Synthesis and Crystal Structures of Tetraethylammonium μ_3-Acetyl-*C*^{1}-(Fe^{1}Fe^2)*O*(Fe^{1}Fe^3)-nonacarbonyl-*triangulo*-triferrate and Tetraethylammonium μ-Carbonyl-nonacarbonyl-μ_3-2,4-dioxapentylidyne-*triangulo*-triferrate

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The iron carbonylate anion $[Fe_2(CO)_8]^{2-}$ reacts with iodomethane and with chloromethyl methyl ether to give the tri-iron cluster anions $[Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]^-$ (1) and $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]^-$ (2) respectively. The structures of the cluster anions have been determined by *X*-ray diffraction studies of their tetraethylammonium salts. The compound $[NEt_4][Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]$ is orthorhombic, space group $Pna2_1$, with a = 16.559(2), b = 11.986(2), c = 12.142(2) Å, and Z = 4, while $[NEt_4][Fe_3(CO)_{10}(\mu_3\text{-}COCH_2OCH_3)]$ is monoclinic, space group $P2_1/n$, with a = 12.806(2), b = 14.922(2), c = 15.098(2) Å, β = 105.34(2)°, and Z = 4. The structures have been solved and refined by standard procedures to R values of 0.068 and 0.080 respectively using 2 273 and 2 677 observed $[I > 1.5\sigma(I)]$ diffractometer data. Possible mechanisms for the formation of the anions are considered.

THE reaction of a carbocation reagent with metal carbonyl anions provides a convenient method for the preparation of metal σ-alkyl complexes. However, little attention has been paid to the analogous reaction with polynuclear carbonyl anions. Recently, the reactivity of $[Fe_3(CO)_{12}]^{2-}$,[1] $[Fe_4(CO)_{13}]^{2-}$,[2,3] and their derivatives with some carbocation reagents was reported. We now describe the reaction of $[Fe_2(CO)_8]^{2-}$ with methyl iodide and chloromethyl methyl ether.

The anion $[Fe_2(CO)_8]^{2-}$ is known to react with acetic acid to give the hydrido-bridged complex $[Fe_2(CO)_8H]^-$ [4] and with di-iodomethane [5] to form the methylene-bridged complex $Fe_2(CO)_8(\mu\text{-}CH_2)$. However, when $[NEt_4]_2[Fe_2(CO)_8]$ was treated with methyl iodide and chloromethyl methyl ether in tetrahydrofuran, solutions were obtained from which the tri-iron clusters of stoicheiometry $[NEt_4][Fe_3(CO)_{10}(CH_3)]$ (1) and $[NEt_4]$-$[Fe_3(CO)_{11}(CH_2OCH_3)]$ (2) respectively, could be isolated.[6] The compound (1) is to be formulated as $[NEt_4][Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]$ and (2) as $[NEt_4][Fe_3(CO)_9$-$(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]$, on the basis of i.r., n.m.r., and *X*-ray diffraction studies.

It is to be noted that whereas alkylation of the anions $[Fe_3(CO)_{12}]^{2-}$ and $[Fe_4(CO)_{13}]^{2-}$ invariably leads to the formation of complexes containing a bridging μ-COR ligand,[1-3] the nature of the alkylation products of the $[Fe_2(CO)_8]^{2-}$ anion depends on the nature of the carbocation reagent.

Spectroscopic data are collected in Tables 1 and 2.

TABLE 1

Infrared spectra (cm^{-1}) of iron complexes

Complex	Medium	ν_{CO} (terminal)
$[NEt_4][Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]$	Mull [a]	2 038m, 1 983(sh), 1 954s, 1 942s, 1 928s, 1 906s, 1 878m
	CH_2Cl_2 [b]	2 042m, 1 984s, 1 952s, 1 940(sh), 1 858w(sh)
$[NEt_4][Fe_3(CO)_9$-$(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]$	Mull [a,c]	2 046w(sh), 1 980(sh), 1 974s, 1 954s, 1 938s, 1 920s, 1 898m
	CH_2Cl_2 [b,d]	2 040w, 1 990s, 1 970s, 1950s, 1 906m

[a] Nujol in KBr plates. [b] In 0.1-mm cell with CH_2Cl_2 in the reference beam. [c] ν_{CO}(bridging) at 1 769m cm^{-1}. [d] ν_{CO}-(bridging) at 1 760m cm^{-1}.

RESULTS AND DISCUSSION

Synthesis and Structure of $[NEt_4][Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]$, (1).—When the $[Fe_2(CO)_8]^{2-}$ anion is treated with one equivalent of methyl iodide in tetrahydrofuran (thf) a red solution is obtained from which the crystalline complex may be isolated in moderate yield. Solution and solid-state i.r. spectra of (1) show terminal carbonyl stretches between 1 890 and 2 040 cm^{-1}; a bridging carbonyl stretch is not observed. At −60 °C the ^{13}C n.m.r. spectrum of the complex in the carbonyl region shows a singlet at δ 233.64 p.p.m. and two broad singlets

TABLE 2

Nuclear magnetic resonance spectra of iron complexes

	^1H [a]		^{13}C [b]	
Complex	δ	Assignment	δ	Assignment
$[NEt_4][Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]$	3.50 (q, J = 8)	CH_3CH_2N (*CH*$_2$)	233.6	$\mu_3\text{-}CH_3$*CO*
	2.56 (s)	μ_3-(*CH*$_3$)CO	214.9 212.5	terminal *CO*
	1.41 (t of t, J = 8, 2)	*CH*$_3$CH$_2$N		
$[NEt_4][Fe_3(CO)_9$-$(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]$	5.55 (s)	O*CH*$_2$O	338.2	μ_3-*C*OCH$_2$OCH$_3$
	3.71 (s)	*CH*$_3$O	267.3	μ-*CO*
	3.52 (q, J = 8)	CH$_3$*CH*$_2$N	220.8	terminal *CO*
	1.41 (t of m, J = 8)			

[a] In p.p.m. relative to $SiMe_4$ (δ 0) in [$^2H_6$]acetone. [b] In p.p.m. relative to $SiMe_4$ (δ 0) at −60 °C in CD_2Cl_2.

at δ 214.88 and 212.45 p.p.m. which can be assigned to terminal CO resonances. The chemical shift of the first peak suggests that it is probably due to some type of bridging carbonyl. An *X*-ray diffraction study shows, in fact, the presence of a μ_3-$CH_3C{=}O$ group sitting above the surface formed by the three iron atoms as shown in Figure 1.

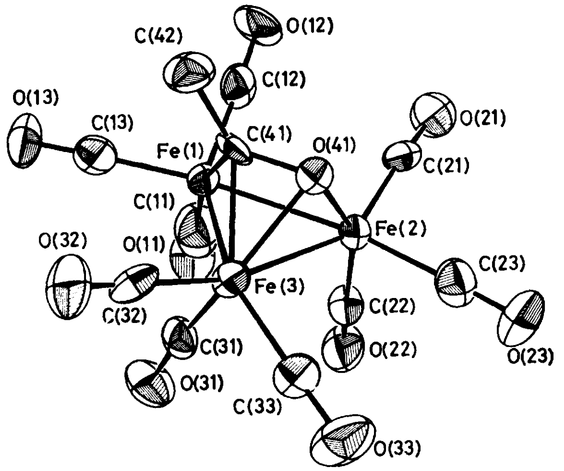


FIGURE 1 Structure of complex (1) showing the atomic numbering scheme

Selected bond lengths and angles are given in Table 3. The mode of bonding of the acetyl group is rather unusual. Previous structural characterisations [7] of bridging acyl groups indicate a μ-bonding mode corresponding to that shown in (Ia) [with a small contribution from the oxocarbene resonance form (Ib)] where two metal atoms are linked, and where the C–O group retains most of its double-bond character. The present complex is interesting in that the bonding can be represented by two canonical forms, (IIa) and (IIb), both of which give all three Fe atoms 18-electron configurations, and where (IIa) is related to the type (Ia) system. The bond lengths indicate strong bonding of C(41) and O(41) to Fe(1) and Fe(2) respectively, whilst Fe(3) is essentially equidistant from the two light atoms, perhaps indicating that (IIa) is the major contributing form. Nevertheless, the C–O bond length of 1.32(2) Å indicates considerable weakening and a significant contribution from form (IIb). A further point of interest is that the Fe_3 ring in this system is distorted away from an equilateral triangle. The Fe(1)–Fe(3) bond distance is close to those in the equilateral Fe_3 system in compound (2) (see below). The Fe(1)–Fe(2) bond appears to have been lengthened, possibly to maximise overlap in the Fe–C, Fe–O bonds of this two-atom bridge system. In contrast, the Fe(2)–Fe(3) bond appears to have been shortened. In this case we presume that the oxygen bridging may involve the formation of a filled molecular orbital which is bonding with respect to the Fe(2)–Fe(3) interaction.

TABLE 3

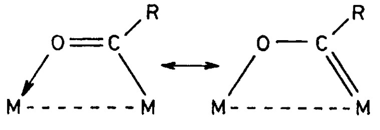
Selected bond lengths and angles for compound (1), $[NEt_4][Fe_3(CO)_9(\mu_3\text{-}COCH_3)]$

(a) Bond lengths (Å)

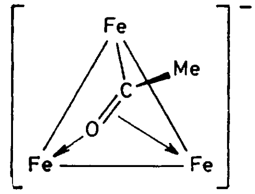
Fe(1)–Fe(2)	2.592(5)	Fe–C (carbonyl)	1.74(2)—1.83(2)
Fe(1)–Fe(3)	2.541(6)		
Fe(2)–Fe(3)	2.478(5)		
Fe(1)–C(41)	1.89(1)	C(41)–O(41)	1.32(2)
Fe(3)–C(41)	1.98(1)	C(41)–C(42)	1.54(2)
Fe(2)–O(41)	1.93(1)		
Fe(3)–O(41)	1.98(1)		

(b) Interbond angles (°)

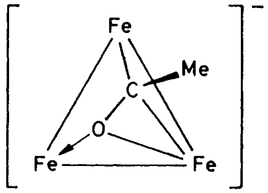
Fe(2)–Fe(1)–Fe(3)	57.7(2)	Fe(1)–C(41)–O(41)	117(1)
Fe(1)–Fe(2)–Fe(3)	60.1(2)	Fe(1)–C(41)–C(42)	128(1)
Fe(1)–Fe(3)–Fe(2)	62.2(2)	Fe(1)–C(41)–Fe(3)	83(1)
		C(42)–C(41)–O(41)	114(1)
C(41)–O(41)–Fe(2)	103(1)	Fe(3)–C(41)–O(41)	71(1)
C(41)–O(41)–Fe(3)	71(1)	C(4)–Fe(3)–O(41)	38.9(4)
Fe(2)–O(41)–Fe(3)	79(1)		



(Ia) (Ib)



(IIa)



(IIb)

Synthesis and Structure of $[NEt_4][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]$, (2).—From the reaction of $[Fe_2(CO)_8]^{2-}$ with one equivalent of chloromethyl methyl ether the red crystalline complex (2) was isolated. The i.r. spectrum had terminal carbonyl stretches between 1 890 and 2 042 cm^{-1} and a bridging carbonyl stretch at 1 776 cm^{-1}. The ^{13}C n.m.r. spectrum in the carbonyl region shows singlets at δ 338.2, 267.3, and 220.8 p.p.m., with relative intensity 1 : 1 : 9 respectively. The i.r. and n.m.r. data are thus consistent with a structure similar to that suggested [1] for the analogous methyl complex $[N(PPh_3)_2][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}COCH_3)]$. The structure of (2) was fully established by *X*-ray diffraction study and is shown in Figure 2, whilst selected bond lengths and angles are given in Table 4. This anion comprises an essentially equilateral triangle of Fe atoms bridged along one side by a carbonyl group and capped by an alkylidyne-type ligand. The basic skeleton has approximate mirror symmetry with a symmetrical $\overline{\mathrm{Fe{-}C(O){-}Fe}}$ bridge. The Fe–C (alkylidyne) bonds fall into two types: those to the iron atoms linked by the carbonyl bridge are essentially equal with lengths of 1.98(1) and 2.01(1) Å, whilst the third, to the remaining iron atom, is shorter at 1.83(1) Å. Again, the three metal atoms are 18-electron systems if the anionic charge is formally localised on the unique

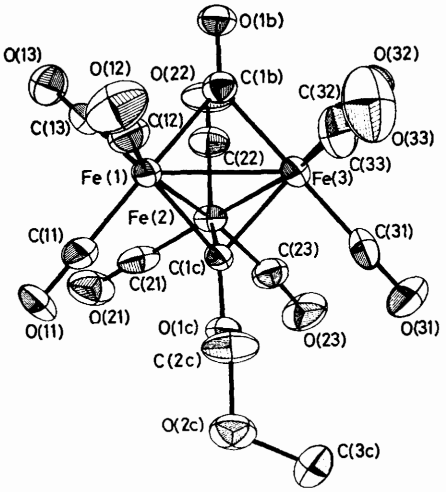


FIGURE 2 Structure of complex (2) showing the atomic numbering scheme

TABLE 4

Selected bond lengths and angles for compound (2), $[NEt_4][Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]$

(*a*) Bond lengths (Å)

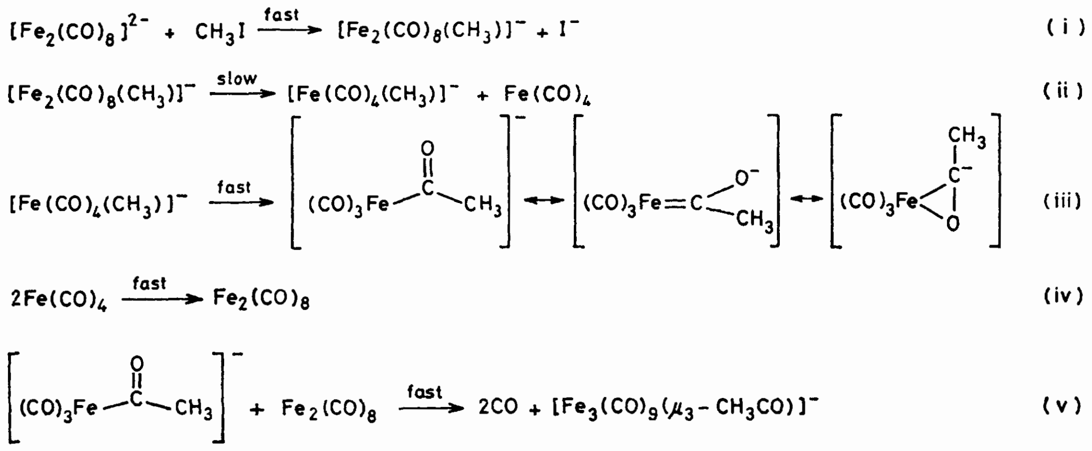
Fe(1)–Fe(2)	2.558(5)	Fe–C (carbonyl)	1.72(2)–1.84(2)
Fe(1)–Fe(3)	2.565(5)		
Fe(2)–Fe(3)	2.553(5)		
Fe(1)–C(1b)	1.96(1)	Fe(1)–C(1c)	1.98(1)
Fe(3)–C(1b)	1.99(1)	Fe(2)–C(1c)	1.83(1)
C(1b)–O(1b)	1.18(2)	Fe(3)–C(1c)	2.01(1)
C(1c)–O(1c)	1.36(2)		
C(2c)–O(1c)	1.48(2)		

(*b*) Interbond angles (°)

Fe(2)–Fe(1)–Fe(3)	59.8(2)	Fe(1)–C(1c)–Fe(2)	84.2(5)
Fe(1)–Fe(2)–Fe(3)	60.2(2)	Fe(1)–C(1c)–Fe(3)	80.1(5)
Fe(1)–Fe(3)–Fe(2)	60.0(2)	Fe(2)–C(1c)–Fe(3)	83.3(5)
Fe(1)–C(1b)–Fe(3)	81.1(5)	Fe(1)–C(1c)–O(1c)	131(1)
Fe(1)–C(1b)–O(1b)	140(1)	Fe(2)–C(1c)–O(1c)	132(1)
Fe(3)–C(1b)–O(1b)	139(1)	Fe(3)–C(1c)–O(1c)	129(2)

iron atom. The geometry of the Fe_3 triangle does not seem to have been affected by the carbonyl bridge, or the uneven bonding of the alkylidyne carbon atom.

Mechanism of Formation.—The formation reactions of the anions $[Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]^-$ and $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]^-$ from the $[Fe_2(CO)_8]^{2-}$ anion are clearly complicated and the yields are only *ca.* 30%; other products formed in the reaction have not been identified. There is a precedent [8] for the formation of Fe_3 from Fe_2 species in the synthesis of $[Fe_3(CO)_{11}H]^-$ from $[Fe_2(CO)_8H]^-$ where fragmentation reactions involving neutral intermediates were proposed. In the present alkylation reactions the anions could be formed as in Schemes 1 and 2. Both reactions could involve a common type of intermediate $[Fe_2(CO)_8R]^-$, but differ



SCHEME 1

$$[Fe_2(CO)_8]^{2-} + CH_3OCH_2Cl \xrightarrow{\text{very slow}} [Fe_2(CO)_8(CH_2OCH_3)]^- + Cl^- \qquad (i)$$

$$[Fe_2(CO)_8(CH_2OCH_3)]^- \xrightarrow{\text{slow}} [Fe(CO)_4(CH_2OCH_3)]^- + Fe(CO)_4 \qquad (ii)$$

$$2Fe(CO)_4 \xrightarrow{\text{fast}} Fe_2(CO)_8 \qquad (iii)$$

$$Fe_2(CO)_8 + [Fe_2(CO)_8]^{2-} \xrightarrow{\text{fast}} [Fe_3(CO)_{11}]^{2-} + Fe(CO)_5 \qquad (iv)$$

$$[Fe_3(CO)_{11}]^{2-} + CH_3OCH_2Cl \xrightarrow{\text{fast}} Cl^- + [Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}COCH_2OCH_3)]^- \qquad (v)$$

SCHEME 2

in the rates of formation of this intermediate. In the reaction with methyl iodide, which is ' softer ' than chloromethyl methyl ether, the alkylation step, Scheme 1(i), is fast and the rate-determining step is the decomposition of this intermediate to $Fe(CO)_4$ and $[Fe(CO)_4(CH_3)]^-$. By contrast, in Scheme 2 the alkylation step is the rate-determining step and subsequent reactions fast. Since there is no precedent for alkyl transfers from metal to the oxygen of CO, although transfers to carbon are very well established,[9] the anion (2) must result from carbocation attack on the more basic bridging CO group in a polynuclear (Fe_3 in this case) anion as in other cases where groups of the type μ_3-COR are formed.[1-3] The ion $[Fe_2(CO)_8]^{2-}$ has no bridging groups [10] so that (2) can only result from attack by $CH_3OCH_2^+$ on an Fe_3 cluster anion with a bridging CO group.

EXPERIMENTAL

Microanalyses were by Pascher (Bonn).

Instruments.—A Perkin-Elmer 597 (i.r.), Perkin-Elmer R-32 (^{1}H n.m.r.), and a Bruker WM-250 operating in the Fourier-transform mode at a frequency of 62.9 MHz, or a Varian XL-100 at 25.2 MHz, at −60 °C (^{13}C n.m.r.) were used for spectroscopic measurements. Tris(acetylacetonato)chromium(III) (0.05 mol dm^{-3}) was added as a relaxation agent. Dichloromethane was used as internal standard. Chemical shifts were converted by using $\delta(SiMe_4) = \delta(CH_2Cl_2) + 53.8$ p.p.m.

All manipulations were performed in a nitrogen atmosphere. $[NEt_4]_2[Fe_2(CO)_8]$ was prepared according to the literature method.[10] All chemicals used were of reagent grade. Solvents were dried by standard procedures, distilled, and deaerated prior to use. Melting points were taken in sealed capillaries and are uncorrected.

Tetraethylammonium μ_3-*Acetyl*-C^1(Fe^{1}Fe^2)O(Fe^{1}Fe^3)-*nonacarbonyl*-triangulo-*triferrate* (1).—To $[NEt_4]_2[Fe_2(CO)_8]$ (7.8 g, 13 mmol) suspended in thf (100 cm^3), was added methyl iodide (0.82 cm^3, 13 mmol) and the mixture stirred overnight at ambient temperature. A white precipitate was filtered off and the filtrate evaporated to dryness under vacuum. The residue was redissolved in thf (50 cm^3) and the solution filtered and concentrated (20 cm^3). Diethyl ether was added to afford a precipitate of red microcrystals which were collected, washed with diethyl ether, and dried *in vacuo*. Yield 2.8 g, 36% based on $[NEt_4]_2[Fe_2(CO)_8]$; m.p. >320 °C (Found: C, 39.0; H, 4.0; O, 27.3. $C_{19}H_{23}Fe_3NO_{10}$ requires C, 38.5; H, 3.9; O, 27.0%).

Suitable crystals for *X*-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated thf solution.

Tetraethylammonium μ-*Carbonyl-nonacarbonyl*-μ_3-2,4-*dioxapentylidyne*-triangulo-*triferrate*, (2).—**CAUTION**: Due to the extreme toxicity and carcinogenicity of chloromethyl methyl ether, the reaction must be carried out in a well ventilated hood. To a thf suspension of $[NEt_4]_2[Fe_2(CO)_8]$ (1.78 g, 3 mmol) in thf (50 cm^3) was added chloromethyl methyl ether (0.25 cm^3, 3.3 mmol). The reaction mixture was stirred overnight at ambient temperature. After filtering and concentrating (10 cm^3), diethyl ether was added to afford dark red crystals which were collected, washed with diethyl ether, and dried *in vacuo*. Yield 0.42 g, 22% based

TABLE 5

Atom co-ordinates (× 10^4) for compound (1)

Atom	*x*	*y*	*z*
Fe(1)	2 451(1)	1 425(2)	−453(2)
Fe(2)	3 776(1)	2 237(2)	350(1)
Fe(3)	2 458(1)	3 026(2)	918(2)
C(11)	2 537(8)	41(13)	149(13)
O(11)	2 588(7)	−863(8)	475(12)
C(12)	2 877(10)	1 186(14)	−1 744(15)
O(12)	3 127(8)	1 088(11)	−2 611(10)
C(13)	1 418(9)	1 269(14)	−837(13)
O(13)	753(7)	1 157(13)	−1 061(12)
C(21)	4 412(9)	1 679(14)	−679(11)
O(21)	4 851(7)	1 261(13)	−1 283(11)
C(22)	3 874(8)	1 109(11)	1 295(12)
O(22)	3 963(7)	382(11)	1 897(11)
C(23)	4 531(9)	3 078(13)	1 073(15)
O(23)	5 014(8)	3 525(12)	1 543(12)
C(31)	2 111(8)	1 801(13)	1 632(14)
O(31)	1 875(8)	1 121(10)	2 222(10)
C(32)	1 521(9)	3 807(12)	944(13)
O(32)	935(6)	4 257(10)	961(12)
C(33)	2 904(9)	3 659(13)	2 114(13)
O(33)	3 205(8)	4 057(12)	2 862(11)
C(41)	2 548(7)	2 974(10)	−704(9)
C(42)	2 083(10)	3 692(14)	−1 546(12)
O(41)	3 190(5)	3 470(8)	−292(8)
N(1a)	4 968(6)	7 292(9)	200(9)
C(1a)	5 165(10)	7 374(13)	1 408(10)
C(1b)	5 660(10)	6 381(16)	1 851(14)
C(2a)	5 710(7)	7 175(13)	−518(13)
C(2b)	6 294(8)	8 170(14)	−415(16)
C(3a)	4 459(8)	6 277(12)	−21(14)
C(3b)	3 669(9)	6 225(17)	657(17)
C(4a)	4 518(9)	8 352(12)	−53(12)
C(4b)	4 239(11)	8 411(19)	−1 264(13)

TABLE 6

Atom co-ordinates (× 10^4) for compound (2)

Atom	*x*	*y*	*z*
Fe(1)	2 608(1)	2 927(1)	−233(1)
Fe(2)	2 956(1)	1 967(1)	1 219(1)
Fe(3)	3 781(1)	3 532(1)	1 298(1)
C(1c)	2 266(7)	3 048(7)	965(6)
O(1c)	1 375(5)	3 386(4)	1 170(4)
C(2c)	1 043(12)	4 299(11)	829(12)
O(2c)	121(6)	4 499(6)	1 087(6)
C(3c)	324(20)	4 804(16)	1 998(16)
C(1b)	4 186(8)	3 025(7)	219(7)
O(1b)	4 973(6)	2 879(5)	−23(5)
C(11)	1 179(10)	2 743(11)	−609(7)
O(11)	279(7)	2 608(10)	−851(6)
C(12)	2 586(10)	3 845(9)	−971(7)
O(12)	2 560(9)	4 445(7)	−1 441(6)
C(13)	2 953(9)	1 980(9)	−820(8)
O(13)	3 159(8)	1 396(7)	−1 213(6)
C(21)	1 934(11)	1 207(9)	809(9)
O(21)	1 238(9)	701(7)	514(8)
C(22)	4 128(11)	1 279(9)	1 155(9)
O(22)	4 832(8)	842(7)	1 113(7)
C(23)	2 908(10)	1 866(9)	2 362(9)
O(23)	2 794(9)	1 790(8)	3 097(6)
C(31)	3 407(10)	3 929(10)	2 268(9)
O(31)	3 195(9)	4 128(10)	2 933(8)
C(32)	5 040(9)	3 092(9)	1 915(7)
O(32)	5 865(7)	2 828(8)	2 295(6)
C(33)	4 150(11)	4 637(11)	1 008(10)
O(33)	4 367(12)	5 338(7)	853(9)
N	3 317(5)	3 209(5)	−3 922(5)
C(1)	2 154(9)	3 530(14)	−4 230(9)
C(2)	1 802(11)	3 817(10)	−5 258(8)
C(3)	4 056(13)	3 968(8)	−4 023(12)
C(4)	3 912(12)	4 783(6)	−3 426(8)
C(5)	3 506(12)	2 442(7)	−4 512(10)
C(6)	2 769(11)	1 619(7)	−4 484(11)
C(7)	3 526(9)	2 944(14)	−2 938(7)
C(8)	4 726(9)	2 662(10)	−2 499(8)

on $[NEt_4]_2[Fe_2(CO)_8]$; m.p. >320 °C (Found: C, 39.8; H, 4.2; O, 28.3. $C_{21}H_{25}Fe_3NO_{12}$ requires C, 38.8; H, 3.9; O, 29.5%).

Suitable crystals for *X*-ray diffraction study were obtained by recrystallising the complex from a thf–Et_2O mixture.

X-*Ray Crystallography*.—Crystals of both compounds were sealed in Lindemann capillaries for *X*-ray examination.

Crystal data. *Compound* (1). $C_{19}H_{23}Fe_3NO_{10}$, $M = 592.98$, Orthorhombic, $a = 16.559(2)$, $b = 11.986(2)$, $c = 12.142(2)$ Å, $U = 2\,410.0$ Å^3, space group $Pna2_1$, $Z = 4$, $D_c = 1.63$ g cm^{-3}, μ(Mo-K_α) = 17.4 cm^{-1}, $F(000) = 1\,208$.

Compound (2). $C_{21}H_{25}Fe_3NO_{12}$, $M = 651.01$, Monoclinic, $a = 12.806(2)$, $b = 14.922(2)$, $c = 15.098(2)$ Å, $\beta = 105.34(2)°$, $U = 2\,782.3$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.55$ g cm^{-3}, μ(Mo-K_α) = 15.2 cm^{-1}, $F(000) = 1\,328$.

Intensity data for both compounds were recorded on a CAD4 diffractometer using Mo-K_α radiation ($\lambda = 0.710\,69$ Å) and an ω—2θ scan method.[11] For compound (1), 3 654 data were collected of which 2 273 satisfied the criterion $I > 1.5\sigma(I)$, whilst for (2), 2 677 data out of 4 580 recorded were observed. The structures were solved by Patterson (1) and direct methods (2) and refined by least squares to final R values ($= \Sigma\Delta F/\Sigma|F_o|$) of 0.068 (1) and 0.080 (2). Unit weights were applied in the case of (1), whilst for (2) weights of $w = 1/[\sigma^2(F_o) + 0.001(F_o)^2]^{\frac{1}{2}}$ gave the best agreement analyses. Final atomic co-ordinates are given in Tables 5 and 6. Thermal parameters and lists of F_o/F_c have been deposited as Supplementary Publication No. SUP 23150 (25 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.