# Electrophilic Attack on the [$\mu_3$-Acetyl-*C*$^1$(Fe$^1$ : Fe$^2$)*O*(Fe$^1$ : Fe$^3$)]-nonacarbonyl-*triangulo*-triferrate(1 −) Anion by Fluoroboric Acid and Methyl Fluorosulphate. Carbon–Oxygen Bond Cleavage to give $\mu_3$-Ethylidyne and $\mu$-Methoxo-groups. *X*-Ray Crystal Structures of $Fe_3(CO)_9(\mu_3\text{-}MeCO)(\mu\text{-}H)$, $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)$, and $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$ †

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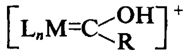
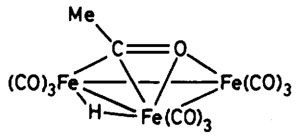
The ($\mu_3$-acetyl)-nonacarbonyltriferrate(1−) ion, $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$, reacts with fluoroboric acid to give the neutral clusters $Fe_3(CO)_9(\mu_3\text{-}MeCO)(\mu\text{-}H)$ (1), $Fe_3(CO)_{10}(\mu\text{-}CMe)(\mu\text{-}H)$ (2), and in small yield, $Fe_3(CO)_9(\mu_3\text{-}MeCOH)$ (3). With methyl fluorosulphate the anion reacts to give either $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)$ (4) or $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$ (5), depending upon the reaction conditions. The crystal structures of (1), (4), and (5) have been determined by *X*-ray diffraction studies. Mechanisms for the electrophilic attacks and for the C–O bond cleavage of the $\mu_3$-acetyl group are discussed.

Since the discovery by E. O. Fischer of mononuclear acylate anions, *e.g.*, $[(CO)_5Cr\{C(O)Me\}]^-$, and of their conversion to carbene complexes by reagents such as $[Me_3O]BF_4$, there have been extensive studies on such $\sigma$-C(O)R anions of various metals and of their reactions with electrophiles.[1,2] The only report of attack on the few known bridging acyl anions is that of methyl fluorosulphate on $[Os_3(CO)_{10}(\mu\text{-}OCMe)]^-$, which forms a highly unstable intermediate converted by silica gel to a $\mu$-acetyl-(carbene)hydrido-complex.[3] Electrophilic attacks on the basic oxygen of *neutral* $\sigma$-acyl species by $H^+$ or $R_3O^+$ give carboxonium species of the type  $\left[L_nM{=}C\begin{smallmatrix}OH\\R\end{smallmatrix}\right]^+$,[4–6] while attack by $(CF_3SO_2)_2O$ on an iron acyl forms a  $Fe{-}C\begin{smallmatrix}OSO_2CF_3\\CHR_2\end{smallmatrix}$ grouping.[7] Protonation of the acyl oxygen was also proposed to account for solvolytic reactions of $(CO)_5MnC(O)Me$.[8] For *neutral* bridging acyls [9] the only report appears to be the reaction of trifluoroacetic acid with $(\eta\text{-}C_5H_5)_2Zr(\mu\text{-}CO)(\mu\text{-}OCMe)Mo(CO)(\eta\text{-}C_5H_5)$ to give ethanol by an unknown pathway.[10]

We now give details [11] of electrophilic attacks on the unique triply bridging acetyl anion, $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$.[12]

## Results and Discussion

(*a*) *Interaction with Fluoroboric Acid.*—When the $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$ anion is treated with 1.5 equivalents of aqueous fluoroboric acid in tetrahydrofuran (thf) at 0 °C a complex mixture is obtained from which compounds of stoicheiometry $Fe_3(CO)_{10}(CH_4)$ (1) and $Fe_3(CO)_{10}(C_2H_4)$ (2) can be isolated in moderate yield. Compound (1) is readily soluble in most organic solvents and can be recrystallised from diethyl ether as dark red crystals. The mass spectrum of (1) shows the parent ion at 464 and peaks corresponding to successive loss of nine CO molecules. The solid-state i.r. spectrum shows terminal carbonyl stretches between 1 950 and 2 100 cm$^{-1}$, as well as stretches at 1 362 and 1 430 cm$^{-1}$. The low-frequency stretches suggest that (1) has an unusual bridging-carbonyl function. The $^1$H n.m.r. spectrum has two singlets of relative intensity of 3 : 1 at $\delta$ 2.14 and −25.09 p.p.m. which correspond to a methyl group and a bridging metal–hydride, respectively. The chemical shift of the methyl group is very similar to that of the $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$ anion,[12] $\delta$ 2.56 p.p.m., and this suggests that the methyl group of (1) has a chemical environment similar to that of the $\mu_3$-MeCO group in $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$. The room-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (1) in the carbonyl region shows a singlet at $\delta$ 242.47 p.p.m. and singlets at $\delta$ 212.18, 210.44, 207.37, and 206.73 p.p.m., which can be assigned to terminal CO resonances. The chemical shift of the first peak is similar to the carbonyl carbon on the $\mu_3$-MeCO group of the parent anion which occurs at $\delta$ 233.6 p.p.m. Based on this spectroscopic evidence, (1) can be formulated as $Fe_3(CO)_9(\mu_3\text{-}MeCO)(\mu\text{-}H)$ with the structure above. This is confirmed by an *X*-ray diffraction study which shows the molecule to contain a $\mu_3$-MeCO group sitting above the surface formed by the three iron atoms and a bridging hydride, as shown in Figure 1.



(1)

Selected bond lengths and angles are given in Table 1. The molecule of (1) is isoelectronic with the anion of the starting material and simply corresponds to its protonation. The proton has added across the Fe–Fe bond [Fe(1)–Fe(3)] parallel to the bridging acyl function, and has caused a significant increase in the Fe–Fe distance from 2.592(5) Å in the anion to 2.737(1) Å here. This is to be expected since the hydride bridge *replaces* the Fe–Fe bond present in the anion. Of the remaining Fe–Fe bonds, one [Fe(1)–Fe(2) in the present structure] does not change significantly [2.478(5) *versus*

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† [$\mu_3$-Acetyl-*C*$^1$(Fe$^1$ : Fe$^2$)*O*(Fe$^1$ : Fe$^3$)]-nonacarbonyl-$\mu$-hydrido-*triangulo*-tri-iron, nonacarbonyl-$\mu_3$-ethylidyne-$\mu_3$-methoxo-tri-iron(2*Fe*–*Fe*), and nonacarbonyl-$\mu_3$-ethylidyne-$\mu_3$-methoxy-methylidyne-*triangulo*-tri-iron.

*Supplementary data available* (No. SUP 23606, 60 pp.): anisotropic thermal parameters, observed and calculated structure factors. See Notices to Authors, No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

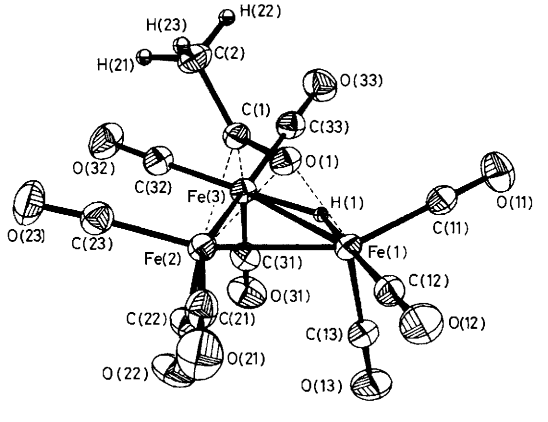
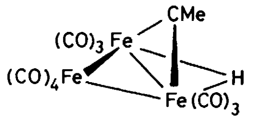


Figure 1. Structure of $Fe_3(CO)_9(\mu_3\text{-}MeCO)(\mu\text{-}H)$ (1)

2.485(1) Å] whilst the other [Fe(2)–Fe(3)] shows an increase, from 2.541(6) to 2.578(1) Å. The only other significant change is a lengthening of the Fe(2)–C(1) bond to the acyl carbon, which increases from 1.98(1) Å in the anion to 2.07(1) Å in the present compound. The C(1)–Fe(3) distance, however, seems unchanged.

Compound (2) is soluble in most organic solvents and can be recrystallised from light petroleum as dark red crystals. It is quite volatile and can be sublimed at room temperature under high vacuum. The mass spectrum shows the parent ion at 476 and peaks corresponding to successive loss of ten CO molecules. The i.r. spectrum shows terminal carbonyl stretches between 2 000 and 2 100 $cm^{-1}$; no stretches are observed between 1 350 and 2 000 $cm^{-1}$, which confirms the absence of any bridging carbonyl or acyl groups. The $^1H$ n.m.r. spectrum shows two singlets of relative intensity 3 : 1 at δ 3.97 and −23.78 p.p.m. which correspond to a methyl group and a bridging metal–hydride, respectively. The chemical shift of the methyl group is very similar to that of a bridging ethylidyne group (see below) and suggests the presence of a μ-CMe group. This view is further supported by the room-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum which shows a singlet at δ 325.7 p.p.m. for a carbyne carbon. The compound can thus be formulated as $Fe_3(CO)_{10}(\mu\text{-}CMe)(\mu\text{-}H)$, with the structure shown below.



(2)

Table 1. Selected bond lengths (Å) and angles (°) for $Fe_3(CO)_9(\mu_3\text{-}MeCO)(\mu\text{-}H)$

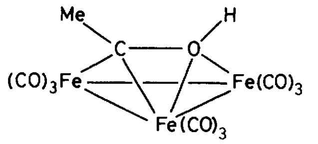
(a) Bond lengths

| | | | |
|---|---|---|---|
| Fe(1)–Fe(2) | 2.485(1) | Fe(2)–Fe(3) | 2.578(1) |
| Fe(1)–Fe(3) | 2.737(1) | | |
| Fe(1)–C(1) | 1.824(1) | Fe(2)–C(1) | 2.073(4) |
| Fe(3)–C(1) | 1.910(1) | | |
| C(1)–O(1) | 1.325(5) | C(1)–C(2) | 1.499(6) |
| Fe(1)–O(1) | 1.958(3) | Fe(2)–O(1) | 2.003(3) |
| Fe(1)–H(1) | 1.68(4) | Fe(3)–H(1) | 1.51(4) |
| Fe(1)–C(11) | 1.824(4) | Fe(2)–C(21) | 1.796(5) |
| Fe(1)–C(12) | 1.805(5) | Fe(2)–C(22) | 1.766(5) |
| Fe(1)–C(13) | 1.782(5) | Fe(2)–C(23) | 1.787(5) |
| Fe(3)–C(31) | 1.836(5) | Fe(3)–C(32) | 1.785(5) |
| Fe(3)–C(33) | 1.788(5) | | |
| C–O (carbonyl) | 1.125(6)—1.143(6) | | |

(b) Bond angles

| | | | |
|---|---|---|---|
| Fe(2)–Fe(1)–Fe(3) | 58.9 | Fe(1)–Fe(2)–Fe(3) | 65.4 |
| Fe(1)–Fe(3)–Fe(2) | 55.7 | | |
| Fe(1)–O(1)–C(1) | 108.0(3) | Fe(3)–C(1)–O(1) | 114.8(3) |
| Fe(1)–H(1)–Fe(3) | 118.0(3) | O(1)–C(1)–C(2) | 113.9(4) |

A small quantity of an orange compound, (3), also may be isolated from the reaction mixture. Due to the limited amount of material, microanalytical data have not been obtained; however, the mass spectrum of the compound shows the highest observed mass at 394 corresponding to a '$Fe_3(CO)_8H_2$' fragment and peaks corresponding to successive loss of eight CO molecules. The complex thus appears to be a tri-iron carbonyl cluster. The i.r. spectrum shows a sharp OH stretch at 3 510 $cm^{-1}$, terminal carbonyl stretches between 1 910 and 2 100 $cm^{-1}$, and bridging carbonyl stretches at 1 372, 1 395, and 1 465 $cm^{-1}$. The $^1H$ n.m.r. spectrum shows two singlets of relative intensity 1 : 3 at δ 4.64 and 1.60 p.p.m. which can be assigned to hydroxyl and methyl groups, respectively. The chemical shift of the methyl group is similar to that of $\mu_3$-MeCO of (1) (δ 2.14 p.p.m.) and quite different from that of the $\mu_3$-CMe group of (2) (δ 3.97 p.p.m.). The spectroscopic data for (3) suggest the presence of a $\mu_3$-MeCOH group and the complex probably has the structure shown below. The methyl analogue of this complex is postulated as an intermediate in the C–O cleavage reaction described below.



(3)

(b) *Interaction with Methyl Fluorosulphate.*—(i) *At room temperature.* When the $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$ anion is allowed to react with a ten-fold excess of $MeSO_3F$ in dichloromethane for about a week, a compound of stoicheiometry $Fe_3(CO)_{10}(C_2H_6)$ (4) may be isolated from this reaction mixture and crystallised from light petroleum as dark red crystals. The mass spectrum shows the parent ion at 478 together with peaks corresponding to successive loss of nine CO molecules. The i.r. spectrum shows terminal carbonyl stretches between 1 990 and 2 100 $cm^{-1}$; no stretches corresponding to bridging carbonyl are observed. The room-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum in the carbonyl region shows a singlet at δ 334.0 p.p.m. corresponding to a carbyne carbon and a singlet at δ 208.6 p.p.m. for the terminal carbonyls. The $^1H$ n.m.r. spectrum shows two singlets of relative intensity 1 : 1 at δ 3.22 and 1.74 p.p.m. which can be assigned to $\mu_3$-CMe and $\mu_3$-OMe groups respectively. The compound (4) can thus be formulated as $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)$ with the structure shown below which is confirmed by *X*-ray diffraction (Figure 2).

Details of the molecular geometry are given in Table 2. In contrast to the hydrido-species (1), which has a *closo* structure (48 electrons, if the acyl is a five-electron ligand), the complex (4) has an open structure (50 electrons, if the $\mu_3$-OMe group is also classed as a five-electron ligand), with the $Fe_3$ triangle broken at the Fe(1)–Fe(2) bond. The Fe–Fe distance here is

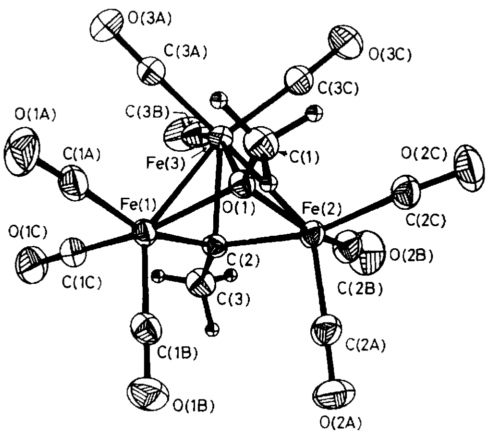
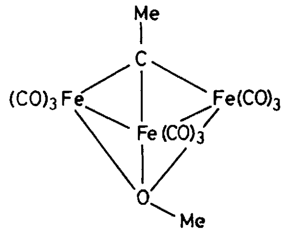


**Figure 2.** Structure of $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)$ (4)



(4)

**Table 2.** Selected bond lengths (Å) and angles (°) for $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)$

(*a*) Bond lengths

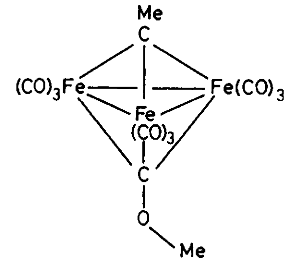
| | | | |
|---|---|---|---|
| Fe(1)-Fe(2) | 3.059(4) | Fe(1)-Fe(3) | 2.472(3) |
| Fe(2)-Fe(3) | 2.459(3) | | |
| Fe(1)-C(2) | 1.937(3) | Fe(2)-C(2) | 1.942(5) |
| Fe(3)-C(2) | 2.063(5) | | |
| Fe(1)-O(1) | 1.984(4) | Fe(2)-O(1) | 1.989(4) |
| Fe(3)-O(1) | 1.940(4) | | |
| Fe(1)-C(1a) | 1.853(6) | Fe(2)-C(2a) | 1.792(6) |
| Fe(1)-C(1b) | 1.785(6) | Fe(2)-C(2b) | 1.754(6) |
| Fe(1)-C(1c) | 1.762(6) | Fe(2)-C(2c) | 1.844(6) |
| Fe(3)-C(3a) | 1.806(6) | Fe(3)-C(3b) | 1.758(6) |
| Fe(3)-C(3c) | 1.805(6) | | |
| C(1)-O(1) | 1.435(5) | C(2)-C(3) | 1.509(7) |

(*b*) Bond angles

| | | | |
|---|---|---|---|
| Fe(1)-Fe(2)-Fe(3) | 76.7 | | |
| C(1)-O(1)-Fe(1) | 126.7(3) | C(3)-C(2)-Fe(1) | 125.9(4) |
| C(1)-O(1)-Fe(2) | 128.2(3) | C(3)-C(2)-Fe(2) | 125.4(4) |
| C(1)-O(1)-Fe(3) | 126.9(3) | C(3)-C(2)-Fe(3) | 131.8(2) |

3.059(4) Å whilst the two bonded distances are 2.459(3) and 2.472(3) Å. Apart from the small but apparently significant differences in the two bonded Fe-Fe distances, the molecule has essentially $C_s$ symmetry. Thus, the Fe-O(1) and Fe-C(2) distances to the two $\mu_3$ ligands each fall into two groups, with distances to the equivalent Fe atoms equal within experimental error [Fe(1),Fe(2)-O(1) = 1.984(4),1.989(4) Å; Fe(1),Fe(2)-C(2) = 1.937(3),1.942(5) Å]. However, whereas the Fe(1),-Fe(2)-O distances are longer than the corresponding distance to the unique iron atom [Fe(3)-O(1) = 1.940(4) Å], the Fe(1),Fe(2)-C(2) distances are much shorter than the Fe(3)-C(2) distance, which is 2.063(5) Å. The reasons for this difference are not immediately obvious, but a possible explanation could involve steric repulsions between the CMe group and the unique carbonyl on Fe(3). Thus, the angle Fe(3)-C(2)-C(3), at 131.8(2)° is larger than the angles Fe(2),Fe(1)-C(2)-C(3) (*ca.* 126°) and the Fe(3)-O(1)-C(1) angle (*ca.* 127°) [which is almost equal to the other two Fe-O(1)-C(1) angles] suggesting that the CMe group may be under steric pressure from the carbonyl.

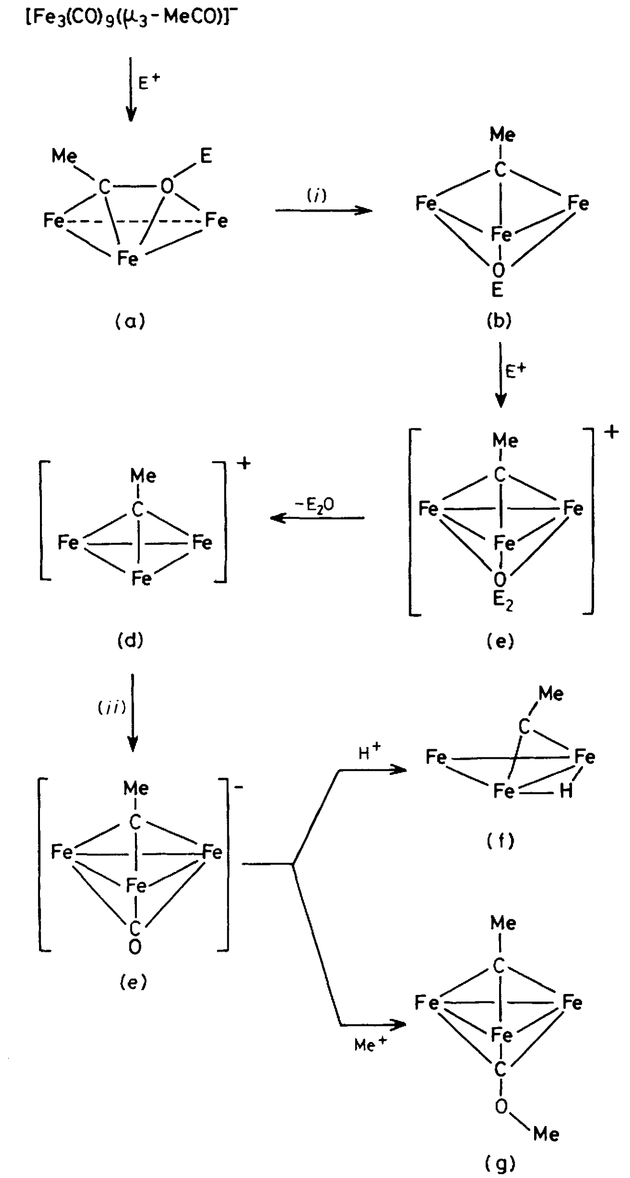
(*ii*) *At elevated temperature.* When the $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$ anion is treated with a ten-fold excess of $MeSO_3F$ in dichloromethane and the solution refluxed, after two days, a complex mixture is obtained from which a compound of stoicheiometry $Fe_3(CO)_{10}(C_3H_6)$ (5) may be isolated in low yield. This is soluble in most organic solvents and can be obtained from light petroleum as red crystals. The mass spectrum shows the parent ion at 490 with peaks corresponding to successive loss of nine CO molecules. The i.r. spectrum shows terminal carbonyl stretches between 1 980 and 2 100 $cm^{-1}$ and stretches at 1 442 and 1 362 $cm^{-1}$. Infrared stretches between 1 360 and 1 500 $cm^{-1}$ have been reported [13] for the $\mu_3$-COR group in the species $[Fe_3(CO)_{10}(COR)]^-$ and $Fe_3(CO)_{10}(COR)H$. Thus, the stretches at 1 362 and 1 442 $cm^{-1}$ may be attributed to the presence of a $\mu_3$-COMe group. The $^1H$ n.m.r. spectra shows two singlets of relative intensity 1 : 1 at δ 4.24 and 3.98 p.p.m. From the chemical shift, the resonance at δ 3.98 p.p.m. can be assigned to a $\mu_3$-CMe group by comparison with the μ-CMe group of (2) which has a resonance at δ 3.97 p.p.m.; the resonance at δ 4.24 p.p.m. can be assigned to a $\mu_3$-COMe group since the $\mu_3$-COMe group in $Fe_3(CO)_{10}(\mu_3\text{-}COMe)H$ has [13] a resonance at δ 4.23 p.p.m. Thus, both i.r., and $^1H$ n.m.r. data indicate the presence of a $\mu_3$-COMe group and (5) can be formulated as $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$, with a bicapped *closo* structure (see below).



(5)

The structure of the molecule is shown in Figure 3; important bond lengths and angles are given in Table 3. Chemically, the three iron atoms are equivalent, and the structure and molecular geometry parameters would be expected to reflect this. In fact, the $Fe_3(CO)_9(CMe)(CO)$ nucleus has approximately $C_3$ symmetry along the O(3)-C(3)-C(2)-C(1) axis, with the $Fe(CO)_3$ units oriented to place one CO group on each unit 'equatorial', *i.e.*, almost in the $Fe_3$ plane [C(11),C(23),C(31)] and the other two groups are above and one below this plane. The one feature which destroys this potential $C_3$ symmetry is the bend at the ether oxygen O(3) which may be responsible for the small distortions from $C_3$ symmetry in the $Fe_3(CO)_9$ nucleus and, possibly, the small variations in bond parameters [*e.g.*, Fe-Fe, Fe-C(2), Fe-C(3), see Table 3], which are expected to be equal.

(*c*) *Mechanism of Formation.*—The above results show that in electrophilic attacks on $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$ cleavage of the C-O bond of the acetyl group may occur. A suggested



**Scheme.** Electrophilic attack on the $\mu_3$-acylate anion $[Fe_3(CO)_9(\mu_3\text{-}MeCO)]^-$: $E^+ = H^+$ or $Me^+$; (*i*) C–O bond cleavage; (*ii*) fragmentation or disproportionation. Terminal carbon monoxide groups are omitted for clarity

mechanism for the formation of the products identified in the reactions is shown in the Scheme.

Initial electrophilic attack on the lone pair of the acyl oxygen gives a species (a) in which the C–O bond would be much weakened and lengthened. This species then undergoes C–O bond cleavage to give (b). Species (a) has been observed spectroscopically for $E = H$; species (b) has been fully characterised by *X*-ray diffraction study for $E = CH_3$. Species (b) may react with excess electrophile to give species (c) which then undergoes facile $E_2O$ elimination to produce species (d); this in turn then disproportionates or fragments or undergoes ' sacrificial oxidation ',[14] to give (e). Finally, (e) then reacts either with acid to give (f), *i.e.* compound (2), or with $MeSO_3F$ to give (g), *i.e.* compound (5). Sacrificial oxidation was proposed in the proton-assisted C–O bond cleavage in the conversion of $[Fe_4(CO)_{13}]^{2-}$ through $Fe_4(CO)_{12}(\eta^2\text{-}COH)(\mu\text{-}H)$ to $Fe_4(CO)_{12}(\eta^2\text{-}CH)(\mu\text{-}H)$.[14]

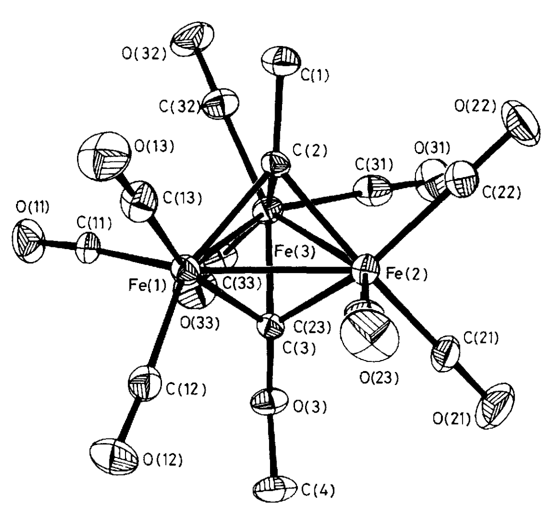


**Figure 3.** Structure of $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$ (5)

**Table 3.** Selected bonds lengths (Å) and angles (°) for $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu\text{-}COMe)$

| | | | |
|---|---|---|---|
| (*a*) Bond lengths | | | |
| Fe(1)–Fe(2) | 2.518(1) | Fe(1)–Fe(3) | 2.508(1) |
| Fe(2)–Fe(3) | 2.519(1) | | |
| Fe(1)–C(2) | 1.979(7) | Fe(1)–C(3) | 1.920(8) |
| Fe(2)–C(2) | 1.962(7) | Fe(2)–C(3) | 1.937(7) |
| Fe(3)–C(2) | 1.936(7) | Fe(3)–C(3) | 1.919(7) |
| (*b*) Bond angles | | | |
| Fe(2)–Fe(1)–Fe(3) | 60.2 | Fe(1)–Fe(2)–Fe(3) | 59.7 |
| Fe(1)–Fe(3)–Fe(2) | 60.1 | | |
| C(1)–C(2)–Fe(1) | 133.1(6) | O(3)–C(3)–Fe(2) | 134.3(5) |
| C(1)–C(2)–Fe(2) | 130.1(6) | O(3)–C(3)–Fe(2) | 133.5(6) |
| C(1)–C(2)–Fe(3) | 132.9(6) | O(3)–C(3)–Fe(3) | 125.0(6) |
| | C(3)–O(3)–C(4) | 119.7(6) | |

According to the Scheme, species (b) might be expected to react first with excess acid to give $Fe_3(CO)_{10}(\mu\text{-}CMe)(\mu\text{-}H)$ (2) and second with excess $MeSO_3F$ to give $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$ (5). The electrophilically induced C–O bond cleavage is further supported by the formation of (2) from the reaction of (4) with excess acid.

The $Fe_3(CO)_9$ moiety can thus act as an ' electron sink ' by rearrangement of the three iron atoms from a *closo* to an open structure, then back to a *closo* structure to assist the C–O bond cleavage process. Although C–O bond scission has long been considered a potential step in Fischer-Tropsch type reactions and many examples of C–O bond lengthening are known, the mechanism of C–O bond cleavages in acyl and related compounds are obscure. The isolation of (4) provides evidence for such C–O scission and some support for the proposal of the intermediacy of surface-bound alkylidynes.[15]

## Experimental

Microanalyses were by Pascher, Bonn. Melting points were determined in sealed capillaries.

All manipulations were performed under oxygen-free nitrogen or *in vacuo*. $[NEt_4][Fe_3(CO)_9(\mu_3\text{-}MeCO)]$ was prepared as before.[12] All chemicals used were of reagent grade; solvents were dried over sodium (except dichloromethane which was dried over P$_2$O$_5$) and distilled from sodium–benzophenone under nitrogen immediately before use. Light petroleum used was that fraction of b.p. 40—60 °C.

*Spectrometers.*—Perkin-Elmer R32 ($^1$H, 90 MHz) and Bruker WM 250 ($^1$H, 250 MHz; $^{13}$C-{$^1$H} 62.9 MHz) instruments were used for n.m.r.; data ($\delta$/p.p.m.) are referenced to SiMe$_4$ in C$_6$D$_6$ unless otherwise stated. A Perkin-Elmer 683 instrument was used for i.r.; spectra were run in Nujol and Fluorolube mulls. Mass spectra were run using V.G. Micromass 7070 and MS-9 instruments.

*Reaction of* [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] *with Aqueous Fluoroboric Acid.*—[$\mu_3$-*Acetyl*-C$^1$(*Fe*$^1$:*Fe*$^2$)O(*Fe*$^1$:*Fe*$^3$)]-*nonacarbonyl*-$\mu$-*hydrido-tri-iron* (1), Fe$_3$(CO)$_9$($\mu_3$-MeCOH) (3), *and decacarbonyl*-$\mu$-*ethylidyne*-$\mu$-*hydrido-tri-iron* (2). (*a*) Aqueous fluoroboric acid (0.25 cm$^3$, *ca.* 1.5 mmol) was added to a thf solution (50 cm$^3$) of [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] (0.6 g, 1 mmol) at 0 °C. The solution was stirred for 2 h at 0 °C, allowed to warm to room temperature and stirred for an additional hour. The resulting red solution was filtered from the white precipitate and the solvent removed under vacuum at 0 °C. The residue was then extracted with diethyl ether (2 × 30 cm$^3$), filtered, concentrated to *ca.* 20 cm$^3$, and cooled at $-20$ °C to give dark red crystals of compound (1), which were collected and washed with cold light petroleum at $-78$ °C. Yield 0.18 g, 38%; m.p. 74—76 °C [Found: C, 28.5; H, 1.0; O, 34.3; *M* (mass spectrum), 464. C$_{11}$H$_4$Fe$_3$O$_{10}$ requires C, 28.4; H, 0.9; O, 34.5%; *M* 463.7]. I.r.: 2 930w, 2 096m, 2 062s, 2 038s, 2 016s, 1 998s, 1 972s, 1 958s, 1 430w, and 1 362w cm$^{-1}$. N.m.r. $^1$H: 2.14 (s, 3 H, $\mu_3$-MeCO), $-25.09$ (s, 1 H, $\mu$-H). $^{13}$C-{$^1$H}: 242.5 ($\mu_3$-Me*C*O); 212.2, 210.4, 207.4, and 206.7 (terminal CO); 42.3 ($\mu_3$-*Me*CO).

(*b*) The filtrate from above was evaporated under vacuum at 0 °C and the residue extracted with light petroleum (2 × 20 cm$^3$). This solution was concentrated to *ca.* 10 cm$^3$ and cooled at $-20$ °C to give a small amount of orange crystals of the compound formulated as Fe$_3$(CO)$_9$($\mu_3$-MeCOH) (3), m.p. 123—126 °C [Found: *M*, 394 (mass spectrum). C$_{11}$H$_4$Fe$_3$O$_{10}$ requires *M*, 463.7]. I.r.: 3 510m, 2 930w, 2 070m, 2 040s, 1 996s, 1 980m, 1 910m, 1 465w, 1 395w, and 1 372w cm$^{-1}$. N.m.r. $^1$H: 4.64 (s, 1 H, OH); 1.60 (s, 3 H, $\mu$-MeCO).

(*c*) The above filtrate in light petroleum was evaporated under vacuum at 0 °C and the residue was sublimed at 30 °C. Compound (2) was obtained as dark red crystals on crystallisation of the sublimate from the minimum amount of light petroleum. Yield 0.12 g, 25%; m.p. 121—125 °C [Found: C, 30.4; H, 1.0; O, 33.4; *M* (mass spectrum), 476. C$_{12}$H$_4$Fe$_3$O$_{10}$ requires C, 30.3; H, 0.8; O, 33.6%; *M* 476]. I.r.: 2 960w, 2 930w, 2 096w, 2 080vw, 2 060s, 2 046ms, 2 036s, 2 026s, and 2 000m (sh) cm$^{-1}$. N.m.r. $^1$H: 3.97 (s, 3 H, $\mu$-CMe); $-23.78$ (s, 1 H, $\mu$-H). $^{13}$C-{$^1$H}: 325.7 ($\mu$-*C*Me); 210.2, 209.2, 206.1, and 205.6 (terminal CO); 46.2 ($\mu$-C*Me*).

*Reaction of* [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] *with Methyl Fluorosulphate.*—*Nonacarbonyl*-$\mu_3$-*ethylidyne*-$\mu_3$-*methoxo-tri-iron* (4) *and nonacarbonyl*-$\mu_3$-*ethylidyne*-$\mu_3$-*methoxymethylidyne-tri-iron* (5). (*a*) *At room temperature.* Methyl fluorosulphate (1.14 g, 10 mmol) was added to a dichloromethane solution (50 cm$^3$) of [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] (0.6 g, 1 mmol) at room temperature. The progress of the reaction was monitored by i.r. periodically. After stirring at room temperature for 7 d the solvent was removed under vacuum at 0 °C. The residue was then extracted with light petroleum (2 × 30 cm$^3$), the solution filtered, concentrated to *ca.* 20 cm$^3$ and cooled at $-20$ °C to give dark red crystals of (4). Yield 0.14 g, 60%, based on the amount of [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] reacted; m.p. >250 °C (decomp.) [Found: C, 30.2; H, 1.4; O, 33.2; *M* (mass spectrum), 478. C$_{12}$H$_6$Fe$_3$O$_{10}$ requires C, 30.1; H, 1.3; O, 33.2%; *M*, 477.7]. I.r. 2 930w, 2 080w, 2 038s, 2 020s, and 1 998s cm$^{-1}$. N.m.r. $^1$H: 3.22 (s, 3 H, $\mu_3$-CMe); 1.74 (s, 3 H, $\mu_3$-OMe). $^{13}$C-{$^1$H}: 334.0 ($\mu_3$-*C*Me); 208.6 (terminal CO); 79.1 ($\mu_3$-OMe); 45.7 ($\mu_3$-C*Me*).

The residue from the above petroleum extraction was then extracted into thf (20 cm$^3$). A test of the filtrate indicated that this contained starting material, [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)], 0.3 g of which was recovered upon addition of diethyl ether (50 cm$^3$) to the thf solution.

(*b*) *At elevated temperature.* Methyl fluorosulphate (1.14 g, 10 mmol) was added to a dichloromethane solution (50 cm$^3$) of [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] (0.6 g, 1 mmol) at room temperature. The solution was then heated to reflux and the progress of the reaction was monitored by i.r. After refluxing for 2 d the solution was allowed to cool at room temperature when the solvent was removed under vacuum at 0 °C. The residue was then extracted with petroleum (2 × 30 cm$^3$) and filtered. [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] (0.15 g, 25%) was recovered from the residue. The petroleum filtrate was concentrated to *ca.* 5 cm$^3$, loaded on preparative t.l.c. plates (silica gel) and eluted with light petroleum. Several bands were obtained. The first band obtained was orange, which upon recrystallisation from light petroleum gave (5) as orange red crystals. Yield 0.04 g, 10%, based on the amount of [NEt$_4$][Fe$_3$(CO)$_9$($\mu_3$-MeCO)] reacted, m.p. >200 °C (decomp.) [Found: C, 31.9; H, 1.6; O, 32.3; *M* (mass spectrum), 490. C$_{13}$H$_6$Fe$_3$O$_{10}$ requires C, 31.8; H, 1.6; O, 32.7%; *M* 489.7]. I.r. 2 940w, 2 850w, 2 078w, 2 030s, 2 010s, 1 985s, 1 442w, and 1 362w cm$^{-1}$. N.m.r. $^1$H: 4.24 (s, 3 H, $\mu_3$-COMe); 3.98 (s, 3 H, $\mu_3$-CMe). $^{13}$C-{$^1$H}: 359.8 ($\mu_3$-*C*OMe); 334.6 ($\mu_3$-*C*Me); 209.6 (terminal CO); 72.4 ($\mu_3$-CO*Me*); 46.9 ($\mu_3$-C*Me*). Attempts to obtain crystals from the other bands were unsuccessful.

*Reaction of* Fe$_3$(CO)$_9$($\mu_3$-CMe)($\mu_3$-OMe) *with Fluoroboric Acid.*—Aqueous fluoroboric acid (0.1 cm$^3$, *ca.* 0.6 mmol) was added to a thf solution (20 cm$^3$) of Fe$_3$(CO)$_9$($\mu_3$-CMe)($\mu_3$-OMe) (0.1 g, 0.2 mmol) at 0 °C. After stirring and warming to room temperature for 2 h, the solvent was removed under vacuum. The residue was sublimed in vacuum at 30 °C to give 0.03 g (30% yield) of Fe$_3$(CO)$_{10}$($\mu$-CMe)($\mu$-H) which was identified by i.r. and $^1$H n.m.r. spectroscopy, and shown to be identical with (2) obtained directly from [Fe$_3$(CO)$_9$($\mu_3$-MeCO)]$^-$.

*Crystallographic Studies.*—Crystals of all three compounds were sealed in Lindemann capillaries under argon. All diffraction measurements [16] were made using an Enraf-Nonius CAD4F diffractometer, with graphite-monochromatised Mo-$K_\alpha$ radiation ($\lambda$ = 0.710 69 Å), and the $\omega/2\theta$ scan method.

*Crystal data for compound* (1). C$_{11}$H$_4$Fe$_3$O$_{10}$, $M$ = 463.69, Triclinic, $a$ = 7.884(1), $b$ = 8.257(1), $c$ = 12.941(2) Å, $\alpha$ = 96.03(2), $\beta$ = 99.46(2), $\gamma$ = 106.85(2)°, $U$ = 748.8 Å$^3$, $Z$ = 2, $D_c$ = 1.96 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 27.84 cm$^{-1}$, $F$(000) = 456, space group $P\bar{1}$. 3 065 Data were collected, 2 260 were considered observed [$I > 1.5\sigma(I)$], with $\omega$ scan = 0.85 + 0.35tan$\theta$, scan speed = 1.27—6.77° min$^{-1}$, 1.5 < $\theta$ < 25.

*Crystal data for compound* (4). C$_{12}$H$_6$Fe$_3$O$_{10}$, $M$ = 477.72, Triclinic, $a$ = 7.659(1), $b$ = 9.051(1), $c$ = 13.142(2) Å, $\alpha$ = 98.77(2), $\beta$ = 100.03(2), $\gamma$ = 108.86(2), $U$ = 848.11 Å$^3$, $Z$ = 2, $D_c$ = 1.87 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 27.10 cm$^{-1}$, $F$(000) = 464, space group $P\bar{1}$. 2 973 Data were collected, 2 582 were considered observed [$I > 1.5\sigma(I)$], $\omega$ scan = 0.85 + 0.35tan$\theta$, scan speed = 1.27—6.77° min$^{-1}$, 1.5 $\leqslant \theta \leqslant$ 25.

**Table 4.** Fractional atomic co-ordinates for $Fe_3(CO)_9(\mu_3\text{-}MeCO)(\mu\text{-}H)$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Fe(1) | 0.212 47(7) | 0.247 98(7) | 0.109 08(4) | C(12) | 0.959 6(5) | 0.720 6(5) | −0.009 9(3) |
| Fe(2) | 0.058 64(7) | 0.276 08(7) | 0.259 83(4) | C(13) | 0.362 5(6) | 0.457 4(5) | 0.111 9(3) |
| Fe(3) | 0.352 60(7) | 0.197 86(7) | 0.306 74(4) | C(21) | 0.115 6(5) | 0.650 2(6) | 0.808 0(3) |
| O(11) | 0.352 6(4) | 0.057 3(4) | 0.956 4(3) | C(22) | 0.213 7(6) | 0.478 7(5) | 0.319 1(4) |
| O(12) | 0.062 9(4) | 0.698 6(4) | 0.053 7(3) | C(23) | 0.956 1(6) | 0.239 6(5) | 0.372 1(3) |
| O(13) | 0.460 6(5) | 0.590 1(4) | 0.115 5(3) | C(31) | 0.449 0(6) | 0.610 0(6) | 0.648 0(4) |
| O(21) | 0.227 1(4) | 0.603 5(5) | 0.849 6(3) | C(32) | 0.335 1(6) | 0.162 2(6) | 0.438 8(3) |
| O(22) | 0.301 1(5) | 0.614 7(4) | 0.357 9(3) | C(33) | 0.464 0(6) | 0.041 7(5) | 0.282 1(3) |
| O(23) | 0.103 9(5) | 0.776 2(5) | 0.554 2(3) | C(1) | 0.113 5(5) | 0.044 8(4) | 0.251 7(3) |
| O(31) | 0.325 0(5) | 0.494 5(5) | 0.620 7(3) | C(2) | −0.008 7(6) | 0.112 7(5) | 0.711 0(3) |
| O(32) | 0.321 1(5) | 0.136 2(5) | 0.521 6(3) | H(1) | 0.382(5) | 0.223(5) | 0.197(3) |
| O(33) | 0.470 2(5) | 0.058 9(4) | 0.736 5(3) | H(21) | 0.028(6) | 0.902(6) | 0.367(4) |
| O(1) | 0.036 2(3) | 0.067 5(3) | 0.157 7(2) | H(22) | 0.032(6) | 0.793(5) | 0.261(3) |
| C(11) | 0.296 8(5) | 0.129 1(5) | 0.013 7(3) | H(23) | 0.126(7) | 0.143(7) | 0.739(4) |

**Table 5.** Fractional atomic co-ordinates for $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}OMe)$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Fe(1) | 7 943(1) | 429(1) | 2 788 | O(2b) | 10 817(6) | 6 056(4) | 1 297(3) |
| Fe(2) | 9 373(1) | 4 003(1) | 2 862 | C(2c) | 8 978(5) | 5 601(4) | 3 551(3) |
| Fe(3) | 6 341(1) | 2 215(1) | 1 958 | O(2c) | 8 832(5) | 6 639(3) | 3 961(3) |
| O(1) | 7 498(3) | 2 247(2) | 3 398(2) | C(3a) | 4 158(5) | 655(4) | 1 953(3) |
| C(1) | 6 652(6) | 2 267(5) | 4 287(3) | O(3a) | 2 757(4) | −301(4) | 1 941(3) |
| C(2) | 9 025(4) | 2 174(3) | 1 982(2) | C(3b) | 6 119(5) | 2 096(5) | 604(3) |
| C(3) | 10 090(6) | 2 134(5) | 1 125(3) | O(3b) | 6 001(5) | 2 014(5) | −271(2) |
| C(1a) | 6 194(5) | −1 103(4) | 3 363(3) | C(3c) | 5 558(5) | 3 893(4) | 1 962(3) |
| O(1a) | 5 137(5) | −2 101(4) | 3 674(3) | O(3c) | 5 005(4) | 4 919(4) | 1 917(3) |
| C(1b) | 10 044(5) | 346(4) | 3 586(3) | | | | |
| O(1b) | 11 420(4) | 317(4) | 4 066(3) | H(1a) | 5 432(57) | 1 445(49) | 4 233(29) |
| C(1c) | 7 971(5) | −935(4) | 1 844(3) | H(1b) | 7 479(67) | 2 237(55) | 4 844(39) |
| O(1c) | 8 022(5) | −1 799(4) | 1 236(4) | H(1c) | 6 371(67) | 3 217(65) | 4 365(38) |
| C(2a) | 11 633(5) | 4 098(4) | 3 569(3) | H(3a) | 11 365(65) | 2 329(51) | 1 526(38) |
| O(2a) | 13 090(4) | 4 150(4) | 3 968(3) | H(3b) | 10 289(61) | 2 992(55) | 692(35) |
| C(2b) | 10 270(6) | 5 271(4) | 1 925(3) | H(3c) | 9 596(60) | 1 213(60) | 707(36) |

**Table 6.** Fractional atomic co-ordinates for $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Fe(1) | 0.186 3(1) | 0.094 8(1) | 0.250 | C(31) | 0.463(1) | −0.084(1) | 0.317(1) |
| Fe(2) | 0.219 7(1) | −0.089 8(1) | 0.255 5(2) | O(31) | 0.516 8(8) | −0.151 3(7) | 0.327(1) |
| Fe(3) | 0.380 9(1) | 0.028 8(1) | 0.297 1(2) | C(33) | 0.481 1(9) | 0.092 9(9) | 0.199(1) |
| C(11) | 0.258(1) | 0.211 9(7) | 0.256(1) | C(2) | 0.240 5(8) | 0.009 2(7) | 0.388(1) |
| O(11) | 0.299 1(8) | 0.286 6(6) | 0.252(1) | C(1) | 0.212(1) | 0.004(1) | 0.529(1) |
| C(12) | 0.097(1) | 0.122 5(9) | 0.119(1) | C(3) | 0.286 2(9) | 0.013 1(7) | 0.152(1) |
| O(12) | 0.036 3(8) | 0.143 6(8) | 0.039(1) | O(3) | 0.323 7(7) | 0.015 7(7) | 0.030 6(8) |
| C(21) | 0.259(1) | −0.176 7(9) | 0.136(1) | C(13) | 0.073(1) | 0.126 9(9) | 0.363(1) |
| O(21) | 0.282(1) | −0.231 5(8) | 0.059(1) | O(13) | 0.005 8(9) | 0.150 7(9) | 0.430(1) |
| C(22) | 0.230(1) | −0.183 7(9) | 0.382(1) | O(33) | 0.545 4(9) | 0.130 4(9) | 0.134(1) |
| O(22) | 0.232(1) | −0.239 5(7) | 0.458(1) | C(32) | 0.429(1) | 0.091(1) | 0.440(1) |
| C(23) | 0.066 9(9) | −0.098 1(8) | 0.236(1) | O(32) | 0.456 9(9) | 0.128 6(8) | 0.529(1) |
| O(23) | −0.025 6(7) | −0.107 6(8) | 0.235(1) | C(4) | 0.245(1) | 0.000(1) | −0.069(1) |

*Crystal data for compound* (5). $C_{13}H_6Fe_3O_{10}$, $M = 489.73$, Orthorhombic, $a = 11.796(3)$, $b = 13.496(2)$, $c = 10.674(3)$ Å, $U = 1\,692.05$ Å$^3$, $Z = 4$, $D_c = 1.92$ g cm$^{-3}$, $\mu(\text{Mo-}K_\alpha) = 26.95$ cm$^{-1}$, $F(000) = 968$, space group $Pna2_1$. 2 795 Data were collected, 1 816 were considered observed [$I > 1.5\sigma(I)$], ω scan = $0.80 + 0.35\tan\theta$, scan speed = 1.27—6.77° min$^{-1}$, $1.5 \leqslant \theta \leqslant 30°$.

*Structure determination and refinement.* The structures of compounds (1) and (4) were determined using direct methods (Fe positions) and difference syntheses, whilst that of (5) was determined from Patterson and difference syntheses. All three were refined by full-matrix least-squares methods with non-hydrogen atoms assigned anisotropic thermal parameters. For compounds (1) and (4), hydrogen atoms were located from difference syntheses and successfully refined with individual isotropic thermal parameters. For compound (5) hydrogen atoms could not be located and were ignored. For compounds (1) and (4) unit weights were used, whilst for compound (5) weights were calculated as $w = 1/[\sigma^2(F_o) + 0.0005\,F_o^2]$. Final $R$ values were 0.029 [for (1)], 0.0379 [for (4), $R' = 0.0385$], and 0.057 [for (5)]. Final atomic positional parameters are given in Tables 4—6.

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