The Reaction of a Bridged Vinylidenedi-iron Complex with Cobalt, Iron, and Manganese Carbonyl Species; *X*-Ray Crystal Structures of the Complexes $[\mathrm{Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)}]$ and $[\mathrm{Co_3Fe(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)}]$ [†]

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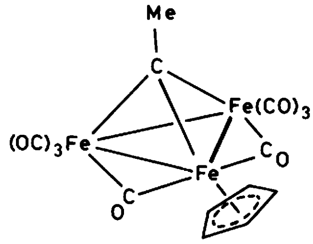
Treatment of *trans*-$[\mathrm{Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2}]$ with $[\mathrm{Fe_2(CO)_9}]$ in diethyl ether affords $[\mathrm{Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)}]$ (1), which was characterised by *X*-ray crystallography, and shown to contain a tetrahedral $\mathrm{CFe_3}$ core which has near, but not exact, mirror symmetry. The $\mathrm{Fe_3}$ triangle has two nearly equal sides [2.519(1) and 2.509(1) Å] and one longer side [2.602(1) Å], the two former being bridged approximately symmetrically by carbonyl ligands. The $\mathrm{Fe_3}$ triangle is triply bridged by the μ_3-CMe ligand, but with the C atom significantly closer to the unique iron atom, which also carries the cyclopentadienyl ligand. The C–Me vector is perpendicular to the $\mathrm{Fe_3}$ plane, and the terminal carbonyl ligands form two mutually orthogonal sets of three on each of the ' basal ' iron atoms. Crystals of (1) are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions a = 8.943(4), b = 12.156(4), c = 15.904(8) Å, and β = 103.57(4)°; R = 0.026 for 2 771 intensities [$I \geqslant 3.0\sigma(I)$]. Reaction of compound (1) with $\mathrm{C_5H_6}$ in toluene, or thermolysis of the complex *trans*-$[\mathrm{Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2}]$, gives $[\mathrm{Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3}]$. Treatment of *trans*-$[\mathrm{Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2}]$ with $[\mathrm{Co_2(CO)_8}]$ in diethyl ether yields as the principal product $[\mathrm{Co_3Fe(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)}]$ (3). The latter complex was shown by *X*-ray crystallography to have a $\mathrm{Co_3Fe}$ core arranged as a ' butterfly ' (interplanar angle 124°) with the iron atom occupying one of the ' wingtips ' and carrying the cyclopentadienyl ligand. The molecule has overall C_s symmetry (required crystallographically), the mirror being defined as the perpendicular bisector of the body of the butterfly. The μ_4-C atom bridges the four metal atoms on the concave side, and the $\mathrm{-C{=}CH_2}$ moiety is η^2-bonded to the wingtip cobalt atom. Two of the nine carbonyl ligands bridge the Co–Fe edges, approximately symmetrically; the other seven are terminal and form orthogonal sets (2 + 2 + 3). Crystals of (3) are orthorhombic, space group *Pcam*, with four molecules in a unit cell of dimensions a = 18.135(16), b = 8.194(9), and c = 12.711(10)Å; R = 0.054 for 1 772 intensities [$I \geqslant 2.0\sigma(I)$]. The trimanganese complex $[\mathrm{Mn_3(\mu\text{-}H)_3(CO)_{12}}]$ reacts with *trans*-$[\mathrm{Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2}]$ in benzene to form the mixed-metal cluster $[\mathrm{Fe_2Mn(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5H_5)_2}]$.

Although dimetal complexes[1] containing bridging $\mathrm{C{=}CR_2}$ ligands have been known for some time there has been no attempt to utilize the unsaturation present in their dimetalla(methylene)cyclopropane ring systems $\mathrm{\overset{|}{M}{-}M{-}\overset{|}{C}{=}CR_2}$ to construct metal cluster compounds containing the $\mathrm{C{=}CR_2}$ fragment. At the start of our investigation the only examples of such species were $[\mathrm{Os_3(\mu_3\text{-}C{=}CH_2)(\mu\text{-}H)_2(CO)_9}]$,[2] $[\mathrm{NiRu_3(\mu_4\text{-}C{=}CHBu^t)(CO)_9(\eta\text{-}C_5H_5)}]$,[3] and $[\mathrm{Ru_4(\mu_4\text{-}C{=}CHPr^i)(\mu_3\text{-}OR)(\mu\text{-}PPh_2)(CO)_{10}}]$ (R = H or Et).[4] The osmium complex was formed from a reaction involving ethylene, whilst the other two clusters were synthesised from acetylide and acetylene complexes. The observation[2] that the $\mathrm{Os_3}$ complex could be readily transformed into $[\mathrm{Os_3(\mu\text{-}H)_3(\mu_3\text{-}CCH_3)(CO)_9}]$ suggested that bridged methylidyne complexes might be accessible from species containing $\mu\text{-}\mathrm{C{=}CH_2}$ ligands. The development[5] of a simple synthesis of *trans*-$[\mathrm{Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2}]$ provided an opportunity to explore these ideas. A preliminary communication has described[6] some of the aspects of this work.[‡]

Results and Discussion

Reaction of an excess of $[\mathrm{Fe_2(CO)_9}]$ with *trans*-$[\mathrm{Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2}]$ in diethyl ether at room temperature over several days gave $[\mathrm{Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2}]$ together with a black crystalline compound (1), which was isolated by



(1)

[†] 1,3;2,3-Di-μ-carbonyl-1,1,1,2,2,2-hexacarbonyl-3-(1′—5′-η^5-cyclopentadienyl)-μ_3-ethylidyne-*triangulo*-tri-iron and 2,4;3,4-di-μ-carbonyl-1,1,1,2,2,3,3-heptacarbonyl-4-(1′—5′-η-cyclopentadienyl)-μ_4-vinylidene-$C^{1''}(\mathrm{Co}^{2,3},\mathrm{Fe}^4)$:$C^{1''}$—$C^{2''}(\mathrm{Co}^1)$-*cyclo*-tricobaltiron (3 *Co*–*Co*) (2*Fe*–*Co*) respectively.

Supplementary data available (No. SUP 23589, 50 pp.): structure factors, thermal parameters, full atomic co-ordinates, full bond distances and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

[‡] Our preliminary communication[6] included essential features of the crystal structure of $[\mathrm{Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)}]$ (1); full details are included in this paper, despite the recent publication[7] of a separate structural study from the U.S.S.R., because of the appreciably higher accuracy of the study reported here.

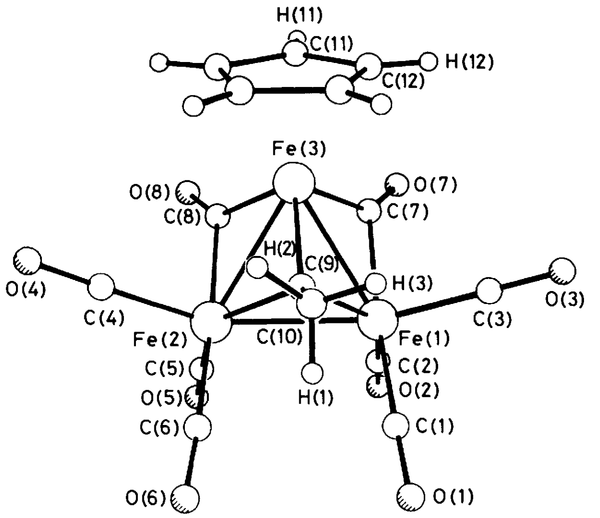


Figure 1. Molecular structure of $[Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)]$ (1) showing the crystallographic numbering

column chromatography, and characterised by elemental analysis, i.r., and n.m.r. spectroscopy. The i.r. spectrum showed bands characteristic of both terminal and bridging CO environments. The ^1H n.m.r. spectrum exhibited two resonances with relative intensities of 5 : 3 with chemical shifts typical of cyclopentadienyl and CMe ligands. The presence in (1) of the latter structural feature was supported by the ^{13}C spectrum which showed a low-field resonance at δ 333 p.p.m. typical of the contact carbon of a μ_3-CMe fragment, and a Me signal at δ 52 p.p.m., which appeared as a quartet [J(CH) = 128 Hz] in a fully coupled spectrum.

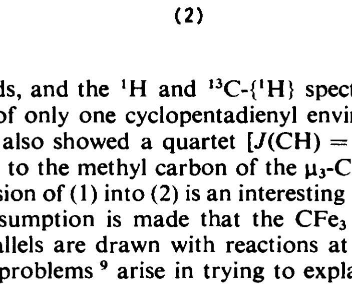
A single-crystal *X*-ray diffraction study established the molecular structure of (1), which is illustrated in Figure 1 with the crystallographic numbering. A stereoscopic view of the molecule (drawn perpendicular to the plane of the cyclopentadienyl ligand) is shown in Figure 2. It is at once evident from Figure 2 that the molecule possesses almost exact mirror symmetry, although this is not required crystallographically. Relevant bond lengths and angles are in Table 1, grouped to show comparable parameters side by side. The Fe_3 triangle is near-isosceles, and the μ_3-CMe ligand has C(9) slightly asymmetrically related to Fe(1) and Fe(2), which form the base of the triangle [Fe(1)–C(9) 1.934(2), Fe(2)–C(9) 1.959(3) Å] and significantly closer to Fe(3) [Fe(3)–C(9) 1.902(3) Å]. A similar asymmetry in the location of the μ_3-C atom was found[8] in the formally analogous structure $[Fe_3(\mu_3\text{-}CEt)(CO)_8(\eta\text{-}C_5H_2Me_2Et)]$ where the comparable distances are 1.928(4), 1.974(5), and 1.910(4) Å respectively. The C(9)–C(10) vector is perpendicular to the plane of the metal atom triangle. Of the eight carbonyl ligands, two bridge the 'equal' sides of the metal triangle [Fe(1)–C(7) 2.023(3), Fe(3)–C(7) 1.889(3), Fe(2)–C(8) 2.020(3), Fe(3)–C(8) 1.885(3) Å]; the other six are terminal and form mutually orthogonal groups of three on each of Fe(1) and Fe(2). The cyclopentadienyl ligand lies astride the mirror plane with C(11) and H(11) in the plane. There appears to be slight 'slippage' in the bonding of the C_5 ring to Fe(3), atoms C(13) and C(14) being some 0.02 Å further away than are C(11), C(12), and C(15).

The formation of (1) and $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ under mild conditions clearly involves a complex sequence of reactions, and it is interesting that only one $Fe(C{=}CH_2)(\eta\text{-}C_5H_5)$ fragment is incorporated into the cluster suggesting the possible involvement of a mononuclear vinylidene species. When this reaction, which also involves transfer of cyclopentadienyl ligands, is conducted in $[^2H_6]$benzene, a slower reaction occurs, but again the same products are formed, there being no deuterium incorporation into the cluster (1). Thus, the origin of the extra hydrogen atom needed to transform the $C{=}CH_2$ group into CMe remains obscure.

Table 1. Bond distances (Å) and angles (°) for $[Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)]$ (1)

Fe(1)–Fe(3)	2.519(1)	Fe(2)–Fe(3)	2.509(1)
Fe(1)–Fe(2)	2.602(1)	Fe(3)–C(9)	1.902(3)
Fe(1)–C(9)	1.934(2)	Fe(2)–C(9)	1.959(3)
Fe(1)–C(7)	2.023(3)	Fe(2)–C(8)	2.020(3)
Fe(3)–C(7)	1.889(3)	Fe(3)–C(8)	1.885(3)
C(7)–O(7)	1.170(3)	C(8)–O(8)	1.172(4)
Fe(1)–C(3)	1.797(4)	Fe(2)–C(4)	1.792(3)
C(3)–O(3)	1.144(5)	C(4)–O(4)	1.148(4)
Fe(1)–C(1)	1.800(3)	Fe(2)–C(6)	1.798(3)
C(1)–O(1)	1.137(4)	C(6)–O(6)	1.135(4)
Fe(1)–C(2)	1.831(3)	Fe(2)–C(5)	1.821(3)
C(2)–O(2)	1.138(3)	C(5)–O(5)	1.133(3)
Fe(3)–C(12)	2.104(3)	Fe(3)–C(15)	2.102(3)
Fe(3)–C(13)	2.126(3)	Fe(3)–C(14)	2.122(3)
Fe(3)–C(11)	2.106(3)	C–C (C_5H_5, mean)	1.413(4)
Fe(1)–Fe(2)–Fe(3)	59.0(1)	Fe(2)–Fe(1)–Fe(3)	58.7(1)
Fe(1)–Fe(3)–Fe(2)	62.3(1)	Fe(1)–C(9)–Fe(2)	83.9(1)
Fe(1)–C(9)–Fe(3)	82.1(1)	Fe(2)–C(9)–Fe(3)	81.0(1)
Fe(1)–C(9)–C(10)	129.5(2)	Fe(2)–C(9)–C(10)	131.0(2)
		Fe(3)–C(9)–C(10)	131.1(2)
Fe(1)–C(7)–O(7)	137.6(2)	Fe(2)–C(8)–O(8)	138.1(2)
Fe(3)–C(7)–O(7)	142.1(2)	Fe(3)–C(8)–O(8)	141.9(2)
Fe(1)–C(7)–Fe(3)	80.1(1)	Fe(2)–C(8)–Fe(3)	79.9(1)
C(1)–Fe(1)–C(3)	89.8(1)	C(6)–Fe(2)–C(4)	90.0(1)
C(1)–Fe(1)–C(2)	94.5(1)	C(6)–Fe(2)–C(5)	94.4(1)
C(2)–Fe(1)–C(3)	105.2(1)	C(5)–Fe(2)–C(4)	106.6(1)

The cluster (1) reacts with an excess of cyclopentadiene in refluxing toluene to form in moderate yield the symmetrical complex $[Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]$ (2), characterised by elemental analysis, mass, i.r., and n.m.r. spectroscopy. The i.r. spectrum in the carbonyl region showed only bridging carbonyl bands, and the ^1H and $^{13}C\text{-}\{^1H\}$ spectra confirmed the presence of only one cyclopentadienyl environment. The ^{13}C spectrum also showed a quartet [J(CH) = 127 Hz] at δ 57 p.p.m. due to the methyl carbon of the μ_3-CMe ligand.



(2)

The conversion of (1) into (2) is an interesting reaction if the reasonable assumption is made that the CFe_3 core remains intact. If parallels are drawn with reactions at mononuclear centres, then problems[9] arise in trying to explain how H_2 is eliminated from the system $(\eta\text{-}C_5H_5)HFe{\cdot}FeH(\eta\text{-}C_5H_5)$. As if to underline the complexity of this chemistry, it was observed

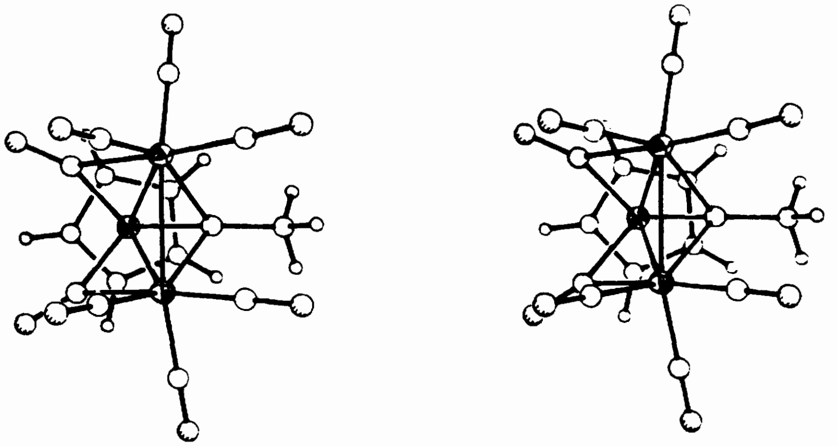
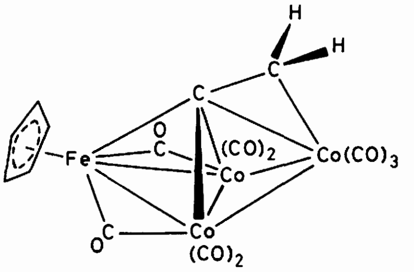


Figure 2. Stereopair drawing of the structure of (1) projected onto the plane of the cyclopentadienyl ligand and showing the near-mirror symmetry

that (2) is also formed in moderate yield when *trans*-[$Fe_2(\mu$-$C{=}CH_2)(\mu$-$CO)(CO)_2(\eta$-$C_5H_5)_2$] is refluxed in the high-boiling solvent di-n-butyl ether.

Dicobalt octacarbonyl reacted at room temperature with *trans*-[$Fe_2(\mu$-$C{=}CH_2)(\mu$-$CO)(CO)_2(\eta$-$C_5H_5)_2$] in diethyl ether. Low-temperature column chromatography of the reaction mixture gave [$CoFe(\mu$-$CO)_2(CO)_4(\eta$-$C_5H_5)$], [$Fe_2(\mu$-$CO)_2$-$(CO)_2(\eta$-$C_5H_5)_2$], [$Co_4(CO)_{12}$], and a new cluster (3) containing a Co_3Fe core, which was structurally identified by single-crystal *X*-ray diffraction.



(3)

The molecular structure of (3) is shown in Figure 3 with the crystallographic numbering, and a stereoscopic view of the molecule, drawn so as to show the crystallographically required mirror symmetry, is in Figure 4. Relevant bond lengths and angles are in Table 2. The molecule comprises a ' butterfly ' Co_3Fe core [Co(1)–Co(2) 2.581(3), Co(1)–Fe 2.499(2), Co(1)–Co(1′) 2.456(3) Å], with the Fe atom in a wingtip position carrying the cyclopentadienyl ligand. The interplanar angle of the butterfly is 124°, and on its concave side, centrally located, lies the μ_4-$C{=}CH_2$ moiety, such that the atom C(21) is bonded to all four metal atoms [Co(1)–C(21) 1.917(6), Co(2)–C(21) 2.087(8), Fe–C(21) 1.933(8) Å] and C(22) is also bonded to Co(2) [Co(2)–C(22) 2.085(10) Å]. Two of the nine carbonyl ligands bridge the Co–Fe bonds, approximately symmetrically [Co(1)–C(5) 1.972(5), Fe–C(5) 1.885(5) Å]; the other seven are terminal and form orthogonal sets [two each on Co(1) and Co(1′), three on Co(2)]. The cyclopentadienyl ligand lies astride the mirror plane with C(11) and H(11) in the plane and again there appears to be slight ' slippage ', atoms C(13) and C(13′) being some 0.05 Å further away than are C(11), C(12), and C(12′).*

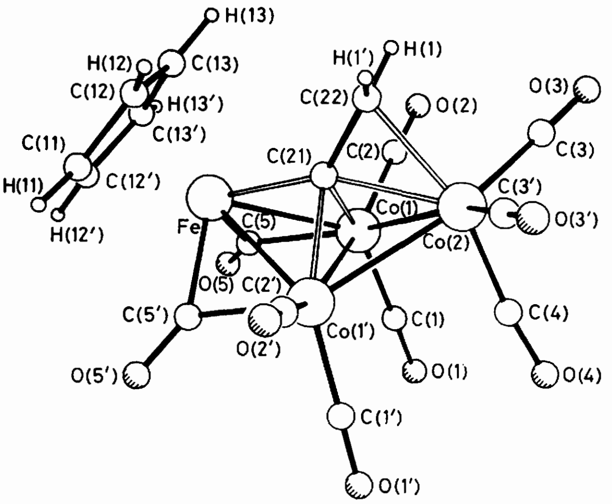


Figure 3. Molecular structure of [$Co_3Fe(\mu_4$-$C{=}CH_2)(\mu$-$CO)_2(CO)_7$-$(\eta$-$C_5H_5)$] (3) showing the crystallographic numbering

In agreement with the solid-state structure, the ^{13}C-{^1H} n.m.r. spectrum of (3) showed a resonance at δ 304 p.p.m. assigned to the contact μ_4-*C*$=CH_2$ carbon. A low-temperature spectrum (−70 °C) gave peaks at δ 245, 208, and 197 p.p.m., the low-field peak being assigned to the bridging carbonyls, the remaining peaks being associated with the $Co(CO)_2$ and Co-$(CO)_3$ groups. The ^1H n.m.r. spectrum was in agreement, showing signals due to η-C_5H_5 and μ_4-$C{=}CH_2$ ligands.

In the formation of both (1) and (3), it is clear that a com-

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* The structure of (3) involves a space group ambiguity (either *Pca*2_1 or *Pcam*). The structure was solved in *Pca*2_1, but the resulting positional parameters suggested that the molecule lies astride a mirror plane perpendicular to *c*. The molecular parameters quoted here are those derived from final refinement in space group *Pcam*. Several atoms, however [notably Co(2), C(22), and the terminal carbonyl ligands], apparently show high thermal activity, despite data collection at 220 K, and there is no way of being certain whether the true space group is *Pca*2_1 with slight deviation of the molecular structure from mirror symmetry, or whether the molecule has true mirror symmetry but with slight positional disorder across the crystallographic mirror plane of *Pcam*. In either event there can be no doubt that the overall molecular configuration is as described here, but the estimates of error may be too small.

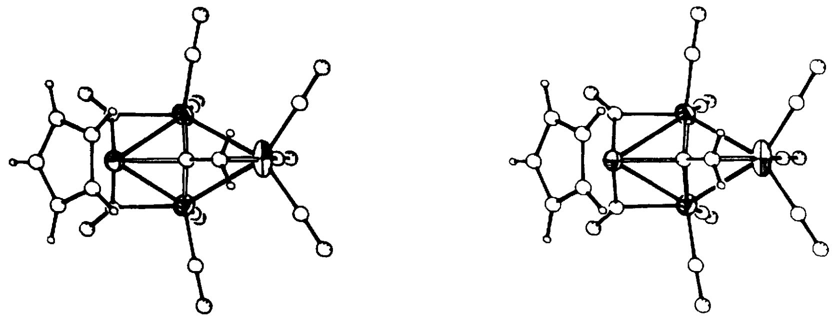


Figure 4. Stereopair drawing of the structure of (3) showing the (crystallographically required) mirror symmetry

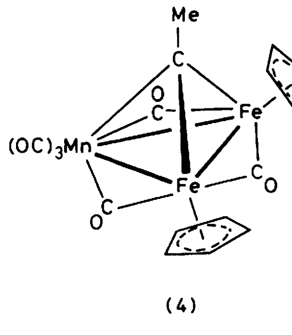
Table 2. Bond distances (Å) and angles (°) for [$Co_3Fe(\mu_4$-C=CH_2)-(μ-CO$)_2$(CO$)_7$(η-C_5H_5)] (3) *

Fe–Co(1)	2.499(2)	Co(1)–Co(2)	2.581(3)
Co(1)–Co(1′)	2.456(3)	Fe–C(21)	1.933(8)
Co(1)–C(21)	1.917(6)	Co(2)–C(21)	2.087(8)
C(21)–C(22)	1.431(12)	Co(2)–C(22)	2.085(10)
Fe–C(5)	1.885(5)	Co(1)–C(5)	1.972(5)
C(5)–O(5)	1.168(7)	Co(1)–C(1)	1.789(7)
C(1)–O(1)	1.124(10)	Co(1)–C(2)	1.770(9)
C(2)–O(2)	1.140(11)	Co(2)–C(3)	1.813(10)
C(3)–O(3)	1.120(13)	Co(2)–C(4)	1.792(10)
C(4)–O(4)	1.140(12)	Fe–C(11)	2.070(8)
Fe–C(12)	2.089(6)	Fe–C(13)	2.126(6)
C–C (Cp, mean)	1.38(2)		

Fe–Co(1)–Co(2)	101.3(1)	Fe–Co(1)–Co(1′)	60.6(1)
Co(2)–Co(1)–Co(1′)	61.6(1)	Co(1)–Fe–Co(1′)	58.9(1)
Co(1)–Co(2)–Co(1′)	56.8(1)	Fe–C(21)–Co(1)	80.9(3)
Co(2)–C(21)–Co(1)	80.2(2)	Co(1)–C(21)–Co(1′)	79.7(3)
Fe–C(21)–Co(2)	155.3(4)	Fe–C(5)–O(5)	144.1(4)
Co(1)–C(5)–O(5)	135.2(4)	Fe–C(5)–Co(1)	80.7(2)
C(1)–Co(1)–C(2)	102.7(4)	C(3)–Co(2)–C(4)	97.7(3)
C(3)–Co(2)–C(3′)	106.6(6)		

* Primes are used to indicate the symmetry operation *m* at $z = \frac{1}{4}$ (*i.e.* $x, y, z \longrightarrow x, y, \frac{1}{2} - z$).

plex scrambling of the ligands occurs, and it is difficult to formulate reaction pathways to these clusters. In contrast, a relatively straightforward reaction occurs between *trans*-[Fe_2(μ-C=CH_2)(μ-CO)(CO$)_2$(η-$C_5H_5$$)_2$] and [$Mn_3$($\mu$-H$)_3$-(CO$)_{12}$] [10] in refluxing benzene, which may be understood in terms of co-ordination of the Fe_2(μ-C=CH_2) system onto an unsaturated MnH(CO$)_4$ fragment,[11] followed by migration of the hydrogen onto the CH_2 carbon, carbon monoxide loss, and metal–metal bond formation (see Scheme). The structure of the resultant Fe_2Mn cluster (4) was established by analysis, mass, i.r., and n.m.r. spectroscopy.



(4)

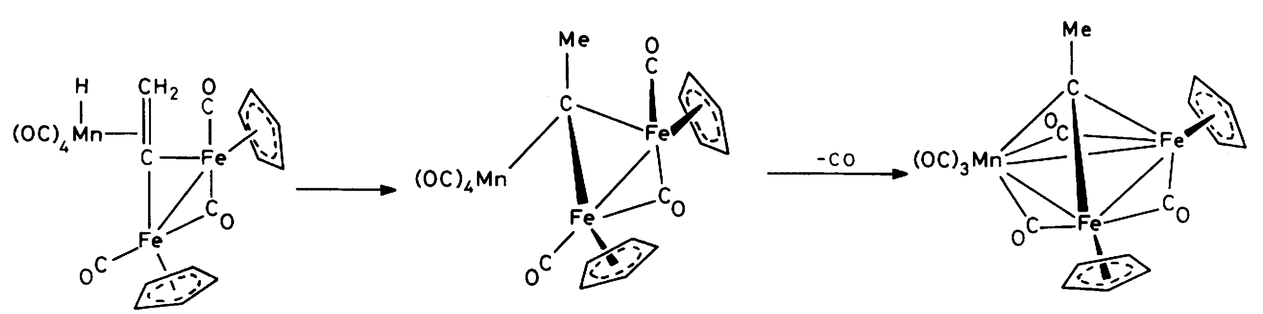
The ^{13}C-{^{1}H} spectrum exhibited a resonance at δ 350 p.p.m., which is assigned to the ligated μ_3-C carbon, and a resonance at δ 54 p.p.m. associated with the methyl group. As in the case of the related complexes described, in a fully coupled spectrum this signal appeared as a quartet, due to ^{1}H–^{13}C coupling. Signals were observed in the carbonyl region of the ^{13}C spectrum corresponding to two bridging and two terminal environments (see Experimental section).

Experimental

The n.m.r. measurements were made with JEOL PS-100, FX-90Q, and FX 200 instruments. Chemical shifts, δ (p.p.m.), are relative to $SiMe_4$ for the ^{1}H and ^{13}C-{^{1}H} spectra. A Perkin-Elmer 257 i.r. spectrometer was used to record i.r. spectra. Mass spectra for the measurement of molecular ions were recorded on an A.E.I. MS 902 instrument. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere. Chromatography was carried out on columns of alumina (Brockman Activity II) unless otherwise stated. Light petroleum refers to the fraction boiling in the range 40—60 °C.

Synthesis of the Complex [Fe_3(μ_3-CMe)(μ-CO$)_2$(CO$)_6$(η-C_5H_5)] (1).—Nonacarbonyldi-iron (0.207 g, 0.57 mmol) was added to a stirred diethyl ether (10 cm^3) solution of *trans*-[Fe_2(μ-C=CH_2)(μ-CO)(CO$)_2$(η-$C_5H_5$$)_2$] (0.20 g, 0.57 mmol). After 24 h at room temperature a further portion of [Fe_2-(CO$)_9$] (0.20 g, 0.57 mmol) was added. This procedure was repeated until a total of 4 mmol of [Fe_2(CO$)_9$] had been added. After the last addition, stirring was continued for a further 24 h, and the volatile material removed *in vacuo*. The solid was extracted with dichloromethane (4 × 20 cm^3), and the extract filtered through a Celite plug (1 × 4 cm). The solvent was removed to give a residue which was extracted with hot toluene (3 × 10 cm^3) and chromatographed (column 35 × 2.5 cm). Elution with toluene afforded a grey band which was collected. Recrystallisation of the residue, after solvent evaporation from thf (tetrahydrofuran)–light petroleum (1 : 3) afforded black *crystals* of [Fe_3(μ_3-CMe)(μ-CO$)_2$(CO$)_6$(η-C_5H_5)] (1) (0.06 g, 22%), m.p. 211 °C (Found: C, 37.2; H, 1.4. $C_{15}H_8Fe_3O_8$ requires C, 37.2; H, 1.6%); $\nu_{max.}$(CO) at 2 068s, 2 021vs, 2 013s, 1 981m, 1 871m, 1 859m, and 1 825w cm^{-1} (cyclohexane). N.m.r.: ^{1}H ([$^2H_6$]benzene), δ 4.02 (s, 5 H, C_5H_5), 4.58 (s, 3 H, Me); ^{13}C-{^{1}H} ([$^2H_6$]acetone), δ 332.7 (μ_3-*C*Me), 221.0 (CO), 95.4 (C_5H_5), and 52.2 p.p.m. [Me, quartet in coupled spectrum, *J*(CH) = 128 Hz]. Further elution with toluene gave [Fe_2(μ-CO$)_2$(CO$)_2$(η-$C_5H_5$$)_2$] and an unidentified red material.

Reaction of (1) *with Cyclopentadiene.*—A solution of (1) (0.065 g, 0.13 mmol) and cyclopentadiene (1 cm^3) in toluene



(4)

Scheme.

(15 cm^3) was stirred and heated under reflux for 4 h. The reaction mixture was applied directly to an alumina packed column (8 × 2.5 cm). Elution with toluene gave $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$. Further elution with thf gave a black band, which on recrystallisation from thf–diethyl ether (1 : 3) gave black *crystals* of $[Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3]$ (2) (0.023 g, 35%) (Found: C, 51.0; H, 3.9%; *M*, 474. $C_{20}H_{18}Fe_3O_3$ requires C, 50.6; H, 3.8%; *M*, 474); $\nu_{max.}$(CO) at 1 831s and 1 761m cm^{-1} (thf). N.m.r. ([$^2H_6$]acetone): ^1H, δ 4.58 (s, 15 H, C_5H_5), 6.22 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 364.5 (μ_3-*C*Me), 267.7 (μ-CO), 91.9 (C_5H_5), and 57.3 p.p.m. [Me, quartet in coupled spectrum, *J*(CH) = 127 Hz].

The Thermolysis of trans-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$.—A solution of *trans*-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ (0.10 g, 0.28 mmol) in di-n-butyl ether (20 cm^3) was heated (48 h) under reflux. The supernatant liquid was applied to an alumina packed column (35 × 2.5 cm). Elution with toluene afforded a red band containing starting material, $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5H_5)_2]$, all identified spectroscopically. The remaining solid was extracted with thf and the extract applied to the column. Elution with thf gave a black band. Removal of solvent and recrystallisation of the residue from thf–diethyl ether (1 : 3) afforded black crystals of (2) (0.045 g, 50%).

Synthesis of $[Co_3Fe(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)]$ (3).—(*a*) A solution of $[Co_2(CO)_8]$ (0.97 g, 2.84 mmol) and *trans*-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ (0.50 g, 1.42 mmol) in diethyl ether (25 cm^3) was stirred at room temperature for 40 h. Solvent was removed *in vacuo*, and the residue extracted with toluene (15 cm^3), and chromatographed (−20 °C, 30 × 2.5 cm). Elution with toluene gave $[CoFe(\mu\text{-}CO)_2(CO)_4(\eta\text{-}C_5H_5)]$ (0.125 g, 25%). Further elution afforded a black band, which was collected and recrystallised from diethyl ether to give black *crystals* of $[Co_3Fe(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)]$ (3) (0.45 g, 55%), m.p. 188 °C (Found: C, 33.6; H, 1.4%; *M*, 575. $C_{16}H_7Co_3FeO_9$ requires C, 33.4; H, 1.4%; *M*, 575); $\nu_{max.}$(CO) at 2 081s, 2 040vs, 2 003m, 1 994w, 1 851s, and 1 809w cm^{-1} (pentane). N.m.r.: ^1H ([$^2H_6$]acetone), δ 4.23 (s, 5 H, C_5H_5), 4.64 [s, 2 H, $C{=}CH_2$]; $^{13}C\text{-}\{^1H\}$ ([$^2H_6$]benzene–benzene), δ 304.3 (μ-*C*=CH_2), 212 (br, CO), 94.4 (C_5H_5), 63.0 (C=*C*H_2); $^{13}C\text{-}\{^1H\}$ ([$^2H_8$]toluene, −70 °C), δ 244.8 (μ-CO), 208.4 (CO), and 197.4 p.p.m. (CO).

(*b*) A solution of $[Co_4(CO)_{12}]$ (0.48 g, 0.85 mmol) and *trans*-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ (0.30 g, 0.85 mmol) in toluene (20 cm^3) was heated under reflux for 14 h. The volume of the solvent was reduced to 5 cm^3, and the solution chromatographed. Elution with toluene afforded a purple band containing (i.r.) traces of $[Co_3(\mu_3\text{-}CMe)(CO)_9]$. Further elution with toluene gave a black band, which was collected. Solvent was removed and the residue recrystallised from diethyl ether to give (3) (0.15 g, 31%).

Synthesis of $[Fe_2Mn(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5H_5)_2]$ (4).—A solution of $[Mn_3(\mu\text{-}H)_3(CO)_{12}]$ (0.095 g, 0.19 mmol)[5] and *trans*-$[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ (0.20 g, 0.57 mmol) in benzene (15 cm^3) was heated under reflux. At 15 min intervals, further portions of the manganese hydride were added up to a total of 0.67 g (1.3 mmol). When the addition was complete, the solution was refluxed for a further hour (total 3 h), and the volatile material removed *in vacuo*. The residue was extracted with toluene, and the combined extracts chromatographed. Elution with toluene afforded a band containing a mixture of $[Mn_2(CO)_{10}]$ and the iron starting material. Further elution gave a blue-black band which was collected and the solvent removed. Recrystallisation of the product from thf–light petroleum gave black *crystals* of $[Fe_2Mn(\mu_3\text{-}CMe)(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5H_5)_2]$ (4) (0.164 g, 60%), m.p. 180 °C (decomp.) (Found: C, 43.8; H, 3.0%; *M*, 492. $C_{18}H_{13}Fe_2MnO_6$ requires C, 43.9; H, 2.6%; *M*, 492); $\nu_{max.}$(CO) at 2 025s, 1 974s, 1 944s, 1 846s, 1 820s, and 1 790m cm^{-1} (cyclohexane). N.m.r. ([$^2H_6$]acetone): ^1H, δ 4.92 (s, 10 H, C_5H_5), 5.84 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$, δ 350.4 (μ_3-*C*Me), 263.1 (1 μ-CO), 253.6 (2 μ-CO), 223.8 (1 CO), 219.3 (2 CO), 93.8 (C_5H_5), and 53.8 p.p.m. [Me, quartet in coupled spectrum, *J*(CH) 127 Hz].

Thermolysis of (4).—A solution of (4) (0.08 g, 0.16 mmol) in toluene (20 cm^3) was heated under reflux for 55 h. The supernatant liquid was applied directly to an alumina packed column (4 × 2 cm). Elution with toluene afforded a brown band containing $[Fe_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (i.r. identified). The remaining solid was extracted with thf, and the extract applied to the column. Elution with thf gave a black band containing (2) (0.025 g, 49%), identified by i.r. and n.m.r. spectroscopy.

Crystal Structure Determinations.—(*a*) $[Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)]$ (1). Crystals of (1) grow as multi-faceted black spheroids from thf–light petroleum at 0 °C. Intensities were collected at 220 K from a crystal of dimensions 0.25 × 0.28 × 0.30 mm (Lindemann capillary) in the range $2.9 \leqslant 2\theta \leqslant 55°$ (θ—2θ scan) on a Nicolet $P2_1$ four-circle diffractometer. Of the total 3 418 independent intensities, 2 771 for which $I \geqslant 3.0\sigma(I)$ were used for the solution and refinement of the structure. Check reflections $1\,\bar{7}\,\bar{4}$ and $\bar{3}\,6\,\bar{2}$ were remeasured every 48 reflections and showed no significant decay over 97 h of exposure. Correction was made for Lorentz, polarisation, and *X*-ray absorption effects, the last by empirical correction based on an ellipsoidal model with 400 azimuthal scan data from six independent reflections.

Table 3. Atomic positional parameters (fractional co-ordinates) for $[Fe_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)]$ (1)

Atom	x	y	z
Fe(1)	0.432 44(4)	0.832 43(3)	0.149 89(2)
Fe(2)	0.188 24(4)	0.900 88(3)	0.196 49(2)
Fe(3)	0.190 10(4)	0.719 00(3)	0.122 09(2)
C(1)	0.483 4(3)	0.966 5(3)	0.117 6(2)
O(1)	0.515 3(3)	1.049 8(2)	0.094 23(15)
C(2)	0.562 8(4)	0.839 1(3)	0.257 3(2)
O(2)	0.644 0(3)	0.846 2(2)	0.323 93(14)
C(3)	0.543 1(4)	0.770 4(3)	0.081 7(3)
O(3)	0.612 9(4)	0.730 8(3)	0.037 9(2)
C(4)	−0.014 0(4)	0.914 7(3)	0.188 9(2)
O(4)	−0.144 0(3)	0.921 4(3)	0.183 1(2)
C(5)	0.284 2(4)	0.924 3(3)	0.309 3(2)
O(5)	0.345 2(3)	0.941 4(3)	0.378 95(14)
C(6)	0.200 0(4)	1.042 2(3)	0.165 4(2)
O(6)	0.202 2(3)	1.131 8(2)	0.145 4(2)
C(7)	0.389 5(4)	0.677 0(3)	0.183 0(2)
O(7)	0.459 6(3)	0.601 7(2)	0.217 41(15)
C(8)	0.163 5(4)	0.744 7(3)	0.234 6(2)
O(8)	0.136 9(3)	0.699 3(2)	0.294 40(14)
C(9)	0.226 1(3)	0.862 6(2)	0.083 6(2)
C(10)	0.173 9(4)	0.916 6(3)	−0.003 3(2)
C(11)	0.109 9(4)	0.555 5(3)	0.112 3(2)
C(12)	0.186 9(4)	0.577 3(3)	0.045 7(2)
C(13)	0.108 5(4)	0.662 1(3)	−0.007 0(2)
C(14)	−0.016 9(4)	0.694 8(3)	0.026 6(2)
C(15)	−0.016 4(4)	0.629 3(3)	0.100 1(2)

Crystal data for (1). $C_{15}H_8Fe_3O_8$, $M = 483.4$, Monoclinic, $a = 8.943(4)$, $b = 12.156(4)$, $c = 15.904(8)$ Å, $\beta = 103.57(4)°$, $U = 1\,681(2)$ Å^3, $Z = 4$, $D_c = 1.91$ g cm^{-3}, $F(000) = 960$, space group $P2_1/c$ (no. 14), Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 26.0 cm^{-1}.

(*b*) $[Co_3Fe(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)]$ (3). Crystals of (3) grow as black hexagonal plates, elongated along *a*, from diethyl ether at −20 °C. Intensities were collected as for (1) except: crystal dimensions 0.48 × 0.33 × 0.13 mm, $2\theta \leqslant 60°$, check reflections 1 3 6 and 0 3 $\bar{2}$, X-ray exposure 81 h, total independent intensities 2 884, those with $I \geqslant 2.0\sigma(I) = 1\,772$, absorption correction from 400 azimuthal scan data from five independent reflections.

Crystal data for (3). $C_{16}H_7Co_3FeO_9$, $M = 575.6$, Orthorhombic, $a = 18.135(16)$, $b = 8.194(9)$, $c = 12.711(10)$ Å, $U = 1\,889(3)$ Å^3, $Z = 4$, $D_c = 2.03$ g cm^{-3}, $F(000) = 1\,128$, space group *Pcam* (non-standard setting of *Pbcm*, no. 57), μ(Mo-K_α) = 33.9 cm^{-1}.

Structure solution and refinement for (1) *and* (3). Both structures were solved by heavy-atom methods and refined by blocked-cascade least squares, with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the methyl group in (1) and of the vinylidene ligand in (3) were refined isotropically. All cyclopentadienyl hydrogen atoms were refined in the ' riding ' mode with a common isotropic thermal parameter. Weights were applied according to the scheme $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$ with $g = 0.000\,10$ for (1) and 0.000 82 for (3). Scattering factors and corrections for anomalous dispersion were from ref. 12. Refinement converged at $R = 0.026$ ($R' = 0.026$) for (1), $R = 0.054$ ($R' = 0.054$) for (3). All calculations were carried out within the laboratory on an ' Eclipse ' Data General Minicomputer with the ' SHELXTL ' system of programs.[13] Atomic positional parameters for (1) are in Table 3, and for (3) in Table 4.

Table 4. Atomic positional parameters (fractional co-ordinates) for $[Co_3Fe(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)_2(CO)_7(\eta\text{-}C_5H_5)]$ (3)

Atom	x	y	z
Co(1)	0.112 66(4)	0.718 06(9)	0.153 39(6)
Co(2)	0.155 81(6)	0.978 18(13)	0.250 00 *
Fe	−0.003 82(5)	0.654 29(13)	0.250 00
C(21)	0.056 8(4)	0.848 3(10)	0.250 00
C(22)	0.042 4(6)	1.020 0(12)	0.250 00
C(1)	0.192 5(4)	0.594 6(11)	0.130 9(7)
O(1)	0.242 0(4)	0.515 0(11)	0.117 5(7)
C(2)	0.095 0(5)	0.801 5(11)	0.027 5(7)
O(2)	0.085 6(5)	0.856 7(18)	−0.053 7(5)
C(3)	0.171 2(4)	1.106 0(10)	0.135 7(9)
O(3)	0.179 6(4)	1.183 2(9)	0.064 0(8)
C(4)	0.243 2(6)	0.876 1(11)	0.250 00
O(4)	0.301 9(4)	0.826 2(9)	0.250 00
C(5)	0.046 1(3)	0.527 8(7)	0.148 7(4)
O(5)	0.044 4(3)	0.405 6(6)	0.101 5(4)
C(11)	−0.099 0(5)	0.515 0(12)	0.250 00
C(12)	−0.099 4(3)	0.615 8(10)	0.161 7(5)
C(13)	−0.100 1(3)	0.776 6(9)	0.196 5(7)

* Atoms lying in the mirror plane have a fixed *z* co-ordinate (0.25).

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