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THE PURPORTED REACTION OF TRICARBONYL-η^5-CYCLOHEXADIENYLIUMIRON TETRAFLUOROBORATE WITH FLUORIDE ION

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Summary

The product of reaction between tricarbonyl-η^5-cyclohexadienyliumiron tetrafluoroborate and fluoride ion has been shown to be the diastereomeric ether complex and not the fluorodiene complex as previously reported.

Introduction

It has been reported that the tricarbonyl-η^5-cyclohexadienyliumiron complex (**1**) is captured by fluoride ion to form the fluorodiene complex **2** (70% yield) [1], the structure of which was determined spectroscopically. Because of the medicinal importance of specifically fluorinated aromatics and alicyclics, this reaction could be of considerable interest as a novel route to such compounds. Consequently, we have reexamined the process in detail and present here the conclusions of this study.

Results and discussion

The complex **1** was synthesised as described by Fischer et al. [2] and the reactivity of our sample checked by its reaction with standard nucleophiles, ethoxide [3] (NaOEt in ethanol) and cyanide [4] (KCN in acetonitrile) ions. In each case, the corresponding adduct **3** (X = OEt, CN) was isolated in high yield and fully spectroscopically characterised.

With this established, we attempted the reaction of the complex **1** with fluoride ion under rigorously anhydrous conditions. Thus the acetonitrile solvent was distilled from P_2O_5 and stored under nitrogen over 3 Å molecular sieves [5]; the 18-crown-6 was complexed with dry acetonitrile and stored in vacuo [6]; the potassium fluoride was dried by heating to > 200°C in a nickel crucible and cooled and stored in vacuo [7]. All glassware was meticuously flame dried and purged with dry nitrogen.

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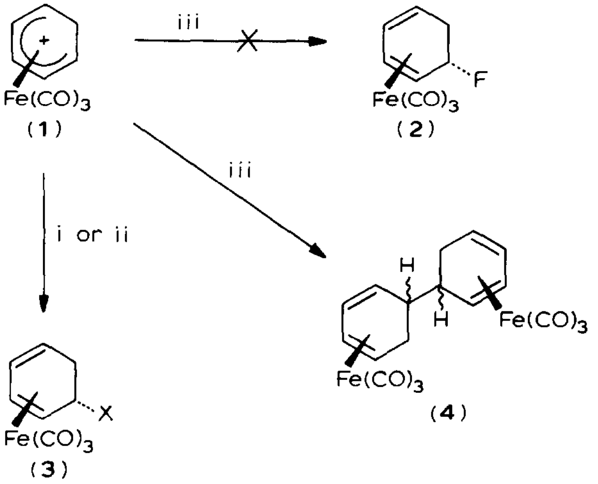
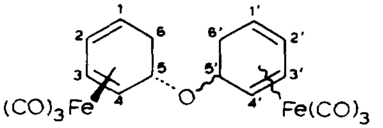


SCHEME 1. Reagents: i, KCN/CH_3CN; ii, NaOEt/EtOH; iii, KF/18-crown-6/CH_3CN.

Reaction of the cation **1** with KF/18-crown-6 was carried out many times and under a variety of conditions, but no high-yield component was ever detectable. Instead a complex mixture of products was produced which contained no fluorine (by ^{19}F NMR analysis) and from which the only isolable component (other than starting material), had mass and NMR spectra consistent with the dimeric species **4** [8].

When the reaction was carried out without special precautions in drying the fluoride, and by the procedure described previously [1], a major product (55%) resulted which showed identical spectroscopic properties (other than mass spectral, see below) to those reported for the "fluorinated" compound. No ^{19}F NMR had been reported. Our product showed no fluorine in the ^{19}F NMR. The proton decoupled ^{13}C NMR spectrum, as before showed some of the peaks as "doublets" but the separation of these varied only between 2 and 15 Hz. This latter had been ascribed to a $^1J(CF)$ coupling of C(5) [1], but such coupling constants are invariably in the region 170–200 Hz [9]. Similarly, in the PMR spectrum a coupling of 10 Hz had been ascribed to a $^2J(HF)$ coupling of H(5) and these coupling constants are normally in the range 40–60 Hz [9]. These considerations alone preclude the structure **3** (X = F) for the product.



(**5**)

TABLE 1

PMR SPECTRAL DATA OF **5** (δ (ppm))

	H(1)	H(2)	H(3)	H(4)	H(5)	H(6*endo*)	H(6*exo*)
Ref. 1	2.9	5.43	5.43	2.9	3.88	2.22	1.45
5	2.92	5.48	5.48	2.92	3.94	2.23	1.40
Ref. 10	2.82	5.37	5.37	2.82	3.72	2.11	1.34

TABLE 2

CMR SPECTRAL DATA OF 5 (δ (ppm))

	C(1/1′)	C(2/2′)	C(3/3′)	C(4/4′)	(C5/5′)	(C6/6′)	CO
Ref. 1	55.5d [a]	84.7	84.1	60.7d [a]	75.6d [a]	31.7d [a]	210.9
5	55.6d [b]	84.7	87.1 [c]	60.8d [b]	75.5d [b]	31.8d [b]	211

[a] In Ref. 1, these peaks were assigned as doublets. [b] Here d refers to the number of peaks, not splitting pattern. [c] This discrepancy is in a carbon remote from the site of substitution and does not alter the argument. The cause is not clear.

The alternative formulation of the product is the ether **5**, previously reported [10] from the reaction of $CsF \cdot 1.5H_2O$ with the cation **1**. Only an unresolved PMR spectrum was recorded by the Russian workers, but the chemical shifts agree closely with those of the Cambridge spectrum. A comparison of all chemical shift data is given in Tables 1 and 2. The reason for the doubling of the proton decoupled CMR peaks is simply that the product is a mixture of diastereomers (as **5**). Although the PMR spectrum (at 90 MHz) generally showed unresolved multiplets, the resonances of the protons at C(6) were well resolved (see Experimental) and confirm the 1/1 diastereomeric mixture.

Despite the accord between the NMR data of the 3 reports of this compound the mass spectra show surprising differences. In the mass spectrum of our samples there was no molecular ion and although the reported spectrum is incomplete and no intensity data are given, fragmentations are generally in accord, except that the peaks are displaced by 2 mass units to lower mass in our spectrum (see Experimental). In the earlier report [1], the initial fragmentation, (238 → 220; −18 m.u.), was ascribed not to a loss water but to a loss of HF (−20 m.u.). The mass spectrum can be interpreted as ready cleavages of **5** to the hydroxydiene complex **3** ($X = OH$) m/z 236 and the cyclohexadiene complex **3** ($X = H$), m/z 220. Subsequent fragmentations of these via losses of hydroxyl, hydrogen, carbon monoxide and ultimately the FeCO group explains all the major peaks in the spectrum.

We conclude that the cation **1** does not capture fluoride ion and therefore this is not a potential source of specifically monofluorinated compounds.

Experimental

All solvents and reagents were freshly purified and rigorously dried by standard methods [5]. NMR spectra were run on a Bruker WH250, Perkin–Elmer R32 or Varian EM360 spectrometers, IR spectra were run on a Perkin–Elmer 298 spectrometer and mass spectra on a VG 7070B spectrometer.

Tricarbonyl-η^5-cyclohexa-1,3-dienyliumiron tetrafluoroborate

This was prepared according to the method of Fischer et al. [2] and had m.p. 190°C.

Tricarbonyl-5-exo-ethoxy-η^5-cyclohexa-1,3-dieneiron and tricarbonyl-5-exo-cyano-η^5-cyclohexa-1,3-dieneiron

Tricarbonyl-η^5-cyclohexa-1,3-dienyliumiron tetrafluoroborate (0.61 g, 2 mmol) was added portionwise to a solution of sodium ethoxide (2 mmol) in ethanol (25 ml) at 0°C. After 1 h the solution was poured into water (50 ml) and extracted with ether (3 × 70 ml). The extract was dried ($MgSO_4$), the solvent removed in vacuo and the residual yellow oil chromatographed over silica gel (eluant: petroleum ether) to give tricarbonyl-5-*exo*-ethoxy-η^5-cyclohexa-1,3-dieneiron **3** (X = OEt), (0.39 g, 74%), as a low melting solid, δ ($CDCl_3$, 250 MHz) 1.13 (3H, t, J 6.6 Hz), 1.52 (1H, dddd, $J_{6endo,6exo}$ 15, $J_{6endo,5}$ 3, $J_{6endo,1}$ 2, $J_{6endo,4}$ 1.5 Hz), 2.25 (1H, ddd, $J_{6exo,6endo}$ 15, $J_{6exo,5}$ 9.8, $J_{6exo,1}$ 4 Hz), 2.91 (1H, ddd, $J_{1,2}$ 8.5, $J_{1,6exo}$ 4, $J_{1,6endo}$ 2 Hz), 3.09 (1H, ddd, $J_{4,3}$ 6, $J_{4,5}$ 3, $J_{4,6endo}$ 1.5 Hz), 3.30 (1H, dq, J 9.1 and 6.8 Hz), 3.46 (1H, dq, J 9.1 and 6.8 Hz), 3.93 (1H, ddd, $J_{5,4}$ 3, $J_{5,6exo}$ 9.8, $J_{5,6endo}$ 3 Hz), 5.45 (1H, br t, $J \sim 7$ Hz), 5.55 (1H, br t, $J \sim 7$ Hz); ν_{max} (neat) 2050, 1960 cm^{-1}; m/z 264 (M^+, 2%), 236 (20%), 208 (13%), 178 (85%), 150 (13%), 134 (22%) and 78 (100%) [3].

The cyano-complex **3** (X = CN) was prepared similarly as yellow crystals (82%); m.p. 89–90°C (lit. 4: m.p. 88–89°C); δ ($CDCl_3$, 60 MHz) 2.09 (1H, m, H(6*endo*)), 2.29 (1H, m, H(6*exo*)), 2.97 (1H, m, H(5)), 3.18 (2H, m, H(1), H(4)), 5.61 (2H, m, H(2), H(3)); ν_{max} (Nujol) 2240, 2050, 1980 cm^{-1}, identical with the reported data [4].

Reaction of 1 with fluoride ion

a. Rigorously anhydrous conditions. Tricarbonyl-η^5-cyclohexadienyliumiron tetrafluoroborate (**1**), (1.53 g, 5 mmol) was dissolved in acetonitrile (30 ml, dried over P_2O_5) in a flame dried apparatus and degassed with nitrogen. Potassium fluoride (4 g, 69 mmol, dried at > 200°C) and 18-crown-6 (50 mg) were added and the mixture refluxed for 30 min. The resultant solution was poured into water and the products extracted with ether. The ether was dried ($MgSO_4$) and evaporated. The crude residue, which contained no fluorine, (by ^{19}F NMR spectroscopy) was fractionated by HPLC (eluant: petroleum ether) to give starting material (1 g) and dimer **4** (45 mg), m.p. 120–121°C (lit. 8: m.p. 120–122°C), δ ($CDCl_3$, 90 MHz) 1.12 (1H, m, H(5)), 1.75 (2H, m, H(6*endo*), H(6*exo*)), 2.95 (2H, m, H(1), H(4)), 5.20 (2H, m, H(2), H(3)); m/z 438 (M^+, 0.5%), 410 (2.5%), 382 (0.5%) and 270 (100%).

b. With partially dried potassium fluoride. The reaction was carried out exactly as above except that the potassium fluoride was dried at $\sim$ 120°C. The product mixture was diluted with ether (100 ml) and washed with water (2 × 30 ml). The organic layer was dried ($MgSO_4$) and chromatographed over silica gel (eluant: ether/petroleum ether (1/4)) to give the diastereomeric ethers **5** (0.62 g, 55%), m.p. 102°C (lit. 10: m.p. 104°C); PMR: δ ($CDCl_3$, 90 MHz) 1.41 (0.5H, br dd, $J_{6endo,6exo}$ 15.4, $J_{6endo,5}$ 12.8 Hz), 1.43 (0.5H, br dd, $J_{6endo,6exo}$ 15.4, *J6endo*,5 9.6 Hz), 2.20 (0.5H, ddd, $J_{6exo,6endo}$ 15.4, $J_{6exo,5}$ 5.5, $J_{6exo,1}$ 3.8 Hz), 2.30 (0.5H, ddd, $J_{6exo,6endo}$ 15.4, $J_{6exo,5}$ 4.5, $J_{6exo,1}$ 3.8 Hz), 2.92 (2H, m, H(1), H(4)), 3.93 (1H, br d, $J_{5,6endo} \sim 10$ Hz), 5.47 (2H, m, H(2), H(3)); for the CMR, see Table 2; ν_{max} (Nujol) 3020, 2900, 2045, 1970, 1020, 618 cm^{-1}; m/z 236 (20%), 220 (3%), 219 (5%), 218 (2%), 208 (17%), 206 (15%), 192 (9%), 191 (3%), 179 (12%), 178 (87%), 150 (28%), 135 (22%), 134 (55%), 121 (22%), 119 (21%), 86 (64%), 84 (100%), 78 (19%).

Acknowledgements

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