Bull Soc Chim Fr (1997) 134, 955-958

Aromatic stacking between ferrocene and perfluorophenanthrene to give a 2 + 2 supramolecular assembly in the solid state

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(Received 23 October 1997; accepted 18 December 1997)

Summary — The title compounds assemble in the solid state to give a 2 + 2 assembly in which two ferrocene units join two perfluorophenanthrene units via face-to-face aromatic stacking without mutual offset of the rings. The metallocene–perfluoroarene pair may be a useful general design element for supramolecular assemblies.

supramolecular chemistry / charge transfer complex

Résumé — Entassement aromatique entre ferrocène et perfluorophenanthrène à l'état solide dans un ensemble supramoléculaire du type 2 + 2. Deux unités de ferrocène cocristallisent avec deux unités de perfluorophénanthrène pour former un ensemble 2 + 2 dans lequel les deux métallocènes sont liés aux deux arènes par entassement aromatique du type face à face sans décalage. Cet assemblage peut être un motif de base en génie supramoléculaire.

chimie supramoleculaire /complexe transfert charge

Introduction

Supramolecular chemistry [1] is a topic of intense current interest in organic [1] and more recently also in inorganic chemistry [2]. Among inorganic examples, hydrogen bonding [3] and coordination polymerization [4] have been the chief intermolecular interactions employed. Aromatic stacking has long been recognized as one of the most important intermolecular forces in organic and biochemical systems [5], but it has less commonly been studied in the inorganic and organometallic realm. Charge transfer complexes of ferrocenes, especially of Cp^*_2Fe, are well known with conventional acceptors such as TCNE [6]. A search is currently under way for intermolecular interactions that can be relied upon to enforce a particular supramolecular architecture in a crystal [7]. Many of these have involved hydrogen bonding groups, but here we examine a candidate interaction based on aromatic stacking interactions.

In a number of recent reports [8], it has been shown that perfluoroalkanes can be defluorinated to perfluoroarenes by thermal reaction with Cp_2Co [8a] or photochemical reaction with Cp^*_2Fe [8b]; in both cases electron transfer (ET) from the metallocene to the perfluoro compound was proposed as the key step. It seemed possible that a charge transfer (CT) adduct might form prior to the ET step, and we therefore looked at the interaction of ferrocenes with perfluoroalkanes, but so far we have had no success in detecting an interaction. Perfluoroarenes are good acceptors and the structurally characterized face-to-face $C_6F_6\cdots C_6H_6$ complex, for example, has long been known [9]; $C_6F_6\cdots$donor complexes have recently been studied quantum chemically for cases such as $HCN\cdots C_6F_6$ where the donor approaches the ring along the sixfold axis and an energy minimum was located at a ΔE of -1.65 kcal/mol with a d(N$\cdots$ring centroid) of 3.3 Å [10]. We found that cocrystallization of Cp^*_2Fe with perfluorophenanthrene gave a 1:1 adduct in which the ferrocene and arene planes were near-parallel; the plane-to-plane distance was 3.6 Å, somewhat longer than the 3.5 Å normally found for true aromatic stacking [11]. A possible reason was the presence of the bulky methyl groups on the ferrocene and so we decided to look at the corresponding unsubstituted compound with the results described here.

Results and discussion

Perfluorophenanthrene seemed a good choice for the acceptor component of the complex because aromatic stacking is known to be enhanced in larger arenes [5]. In addition, the presence of three rings in principle allows the ferrocene to bind in edge-to-face or face-to-face manner, both well recognized structural motifs in aromatic stacking. This arene has recently become available in synthetic quantities by defluorination of the corresponding commercial perfluoroalkane with hot sodium oxalate or ferrous oxalate [12].

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Evaporation of a 1:1 pentane solution of the components gave vermilion-colored crystals that were mounted and studied by X-ray diffraction. The resulting structure (figs 1 and 2, tables I–III) shows that two ferrocenes and two perfluorophenanthrenes assemble in a 2 + 2 arrangement with two ferrocenes forming the meat of a sandwich in which the perfluoroarenes constitute the bread. This is shown diagramatically in figure 3a and differs from the situation we found for Cp^*_2Fe-perfluorophenanthrene, where the 'ladder' arrangement of arene and metallocene was found (fig 3b).

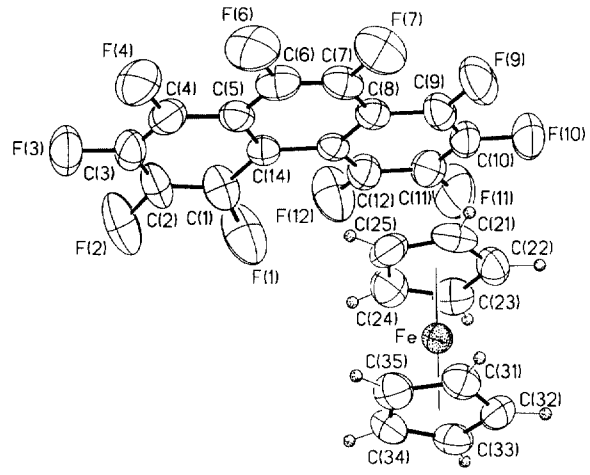

Fig 1. A view of the interaction of one ferrocene with one perfluorophenanthrene molecule in the 2 + 2 assembly of the title complex.

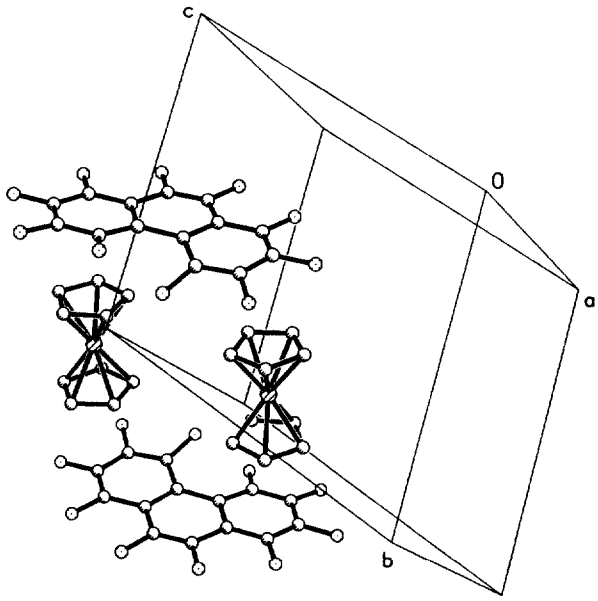

Fig 2. A diagram showing the full 2 + 2 assembly of the title complex.

The ferrocenes are located above or below the wingtip arene rings of the phenanthrene, which are expected to be more electron deficient because they have the largest number of F substituents. The Cp centroid to wingtip arene ring centroid distance of 3.52 Å is appropriate for aromatic stacking although the interplanar distance of 3.40 Å in graphite [13] is somewhat shorter.

Table I. Crystal data and structure refinement for the title complex.

Empirical formula	$C_{24}H_{10}F_{10}Fe$
Formula weight	544.17
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.843(1) Å, α = 111.72(1)°
	b = 9.999(1) Å, β = 90.62(1)°
	c = 11.180(2) Å, γ = 91.56(1)°
Volume, Z	1021.6 (4) Å^3, 2
Density (calculated)	1.769 g/cm^3
Absorption coefficient	0.839 mm^{-1}
$F(000)$	540
Crystal size	0.40 × 0.30 × 0.30 mm
Crystal color	Orange block
θ range for data collection	2.07 to 22.50°
Limiting indices	$-1 \leqslant h \leqslant 10$, $-9 \leqslant k \leqslant 9$,
	$-12 \leqslant l \leqslant 12$
Reflections collected	3077
Independent reflections	2558 (R_{int} = 0.0435)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2558 / 0 / 316
Goodness-of-fit on F^2	0.970
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0590, w$R2$ = 0.1558
R indices (all data)	$R1$ = 0.0844, w$R2$ = 0.1662
Largest diff peak and hole	0.772 and −0.476 e Å^{-3}

Perhydroarenes tend to mutually interact either by an edge-to-face T-shaped interaction without any offset or by a face-to face interaction with one arene significantly offset relative to the other. These geometries are consistent with the main interaction between the two rings being electrostatic, and the charge distributions of the rings being as shown in figure 4a. In the case of arene-perfluoroarene interactions, the perfluoroarene charge distribution of figure 4b is expected to strongly favor the observed face to face arrangement. Examination of models suggested that both edge-to-face and face-to-face arrangements would in principle be possible for $FeCp_2$-perfluoronaphthalene on geometric grounds but in the former case, only one ferrocene would be expected to fit between the arene planes. Electronically, the observed structure is expected to be strongly favored, however.

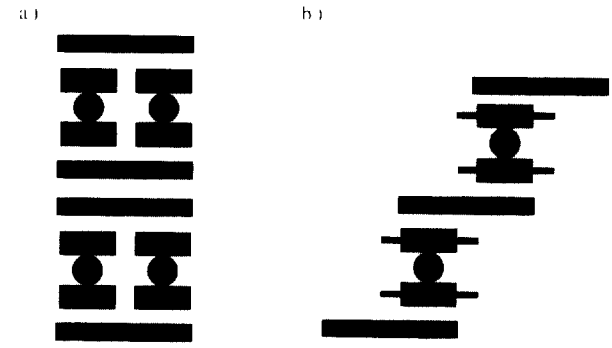

Fig 3. A comparison of (a) the 2 + 2 'supersandwich' packing arrangement found here, compared with (b) the ladder packing arrangement found in the decamethylferrocene analogue.

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for the title complex.

	x	y	z	$U(eq)$[a]
Fe	4486.9(9)	11037.8(9)	12856.8(8)	67(1)
F(1)	−3(7)	8073(9)	8572(6)	203(3)
F(2)	485(6)	6782(9)	6122(5)	194(3)
F(3)	2161(7)	4581(7)	5253(5)	178(3)
F(4)	3360(7)	3635(6)	6886(6)	181(3)
F(6)	3773(6)	3798(6)	9181(6)	166(2)
F(7)	3262(6)	4890(7)	11615(6)	163(2)
F(9)	1945(6)	6450(7)	13462(5)	155(2)
F(10)	−4(6)	8289(6)	14367(5)	159(2)
F(11)	−1497(8)	9088(8)	12765(6)	204(3)
F(12)	−1141(6)	8103(8)	12288(6)	181(3)
C(1)	693(8)	6799(11)	8192(9)	112(3)
C(2)	995(10)	6188(14)	6914(9)	119(3)
C(3)	1870(12)	5118(13)	6503(9)	115(3)
C(4)	2477(10)	4656(10)	7335(10)	114(3)
C(5)	2161(8)	5233(8)	8679(7)	87(2)
C(6)	2831(8)	4801(9)	9572(11)	106(3)
C(7)	2577(8)	5336(9)	10818(10)	97(2)
C(8)	1559(7)	6346(7)	11330(7)	79(2)
C(9)	1247(9)	6872(10)	12644(8)	100(2)
C(10)	264(12)	7800(11)	13098(8)	108(3)
C(11)	−475(10)	8232(9)	12300(10)	111(3)
C(12)	−192(9)	7740(9)	11008(8)	98(2)
C(13)	820(6)	6817(6)	10467(6)	68(2)
C(14)	1195(6)	6280(7)	9103(6)	72(2)
C(21)	4095(8)	9187(9)	13151(11)	105(3)
C(22)	3225(9)	10220(10)	13859(8)	99(2)
C(23)	2492(8)	10666(9)	13033(10)	103(2)
C(24)	2876(9)	9902(11)	11784(9)	108(2)
C(25)	3867(10)	8974(8)	11851(9)	107(3)
C(31)	6415(7)	11728(8)	13457(8)	91(2)
C(32)	5523(8)	12819(8)	14118(7)	93(2)
C(33)	4785(8)	13170(8)	13207(9)	96(2)
C(34)	5238(10)	12344(9)	11985(8)	106(2)
C(35)	6263(8)	11437(8)	12148(9)	99(2)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond lengths (Å) and angles (°) for the title complex.

Fe-C(23)	2.014(7)	Fe-C(35)	2.018(7)
Fe-C(31)	2.022(7)	Fe-C(24)	2.024(8)
Fe-C(34)	2.026(7)	Fe-C(21)	2.024(7)
Fe-C(25)	2.023(7)	Fe-C(22)	2.030(7)
Fe-C(33)	2.032(7)	Fe-C(32)	2.052(7)
F(1)-C(1)	1.388(10)	F(2)-C(2)	1.337(10)
F(3)-C(3)	1.336(9)	F(4)-C(4)	1.315(10)
F(6)-C(6)	1.339(8)	F(7)-C(7)	1.322(8)
F(9)-C(9)	1.332(9)	F(10)-C(10)	1.350(9)
F(11)-C(11)	1.320(9)	F(12)-C(12)	1.367(8)
C(1)-C(2)	1.370(12)	C(1)-C(14)	1.395(9)
C(2)-C(3)	1.339(13)	C(3)-C(4)	1.325(13)
C(4)-C(5)	1.437(11)	C(5)-C(14)	1.386(9)
C(5)-C(6)	1.392(11)	C(6)-C(7)	1.323(11)
C(7)-C(8)	1.411(10)	C(8)-C(9)	1.406(10)
C(8)-C(13)	1.421(9)	C(9)-C(10)	1.329(11)
C(10)-C(11)	1.342(12)	C(11)-C(12)	1.378(11)
C(12)-C(13)	1.364(9)	C(13)-C(14)	1.471(9)
C(21)-C(22)	1.372(11)	C(21)-C(25)	1.404(11)
C(22)-C(23)	1.372(10)	C(23)-C(24)	1.383(11)
C(24)-C(25)	1.384(11)	C(31)-C(35)	1.388(10)
C(31)-C(32)	1.406(10)	C(32)-C(33)	1.397(10)
C(33)-C(34)	1.395(10)	C(34)-C(35)	1.429(10)
C(23)-Fe-C(35)	161.7(4)	C(23)-Fe-C(31)	156.8(4)
C(35)-Fe-C(31)	40.2(3)	C(23)-Fe-C(24)	40.0(3)
C(35)-Fe-C(24)	125.2(4)	C(31)-Fe-C(24)	161.8(4)
C(23)-Fe-C(34)	124.4(4)	C(35)-Fe-C(34)	41.4(3)
C(31)-Fe-C(34)	68.4(3)	C(24)-Fe-C(34)	107.7(3)
C(23)-Fe-C(21)	67.0(3)	C(35)-Fe-C(21)	122.3(4)
C(31)-Fe-C(21)	108.7(3)	C(24)-Fe-C(21)	67.8(3)
C(34)-Fe-C(21)	158.1(4)	C(23)-Fe-C(25)	66.9(3)
C(35)-Fe-C(25)	108.8(3)	C(31)-Fe-C(25)	125.8(4)
C(24)-Fe-C(25)	40.0(3)	C(34)-Fe-C(25)	122.2(4)
C(21)-Fe-C(25)	40.6(3)	C(23)-Fe-C(22)	39.7(3)
C(35)-Fe-C(22)	157.0(4)	C(31)-Fe-C(22)	122.4(3)
C(24)-Fe-C(22)	67.2(3)	C(34)-Fe-C(22)	160.4(4)
C(21)-Fe-C(22)	39.6(3)	C(25)-Fe-C(22)	66.9(3)
C(23)-Fe-C(33)	108.1(3)	C(35)-Fe-C(33)	68.4(3)
C(31)-Fe-C(33)	68.0(3)	C(24)-Fe-C(33)	121.2(4)
C(34)-Fe-C(33)	40.2(3)	C(21)-Fe-C(33)	160.7(4)
C(25)-Fe-C(33)	156.6(4)	C(22)-Fe-C(33)	124.8(4)
C(23)-Fe-C(32)	122.0(4)	C(35)-Fe-C(32)	67.6(3)
C(31)-Fe-C(32)	40.4(3)	C(24)-Fe-C(32)	156.3(4)
C(34)-Fe-C(32)	67.5(3)	C(21)-Fe-C(32)	125.4(4)
C(25)-Fe-C(32)	162.3(4)	C(22)-Fe-C(32)	109.1(3)
C(33)-Fe-C(32)	40.0(3)	C(2)-C(1)-F(1)	116.7(9)
C(2)-C(1)-C(14)	122.2(9)	F(1)-C(1)-C(14)	120.7(8)
F(2)-C(2)-C(3)	121.4(10)	F(2)-C(2)-C(1)	117.6(11)
C(3)-C(2)-C(1)	120.7(9)	C(4)-C(3)-F(3)	121.2(12)
C(4)-C(3)-C(2)	120.2(9)	F(3)-C(3)-C(2)	118.5(12)
F(4)-C(4)-C(3)	117.7(10)	F(4)-C(4)-C(5)	121.1(10)
C(3)-C(4)-C(5)	121.1(9)	C(14)-C(5)-C(6)	119.1(7)
C(14)-C(5)-C(4)	119.1(8)	C(6)-C(5)-C(4)	121.7(9)
C(7)-C(6)-F(6)	117.2(9)	C(7)-C(6)-C(5)	122.9(7)
F(6)-C(6)-C(5)	120.0(9)	F(7)-C(7)-C(6)	119.7(8)
F(7)-C(7)-C(8)	118.2(8)	C(6)-C(7)-C(8)	122.1(7)
C(9)-C(8)-C(7)	122.3(8)	C(9)-C(8)-C(13)	119.8(7)
C(7)-C(8)-C(13)	118.0(7)	F(9)-C(9)-C(10)	118.7(9)
F(9)-C(9)-C(8)	120.2(9)	C(10)-C(9)-C(8)	121.1(8)
C(9)-C(10)-C(11)	120.4(8)	C(9)-C(10)-F(10)	119.6(10)
C(11)-C(10)-F(10)	120.0(10)	F(11)-C(11)-C(10)	119.1(9)
F(11)-C(11)-C(12)	121.0(10)	C(10)-C(11)-C(12)	119.8(8)
C(13)-C(12)-F(12)	122.6(7)	C(13)-C(12)-C(11)	123.6(8)
F(12)-C(12)-C(11)	113.3(8)	C(12)-C(13)-C(8)	115.2(6)
C(12)-C(13)-C(14)	126.3(6)	C(8)-C(13)-C(14)	118.5(6)
C(5)-C(14)-C(1)	116.2(7)	C(5)-C(14)-C(13)	119.2(6)
C(1)-C(14)-C(13)	124.6(7)	C(22)-C(21)-C(25)	107.2(7)
C(22)-C(21)-Fe	70.5(4)	C(25)-C(21)-Fe	69.7(4)
C(21)-C(22)-C(23)	108.5(8)	C(21)-C(22)-Fe	70.0(4)
C(23)-C(22)-Fe	69.5(4)	C(24)-C(23)-C(22)	109.1(8)
C(24)-C(23)-Fe	70.4(5)	C(22)-C(23)-Fe	70.8(4)
C(23)-C(24)-C(25)	107.0(7)	C(23)-C(24)-Fe	69.6(5)
C(25)-C(24)-Fe	70.0(4)	C(24)-C(25)-C(21)	108.2(7)
C(24)-C(25)-Fe	70.0(5)	C(21)-C(25)-Fe	69.7(4)
C(35)-C(31)-C(32)	108.3(7)	C(35)-C(31)-Fe	69.7(4)
C(32)-C(31)-Fe	71.0(4)	C(33)-C(32)-C(31)	108.1(7)
C(33)-C(32)-Fe	69.2(4)	C(31)-C(32)-Fe	68.6(4)
C(32)-C(33)-C(34)	108.5(7)	C(32)-C(33)-Fe	70.8(4)
C(34)-C(33)-Fe	69.7(4)	C(33)-C(34)-C(35)	107.4(7)
C(33)-C(34)-Fe	70.1(4)	C(35)-C(34)-Fe	69.0(4)
C(31)-C(35)-C(34)	107.7(7)	C(31)-C(35)-Fe	70.0(4)
C(34)-C(35)-Fe	69.6(4)		

The Fe-centroid distance of 1.64 Å definitely shows that charge transfer is minimal, because this distance is appropriate for Fe(II) not Fe(III). Likewise the perfluoroarene distances appear appropriate for the neutral species, not the anion. The Cp rings have an eclipsed geometry and are ordered.

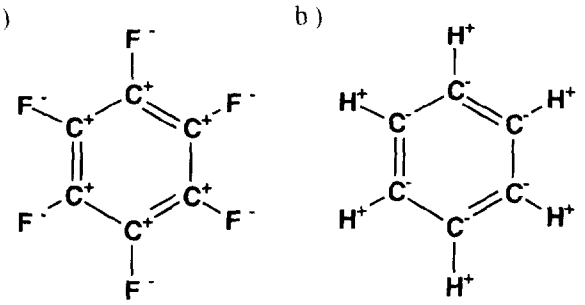

Fig 4. A schematic comparison of the charge distributions expected for (a) C_6F_6 versus (b) C_6H_6.

The perfluoroarene has C–C distances ca 0.03 Å shorter than the corresponding perhydroarene, consistent with a partial positive charge on carbon contracting the C orbitals. The F(4)···F(5) nonbonding distance is an extremely short 2.08 Å, or 0.62 Å shorter than the sum of the van der Waals radii of two fluorine atoms. This shortening, together with the significant angular distortions of the rings shows that the molecule is very strained – in fact it could be useful in developing an improved force field for MM calculations on fluorocarbons. Finally, the structure provides definitive evidence for the structure of the product of defluorination of the corresponding perfluoroalkane with hot sodium oxalate.

Conclusion

We have identified the ferrocene–perfluoroarene pair as a candidate motif for use in the construction of solid state supramolecular assemblies. The ferrocene and arene engage in face-to-face aromatic packing without the mutual offset of the two rings commonly seen [5] in perhydroarene–perhydroarene interactions, but like the arene–perfluoroarene pair [9]. There is no evidence for charge transfer in these species and no CT band was detected in the solid state. In contrast to the ladder packing seen for Cp^*_2Fe–$C_{14}F_{10}$, the smaller Cp_2Fe is able to form a 2 + 2 assembly in which two ferrocenes are sandwiched between two arene groups.

Experimental section

Perfluorophenanthrene was obtained from the corresponding perfluoroalkane by a synthetic method we have developed [12]. Slow evaporation of a solution of the components in 1:1 molar ratio (0.05 M, 2d) gave orange crystals suitable for X-ray analysis. The composition of the crystal was confirmed as 1:1 by GC-MS analysis of a pentane solution of the dissolved crystal.

Crystal data collection and refinement parameters are given in table I. No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. The *E*-statistics suggested a centrosymmetric space group. Solution in $P\bar{1}$ yielded chemically reasonable and computationally stable results. The structure was solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. Absorption corrections were not required because a variation of <10% was observed in the Ψ-scans. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.3) program libraries [14].

Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK as supplementary publication No. SUP 90477 and is available on request from the Document Supply Center.

Acknowledgments

We thank the US Department of Energy for support.

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