Data collection

Siemens R3m/V diffractom-
eter
$\omega/2\theta$ scans
Absorption correction:
empirical (four ψ scans)
(North, Phillips &
Mathews, 1968)
$T_{min} = 0.42$, $T_{max} = 0.48$
5162 measured reflections
4880 independent reflections

3741 reflections with
$F > 4\sigma(F)$
$R_{int} = 0.0155$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 35$
$l = 0 \rightarrow 12$
2 standard reflections
every 250 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.0443$
$wR = 0.0597$
$S = 0.85$
3741 reflections
419 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + 0.0049F^2]$
$(\Delta/\sigma)_{max} = 0.48$

$\Delta\rho_{max} = 1.87$ e $Å^{-3}$
$\Delta\rho_{min} = -1.67$ e $Å^{-3}$
Extinction correction: none
Scattering factors from *Inter-
national Tables for X-ray
Crystallography* (Vol. IV)
Absolute configuration:
Flack (1983)
Flack parameter =
$-0.003\,(19)$

Table 1. *Selected bond lengths (Å) and angles (°)*

	Molecule A	Molecule B
Re—Cl(1)	2.418 (5)	2.428 (5)
Re—Cl(2)	2.355 (7)	2.345 (7)
Re—P(1)	2.468 (4)	2.461 (4)
Re—O(1)	1.680 (13)	1.639 (13)
Re—O(2)	1.923 (13)	1.862 (14)
Re—N(1)	2.205 (18)	2.206 (18)
Cl(1)—Re—Cl(2)	87.8 (3)	87.7 (3)
Cl(1)—Re—P(2)	177.8 (3)	177.4 (2)
Cl(1)—Re—O(1)	97.1 (4)	97.5 (5)
Cl(1)—Re—O(2)	94.4 (4)	92.3 (5)
Cl(1)—Re—N(1)	88.2 (5)	87.0 (5)
Cl(2)—Re—P(1)	89.9 (2)	91.9 (2)
Cl(2)—Re—O(1)	101.8 (6)	100.6 (5)
Cl(2)—Re—O(2)	90.2 (4)	92.0 (6)
Cl(2)—Re—N(1)	164.3 (5)	165.2 (5)
P(1)—Re—O(1)	83.4 (4)	85.1 (4)
P(1)—Re—O(2)	85.6 (4)	85.1 (5)
P(1)—Re—N(1)	93.9 (4)	92.8 (4)
O(1)—Re—O(2)	163.7 (6)	164.3 (7)
O(1)—Re—N(1)	93.8 (7)	93.9 (6)
O(2)—Re—N(1)	75.0 (6)	74.4 (7)

The H atoms, with the exception of the missing water H atoms, were included in calculated positions, but were not refined. Only a common variable displacement parameter was applied to them.

Data collection: *SHELXTL-Plus* (Sheldrick, 1987). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: AB1373). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Tetranuclear Iron Cluster Complex: [{Fe(CO)3}3{μ3-CC[Fe(CO)2(η5-C5H5)]-C(CF3)}]

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Abstract

Undecacarbonyl[4(η^5)-cyclopentadienyl]-μ_3-(4,4,4-trifluorobutaneheptayl)-tetrairon(3 *Fe—Fe*), [{Fe(CO)3}3-{μ_3-CC[Fe(CO)2Cp]C(CF3)}] (Cp is η^5-C5H5) contains a triangular {Fe(CO)3}3 core [Fe—Fe distances 2.482 (1), 2.663 (1) and 2.693 (1) Å] linked *via* an unusual C3CF3 bridging unit to an Fe(CO)2Cp group.

Comment

The dinuclear complex [{Cp(CO)Fe}2{μ-C2(CF3)2-SMe}2] (Cp is η^5-C5H5), (1), reacts with triiron dodecacarbonyl [Fe3(CO)12] to give μ_3-η^2-alkyne

Fe_3C_2 and Fe_2SC_2 five-vertex polyhedral cluster complexes (3) and (4), and di- and triiron derivatives [{Fe(CO)$_3$}$_2$(μ-SMe){μ-C$_2$H(CF$_3$)$_2$}], [{Fe(CO)$_3$}$_2${μ-C(CF$_3$)CCFeCp(CO)$_2$}], (5), and [{Fe(CO)$_3$}$_2${μ-C-(SMe)(CF$_3$)CCF$_2$}], (6) (Rumin, Pétillon, Manojlović-Muir & Muir, 1990). Because of their unusual chemical behaviour (Rumin, Pétillon, Manojlović-Muir, Muir & Yufit, 1995), we have tried to obtain compounds (5) and (6) in greater yield by modifying the preparation. To this end, we examined the thermal reaction of (1) in toluene with diiron nonacarbonyl, Fe$_2$(CO)$_9$ (see scheme). In addition to the previously known compounds (3)–(6), we obtained in low yield a new tetrairon complex [{Fe(CO)$_3$}$_3${μ_3-CC[Fe(CO)$_2$Cp]C(CF$_3$)}], (2), whose structural and spectroscopic characterization we now describe.

(1)

↓ Δ | Toluene

(3) (3%)   (4) (8%)
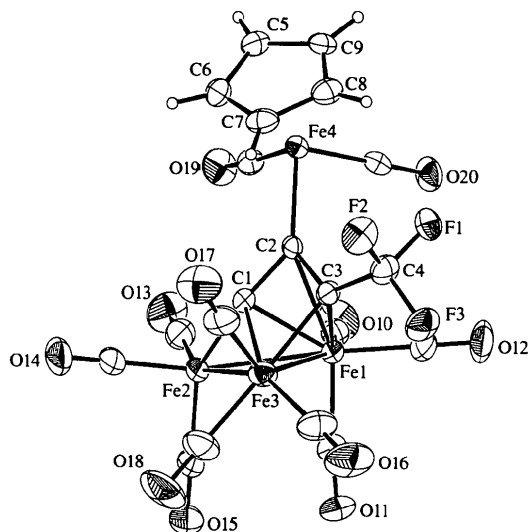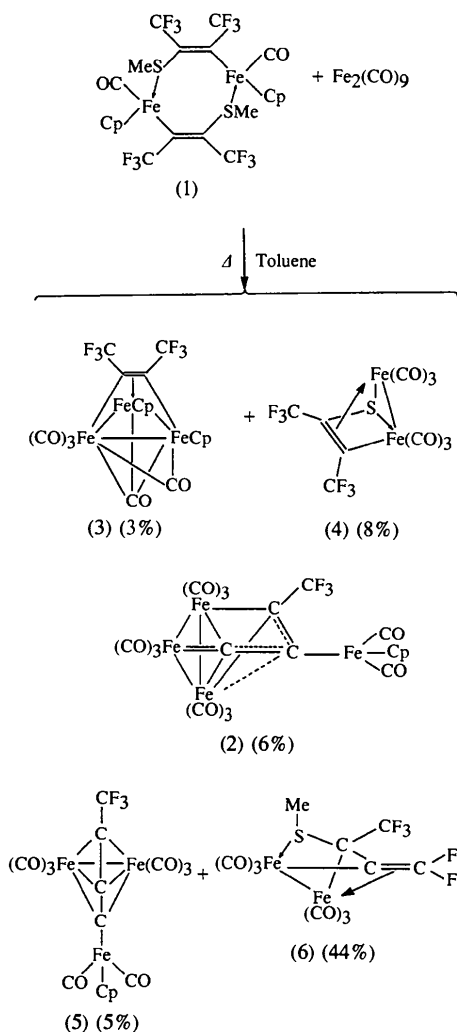
(2) (6%)

(6) (44%)

(5) (5%)

Fig. 1. A view of the title molecule showing 30% probability ellipsoids, except for H atoms which are represented as spheres of arbitrary radii. Carbonyl C atoms are numbered as the O atoms.

As can be seen from Fig. 1, complex (2) contains a triangular Fe1Fe2Fe3(CO)$_9$ unit which completes its expected 48 electron count by accepting six electrons from the unusual C1—C2—C3—CF$_3$ ligand. The

attachment of this chain of four C atoms to the Fe$_3$ triangle can be described in terms of a bridging π-allylic interaction between C1—C2—C3 and the Fe1—Fe3 bond; the terminal C atoms (C1 and C3) interact more strongly with the metal atoms than does C2, which binds weakly to Fe1 [Fe1—C2 2.254 (4) Å] and not at all to Fe3 [Fe3$\cdots$C2 2.716 (4) Å]. In contrast, the Fe2—C1 distance is short enough [1.773 (4) Å] to suggest that the bond has some multiple character and also that C1 adopts sp-hybridization, a view consistent with the near linearity of the Fe2—C1—C2 angle [165.1 (3)°]. An Fe(CO)$_2$Cp substituent is attached to the C2 atom which is almost coplanar with atoms C1, C3 and Fe4 [the torsion angles C4—C3—C2—C1 and C4—C3—C2—Fe4 are 172.6 (4) and −3.1 (7)°, respectively]. Although the lengths of the Fe1—Fe2 and Fe2—Fe3 bonds are normal, the bridged Fe1—Fe3 bond is unusually short [2.482 (1) Å]. A database search gave a mean length for 645 Fe—Fe bonds in trinuclear clusters of 2.621 Å (Allen *et al.*, 1979), with 80% of the individual values in the range 2.505–2.738 Å. Other bond lengths are consistent with the proposed structure and agree with accepted values; the Fe—CO bond lengths range between 1.751 (6) and 1.823 (6) Å, with a mean of 1.789 Å, close to that of 1.782 Å reported by Orpen *et al.* (1992). The C11 and C18 carbonyl ligands are very weakly semi-bridging [Fe3$\cdots$C11 2.715 (5) and Fe2$\cdots$C18 2.726 (6) Å] and appreciably bent, with Fe—C—O angles of 171.8 (5) and 171.1 (6)° [*cf.* 175.7 (6)–179.0 (4)° for the other nine CO groups].

Spectroscopic assignments are consistent with the results of the structure analysis. The IR spectrum thus displays five absorptions between 2085 and 1960 cm^{-1} which are assigned to ν(CO) stretching vibrations. The

^{19}F NMR spectrum exhibits a singlet at δ −56.65 indicating the presence of a single CF_3 group. The $^{13}C\{^1H\}$ NMR spectrum contains a quartet at δ 129.8 (J_{CF} = 277 Hz) attributed to the CF_3 group and three resonances in the CO region, with areas in the ratio 2:6:3 consistent with the IR assignment. Resonances attributable to quaternary C atoms are observed at δ 139.0 (q, $^2J_{CF}$ = 35 Hz), 152.8 (q, $^3J_{CF}$ = 4.5 Hz) and 254.3 (q, $^4J_{CF}$ = 1.5 Hz). The low-field shift of the last carbon resonance suggests carbyne-like character.

In crystals of (2), the intermolecular contacts are consistent with normal van der Waals radii; the shortest intermolecular O$\cdots$O contact is that of 2.948(7) Å between O12 and O16^i [symmetry code: (i) $1-x$, $-y$, $1-z$]. The contacts O14$\cdots$H6^{ii} and O17$\cdots$H5^{iii} meet the criteria suggested by Braga, Grepioni, Biradha, Pedireddi & Desiraju (1995) for C—H$\cdots$O hydrogen bonding in crystals of metal carbonyls [O14$\cdots$H6^{ii} 2.68 Å and C—H$\cdots$O 128°; O17$\cdots$H5^{iii} 2.65 Å and C—H$\cdots$O 122°; symmetry codes: (ii) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$; (iii) x, $1-y$, $\frac{1}{2}+z$; C—H bond lengths were renormalized from 0.93 to 1.08 Å for these calculations].

Experimental

[{Cp(CO)Fe}$_2${μ-C$_2$(CF$_3$)$_2$SMe}$_2$], (1) (6 g, 0.83 mmol), and seven equivalents of Fe$_2$(CO)$_9$ (5.81 mmol) were heated in toluene (200 ml) under reflux for 4 h. The toluene was removed under vacuum and the residue extracted with dichloromethane. Filtration through celite followed by elution with hexane–dichloromethane (75:25) down a silica gel column gave a maroon band of compound (2). Recrystallization gave a maroon solid (yield 6%). Mass spectrum (m/z): 646 [M − 2CO]$^+$, 562 [M − Fe(CO)$_3$]$^+$, 534, 506, 478, 450, 422, 394, 366, 338 [M − Fe(CO)$_3$ − nCO]$^+$ (n = 1–8). Chemical shifts (δ) in p.p.m. measured in CDCl$_3$ at room temperature (J in Hz): ^{1}H 5.20 (s, C$_5$H$_5$); ^{19}F −56.65 (s, CF$_3$); $^{13}C\{^1H\}$ 86.4 (s, C$_5$H$_5$), 129.8 (q, CF$_3$, $^1J_{CF}$ = 277), 139.0 (q, C—CF$_3$, $^2J_{CF}$ = 35), 152.8 [q, C—FeCp(CO)$_2$, $^3J_{CF}$ = 4.5], 208.4 (s, 3CO), 210.8 (s, 6CO), 213.4 [s, 2CO, FeCp(CO)$_2$] and 254.3 (q, Fe≡C, $^4J_{CF}$ = 1.5). IR (cm^{-1}, CH$_2$Cl$_2$ solution) 1960, 1985, 2020, 2040 and 2085.

Crystal data

[Fe$_4$(C$_5$H$_5$)(C$_4$F$_3$)(CO)$_{11}$]
M_r = 701.64
Monoclinic
$C2/c$
a = 29.3869(14) Å
b = 12.1954(8) Å
c = 13.5700(9) Å
β = 103.845(5)°
V = 4722.0(5) Å^3
Z = 8
D_x = 1.974 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 16.1–20.0°
μ = 2.491 mm^{-1}
T = 293 (2) K
Needle
0.40 × 0.10 × 0.10 mm
Maroon

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4836 measured reflections
4624 independent reflections
2784 reflections with $I > 2\sigma(I)$

R_{int} = 0.0322
θ_{max} = 26°
$h = -35 \rightarrow 36$
$k = -15 \rightarrow 0$
$l = -16 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0406
$wR(F^2)$ = 0.0941
S = 1.023
4623 reflections
343 parameters
H atoms riding with U(H) = 1.2U_{eq}(C)

w = 1/[$\sigma^2(F_o^2)$ + (0.0396P)^2 + 3.1396P]
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—C1	2.038(4)	Fe4—C2	1.974(4)
Fe1—C3	2.040(4)	Fe4—C7	2.099(5)
Fe1—C2	2.254(4)	Fe4—C6	2.099(4)
Fe1—Fe3	2.4824(9)	Fe4—C8	2.100(5)
Fe1—Fe2	2.6928(9)	Fe4—C9	2.104(4)
Fe2—C1	1.773(4)	Fe4—C5	2.109(5)
Fe2—Fe3	2.6628(10)	C1—C2	1.414(5)
Fe3—C3	2.004(4)	C2—C3	1.425(6)
Fe3—C1	2.095(4)	C3—C4	1.488(6)
C1—Fe1—C3	60.9(2)	C2—C1—Fe1	79.3(2)
C1—Fe1—C2	38.05(14)	Fe2—C1—Fe1	89.7(2)
C3—Fe1—C2	38.35(15)	C2—C1—Fe3	99.6(3)
C1—Fe1—Fe3	54.15(11)	Fe2—C1—Fe3	86.6(2)
C3—Fe1—Fe3	51.49(12)	Fe1—C1—Fe3	73.82(13)
C2—Fe1—Fe3	69.80(10)	C1—C2—C3	93.4(3)
C1—Fe1—Fe2	41.17(12)	C1—C2—Fe4	129.6(3)
C3—Fe1—Fe2	96.98(12)	C3—C2—Fe4	136.9(3)
C2—Fe1—Fe2	78.86(10)	C1—C2—Fe1	62.7(2)
C1—Fe2—Fe3	51.76(13)	C3—C2—Fe1	62.7(2)
C1—Fe2—Fe1	49.18(13)	Fe4—C2—Fe1	134.9(2)
C3—Fe3—C1	60.5(2)	C2—C3—C4	124.7(4)
C3—Fe3—Fe1	52.79(12)	C2—C3—Fe3	103.5(3)
C1—Fe3—Fe1	52.03(11)	C4—C3—Fe3	127.1(3)
C3—Fe3—Fe2	98.83(12)	C2—C3—Fe1	79.0(2)
C1—Fe3—Fe2	41.64(11)	C4—C3—Fe1	129.4(3)
C2—C1—Fe2	165.1(3)	Fe3—C3—Fe1	75.72(15)

Reactions were performed under argon using standard Schlenk techniques and solvents were deoxygenated and dried by standard methods. IR spectra were obtained with a Perkin Elmer 1430. The mass spectrum was measured on a GC/MS Hewlett Packard 5595C. NMR spectra (^{1}H, ^{13}C and ^{19}F) in CDCl$_3$ were recorded on a Jeol FX 100, a Bruker AC300 or Bruker DRX 400 and were referenced to Me$_4$Si and CFCl$_3$. The irregular shape of the crystal precluded a satisfactory analytical absorption correction. An empirical absorption correction based on ψ scans gave a less satisfactory refinement than that reported here. Transmission factors are estimated to be *ca* 0.72–0.81. The database searches were made with the EPSRC Chemical Database Service at Daresbury Laboratory, Warrington, England, on the January 1996 version of the Cambridge Structural Database (Allen *et al.*, 1979).

Data collection: *CAD-4 Express* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 Express*. Data reduction: *GX* (Mallinson & Muir, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure:

$$[Fe_4(C_5H_5)(C_4F_3)(CO)_{11}]$$

*SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIFWRITE* (Pawson & Muir, 1996) and *PLATON* (Spek, 1995).

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