A Unique Example of an Octahedral Iron(II) Complex containing Four Triflate Anions and Two Nitrile-like Organometallic Cations†

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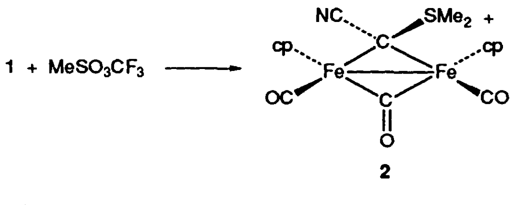
The action of $MeSO_3CF_3$ on $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe\}]$ **1** (cp = $\eta^5\text{-}C_5H_5$) yields $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}][SO_3CF_3]$ **2**. The sulphonium cation is also obtained, trapped in the unusual triflate complex $[Fe(OSO_2CF_3)_4\{Fe_2(cp)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)SMe_2]\}_2]$ **3**, by treating the thiolcarbamate $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)C(O)SMe\}]$ **4** with $MeSO_3CF_3$. The X-ray crystal structure of **3** shows the iron(II) centre co-ordinated by four *O*-bonded triflate anions and by two, mutually *trans*-disposed, *N*-co-ordinated organometallic cations in an octahedral geometry.

We have recently described that S-methylation of the cyanothioalkoxycarbene $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe\}]$[1] **1** (cp = $\eta^5\text{-}C_5H_5$) with $MeSO_3CF_3$ forms the triflate salt $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}][SO_3CF_3]$ **2**, which is an excellent starting material for a broad variety of new C, N, O,S-substituted μ-carbenes of the type $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)X\}]$ *via* SMe_2 replacement with the appropriate nucleophiles (X = Me, OR, SR or NR_2).[2]

We now report on the structure of the sulfonium cation $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}]^+$ of **2**, unexpectedly trapped through *N*-co-ordination at the iron(II) centre in the neutral triflate complex $[Fe(OSO_2CF_3)_4\{Fe_2(cp)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)SMe_2]\}_2]$ **3**, obtained by treating $MeSO_3CF_3$ with $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)C(O)SMe\}]$ **4**.[3] Compound **3** represents the first structurally characterized complex containing more than two covalently bonded triflate ligands.[4] Full details of the synthesis of **2** and **3** together with their spectroscopic properties are also described.

Results and Discussion

The reaction of compound **1** with an excess of $MeSO_3CF_3$ in dichloromethane affords in almost quantitative yield the dark red, air-sensitive precipitate **2** which is soluble in acetonitrile and nitromethane [equation (1)]. The structure of the sulfonium derivative **2**, which is similar in nature to the acylium,[5] phosphonium,[6] nitrilium[7] and ammonium[8] species $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHX)]^+$ (X = CO, PPh_3, $CNBu^t$ or NMe_3) has been established spectroscopically. The *cis* arrangement of the cp and terminal CO ligands was assigned on the basis of the following observations: (*i*) single cp (^1H, δ 5.28; ^{13}C, δ 88.1) and terminal CO (^{13}C, δ 204.2); (*ii*) ν(CO) absorptions at 2013s and 1981m cm^{-1}. The occurrence of the bridging ligands CO and $C(CN)SMe_2$ is supported by the presence of NMR resonances associated with SMe_2 and μ-CO [^1H, δ 3.24 (s); ^{13}C, δ 27.9, 250.6] and on the basis of the IR bands at 1835 [ν(CO)] and 2175 cm^{-1} [ν(CN)]. In agreement with the cationic nature of **2** all the CO stretching vibrations are found shifted to higher wavenumbers with respect to those of the precursor **1**. The spectral data do not allow an assignment of the relative geometry of the SMe_2 and cp groups. However, since in **1**, the precursor of **2**, the SMe group is located on the less-hindered CO face,[1] we tentatively assigned a similar *syn* geometry to **2**.[9] The proposed structure has been confirmed by the X-ray analysis of the dark red, microcrystalline, highly hygroscopic compound obtained in about 40% yield from an excess of $MeSO_3CF_3$ and $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)C(O)SMe\}]$ **4** in CH_2Cl_2 solvent.



(1)

2

The molecular structure (Fig. 1) unexpectedly reveals the presence of the sulfonium cation **2**, nitrile-like, *N*-co-ordinated to the iron(II) centre of the six-co-ordinate trifluoromethanesulfonate complex $[Fe(OSO_2CF_3)_4\{Fe_2(cp)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)SMe_2]\}_2]$ **3**. This complex is insoluble in dichloromethane, benzene and hexane, but readily soluble in polar solvents such as acetone, acetonitrile and nitromethane. Like **2**, it dissolves in methanol to form the neutral cyanomethoxycarbene $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)OMe\}]$.[2,10]

Compounds **2** and **3**, not surprisingly, exhibit identical IR spectra in MeCN in the carbonyl stretching region. However, the IR spectra in KBr reveal substantial differences (see Table 3). For complex **2** the triflate S–O stretches of the free ion are found at comparable wavenumbers to those of ionic triflate salts (*e.g.* 1280 and 1035 cm^{-1} for $Na[O_3SCF_3]$[11]). This two-band pattern is split into a three-band pattern for **3** which is consistent with a reduction in symmetry of the triflate group from C_{3v} (free ion) to C_s upon unidentate co-ordination.[4b] Moreover, the band at 1270 cm^{-1} associated with the free $CF_3SO_3^-$ in **2** is shifted to higher wavenumber (1315 cm^{-3} for **3**) as generally found for monodentate trifluoromethanesulfonate.[12] Finally, in addition to the expected ν(CN) increase, a significant shift towards higher wavenumbers of the ν(CO) groups of the *N*-co-ordinated organometallic moiety with respect to those of the unbonded **2** is found in the KBr IR

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

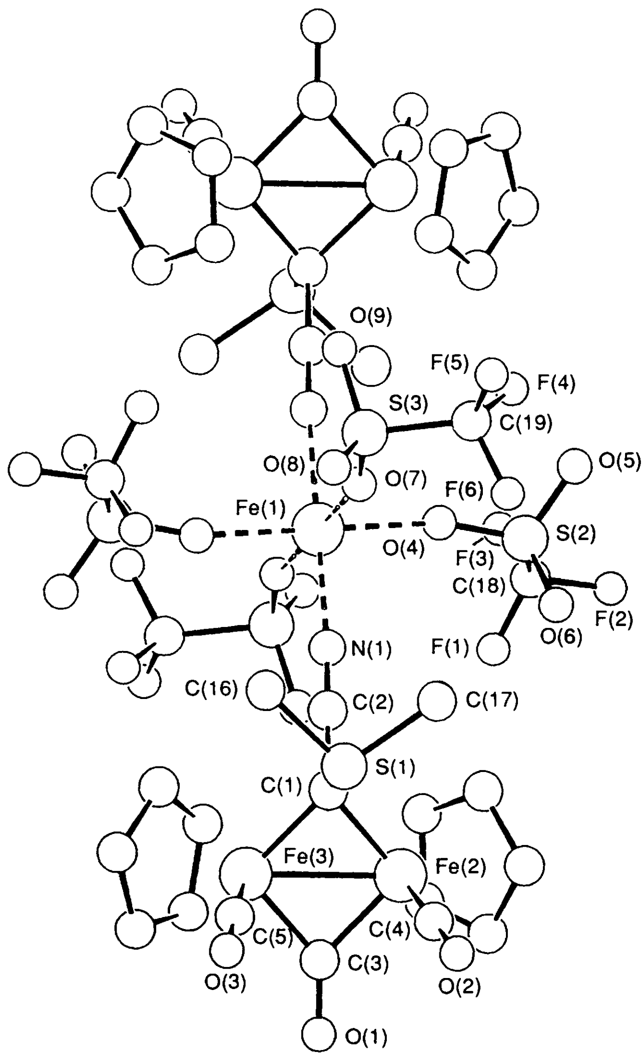
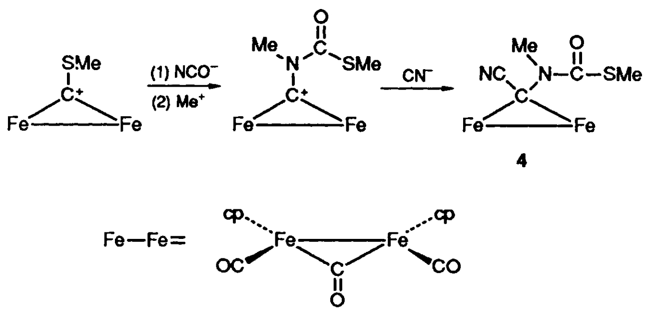


Fig. 1 The molecular structure of compound **3** showing the atomic labelling scheme



Scheme 1

Table 1 Crystal data and details of measurements for compound **3**

Formula	$C_{38}H_{32}F_{12}Fe_5N_2O_{18}S_6{\cdot}CH_2Cl_2$
M	1589.19
Crystal size/mm	0.10 × 0.20 × 0.10
System	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	13.338(2)
b/Å	18.795(3)
c/Å	12.388(5)
α/°	92.44(4)
β/°	93.31(2)
γ/°	81.69(2)
U/Å^3	3065.9
Z	2
$F(000)$	1564
D_c/g cm^{-3}	1.72
μ(Mo-Kα)/cm^{-1}	14.6
2θ range/°	4–40
ω Scan width/°	0.7 + 0.35 tanθ
Requested counting $\sigma(I)/I$	0.02
Prescan rate/° min^{-1}	8
Maximum scan time/s	60
Measured reflections	6186
Unique observed reflections $[I_o > 2.0\sigma(I_o)]$	4238
No. of refined parameters	738
R, R',[a] S,[b] K,[a] g[a]	0.06, 0.07, 2.1, 5.1, 0.001

[a] $R' = \Sigma[(F_o - F_c)w^{\frac{1}{2}}]/\Sigma F_o w^{\frac{1}{2}}$, where $w = K/[\sigma(F) + |g|F^2]$. [b] $S = \Sigma[(F_o - F_c)/\sigma]^2/(n - m)$, where n and m are the numbers of observations and parameters, respectively.

spectrum of the zwitterionic complex **3**. Thus, the net effect of the iron(II) centre is that of transferring a partial positive charge onto the diiron framework upon nitrile co-ordination. The same effect has also been found (Table 3) in $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C[CNW(CO)_5]SMe\}]$ **5** obtained by treating equimolar amounts of $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) with the cyanocarbene derivative **1**. This and the related, recently reported, *N*-metallation reactions of diiron cyanocarbenes[2,13] indicate that these complexes behave like cyanoolefins in their co-ordinating ability towards Lewis-acid metal fragments,[14] *via* the nitrile-N lone pair.

Complex **4**, which can be considered as a thiolcarbamate derivative, was recently prepared from the thiocarbyne complex $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]^+$,[15] through an unprecedented stepwise insertion of MeNCO into the C–S bond followed by CN^- addition at the bridging carbyne carbon (Scheme 1).[3] In this light the reverse elimination of MeNCO from **4** should be feasible in view of the properties of carbamic acid derivatives RHNC(O)XR (X = O or S) which are known to decompose with formation of isocyanates and alcohols (thiols). Therefore, the reaction of **4** with $MeSO_3CF_3$ promotes MeNCO elimination *via* S-methylation, followed by SMe_2 migration to the strong electrophilic μ-C atom of the diiron framework. The described concerted mechanism could explain the formation of **2** by the action of $MeSO_3CF_3$. This latter very likely also causes the oxidation to Fe^{II} which is stabilized by trapping four triflate and two molecules of the nitrile **2**. Further oxidation to Fe^{III} is prevented by the strictly anaerobic conditions used in the preparation of **3**. Similar reactions, in which $MeSO_3X$ (X = F or CF_3) acts as an oxidizing and co-ordinating agent have been reported.[4a] For example, $[Zr(cp)_2L_2]$ (L = $PMePh_2$) when mixed with FSO_3Me loses two L, and the Zr^{II} is oxidized to Zr^{IV}. Some $[Zr(cp)_2(OSO_2F)_2]$ was detected in this reaction.[16]

Crystal Structure of Compound **3**.—The crystal contains discrete complex units $[Fe(OSO_2CF_3)_4\{Fe_2(cp)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)SMe_2]\}_2]$ and dichloromethane molecules in 1 : 1 molar ratio. The complex molecule (Fig. 1) can be described in terms of a six-co-ordinate iron(II) cation to which four *O*-bonded $OSO_2CF_3^-$ anions and two *N*-bonded organometallic cations are co-ordinated in *trans* configuration. The complex has crystallographic C_i symmetry and the independent unit of the crystal structure consists of a pair of half molecules (**A** and **B**). The co-ordination around the iron(II) cation is regular and equivalent in the two independent units. Relevant bond distances and angles for **A** and **B** are reported in Table 4.

The average Fe–N and Fe–O distances are 2.13(1) and 2.10(1) Å respectively. The small difference between these values is in agreement with the size of the donor atoms and indicates substantial equivalence of the Fe–N and Fe–O bonding interactions. As a comparison, for the Fe–O(sulfonate) distances one can cite the value 2.007(3) Å found in $[Fe(\eta^5\text{-}$

Table 2 Fractional atomic coordinates for compound **3**

Atom	x	y	z	Atom	x	y	z
Fe(1A)	0.0	0.0	0.0	O(5B)	−0.132 2(5)	0.396 0(4)	0.218 8(7)
Fe(2A)	0.396 01(9)	0.858 04(7)	0.869 15(11)	O(6B)	0.014 0(6)	0.334 5(3)	0.311 9(7)
Fe(3A)	0.275 36(9)	0.800 12(7)	0.738 98(10)	C(18B)	0.039 0(9)	0.418 9(5)	0.166 9(9)
S(1A)	0.268 5(2)	0.754 9(1)	0.985 0(2)	F(1B)	0.010 4(8)	0.483 5(5)	0.125 3(7)
S(2A)	0.163 6(2)	1.095 7(1)	1.152 5(2)	F(2B)	0.135 4(7)	0.417 9(6)	0.204 2(10)
S(3A)	−0.031 8(2)	0.899 7(1)	1.216 0(2)	F(3B)	0.039 7(8)	0.373 0(5)	0.082 9(7)
C(1A)	0.264 5(6)	0.826 1(4)	0.895 3(7)	O(7B)	0.071 9(4)	0.579 1(3)	0.430 4(6)
C(2A)	0.187 6(7)	0.881 8(5)	0.924 7(8)	O(8B)	0.229 6(5)	0.539 6(4)	0 346 7(6)
N(1A)	0.125 2(7)	0.926 8(5)	0.951 2(8)	O(9B)	0.227 0(5)	0.618 8(4)	0.506 1(5)
C(3A)	0.414 2(8)	0.813 2(6)	0.728 8(9)	C(16A)	0.140 6(8)	0.735 0(7)	0.983 3(12)
O(1A)	0.480 0(6)	0.798 8(5)	0.667 5(7)	C(17A)	0.277 0(10)	0.795 8(7)	1.118 2(8)
C(4A)	0.473 5(7)	0.783 2(6)	0.917 1(9)	O(4A)	0.084 2(7)	1.068 9(4)	1.090 9(7)
O(2A)	0.530 7(6)	0.735 3(5)	0.946 6(8)	O(5A)	0.133 6(7)	1.129 7(4)	1.251 4(6)
C(5A)	0.318 4(8)	0.707 4(6)	0.753 9(9)	O(6A)	0.254 8(6)	1.046 7(5)	1.161 6(8)
O(3A)	0.350 2(6)	0.647 9(4)	0.755 6(7)	C(18A)	0.194 3(7)	1.1657(6)	1.072 2(8)
C(6A)	0.122 8(5)	0.837 3(6)	0.697 8(6)	F(1A)	0.230 6(7)	1.141 1(4)	0.980 9(6)
C(7A)	0.155 6(5)	0.773 5(6)	0.636 4(6)	F(2A)	0.262 0(6)	1.201 5(4)	1.121 5(6)
C(8A)	0.235 7(5)	0.787 1(6)	0.573 1(6)	F(3A)	0.114 7(7)	1.212 4(4)	1.046 4(8)
C(9A)	0.252 4(5)	0.859 3(6)	0.595 4(6)	O(7A)	0.002 0(9)	0.937 8(5)	1.136 5(7)
C(10A)	0.182 7(5)	0.890 3(6)	0.672 5(6)	O(8A)	−0.010 1(10)	0.825 6(4)	1.199 1(9)
C(11A)	0.341 6(5)	0.971 4(4)	0.869 4(11)	O(9A)	−0.130 9(6)	0.930 9(7)	1.243 9(9)
C(12A)	0.377 8(5)	0.949 9(4)	0.974 8(11)	C(19A)	0.045 0(8)	0.920 7(5)	1.332 0(9)
C(13A)	0.481 9(5)	0.920 9(4)	0.970 2(11)	F(4A)	0.036 3(7)	0.989 8(4)	1.357 4(7)
C(14A)	0.510 0(5)	0.924 4(4)	0.861 9(11)	F(5A)	0.023 6(8)	0.889 7(5)	1.418 9(7)
C(15A)	0.423 3(5)	0.955 6(4)	0.799 7(11)	F(6A)	0.140 8(7)	0.895 7(6)	1.323 4(9)
C(3B)	−0.431 8(8)	0.673 9(5)	0.240 1(9)	C(20A)*	0.304 7(10)	0.503 8(7)	0.117 6(14)
O(1B)	−0.500 2(6)	0.681 1(5)	0.176 4(7)	Cl(1A)*	0.390 8(5)	0.433 3(3)	0.148 2(5)
C(4B)	−0.328 4(8)	0.775 4(6)	0.252 0(9)	Cl(2A)*	0.339 4(8)	0.561 6(4)	0.035 8(10)
O(2B)	−0.352 6(7)	0.836 4(5)	0.240 8(8)	Fe(1B)	0.0	0.5	0.5
C(5B)	−0.480 3(8)	0.727 6(7)	0.416 3(9)	Fe(2B)	−0.410 18(9)	0.646 06(7)	0.388 59(12)
O(3B)	−0.536 2(7)	0.781 6(5)	0.431 0(7)	Fe(3B)	−0.291 29(9)	0.682 70(7)	0.255 07(10)
C(6B)	−0.252 4(6)	0.679 0(4)	0.094 6(5)	S(1B)	−0.264 8(2)	0.757 0(1)	0.490 7(2)
C(7B)	−0.280 1(6)	0.611 5(4)	0.118 5(5)	S(2B)	−0.035 5(2)	0.400 5(1)	0.270 4(2)
C(8B)	−0.212 0(6)	0.581 3(4)	0.202 2(5)	S(3B)	0.173 0(2)	0.593 4(1)	0.412 8(2)
C(9B)	−0.142 1(6)	0.630 2(4)	0.230 1(5)	C(1B)	−0.275 5(6)	0.675 8(4)	0.414 4(7)
C(10B)	−0.167 0(6)	0.690 6(4)	0.163 6(5)	C(2B)	−0.195 6(7)	0.621 0(5)	0.453 8(7)
C(11B)	−0.364 4(6)	0.532 5(4)	0.404 7(9)	N(1B)	−0.135 2(6)	0.577 5(4)	0.483 7(6)
C(12B)	−0.390 1(6)	0.565 7(4)	0.506 5(9)	C(19B)	0.146 3(6)	0.669 3(6)	0.330 9(8)
C(13B)	−0.493 0(6)	0.598 1(4)	0.497 5(9)	F(4B)	0.101 0(6)	0.655 0(4)	0.235 5(6)
C(14B)	−0.531 0(6)	0.585 0(4)	0.390 1(9)	F(5B)	0.086 2(6)	0.723 2(3)	0.376 8(7)
C(15B)	−0.451 6(6)	0.544 5(4)	0.332 8(9)	F(6B)	0.230 8(6)	0.694 7(4)	0.309 3(8)
C(16B)	−0.135 0(7)	0.773 3(6)	0.483 2(11)	C(20B)*	0.339 4(15)	0.027 5(7)	0.421 7(12)
C(17B)	−0.264 0(9)	0.734 2(6)	0.630 7(7)	Cl(1B)*	0.282 1(5)	0.045 9(3)	0.536 3(5)
O(4B)	−0.037 3(5)	0.463 4(3)	0.340 9(5)	Cl(2B)*	0.404 6(6)	−0.050 9(3)	0.386 4(7)

* The clathrated CH_2Cl_2 molecule is randomly distributed over two independent sites (site occupation factor 0.50).

Table 3 IR data, ν/cm^{-1}

		CO			SO			CF	
Compound	CN								
2[a]	2177	2008	1979	1834	1270	1033		1226	1156
3[a]	2201	2017	1990	1839	1315	1243	1040	1235	1175
$[Co(py)_4(OSO_2CF_3)_2]$[a,b]					1310	1240	1040	1230	1170
1[c,d]	2155	2002	1969	1806					
5[d]	2181	2006	1972	1812 [Fe(CO)]					
		2073	1935	1902 [W(CO)]					

[a] Dispersed in KBr. [b] Ref. 11; py = pyridine. [c] Ref. 1. [d] In CH_2Cl_2 solution.

$C_5Me_5)(CO)_2(OSO_2CF_3)]$.[17] The shorter bond distance in the latter is indicative of a better σ donation in species in which the other ligands are π acceptors.

The organometallic cation $Fe_2(cp)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)SMe_2]^+$ contains the bridging carbene unit μ-C(CN)SMe_2. This fragment is placed with the SMe_2 grouping *syn* to the terminal CO ligands, preserving the orientation of the μ-C substituents found in its precursor **4**.[3] The retained geometry indicates that the proposed $MeSO_3CF_3$-promoted rearrangement from the thiolcarbamate to the SMe_2 function occurs in the same region of space, that is the less-hindered CO face of **4**. It is of interest to compare the geometries of **2** bonded in **3** and the unalkylated *cis-syn*-**1**. Table 5 shows that the bond lengths at the carbene carbon are slightly but systematically shorter in the cation **3**. The comparison is not statistically significant if pairs of distances are considered separately but it improves when the whole set of values is examined. Another experimental finding that fits well with the bond distances is that the μ-C alkylidene carbon of **2** is easily attacked by nucleophilic agents.[2] The combined geometrical and chemical evidence shows that the

Table 4 Relevant bond distances (Å) and angles (°) for the two independent 'half' molecules (**A** and **B**) present in the crystal of compound **3**

	A	B		A	B
Fe(1)–N(1)	2.11(1)	2.15(1)	C(1)–C(2)	1.41(1)	1.45(1)
Fe(1)–O(4)	2.09(1)	2.12(1)	C(2)–N(1)	1.15(1)	1.12(1)
Fe(1)–O(7)	2.09(1)	2.12(1)	S(1)–C(1)	1.77(1)	1.78(1)
S(2)–O(4)	1.41(1)	1.44(1)	S(1)–C(16)	1.80(1)	1.81(1)
S(2)–O(5)	1.41(1)	1.42(1)	S(1)–C(17)	1.79(1)	1.80(1)
S(2)–O(6)	1.42(1)	1.42(1)	Fe(2)–C(1)	1.98(1)	1.96(1)
S(2)–C(18)	1.79(1)	1.74(1)	Fe(3)–C(1)	1.99(1)	1.98(1)
C(18)–F(1)	1.30(1)	1.34(1)	C(1)–C(2)	1.41(1)	1.45(1)
C(18)–F(2)	1.31(1)	1.34(2)	C(2)–N(1)	1.15(1)	1.12(1)
C(18)–F(2)	1.31(1)	1.32(1)	S(1)–C(1)	1.77(1)	1.78(1)
S(3)–O(7)	1.38(1)	1.44(1)	S(1)–C(16)	1.79(1)	1.81(1)
S(3)–O(8)	1.39(1)	1.43(1)	S(1)–C(17)	1.80(1)	1.80(1)
S(3)–O(9)	1.42(1)	1.43(1)	Fe(2)–C(3)	1.92(1)	1.93(1)
S(3)–C(19)	1.78(1)	1.77(1)	Fe(3)–C(3)	1.91(1)	1.90(1)
C(19)–F(4)	1.31(1)	1.33(1)	C(3)–O(1)	1.19(1)	1.17(1)
C(19)–F(5)	1.31(2)	1.33(1)	Fe(2)–C(4)	1.73(1)	1.71(1)
C(19)–F(6)	1.30(1)	1.33(1)	Fe(3)–C(5)	1.77(1)	1.74(1)
Fe(2)–Fe(3)	2.536(2)	2.538(2)	C(4)–O(2)	1.15(1)	1.16(2)
C(1)–Fe(2)	1.98(1)	1.96(1)	C(5)–O(3)	1.14(1)	1.18(1)
C(1)–Fe(3)	1.99(1)	1.98(1)			
Fe(2)–C(cp)	2.12(1) (av.)	2.12(1) (av.)	Fe(3)–C(cp)	2.11(1) (av.)	2.11(1) (av.)
C(18)–S(2)–O(4)	103.5(5)	103.1(5)	O(4)–Fe(1)–N(1)	96.1(4)	86.6(3)
C(18)–S(2)–O(5)	105.5(5)	104.6(5)	O(7)–Fe(1)–N(1)	86.8(4)	84.8(3)
C(18)–S(2)–O(6)	104.3(5)	104.8(5)	Fe(1)–N(1)–C(2)	173.4(3)	163.9(4)
S(2)–C(18)–F(1)	112.2(8)	113.6(8)	Fe(1)–O(4)–S(2)	161.9(5)	144.0(4)
S(2)–C(18)–F(2)	112.4(7)	110.1(9)	Fe(1)–O(7)–S(3)	160.2(8)	139.1(4)
S(2)–C(18)–F(3)	112.3(8)	114.4(9)	O(4)–S(2)–O(5)	113.7(6)	111.6(4)
C(19)–S(3)–O(7)	102.9(6)	101.0(4)	O(4)–S(2)–O(6)	114.5(5)	117.0(4)
C(19)–S(3)–O(8)	105.6(6)	104.7(5)	O(5)–S(2)–O(6)	114.5(5)	114.1(5)
C(19)–S(3)–O(9)	103.0(6)	104.0(4)	O(7)–S(3)–O(8)	113.2(7)	113.7(4)
S(3)–C(19)–F(4)	113.6(7)	113.1(8)	O(7)–S(3)–O(9)	110.5(7)	115.3(4)
S(3)–C(19)–F(5)	112.7(8)	112.9(7)	O(8)–S(3)–O(9)	119.5(8)	115.8(4)
S(3)–C(19)–F(6)	112.9(8)	111.3(6)	F(1)–C(8)–Fe(2)	106.7(9)	106.2(9)
C(2)–C(1)–S(1)	109.0(7)	108.0(6)	F(1)–C(18)–F(3)	105.4(9)	104.9(9)
C(1)–S(1)–C(16)	105.3(5)	106.5(5)	F(2)–C(18)–F(3)	107.3(9)	107.1(9)
C(1)–S(1)–C(17)	105.4(5)	105.7(5)	F(4)–C(19)–F(5)	105.7(9)	106.3(8)
C(16)–S(1)–C(17)	99.3(6)	100.2(6)	F(4)–C(19)–F(6)	108.9(9)	106.0(9)
O(4)–Fe(1)–O(7)	88.9(4)	87.7(3)	F(5)–C(19)–F(6)	102.1(9)	106.8(9)

Table 5 Bond distances (Å) in related bridging-carbene units

Compound (partial formula)	Fe–Fe	Fe–(μ-C)	μ-C–S	$S-C_{Me}$	μ-C–CN
3 $[Fe_2\{\mu\text{-}C(CN)SMe_2\}]$	2.537(2)	1.98(1)	1.775(5)	1.800(3)	1.43(2)
1 $[Fe_2\{\mu\text{-}C(CN)SMe\}]$ *	2.540(1)	1.994(5)	1.807(2)	1.805(2)	1.440(5)

* Ref. 1.

positive charge produces its more significant effects on this carbon atom, which therefore is the most positive centre in the molecule.

The *O*-bonded trifluoromethanesulfonate exhibits the expected staggered conformation. The average bond parameters (over four independent anions) are S–O 1.42(1), S–C 1.77(1), C–F 1.32(1) Å, O–S–O 114.4(2) and F–C–F 106.2(2)°. These values are not unusual when compared to those of analogous structures.[4b] It is worth noting, however, that the Fe–O(triflate) distances in the two crystallographically independent units (**A** and **B**) correlate with the Fe–O–S angles: the shorter bonds [Fe(1)–O(4) and Fe(1)–O(7) both 2.09(1) in **A**, 2.12(1) in **B** correspond to wider Fe–O–S angles [Fe(1)–O(4)–S(2) and Fe(1)–O(7)–S(3) 161.9(5) and 160.2(8) in **A**, 144.0(4) and 139.1(4)° in **B**]. This is indicative that the different packing environments around the two independent molecules in the lattice exert a significant control on the iron–ligand interactions. This is substantiated by the comparable relationship between the Fe(1)–N(1) distances [2.11(1) in **A** and 2.15(1) Å in **B**] and the Fe(1)–N(1)–C(2) angles [173.4(3) in **A** and 163.9(4)° in **B**].

Experimental

General Procedures.—All reactions were carried out under a dry and oxygen-free atmosphere of N_2 by using standard Schlenk techniques. All the solvents were appropriately dried and degassed prior to use under dinitrogen. Dichloromethane was distilled over CaH_2 and passed through a column of activated alumina in order to remove traces of ethanol.[18] Reagent-grade chemicals were used as received. The complexes $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe\}]$ **1**[1] and $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)N(Me)C(O)SMe\}]$ **4**[3] were prepared according to literature procedures.

Infrared spectra were recorded on a Perkin-Elmer 983-G spectrometer in solution using a pair of matched 1.0 mm NaCl cells or as KBr pellets, ^1H and ^{13}C NMR spectra on a Varian Gemini 200 spectrometer using $SiMe_4$ as internal standard; $[Cr(acac)_3]$ (acac = acetylacetonate) (0.1 mol dm^{-3}) was added to the ^{13}C samples to reduce data-collection time. Elemental analyses were determined by Pascher Microanalytical Laboratorium (Remagen, Germany). Melting points were uncorrected.

Preparations.—$[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)SMe_2\}][SO_3CF_3]$ **2**. To a stirred solution of compound **1** (1.21 g, 2.94 mmol) in dichloromethane (20 cm^3) was added a slight excess of $MeSO_3CF_3$ (0.34 cm^3, 3.05 mmol). After a few minutes a dark red precipitate was obtained. The solvent was then removed by cannula and the solid washed with dry Et_2O (3 × 10 cm^3). The red microcrystalline solid was dried under vacuum and stored in the sealed ampoules under an argon atmosphere, affording compound **2** (1.57 g, 93%), m.p. 185–187 °C (decomp.) (Found: C, 37.40; H, 2.80; Fe, 19.20; N, 2.50. $C_{18}H_{16}F_3Fe_2NO_6S_2$ requires C, 37.60; H, 2.80; Fe, 19.40; N, 2.45%); IR ν_{max}/cm^{-1} (MeCN): 2175w (CN), 2013s, 1981m (CO) and 1835m (μ-CO). NMR: $\delta_H(CD_3CN)$ 5.28 (10 H, s, cp) and 3.24 (6 H, s, SMe_2); $\delta_C(CD_3NO_2)$ 250.6 (μ-CO), 204.2 (CO), 88.1 (cp), 84.5 (μ-C) and 27.9 (Me).

$[Fe(OSO_2CF_3)_4\{Fe_2(cp)_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)SMe_2]\}_2]\cdot CH_2Cl_2$ **3**. To a stirred solution of compound **4** (0.60 g, 1.32 mmol) in dichloromethane (15 cm^3) was added $MeSO_3CF_3$ (0.30 cm^3, 2.65 mmol). When the addition was complete the stirring was stopped and the reaction mixture set aside for 48 h at room temperature. Red-brown crystals were then formed. The solvent was removed by cannula and the crystals washed with dry Et_2O affording compound **3** (0.84 g, 40%), m.p. 133–135 °C (Found: C, 30.0; H, 2.35. $C_{39}H_{34}Cl_2F_{12}Fe_5N_2O_{18}S_6$ requires C, 29.45; H, 2.15%).

$[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C[CNW(CO)_5]SMe\}]$ **5**. Complex **1** (0.20 g, 0.49 mmol) was dissolved in thf (20 cm^3) and treated with an equimolar amount of $[W(CO)_5(thf)]$ which was obtained by photolysis of $[W(CO)_6]$ (0.35 g, 1.00 mmol) in tetrahydrofuran (25 cm^3). The reaction mixture was stirred for 1 h and dried under vacuum. The residue, dissolved in CH_2Cl_2, was chromatographed on an alumina column (10 × 3 cm^3). Elution with CH_2Cl_2–hexane (1 : 1, v/v) gave a first red fraction which was collected and evaporated to dryness. Recrystallization of the residue from CH_2Cl_2 layered with pentane gave red crystals of compound **5** (0.13 g, 37%) (Found: C, 34.05; H, 1.90. $C_{21}H_{13}Fe_2NO_8SW$ requires C, 34.30; H, 1.80%); IR ν_{max}/cm^{-1} (CH_2Cl_2): 2180w (CN), 2008s, 1979w (CO), 2073w, 1935vs, 1902 (sh) (W–CO) and 1812m (μ-CO). NMR: $\delta_H(CDCl_3)$ 4.84 (10 H, s, cp) and 2.66 (3 H, s, SMe).

When compound **1** was treated with an excess of $[W(CO)_5(thf)]$, **5** and the S-metallated $[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C[CNW(CO)_5][S(Me)W(CO)_5]\}]$ were formed. These complexes were separated by column chromatography.

X-Ray Structure Determination.—All operations on the crystals of compound **3** had to be carried out in an argon-filled glove-bag to prevent decomposition. The crystals were sealed in Lindemann glass capillaries. Nonetheless, rapid decay under X-ray exposure could not be avoided and the data collection had to be stopped at $2\theta_{max} = 40°$ (decay 60%). The data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.710 69 Å). The intensities were collected in ω–2θ scan mode at room temperature, and corrected for Lorentz polarization and decay effects. No correction for absorption was applied. Empirical absorption corrections were applied by using the Walker and Stuart method.[19] Crystal data and details of measurements are summarized in Table 1.

The structure was solved by using direct methods followed by Fourier-difference syntheses and subsequent least-squares refinement. The C_5H_5 were refined as rigid groups with idealized D_{5h} geometry (C–C 1.42, C–H 1.08 Å). Scattering factors for neutral atoms were taken from ref. 20. For all calculations the SHELX 76 program was used.[21] All atoms, except the H-atoms, were treated anisotropically. A common isotropic thermal parameter was refined for the H atoms [0.12(3) Å^2]. The final Fourier-difference map showed peaks not exceeding 1.2 e Å^{-3} in the proximity of Fe atoms. Fractional atomic coordinates are reported in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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