Reactivity of $[PPh_4][Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)C(CF_3)H\}]$ toward Electrophiles. *X*-Ray Structure of $[Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)CHC(OEt)_2\}]$, a Product resulting from Fluorine Abstraction at a CF_3 Group and Subsequent Fluorine Substitution by Ethoxy-groups†

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The complex $[PPh_4][Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)C(CF_3)H\}]$ reacts with electrophiles like H^+ and $C_2H_5^+$ to give $[Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)CHCF_2\}]$, a product resulting from fluorine abstraction at a CF_3 group. This product reacts with ethanol to give $[Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)CHC(OEt)_2\}]$ whose structure has been established by single-crystal *X*-ray determination. The compound crystallizes in the space group $P2_1/n$ with $a = 10.673(6)$, $b = 20.681(4)$, $c = 13.118(4)$ Å, $\beta = 92.27(3)°$, and $Z = 4$. The structure was refined to $R = 0.027$ ($R' = 0.026$) for 1 137 independent reflections. In this structure, the organic bridge is bonded to one iron by an allylic fragment, $CPhCPhC(CF_3)$, and the $CHC(OEt)_2$ fragment is very asymmetrically bonded to the other iron [Fe–C(H) 2.150(10), Fe–C(OEt)$_2$ 2.864(10) Å].

In a recent paper[1] we have shown that $[PPh_4][Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}CPhC(Ph)H\}]$ reacts with hexafluorobutyne to give complex $[PPh_4][Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)C(CF_3)H\}]$ (1), a product resulting from insertion of the alkyne into the carbon–hydrogen bond of the ethenyl ligand. In this molecule, the $C(CF_3)C(CF_3)H$ part is σ-bonded to the iron atoms.

Considering the anionic nature of the organometallic fragment, we tested its reactivity toward electrophiles such as the proton and carbocations. Surprisingly, in both cases we obtained the same product which results from fluorine abstraction at the CF_3 group in the β position to one iron atom. Moreover, the two fluorines of the remaining CF_2 group are very labile and are easily replaced by ethoxy-groups from the ethanol used as solvent. In this note, we describe these results and give the *X*-ray structure of the resulting product $[Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)CHC(OEt)_2\}]$ (3) in which an olefinic group is π-bonded highly asymmetrically to one iron.

Experimental

All reactions were performed under a nitrogen atmosphere. Proton n.m.r. spectra were recorded on a Bruker WH90 spectrometer, ^{13}C n.m.r. spectra on a Bruker WM250 instrument. I.r. spectra in the ν(CO) region were recorded on a Perkin-Elmer 225 spectrometer for hexadecane solutions. Complex (1) was prepared by published procedures.[1] Elemental analyses were performed in our laboratory.

Preparation of $[Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)CHCF_2\}]$ (2).—To complex (1) (0.5 g) dissolved in dichloromethane (10 cm^3) was added CF_3CO_2H (1 cm^3). The solution was stirred for 10 min and then evaporated under vacuum. Extraction of the residue with pentane (2 × 10 cm^3) and concentration of the solution to 5 cm^3 gave, after cooling, complex (2) as an orange powder (150 mg, 46.3% yield). The same result was obtained by treating the anionic complex with triethyloxonium tetrafluoroborate. M.p. 58 °C (decomp.) (Found: C, 48.05; H, 1.70. Calc. for $C_{24}H_{11}F_5Fe_2O_6$: C, 47.85; H, 1.80%). I.r.: ν(CO) 2 079m, 2 047s, 2 019m, 2013m, and 1 990w cm^{-1}. N.m.r.: ^1H (C_6D_6), 7.15 (m, C_6H_5) and 3.09 p.p.m. (t, $J = 5.7$ Hz, CH); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), except phenyl resonances, 208.1 (CO), 167.2 [Fe–$C(C_6H_5)$], 144.1 (t, $J = 302$, CF_2), 107.9 [$C(C_6H_5)$], 57.9 (q, $J = 32.7$, $C(CF_3)$], and 33.9 p.p.m. (t, $J = 6.5$ Hz, $CH\text{–}CF_2$).

Preparation of $[Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)CHC(OEt)_2\}]$ (3).—Complex (2) was dissolved in a small amount of ethanol in an attempt to obtain suitable crystals. Cooling to −20 °C gave orange crystals of (3), m.p. 174 °C (Found: C, 51.6; H, 3.05. Calc. for $C_{28}H_{21}F_3Fe_2O_8$: C, 51.35; H, 3.20%). I.r.: ν(CO) 2 053m, 2 013s, 1 983m, 1 977m, 1 960w, and 1 947w cm^{-1}. N.m.r.: ^1H (CD_2Cl_2), 7.17 (m, C_6H_5), 4.55 (m, OCH_2), 2.34 (CH), 1.60 (t, $J = 7.34$), and 1.54 p.p.m. (t, $J = 6.75$ Hz, OCH_2CH_3); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), except phenyl resonances, 213.7, 212.7, 212, 211.3 (CO) (intensity 1:3:1:1), 186.2 [$C(OC_2H_5)_2$], 172.2 [Fe–$C(C_6H_5)$], 127.5 (q, $J = 274.7$, CF_3), 113.5 [$C(C_6H_5)$], 60.5, 60.1 (OCH_2), 54.7 (q, $J = 31$ Hz, CCF_3), 27.1 (CH), 14.4, and 13.9 p.p.m. (OCH_2CH_3).

Crystallography.—An equidimensional crystal of complex (3) (0.1 × 0.1 × 0.1 mm) was selected and mounted on an Enraf–Nonius CAD4 diffractometer. The unit cell dimensions were found from 25 reflections with $3 < \theta < 11.2°$. The intensities

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† μ-[1—3:4—5-η-5,5-Diethoxy-1,2-diphenyl-3-trifluoromethylpenta-2,4-dien-1-yl-$C^{1-3}(Fe^1)C^{1,4,5}(Fe^2)$]-bis(tricarbonyliron)(*Fe–Fe*).

Supplementary data available (No. SUP 56259, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Final least-squares co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for complex (**3**)

Atom	*X/a*	*Y/b*	*Z/c*
Fe(1)	9 194(1)	499(1)	2 745(1)
Fe(2)	6 802(1)	392(1)	2 329(1)
C(1)	9 538(7)	1 738(4)	1 823(7)
C(2)	8 773(8)	1 199(5)	1 570(8)
C(3)	7 374(8)	1 267(4)	1 760(7)
C(4)	7 034(7)	1 337(5)	2 816(8)
C(5)	7 778(8)	932(4)	3 456(7)
C(11)	10 009(10)	−2(5)	1 830(9)
O(11)	10 468(8)	−332(4)	1 252(6)
C(12)	9 216(10)	−148(6)	3 625(9)
O(12)	9 260(7)	−589(4)	4 176(6)
C(13)	10 491(10)	909(5)	3 390(8)
O(13)	11 299(7)	1 171(4)	3 792(6)
C(21)	5 168(11)	438(6)	1 989(9)
O(21)	4 106(7)	443(4)	1 796(7)
C(22)	7 283(11)	−35(6)	1 225(11)
O(22)	7 540(10)	−292(5)	493(8)
C(23)	6 507(11)	−296(7)	3 120(10)
O(23)	6 267(10)	−743(5)	3 597(9)
C(31)	6 655(8)	1 587(6)	885(9)
F(32)	5 431(6)	1 647(3)	1 010(4)
F(33)	6 797(5)	1 261(3)	10(4)
F(34)	7 069(5)	2 198(3)	697(4)
C(41)	6 047(8)	1 802(6)	3 176(7)
C(42)	5 096(9)	1 583(6)	3 816(8)
C(43)	4 226(10)	2 032(7)	4 159(9)
C(44)	4 309(11)	2 670(7)	3 906(10)
C(45)	5 243(10)	2 887(6)	3 300(8)
C(46)	6 123(9)	2 457(5)	2 955(7)
C(51)	7 729(9)	971(7)	4 581(8)
C(52)	7 298(9)	500(6)	5 214(11)
C(53)	7 294(10)	561(8)	6 260(12)
C(54)	7 760(13)	1 115(6)	6 719(11)
C(55)	8 200(13)	1 585(7)	6 125(12)
C(56)	8 204(9)	1 531(6)	5 068(10)
O(111)	9 176(5)	2 193(3)	2 443(5)
C(112)	10 063(11)	2 740(6)	2 695(11)
C(113)	9 549(12)	3 159(6)	3 282(10)
O(121)	10 689(5)	1 828(3)	1 520(5)
C(122)	11 254(8)	1 368(5)	826(8)
C(123)	12 463(8)	1 690(5)	567(9)

were collected with graphite-monochromatized Mo-K_α radiation using the θ—2θ scan technique. Three reflections were measured every 2 h for control orientation and intensity. No significant difference was observed. 4 267 Intensities were collected in the range $2 < \theta < 23.5°$ ($hkl = \pm 10, 21, 13$), 1 137 of which were considered as observed [$I > 2.5\sigma(I)$]. Lorentz polarization corrections were made, but absorption was ignored.

Crystal data. $C_{28}H_2F_3Fe_2O_8$, $M = 655.17$, monoclinic, space group $P2_1/n$, $a = 10.673(6)$, $b = 20.681(4)$, $c = 13.118(4)$ Å, $\beta = 92.27(3)°$, $U = 2\,893(3)$ Å^3, $Z = 4$, $D_c = 1.50$ g cm^{-3}, $F(000) = 1\,332$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 11.0 cm^{-1}.

The Fe atoms were located by direct methods, using the MULTAN 80 system.[2] The remaining non-hydrogen atoms were located by the DIRDIF80 system.[3] Atoms were refined isotropically and anisotropically by a full-matrix least-squares method, using the SHELX 76 computer program.[4] The function minimized was $w||F_o| - |F_c||^2$ where $w = [\sigma^2(F_o) + 0.0003|F_o|^2]^{-1}$. Scattering factors were taken from ref. 5. A difference synthesis revealed the position of all hydrogen atoms, which were refined with an overall isotropic thermal parameter, and the bond distances constrained with the exception of HC(2). The final R value was 0.027 ($R' = 0.026$) for all observed reflections. The maximum residual electron density was 0.15 e Å^{-3} from a final difference synthesis. The fractional co-ordinates of the non-hydrogen atoms are listed in Table 1.

Results and Discussion

The complex $[PPh_4][Fe_2(CO)_6\{\mu\text{-}CPhCPhC(CF_3)C(CF_3)H\}]$ (**1**) reacts readily with protons or carbocations leading to the same product, (**2**). Proton n.m.r. spectroscopy of (**2**) gives evidence of the presence of phenyl groups and a triplet whose integration corresponds to one hydrogen and could be attributed to the CH group. The reason for its appearance as a triplet was not clear until the ^{13}C n.m.r. spectrum had shown the presence of a CF_2 group at 144.1 p.p.m. Furthermore, the ^{13}C resonance of the CH group at 33.9 p.p.m. also appears as a triplet due to coupling with the two fluorine atoms. These spectroscopic results suggest that the electrophilic reagents have abstracted one fluorine atom from the CF_3 group bonded to the CH carbon of the anionic starting molecule. There is a precedent for fluoride abstraction by protons from a CF_3 group but in this case the CF_3 group was directly bonded to a metal.[6] Attempts to obtain suitable crystals for an *X*-ray structure determination were not successful with pentane as solvent. With ethanol good crystals were obtained but spectroscopic data indicate that complex (**2**) had reacted with the solvent. The ν(CO) stretching bands moved towards lower frequencies and the proton n.m.r. spectrum showed the presence of two ethoxy-groups. Also, the CH resonance was no longer a triplet but a singlet. This suggests that the two fluorine atoms have been replaced by ethoxy-groups, and is confirmed by the ^{13}C n.m.r. spectrum which shows the disappearance of the CF_2 group and the presence of a new resonance at 186.2 p.p.m. It also confirms the presence of two ethoxy-groups. To elucidate further the nature of complex (**3**), we have performed an *X*-ray structure determination. The molecular structure together with the numbering of the atoms is shown in the Figure. Selected bond distances and angles are gathered in Table 2.

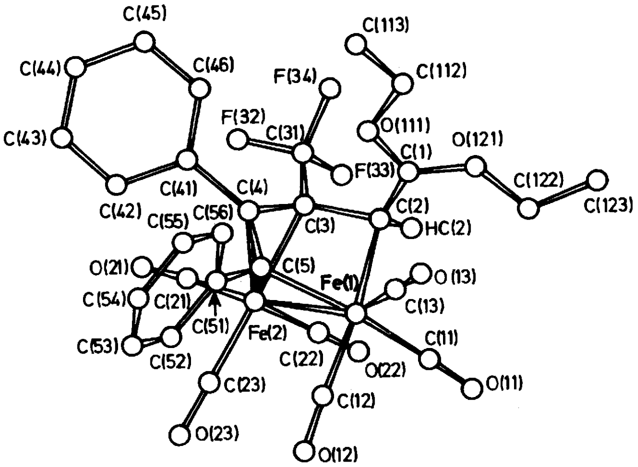

Figure 1. Structure of complex (**3**) showing the atomic numbering scheme

The structure shows that complex (**3**) results from the abstraction of one fluorine atom and the replacement of two

Table 2. Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses for complex (**3**)

Fe(2)–Fe(1)	2.599(2)	C(5)–Fe(2)	2.098(9)	C(31)–C(3)	1.504(15)	O(23)–C(23)	1.150(18)
C(1)–Fe(1)	2.864(10)	C(21)–Fe(2)	1.785(12)	C(5)–C(4)	1.409(12)	F(32)–C(31)	1.339(10)
C(2)–Fe(1)	2.150(10)	C(22)–Fe(2)	1.789(14)	C(41)–C(4)	1.516(14)	F(33)–C(31)	1.343(14)
C(5)–Fe(1)	2.017(9)	C(23)–Fe(2)	1.796(14)	C(51)–C(5)	1.480(13)	F(34)–C(31)	1.360(14)
C(11)–Fe(1)	1.832(11)	C(2)–C(1)	1.414(12)	O(11)–C(11)	1.144(14)	C(112)–O(111)	1.504(13)
C(12)–Fe(1)	1.766(12)	O(111)–C(1)	1.311(11)	O(12)–C(12)	1.163(14)	C(113)–C(112)	1.295(18)
C(13)–Fe(1)	1.805(10)	O(121)–C(1)	1.319(10)	O(13)–C(13)	1.131(13)	C(122)–O(121)	1.463(12)
C(3)–Fe(2)	2.061(9)	C(3)–C(2)	1.530(12)	O(21)–C(21)	1.152(14)	C(123)–C(122)	1.503(13)
C(4)–Fe(2)	2.069(10)	C(4)–C(3)	1.453(14)	O(22)–C(22)	1.141(18)		
C(2)–Fe(1)–Fe(2)	74.4(2)	C(31)–C(3)–C(2)	112.4(8)	O(12)–C(12)–Fe(1)	177.2(10)	C(23)–Fe(2)–C(21)	89.7(6)
C(5)–Fe(1)–Fe(2)	52.2(2)	C(31)–C(3)–C(4)	123.2(8)	O(13)–C(13)–Fe(1)	179.4(10)	C(23)–Fe(2)–C(22)	98.0(6)
C(5)–Fe(1)–C(2)	83.9(4)	C(3)–C(4)–Fe(2)	69.1(5)	O(21)–C(21)–Fe(2)	176.9(11)	O(111)–C(1)–C(2)	122.0(8)
C(11)–Fe(1)–Fe(2)	107.6(3)	C(5)–C(4)–Fe(2)	71.3(5)	O(22)–C(22)–Fe(2)	176.5(12)	O(121)–C(1)–C(2)	125.1(8)
C(11)–Fe(1)–C(2)	90.1(4)	C(21)–Fe(2)–C(5)	126.9(5)	O(23)–C(23)–Fe(2)	176.7(11)	O(121)–C(1)–O(111)	112.8(7)
C(11)–Fe(1)–C(5)	159.8(4)	C(22)–Fe(2)–Fe(1)	84.3(4)	F(32)–C(31)–C(3)	114.5(9)	C(1)–C(2)–Fe(1)	105.1(6)
C(12)–Fe(1)–Fe(2)	93.5(4)	C(22)–Fe(2)–C(3)	92.4(5)	F(33)–C(31)–C(3)	111.4(9)	C(3)–C(2)–Fe(1)	97.0(6)
C(12)–Fe(1)–C(2)	167.4(4)	C(22)–Fe(2)–C(4)	132.9(5)	F(33)–C(31)–F(32)	106.8(8)	C(3)–C(2)–C(1)	116.5(8)
C(12)–Fe(1)–C(5)	91.5(4)	C(5)–C(4)–C(3)	110.7(8)	F(34)–C(31)–C(3)	113.2(8)	C(2)–C(3)–Fe(2)	106.4(6)
C(12)–Fe(1)–C(11)	90.3(5)	C(41)–C(4)–Fe(2)	128.3(6)	F(34)–C(31)–F(32)	104.9(9)	C(4)–C(3)–Fe(2)	69.7(5)
C(13)–Fe(1)–Fe(2)	150.2(3)	C(41)–C(4)–C(3)	124.3(8)	F(31)–C(31)–F(33)	105.5(9)	C(4)–C(3)–C(2)	116.6(8)
C(13)–Fe(1)–C(2)	98.9(4)	C(41)–C(4)–C(5)	125.0(9)	C(112)–O(111)–C(1)	118.5(7)	C(31)–C(3)–Fe(2)	121.1(7)
C(13)–Fe(1)–C(5)	98.6(4)	Fe(2)–C(5)–Fe(1)	78.3(3)	C(113)–C(112)–O(111)	110.9(10)	C(122)–O(121)–C(1)	120.6(7)
C(13)–Fe(1)–C(11)	101.4(5)	C(4)–C(5)–Fe(1)	113.8(6)	C(22)–Fe(2)–C(5)	133.1(5)	C(123)–C(122)–O(121)	103.4(7)
C(13)–Fe(1)–C(12)	93.4(5)	C(4)–C(5)–Fe(2)	69.1(5)	C(22)–Fe(2)–C(21)	97.6(5)		
C(3)–Fe(2)–Fe(1)	72.4(2)	C(51)–C(5)–Fe(1)	122.8(7)	C(23)–Fe(2)–Fe(1)	98.0(4)		
C(4)–Fe(2)–Fe(1)	75.5(2)	C(51)–C(5)–Fe(2)	134.0(7)	C(23)–Fe(2)–C(3)	165.2(5)		
C(4)–Fe(2)–C(3)	41.2(4)	C(51)–C(5)–C(4)	121.4(9)	C(23)–Fe(2)–C(4)	126.3(5)		
C(5)–Fe(2)–Fe(1)	49.5(2)	O(11)–C(11)–Fe(1)	176.8(10)	C(23)–Fe(2)–C(5)	96.2(5)		
C(5)–Fe(2)–C(3)	68.9(3)						
C(5)–Fe(2)–C(4)	39.5(3)						
C(21)–Fe(2)–Fe(1)	171.7(4)						
C(21)–Fe(2)–C(3)	99.4(5)						
C(21)–Fe(2)–C(4)	97.5(5)						

other fluorine atoms by ethoxy-groups in the CF_3 bonded to the CH group of the anionic complex (**1**). This was suggested by the n.m.r. data for complexes (**2**) and (**3**).

The organic part of the molecule that bridges the $Fe_2(CO)_6$ unit is bonded to Fe(2) by the C(3)C(4)C(5) allylic fragment in the same way as in (**1**),[1] but the most salient feature is the mode of bonding of the C(2)C(1) fragment, especially the long Fe(1)–C(1) distance [2.864(10) Å]. Even though it could be considered as nearly σ-bonded by C(2), the short C(1)–C(2) bond [1.414(12) Å] indicates that this fragment retains some olefinic character. The angles around C(1) are nearly those of a *sp*^{2} carbon and the C(1), C(2), O(111), and O(121) atoms are nearly in the same plane. The two ethoxy-groups are not equivalent at room temperature on the n.m.r. time-scale, which shows that the rotational barrier is quite high. The same kind of bonding has been encountered for cationic $Fe(C_5H_5)(CO)_2$(olefin) complexes[7] and we have found recently that in a very similar complex $[Fe_2(CO)_6\{\mu\text{-}C(CF_3)C(CF_3)CHCHCH(OEt)\}]$ the π-bonded end CHCH(OEt) has a slightly unsymmetrical mode of bonding, the iron–carbon distances differing by 0.15 Å.[8] This suggests that the situation observed here is the consequence of the presence of two ethoxy-groups. This seems to be substantiated by the quite short C(1)–O(111) and C(1)–O(121) distances.* Examination of the carbon–carbon distances in the C(2)–C(5) chain shows the expected delocalization in the allylic fragment C(3)C(4)C(5), but C(2)–C(3) has a normal single-bond length. Concerning the bonding to the iron atoms, the C(5)–Fe(1) distance is slightly shorter than C(5)–Fe(2) and Fe(2) is nearly equidistant from C(3), C(4), and C(5).

The Fe(1)–Fe(2) bond length [2.599(2) Å] is normal for an iron–iron single-bond distance[9] and the $Fe(CO)_3$ units have normal bond distances and angles.

To summarize, the structure of complex (**3**) evidences the lability of the fluorine atoms bonded to the CF_3 group in the β position to Fe(1) in (**1**). The first abstraction is the consequence of the action of an electrophilic agent such as a proton or a carbocation on complex (**1**). The remaining two fluorine atoms are also very labile and easily displaced by an ethoxy-group, suggesting that in (**1**) the CH–CF_2 alkyne part of the organic ring is also asymmetrically bonded to Fe(1).[7,8,10]

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* A referee suggested that another possibility would be to consider C(1) as a carbocation centre stabilized by ethoxy-groups and the molecule as a zwitterion. This would be consistent with the short C(1)–O distances and the lowering of the ν(CO) stretching frequencies of complex (**3**) compared to those of (**2**).

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