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Journal of Fluorine Chemistry 76 (1996) 1–2

JOURNAL OF FLUORINE CHEMISTRY

Communication

Charge-transfer salts containing cyclic perfluorinated anions

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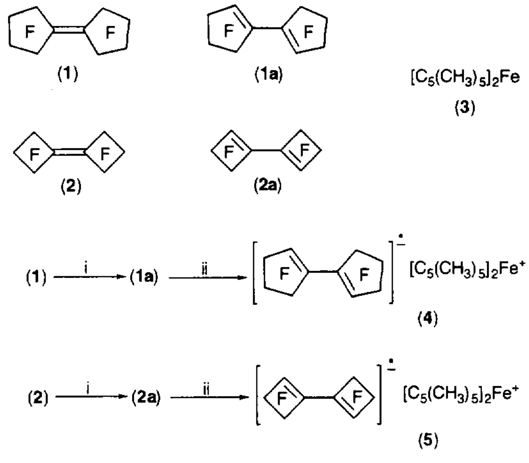
Received 23 May 1995; accepted 1 August 1995

Abstract

Perfluorobicyclopentenyl (**1a**) and -butenyl (**2a**) react with decamethylferrocene (**3**), to give charge-transfer salts **4** and **5**, respectively; perfluorohexakis(trifluoromethyl)cyclo-pentadiene (**6**) forms a salt (**8**) containing the $C_5(CF_3)_5$ anion. Crystal structures of the salts **4** and **5** have been determined; both contain centrosymmetric *trans*-diene radical anions.

Keywords: Charge-transfer salts; Perfluorinated cyclic alkenes; Crystal structure; Cyclic voltammetry



Scheme 1. Reagents and conditions: i, Decamethylferrocene, + 2e⁻, − 2F⁻, room temp., CH_3CN; ii, Decamethylferrocene, + 1e⁻.

There has been much interest in recent years in the synthesis of a variety of donor–acceptor systems, particularly with respect to their electronic properties. Not least is the interesting development by Miller and his co-workers of a so-called 'organic magnet', involving tetracyanoethene and decamethylferrocene [1].

We have been exploring the synthesis and chemistry of some novel perfluorinated cyclic alkenes and derived dienes e.g. **1**, **1a**, **2** and **2a**, and these have relatively low reduction potentials, as revealed by cyclic voltammetry [2].

Consequently, we have investigated the reaction of **1** with decamethylferrocene (**3**) and obtained a product (**4**) which is derived from the starting material (**1**), first by defluorination of the monoene (**1**) via electron transfer from **3** to **1**, similar to the defluorination of **1** using sodium amalgam [2], then further charge transfer to the diene (**1a**) to give a stable electron-transfer salt (**4**, Scheme 1).

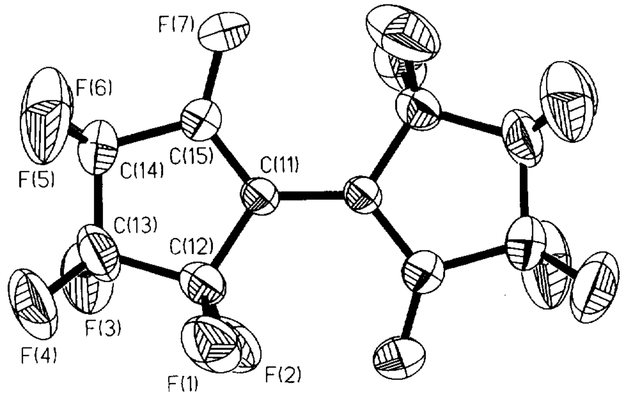


Fig. 1. Structure of the radical anion $[C_{10}F_{14}]^{\dot{-}}$ in **4**. Unique atoms are labelled, the minor disorder component is not shown, and ellipsoids are at the 30% probability level. Key dimensions: C(11)–C(12), 1.455(5) Å; C(12)–C(13), 1.520(6) Å; C(13)–C(14), 1.470(7) Å; C(14)–C(15), 1.499(5) Å; C(11)–C(15), 1.359(5) Å; C(11)–C(11′), 1.438(6) Å; C(15)–C(11)–C(12), 108.9(3)°; C(11)–C(12)–C(13), 107.2(3)°; C(12)–C(13)–C(14), 106.8(3)°; C(13)–C(14)–C(15), 104.6(3)°; C(14)–C(15)–C(11), 112.3(4)°; C(15)–C(11)–C(11′), 127.0(4)°; C(12)–C(11)–C(11′), 124.2(4)°.

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SSDI 0022-1139(95)03335-1

However, the same salt (**4**) was obtained more easily by direct reaction of perfluorobicyclopentenyl (**1a**) with decamethylferrocene (**3**). An analogous salt (**5**) was made from the bicyclobutenyl derivative (**2a**). These constitute the first room-temperature-stable radical anion salts involving a fluorinated diene to be obtained. Both structures **4** and **5** were confirmed by single-crystal X-ray analysis [1]; see Figs. 1 and 2 for the structures of the anions in **4** and **5** respectively. These data show quite clearly the diene-like character of these novel salts.

The magnetic behaviour of **4** and **5** have been investigated, but neither showed ferromagnetism down to 4 K. More recently, we have synthesized the new perfluorinated diene **6** [3], and reaction of this with decamethylferrocene also gave a 1:1 salt, Scheme 2.

Unfortunately we have been unable, so far, to obtain a structure by X-ray analysis, but elemental analysis is consistent with the structure **8**, involving the pentakis(trifluoromethyl)cyclopentadienyl anion. More pertinent, however, is the fact that the ^{19}F NMR spectrum of **8** shows a single sharp resonance at δ_F −49.7 ppm, which corresponds exactly to a value for the caesium salt of the pentakis(trifluoromethyl)cyclopentadienyl anion.

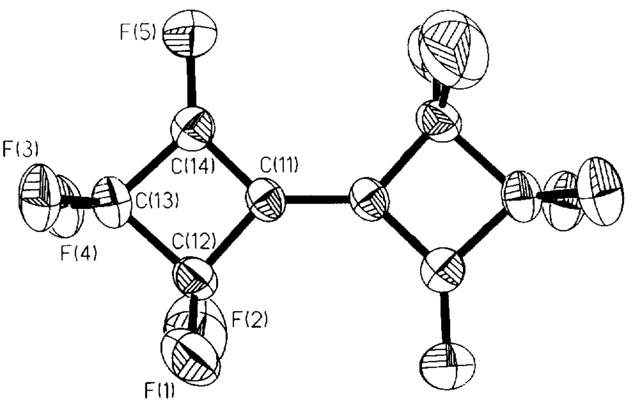
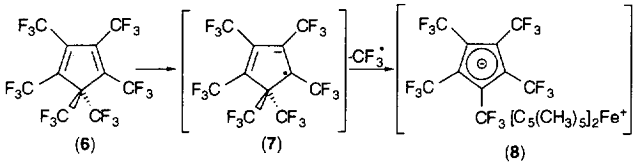


Fig. 2. Structure of the radical anion $[C_8F_{10}]$: in **5**, with 30% ellipsoids and labelling of unique atoms. Key dimensions: C(11)–C(12), 1.450(5) Å; C(12)–C(13), 1.535(6) Å; C(13)–C(14), 1.503(5) Å; C(14)–C(11), 1.390(5) Å; C(11)–C(11′), 1.419(7) Å; C(14)–C(11)–C(12), 92.3(3)°; C(11)–C(12)–C(13), 89.6(3)°; C(12)–C(13)–C(14), 84.8(3)°; C(13)–C(14)–C(11), 93.2(3)°; C(14)–C(11)–C(11′), 135.3(4)°; C(12)–C(11)–C(11′), 132.3(4)°.



Scheme 2. Reagents and conditions: Decamethylferrocene, + 1e⁻, 85 °C, CH_3CN, 17.5 h (64%).

All of the salts **4**, **5** and **8** have the same dark bottle-green colour and, of course, each ion contains the decamethylferrocene unit but with the iron in the Fe(III) state.

Acknowledgements

We thank the EPSRC for studentships and Electricity Association Technology for CASE awards (to MWB, SJM and JFSV), and EPSRC for an equipment grant to WC.

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[1] Crystal data for **4**: $[C_{20}H_{30}Fe][C_{10}F_{14}]$, $M_r = 712.4$, triclinic, $P\bar{1}$, $a = 9.122(2)$ Å, $b = 9.640(2)$ Å, $c = 9.706(2)$ Å, $\alpha = 97.81(2)°$, $\beta = 95.04(2)°$, $\gamma = 115.83(2)°$, $V = 750.7(3)$ Å^3, $Z = 1$, $D_c = 1.576$ g cm^{-3}, $F(000) = 362$, Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 0.61$ mm^{-1}. The structure was determined by direct methods and refined on F^2 for all 2657 independent reflections measured at room temperature with a Stoe–Siemens diffractometer ($2\theta\{\max\} = 50°$), with anisotropic displacement parameters, constrained isotropic hydrogen atoms, and twofold positional disorder for most of the fluorine atoms (representing alternative pseudo-axial and pseudo-equatorial positions on the approximately planar rings): $R' = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^2)^2]^{1/2} = 0.1421$ for all data, conventional R (on F values for 2253 reflections with $F_o^2 > \sigma(F_o^2)) = 0.0449$, goodness of fit = 1.095 on F^2 for 256 parameters, weighting scheme $w^{-1} = s^2(F_o^2) + (0.089P)^2 + 0.22P$, where $P = (F_o^2 + 2F_c^2)/3$, final difference synthesis between +0.30 and −0.45 e Å^{-3}.

Crystal data for **5**: $[C_{20}H_{30}Fe][C_8F_{10}]$, $M_r = 612.4$, triclinic, $P\bar{1}$, $a = 8.222(2)$ Å, $b = 9.150(2)$ Å, $c = 9.650(2)$ Å, $\alpha = 96.67(2)°$, $\beta = 97.34(2)°$, $\gamma = 108.38(2)°$, $V = 673.8(3)$ Å^3, $Z = 1$, $D_c = 1.509$ g cm^{-3}, $F(000) = 314$, μ (Mo Kα) = 0.65 mm^{-1}. Structure determination was as for **4**, with 2360 independent reflections and with no resolved disorder: $R' = 0.1720$ for all data, conventional $R = 0.0479$ (on 2055 F values), goodness of fit = 1.075 for 183 parameters, weighting scheme $w^{-1} = \sigma^2(F_o^2) + (0.1015P)^2 + 0.329P$, final difference synthesis between +0.30 and −0.68 e Å^{-3}. Attempts to collect data at reduced temperatures were unsuccessful, with a deterioration in the quality of the diffraction pattern on cooling. Programs: SHELXTL and SHELXL-93, G.M. Sheldrick, University of Göttingen. Atomic coordinates, bond lengths and angles and displacement parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre.