepared by metathesis of $[NBu_4]Br$ and $Li[Al(OC(CF_3)_3)_4]$ in methanol, recrystallized from dichloroethane/hexanes (m.p. 198–199 °C), and vacuum dried. $[NBu_4][AsF_6]$ was prepared by metathesis of $[NBu_4]Br$ and $[NBu_2H_2][AsF_6]$ (Ozark Mahoning) in aqueous methanol, recrystallized from dichloromethane/ether, and vacuum dried. Ferrocene, ruthenocene and nickelocene (Strem) were vacuum sublimed. The preparation of bis(fulvalene)dinickel, **1**, has been previously described [17]. The sample used for this study was **1** $[PF_6]$. Since the concentration of this sample in electrolyte solution was about 100-fold less than that of the supporting electrolyte, the presence of the $[PF_6]^-$ should have minimal effect on the $\Delta E_{1/2}$ values measured for **1**.

Calculations of electrostatic potentials were carried out with the TURBOMOLE program package (version 6.10) [34]. The geometries were optimized on the DFT-BP86 [35,36] level using the SV(P) [37] basis set, the RI approximation (resolution of identity [38,39]) and the COSMO solvation model (with ε_r = infinity). All geometries were optimized in the highest possible point group symmetry. Electrostatic potential calculations, including core and electronic contributions, were then carried out with the RIDFT module of TURBOMOLE, and visualized with gOpenmol [40].

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.03.001.

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