Crystal Structure and Stereochemical Non-rigidity of Octacarbonyl-(η-1,3-dimethyl-2-vinylcyclopentadienyl)-μ_3-propylidyne-*triangulo*-tri-iron

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The title compound has been obtained by treating $[Fe_3(CO)_{12}]$ with methylacetylene and is characterized by i.r., mass, ^1H, and ^{13}C n.m.r. spectra. The crystal structure has been determined by *X*-ray methods. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$, in a unit cell of dimensions $a = 7.584(7)$, $b = 15.851(9)$, $c = 18.535(11)$ Å, and $\beta = 103.3(1)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least squares to R 0.032 for 3145 observed reflections. The molecule is formed by a Fe_3C cluster very similar to the Co_3C core in $[Co_3(CY)(CO)_9]$ (Y = alkyl, aryl, or other group). Trimerization of the alkyne leads to the formation of a cyclopentadienyl unit (bearing one vinyl and two methyl groups) η-bonded to one iron atom. Of the eight carbonyls co-ordinated to the iron atoms, six are terminal and two are bridging the shortest sides of the cluster. Variable-temperature ^{13}C n.m.r. spectra show that a two-stage exchange process occurs.

IN the reaction of $[Fe_3(CO)_{12}]$ and methylacetylene several tri- and bi-nuclear acetylenic carbonyl compounds are formed;[1] we have isolated two novel tri-nuclear compounds, one of which, $[Fe_3(HC_2Me)_3(CO)_8]$, has been recently studied in detail.[2] We now report the *X*-ray structure determination, and the ^1H and ^{13}C n.m.r. spectra, of the second compound which was first formulated as $[Fe_3(HC_2Me)_4(CO)_8]$, and after the structural analysis as $[Fe_3(CEt)\{C_5H_2Me_2(C_2H_3)\}(CO)_8]$. This compound is characterized by an $Fe_3(CEt)$ unit, similar to those found in the clusters $[Co_3(CY)(CO)_9]$ (Y = alkyl, aryl, or other group).[3] So far, the only compounds of the iron triad showing a similar M_3C core are the hydrides $[M_3(CMe)(CO)_9H_3]$ (M = Ru or Os),[4] which were obtained from ethylene. Thus the title compound is the first M_3C cluster obtained from acetylenes, and this may provide a new preparative route for this sort of compound.

EXPERIMENTAL

Preparation of the Compound $[Fe_3(CEt)\{C_5H_2Me_2(C_2H_3)\}(CO)_8]$.—The compound was obtained from the reaction between $[Fe_3(CO)_{12}]$ and gaseous methylacetylene [2] in very low yield; the methylacetylene was purchased from Merck-Schuchardt and contained trace amounts of acetylene and 0.5% of allene. G.l.c. analyses of the gas from the bottle and of the effluent from the reaction vessel showed no significant variations in the allene content. Separation from the reaction mixture by t.l.c. (preparative plates, Kieselgel P.F., diethyl ether–light petroleum eluant) did not afford the pure compound; the impure specimens were crystallized from dry n-heptane, and the crystals obtained were further dissolved in and recrystallized from n-heptane. Black-violet prismatic crystals were finally obtained (Found: C, 42.95; H, 3.10; Fe, 31.05; O, 23.1. Calc. for $C_{20}H_{16}Fe_3O_8$: C, 43.5; H, 2.90; Fe, 30.35; O, 23.2%), *M* 551.85.

Physical Measurements.—I.r. spectra were recorded on a Beckmann IR-12 (KBr optics), mass spectra on an Hitachi-Perkin-Elmer RMU-6H, ^1H n.m.r. spectra on a Jeol JNM–C 60–HL, and ^{13}C n.m.r. spectra on a Jeol-PS 100–FT instrument operating at 25.1 MHz in the Fourier-transform mode. The chemical shifts are reported as downfield positive with respect to internal tetramethylsilane. Carbon tetrachloride solution was sealed *in vacuo* in 5-mm tubes for ^1H n.m.r. spectra; $CDCl_3$ and CD_2Cl_2 solutions together with 0.05 mol dm^{-3} $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) as inert relaxation agent were sealed *in vacuo* in 10-mm tubes for ^{13}C n.m.r. spectra. Deuteriated solvents were purchased from NMR Ltd. and used directly after drying over molecular sieves.

Crystal Data.—$C_{20}H_{16}Fe_3O_8$, $M = 551.85$, Monoclinic, $a = 7.584(7)$, $b = 15.851(9)$, $c = 18.535(11)$ Å, $\beta = 103.3(1)°$, $U = 2\,168.5$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 1\,112$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 20.75 cm^{-1}, space group $P2_1/c$ from systematic absences.

The unit-cell dimensions, determined from rotation and Weissenberg photographs, were refined by a least-squares procedure applied to the diffractometer measurement of 16 reflections.

Intensity Data.—Intensity data were collected on a Siemens AED single-crystal diffractometer by use of Zirconium-filtered Mo-K_α radiation and the ω—2θ scan technique. A prismatic crystal of dimensions *ca.* 0.40 × 0.25 × 0.40 mm was aligned with its *c* axis along the ϕ axis of the diffractometer and all the reflections with $2\theta < 50°$ were measured. Of 3 806 independent reflections, 3 145 having $I > 2\sigma(I)$ were considered observed and used in the analysis. The intensity data were corrected for Lorentz and polarization factors, but no correction was applied for absorption effects because of the low value of μR. The absolute scale was determined first by Wilson's method and then by correlating observed and calculated values.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares, first with isotropic and then with anisotropic thermal parameters. The vinyl group was disordered with the terminal carbon atom distributed in two positions of almost equivalent occupancy. All the hydrogen atoms except those of the vinyl group were located directly

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from a difference synthesis calculated after several cycles of least squares. Further least-squares cycles were then computed including these hydrogen atoms and the two statistical carbon atoms of the vinyl group with isotropic thermal parameters. Unit weights were chosen at each stage of the refinement after analyzing the variation of $|\Delta F|$ with respect to $|F|$. The final R was 0.032. Atomic scattering factors for non-hydrogen atoms were taken from ref. 5 and for hydrogen atoms from ref. 6. Final atomic co-ordinates and thermal parameters are given in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21859 (20 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$ for Fe, O, and C atoms; $\times 10^3$ for H atoms) with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
Fe(1)	3 184(1)	744(1)	1 319(1)
Fe(2)	4 539(1)	1 660(1)	2 422(1)
Fe(3)	5 211(1)	2 019(1)	1 191(1)
O(1)	8 325(4)	1 494(2)	2 405(2)
O(2)	7 007(6)	3 646(2)	1 509(3)
O(3)	7 696(4)	1 048(2)	503(2)
O(4)	2 998(5)	2 651(3)	−205(2)
O(5)	5 416(4)	−596(2)	864(2)
O(6)	931(4)	933(2)	−180(2)
O(7)	268(4)	−143(2)	1 804(2)
O(8)	5 352(4)	−119(2)	2 665(2)
C(1)	6 790(5)	1 633(3)	2 155(2)
C(2)	6 302(6)	3 016(3)	1 380(3)
C(3)	6 747(5)	1 417(3)	778(2)
C(4)	3 867(6)	2 387(3)	338(3)
C(5)	4 546(5)	−84(2)	1 042(2)
C(6)	1 819(5)	863(3)	405(2)
C(7)	1 379(5)	202(2)	1 611(2)
C(8)	4 746(5)	487(2)	2 341(2)
C(9)	5 823(6)	2 407(3)	3 362(2)
C(10)	4 171(6)	2 779(3)	2 983(2)
C(11)	2 742(6)	2 223(3)	3 000(2)
C(12)	3 498(6)	1 481(2)	3 379(2)
C(13)	5 416(6)	1 596(3)	3 608(2)
C(14)	6 705(8)	997(4)	4 044(3)
C(15) *	7 912(17)	1 068(8)	4 598(7)
C(15′) *	6 798(25)	535(12)	4 551(10)
C(16)	2 396(7)	754(3)	3 560(3)
C(17)	7 651(7)	2 837(4)	3 525(3)
C(18)	2 901(5)	1 934(2)	1 505(2)
C(19)	1 224(5)	2 474(2)	1 288(2)
C(20)	1 474(7)	3 432(3)	1 374(3)
H(10)	394(5)	334(2)	272(2)
H(11)	133(5)	233(2)	275(2)
H(161)	324(5)	30(2)	368(2)
H(162)	212(5)	83(3)	401(2)
H(163)	120(5)	65(2)	316(2)
H(171)	795(5)	314(2)	403(2)
H(172)	866(5)	246(3)	351(2)
H(173)	755(5)	324(2)	311(2)
H(191)	64(4)	232(2)	75(2)
H(192)	32(4)	226(2)	158(2)
H(201)	33(5)	371(2)	113(2)
H(202)	160(5)	354(2)	194(2)
H(203)	230(5)	364(3)	119(2)

* C(15) and C(15′) are distributed in two statistical positions: the population parameters are 0.6 for C(15) and 0.4 for C(15′).

All the calculations were performed on a CDC 6600 computer at the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, with programs written by Immirzi.[7]

RESULTS AND DISCUSSION

I.r. Spectrum.—The compound showed CO-stretching absorptions (in CCl_4 solution) at 2 065vs, 2 020vs, 2 010vs (sh), 1 976s, 1 965s, 1 865s, and 1 818m cm^{-1}; the last two bands are assigned to the bridging carbonyls.

Mass Spectrum.—The cluster appears to be quite stable (68% of trimetallic fragments) and showed the molecular ion and peaks corresponding to the loss of eight CO groups; ions $[Fe_3(C_{12}H_{14})(CO)_n]^+$ and $[Fe_3(C_{12}H_{14})(CO)_n]^{2+}$ (n = 0—2), due to loss of H_2 before the last two CO, were also observed. The ions $[Fe_2(C_{12}H_{16})(CO)_2]^+$, $[Fe_2(C_{12}H_{16})(CO)]^+$, $[Fe_m(C_9H_n)]^+$ (m = 1—3; n = 8—10), and $[C_9H_{12}]^+$ also appeared; no $[Fe_3C]^+$ ion was detected, while in the mass spectra of $[Co_3(CY)(CO)_9]$ the analogous $[Co_3C]^+$ was observed.[8]

X-*Ray Structure.*—The structure of the compound is represented in Figure 1; bond distances and angles in the molecule are in Table 3. The structure consists of a trinuclear cluster of iron atoms bound to eight carbonyls, a triply bridging CEt group, and a substituted cyclopentadienyl group (derived from trimerization of the alkyne, and η-bonded to one of the iron atoms). Six of the carbonyl groups are terminal [three attached to Fe(1), three to Fe(3)] and two are bridging [one between Fe(1) and Fe(2), the other between Fe(3) and Fe(2)]. These bridges are almost symmetrical as shown by the Fe(2)–C(8), Fe(1)–C(8) (1.875 and 2.031 Å) and Fe(2)–C(1), Fe(3)–C(1) (1.884 and 2.004 Å) bond distances. The iron atoms are at the corners of an isosceles triangle and the compound as a whole shows only small departures from m symmetry (Figure 2).

The Fe–Fe bond distances (2.515, 2.525, and 2.583 Å) are at the lower end of the range of values reported for other acetylenic carbonyliron compounds,[9] and this is expected on the grounds of the presence of the CO bridges (the shortest distances are those bridged by CO) and of the triply bridging CEt group, in analogy with the Co–Co distances observed in the binuclear cobalt acetylenic compounds[10] and in $[Co_3(CY)(CO)_9]$[3,10] respectively.

The title compound is the first case of an iron derivative in which an Fe_3C cluster is present and it is comparable with the M_3C core in $[Co_3(CY)(CO)_9]$ and $[M_3(CMe)(CO)_9H_3]$ (M = Ru or Os). The values for the angles Fe–C(18)–Fe (80.7, 82.0, and 82.6°) are in good agreement with the value (86°) found for $[Ru_3(CMe)(CO)_9H_3]$ and quite close to the mean value (81°) found for Co–C–Co in $[Co_3(CY)(CO)_9]$.[3] These values are only slightly larger than those found for the M–C–M angles (mean

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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TABLE 2

Thermal parameters (Å²) with estimated standard deviations in parentheses*

	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	3.33(2)	2.62(2)	2.63(2)	−0.08(2)	0.87(2)	−0.42(2)
Fe(2)	3.07(2)	2.42(2)	2.68(2)	−0.07(2)	0.90(2)	−0.41(2)
Fe(3)	3.28(2)	3.26(2)	3.54(2)	−0.07(2)	1.49(2)	0.34(2)
O(1)	3.16(12)	6.89(18)	5.38(15)	0.51(12)	0.87(11)	−0.31(13)
O(2)	9.30(26)	3.85(16)	14.79(35)	−1.78(17)	6.02(25)	−1.39(19)
O(3)	4.88(15)	7.63(21)	6.76(18)	−0.11(14)	2.88(14)	−2.50(16)
O(4)	7.84(23)	12.04(32)	6.14(20)	0.54(22)	1.70(17)	4.98(21)
O(5)	6.83(18)	4.60(15)	5.67(16)	1.58(13)	2.51(14)	−0.85(13)
O(6)	5.53(16)	7.30(19)	3.51(13)	0.73(14)	0.21(11)	−0.50(13)
O(7)	5.51(16)	5.89(17)	6.61(18)	−1.97(14)	2.78(14)	−0.47(14)
O(8)	7.60(19)	3.18(12)	4.09(13)	1.28(12)	0.58(13)	0.20(10)
C(1)	3.47(16)	3.75(18)	4.04(17)	0.02(14)	1.01(14)	−0.61(15)
C(2)	5.20(23)	3.53(19)	7.68(28)	−0.02(17)	3.44(21)	0.15(19)
C(3)	3.83(18)	4.75(21)	4.26(19)	−0.71(16)	1.24(15)	−0.54(16)
C(4)	5.24(23)	6.57(27)	4.92(22)	−0.50(20)	2.27(19)	1.83(20)
C(5)	4.71(19)	3.34(17)	3.30(16)	−0.07(14)	1.07(15)	−0.26(13)
C(6)	4.04(18)	3.92(18)	3.57(17)	0.14(14)	1.03(14)	−0.62(14)
C(7)	4.34(19)	3.53(17)	3.78(18)	−0.13(15)	1.04(15)	−0.74(14)
C(8)	4.39(18)	2.90(15)	3.06(16)	0.17(13)	0.76(13)	−0.31(13)
C(9)	4.84(21)	4.50(21)	4.01(18)	−0.84(16)	1.06(16)	−2.03(16)
C(10)	5.96(23)	3.14(18)	4.07(18)	0.15(16)	1.65(17)	−1.12(15)
C(11)	4.75(20)	3.92(18)	3.59(17)	0.54(15)	1.72(15)	−1.11(14)
C(12)	5.26(20)	3.78(18)	2.70(15)	−0.29(15)	1.66(14)	−0.81(13)
C(13)	4.77(20)	4.59(20)	2.57(15)	0.45(16)	0.71(14)	−0.87(14)
C(14)	8.91(35)	8.65(36)	3.25(20)	3.44(29)	-0.67(21)	−0.83(22)
C(16)	7.62(29)	4.80(22)	4.77(22)	−1.10(21)	3.17(21)	−0.10(18)
C(17)	6.10(27)	7.88(34)	7.00(30)	−2.77(25)	1.68(23)	−3.34(26)
C(18)	3.31(15)	2.96(15)	2.96(15)	−0.30(12)	0.99(12)	0.00(12)
C(19)	3.31(16)	3.26(17)	4.46(19)	0.44(13)	0.97(14)	0.16(14)
C(20)	5.15(24)	3.54(20)	8.76(32)	0.93(18)	0.64(22)	0.50(20)
C(15)	9.8(3)					
C(15′)	9.8(5)					
H(10)	4.7(9)					
H(11)	4.9(9)					
H(161)	5.5(9)					
H(162)	6.0(10)					
H(163)	5.6(9)					
H(171)	5.6(9)					
H(172)	6.5(1.0)					
H(173)	5.8(1.0)					
H(191)	2.9(7)					
H(192)	3.7(8)					
H(201)	5.6(9)					
H(202)	6.0(1.0)					
H(203)	6.0(1.0)					

* Anisotropic thermal parameters in the form exp[$-0.25(h^2a^{*2}B_{11} + \ldots + 2klb^*c^*B_{23})$].

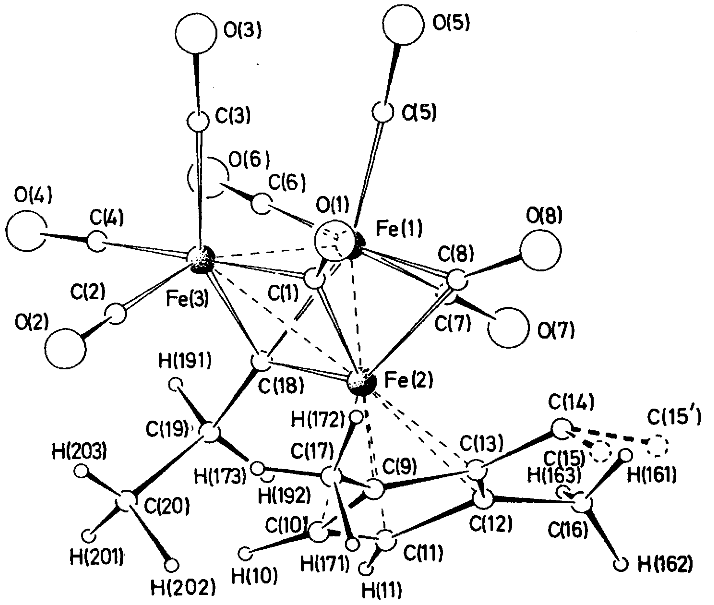

FIGURE 1 View showing the molecular shape and the atomic numbering

TABLE 3

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*i*) In the co-ordination sphere of the iron atoms

Fe(1)–Fe(2)	2.525(3)	Fe(2)–C(10)	2.107(5)
Fe(1)–Fe(3)	2.583(2)	Fe(2)–C(11)	2.115(5)
Fe(2)–Fe(3)	2.515(3)	Fe(2)–C(12)	2.120(5)
Fe(1)–C(5)	1.816(4)	Fe(2)–C(13)	2.148(4)
Fe(1)–C(6)	1.781(4)	Fe(2)–C(18)	1.910(4)
Fe(1)–C(7)	1.802(4)	Fe(3)–C(1)	2.004(4)
Fe(1)–C(8)	2.031(4)	Fe(3)–C(2)	1.781(5)
Fe(1)–C(18)	1.938(4)	Fe(3)–C(3)	1.807(5)
Fe(2)–C(1)	1.884(5)	Fe(3)–C(4)	1.771(5)
Fe(2)–C(8)	1.875(4)	Fe(3)–C(18)	1.974(5)
Fe(2)–C(9)	2.146(5)		
Fe(2)–Fe(1)–Fe(3)	59.0(1)	C(8)–Fe(2)–Fe(1)	52.5(1)
Fe(2)–Fe(1)–C(5)	119.5(1)	C(9)–Fe(2)–C(10)	38.9(2)
Fe(2)–Fe(1)–C(6)	138.5(2)	C(9)–Fe(2)–C(11)	65.2(2)
Fe(2)–Fe(1)–C(7)	103.1(1)	C(9)–Fe(2)–C(12)	65.2(2)
Fe(2)–Fe(1)–C(8)	47.1(1)	C(9)–Fe(2)–C(13)	38.7(2)
Fe(2)–Fe(1)–C(18)	48.5(1)	C(9)–Fe(2)–C(18)	132.7(2)
Fe(3)–Fe(1)–C(5)	98.6(1)	C(9)–Fe(2)–Fe(1)	177.0(1)
Fe(3)–Fe(1)–C(6)	93.3(2)	C(10)–Fe(2)–C(11)	38.8(2)
Fe(3)–Fe(1)–C(7)	155.5(1)	C(10)–Fe(2)–C(12)	65.3(2)
Fe(3)–Fe(1)–C(8)	90.6(1)	C(10)–Fe(2)–C(13)	65.1(2)
Fe(3)–Fe(1)–C(18)	49.3(1)	C(10)–Fe(2)–C(18)	96.6(2)
C(5)–Fe(1)–C(6)	93.0(2)	C(10)–Fe(2)–Fe(1)	143.9(1)
C(5)–Fe(1)–C(7)	105.1(2)	C(11)–Fe(2)–C(12)	39.2(2)
C(5)–Fe(1)–C(8)	82.6(2)	C(11)–Fe(2)–C(13)	65.5(2)
C(5)–Fe(1)–C(18)	147.9(2)	C(11)–Fe(2)–C(18)	89.5(2)
C(6)–Fe(1)–C(7)	91.2(2)	C(11)–Fe(2)–Fe(1)	117.6(1)
C(6)–Fe(1)–C(8)	174.5(2)	C(12)–Fe(2)–C(13)	39.2(2)
C(6)–Fe(1)–C(18)	90.1(2)	C(12)–Fe(2)–C(18)	118.9(2)
C(7)–Fe(1)–C(8)	86.8(2)	C(12)–Fe(2)–Fe(1)	116.1(1)
C(7)–Fe(1)–C(18)	106.7(2)	C(13)–Fe(2)–C(18)	155.0(2)
C(8)–Fe(1)–C(18)	95.4(2)	C(13)–Fe(2)–Fe(1)	140.7(2)
Fe(3)–Fe(2)–C(1)	51.8(1)	C(18)–Fe(2)–Fe(1)	49.5(1)
Fe(3)–Fe(2)–C(8)	96.5(1)	C(1)–Fe(3)–C(2)	86.6(2)
Fe(3)–Fe(2)–C(9)	117.6(1)	C(1)–Fe(3)–C(3)	84.6(2)
Fe(3)–Fe(2)–C(10)	109.6(1)	C(1)–Fe(2)–C(4)	178.1(2)
Fe(3)–Fe(2)–C(11)	130.8(1)	C(1)–Fe(3)–C(18)	96.0(2)
Fe(3)–Fe(2)–C(12)	169.0(1)	C(1)–Fe(3)–Fe(1)	85.7(1)
Fe(3)–Fe(2)–C(13)	149.3(1)	C(1)–Fe(3)–Fe(2)	47.6(1)
Fe(3)–Fe(2)–C(18)	50.8(1)	C(2)–Fe(3)–C(3)	103.7(2)
Fe(3)–Fe(2)–Fe(1)	61.7(1)	C(2)–Fe(3)–C(4)	91.7(2)
C(1)–Fe(2)–C(8)	81.9(2)	C(2)–Fe(3)–C(18)	114.0(2)
C(1)–Fe(2)–C(9)	87.5(2)	C(2)–Fe(3)–Fe(1)	159.3(2)
C(1)–Fe(2)–C(10)	112.3(2)	C(2)–Fe(3)–Fe(2)	101.8(2)
C(1)–Fe(2)–C(11)	150.6(2)	C(3)–Fe(3)–C(4)	95.2(2)
C(1)–Fe(2)–C(12)	138.7(2)	C(3)–Fe(3)–C(18)	142.3(2)
C(1)–Fe(2)–C(13)	100.5(2)	C(3)–Fe(3)–Fe(1)	94.6(2)
C(1)–Fe(2)–C(18)	102.4(2)	C(3)–Fe(3)–Fe(2)	123.4(2)
C(1)–Fe(2)–Fe(1)	89.9(1)	C(4)–Fe(3)–C(18)	85.3(2)
C(8)–Fe(2)–C(9)	125.6(2)	C(4)–Fe(3)–Fe(1)	96.2(2)
C(8)–Fe(2)–C(10)	153.8(2)	C(4)–Fe(3)–Fe(2)	133.6(2)
C(8)–Fe(2)–C(11)	122.3(2)	C(18)–Fe(3)–Fe(1)	48.1(1)
C(8)–Fe(2)–C(12)	89.3(2)	C(18)–Fe(3)–Fe(2)	48.6(1)
C(8)–Fe(2)–C(13)	91.3(2)	Fe(1)–Fe(3)–Fe(2)	59.4(1)
C(8)–Fe(2)–C(18)	101.7(2)		

(*ii*) In the carbonyl groups

O(1)–C(1)	1.171(5)	O(5)–C(5)	1.142(5)
O(2)–C(2)	1.132(6)	O(6)–C(6)	1.143(5)
O(3)–C(3)	1.135(6)	O(7)–C(7)	1.129(5)
O(4)–C(4)	1.148(6)	O(8)–C(8)	1.169(5)
Fe(2)–C(1)–Fe(3)	80.5(2)	Fe(1)–C(5)–O(5)	179.0(3)
Fe(2)–C(1)–O(1)	141.2(3)	Fe(1)–C(6)–O(6)	179.3(4)
Fe(3)–C(1)–O(1)	138.3(3)	Fe(1)–C(7)–O(7)	178.8(4)
Fe(3)–C(2)–O(2)	179.1(5)	Fe(1)–C(8)–Fe(2)	80.5(2)
Fe(3)–C(3)–O(3)	178.4(4)	Fe(1)–C(8)–O(8)	136.0(3)
Fe(3)–C(4)–O(4)	177.8(5)	Fe(2)–C(8)–O(8)	143.5(3)

(*iii*) In the organic ligands

C(9)–C(10)	1.416(6)	C(11)–H(11)	1.08(4)
C(9)–C(13)	1.421(7)	C(16)–H(161)	0.95(3)
C(9)–C(17)	1.512(7)	C(16)–H(162)	0.91(4)
C(10)–C(11)	1.403(7)	C(16)–H(163)	1.04(3)
C(11)–C(12)	1.421(6)	C(17)–H(171)	1.03(4)
C(12)–C(13)	1.430(6)	C(17)–H(172)	0.98(4)

TABLE 3 (*Continued*)

C(12)–C(16)	1.506(7)	C(17)–H(173)	0.99(4)
C(13)–C(14)	1.465(7)	C(19)–H(191)	1.02(3)
C(14)–C(15)	1.214(13)	C(19)–H(192)	1.02(4)
C(14)–C(15′)	1.181(20)	C(20)–H(201)	0.99(3)
C(18)–C(19)	1.509(5)	C(20)–H(202)	1.05(4)
C(19)–C(20)	1.534(5)	C(20)–H(203)	0.85(4)
C(10)–H(10)	1.01(3)		
Fe(2)–C(1)–Fe(3)	80.5(2)	C(15)–C(14)–C(13)	133.2(8)
Fe(2)–C(1)–O(1)	141.2(3)	C(15′)–C(14)–C(13)	138.7(11)
Fe(3)–C(1)–O(1)	138.3(3)	C(19)–C(18)–Fe(1)	128.7(3)
Fe(3)–C(2)–O(2)	179.1(5)	C(19)–C(18)–Fe(2)	134.6(3)
Fe(3)–C(3)–O(3)	178.4(4)	C(19)–C(18)–Fe(3)	129.3(3)
Fe(3)–C(4)–O(4)	177.8(5)	Fe(1)–C(18)–Fe(2)	82.0(2)
Fe(1)–C(5)–O(5)	179.0(3)	Fe(1)–C(18)–Fe(3)	82.6(2)
Fe(1)–C(6)–O(6)	179.3(4)	Fe(2)–C(18)–Fe(3)	80.7(2)
Fe(1)–C(7)–O(7)	178.8(4)	C(20)–C(19)–C(18)	117.2(3)
Fe(1)–C(8)–Fe(2)	80.5(1)	C(11)–C(10)–H(10)	121(2)
Fe(1)–C(8)–O(8)	136.0(3)	H(10)–C(10)–C(9)	130(2)
Fe(2)–C(8)–O(8)	143.5(3)	H(11)–C(11)–C(10)	126(2)
C(10)–C(9)–C(13)	107.6(4)	C(12)–C(11)–H(11)	126(2)
C(10)–C(9)–C(17)	125.3(4)	H(161)–C(16)–H(162)	100(3)
C(10)–C(9)–Fe(2)	69.1(2)	H(161)–C(16)–H(163)	118(3)
C(13)–C(9)–C(17)	126.9(4)	H(162)–C(16)–H(163)	109(3)
C(13)–C(9)–Fe(2)	70.7(2)	H(163)–C(16)–C(12)	113(2)
C(17)–C(9)–Fe(2)	129.4(3)	H(161)–C(16)–C(12)	105(2)
C(11)–C(10)–Fe(2)	70.9(3)	H(162)–C(16)–C(12)	111(2)
C(11)–C(10)–C(9)	109.1(4)	H(171)–C(17)–H(172)	108(3)
Fe(2)–C(10)–C(9)	72.0(3)	H(171)–C(17)–H(173)	112(3)
Fe(2)–C(11)–C(10)	70.3(3)	H(171)–C(17)–C(9)	113(2)
C(12)–C(11)–Fe(2)	70.6(3)	H(172)–C(17)–H(173)	107(3)
C(12)–C(11)–C(10)	107.8(4)	H(172)–C(17)–C(9)	114(3)
Fe(2)–C(11)–C(10)	70.3(3)	H(173)–C(17)–C(9)	103(2)
C(13)–C(12)–C(16)	127.6(4)	H(191)–C(19)–C(18)	106(2)
C(13)–C(12)–Fe(2)	71.5(2)	H(191)–C(19)–H(192)	104(3)
C(13)–C(12)–C(11)	108.0(4)	H(192)–C(19)–C(18)	107(2)
C(16)–C(12)–Fe(2)	128.4(3)	C(20)–C(19)–H(191)	111(2)
C(16)–C(12)–C(11)	124.2(4)	C(20)–C(19)–H(192)	111(2)
Fe(2)–C(12)–C(11)	70.2(2)	H(201)–C(20)–H(202)	105(3)
C(14)–C(13)–Fe(2)	127.3(3)	H(201)–C(20)–H(203)	107(3)
C(14)–C(13)–C(9)	126.6(4)	H(202)–C(20)–H(203)	116(3)
C(14)–C(13)–C(12)	125.8(4)	H(201)–C(20)–C(19)	109(2)
Fe(2)–C(13)–C(9)	70.6(2)	H(202)–C(20)–C(19)	104(2)
Fe(2)–C(13)–C(12)	69.4(2)	H(203)–C(20)–C(19)	115(2)
C(9)–C(13)–C(12)	107.5(4)		

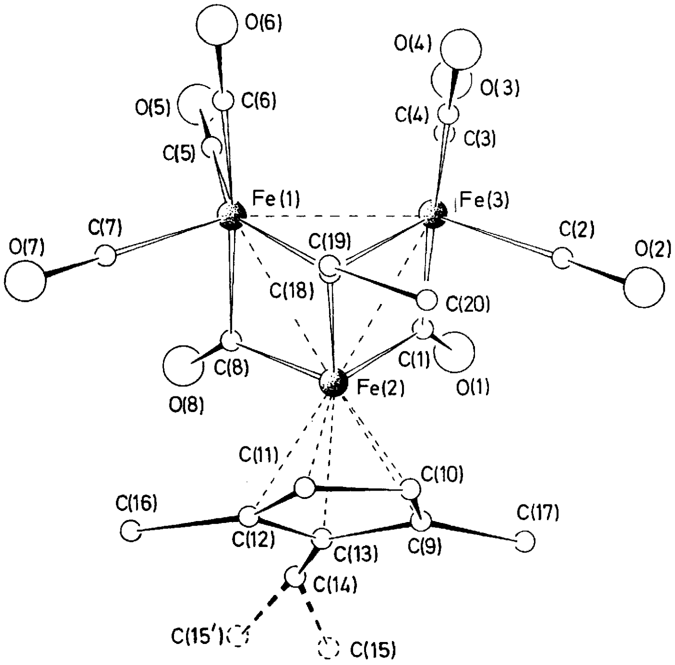

FIGURE 2 Projection of the structure on the plane of the iron cluster showing the approximate *m* symmetry of the compound

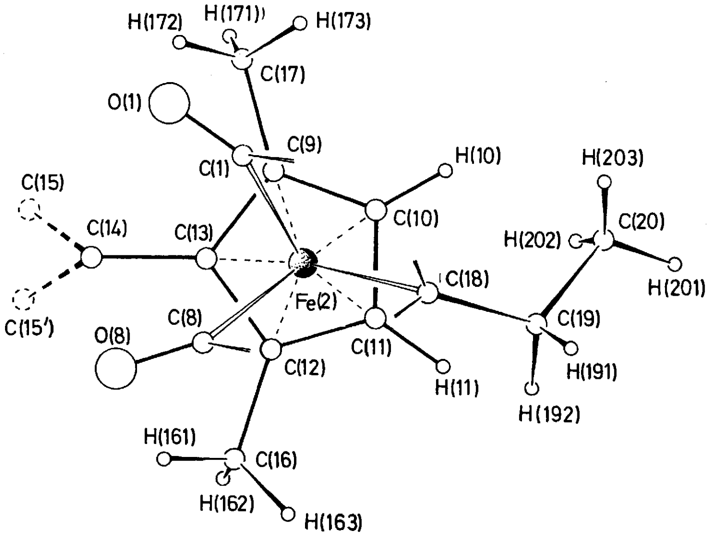

FIGURE 3 Projection of a part of the structure on the cyclopentadienyl plane showing that the two statistically distributed carbons C(15) and C(15') have similar environments

value 78°) when there is a triply bridging CO,[9a,11] but are much smaller than that (109.5°) expected if the triply bridging carbon were in an sp^3 hybridized state. The distortion from the tetrahedral environment for C(18) is essentially determined by the reduced possibility of approach to the iron cluster. Thus the Fe–C(18)–C(19) angles are severely distorted from the tetrahedral value; in particular, they are much larger (128.7, 129.3, and 134.6°) as C(18) cannot approach close to the iron atoms, the observed distances (1.910, 1.938, and 1.974 Å) being shorter than the Fe–C σ bonds found in cases where the sp^3 carbon is not bridging [2.098[12] and 2.123 Å (ref. 13)]. It seems that the situation found in the present compound is a result of a compromise between steric hindrance, which does not allow C(18) to approach close to the iron cluster, and the repulsion of the bonding electron pairs at the carbon atom. Also in the $[Co_3(CY)(CO)_9]$ series the mean value for the Co–C (C triply bridging) distance (1.92 Å[3]) is slightly shorter than the Co–C σ bonds in $[Co_4(C_2Et_2)(CO)_{10}]$ (2.01 Å[14]) and in $[Co_2(C_2Ph_2)(CO)_6]$ (1.96 Å[10]). In any case a simple picture is not adequate to describe the bonding system in this Fe_3C cluster as well as in the other M_3C clusters.

Substitution of CO groups by a cyclopentadienyl ring, together with a shift of some terminal to bridging CO, in order to allow the bonding of the ring to the cluster and to satisfy the electronic requirements of the co-ordinating metal, is a feature also observed in the $[Co_3(CY)(CO)_9]$ series.[3a] The cyclization of acetylenes to cyclopentadienyl on iron carbonyls has been previously reported, a typical example being the 'deep red' isomer $[Fe_2(C_2H_2)_3(CO)_6]$.[13] The cyclopentadienyl unit in the present compound is, however, noteworthy for the vinyl substituent with the terminal carbon statistically distributed in two positions. This particular situation can be justified by the equivalent hindrances which carbons C(15) and C(15') exert on methyl groups at C(16) and C(17) and on the oxygens O(1) and O(8) (Figure 3).

The cyclopentadienyl ring is quite planar. The best plane through the carbons of the ring C(9) ··· C(13)

TABLE 4

N.m.r. data for $[Fe_3(CEt)\{C_5H_2Me_2(C_2H_3)\}(CO)_8]$

		CO									
	C(18)	Bridge	Terminal	C(14)	C(15)	C(9,12)	C(13)	C(10,11)	C(19)	C(20)	C(16,17)
$^1H(\tau)$ [a]				6.81	5.92 [b] 5.72 [c]			4.22	5.30	1.93	1.68
				(1, dd)	(1, dd) (1, dd)			(2, s)	(2, q)	(3, t)	(6, s)
^{13}C (δ/p.p.m.) [d]	345.6	252.8	210.8 214.1, 212.6, 205.0 [e]	126.0	124.2	107.8	102.5	89.5	56.9	22.3	11.8
				(154)	(159)			(178)	(127)	(128)	(129)

[a] Hydrogen atoms have the same number as the carbons to which they are bonded, according to Figure 1. Multiplicities and integrated intensities are given in parentheses. [b] *cis*. [c] *trans*. [d] Values of ^1J(C–H) ± 5 Hz are given in parentheses. [e] At −74 °C.

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has the equation $0.3127X - 0.4007Y - 0.8612Z = -5.814\,8$ [where X, Y, and Z are co-ordinates in Å, $X \equiv x$, $Y \equiv y$, and Z is perpendicular to X, Y. Displacements from this plane are C(9) −0.004, C(10) 0.007, C(11) −0.007, C(12) 0.004, C(13) −0.001, C(14) −0.050, C(15) −0.743, C(15′) −0.589, C(16) −0.101, C(17) −0.119, and Fe(2) 1.752 Å]. The dihedral angle formed by this plane with the plane through the iron atoms is 72.7°. The formation of a vinyl-substituted cyclopentadienyl ring can be simply explained by condensation of two methylacetylenes joined tail-to-tail with a third methylacetylene whose 'reactive hydrogen' side is unaltered; a hydrogen shift from the methyl group to the α-acetylenic carbon is required for the formation of the vinyl group. A hydrogen shift to a fourth molecule of alkyne must be considered to account for the formation of the ethyl group bonded to C(18).

N.M.R. Spectra.—The ^{1}H n.m.r. spectrum showed the resonances expected on the basis of the crystal structure. The pattern and the position of the low-field resonances at τ 6.81, 5.92, and 5.72 [$J(\text{H–H}_{cis})$ 10.8, $J(\text{H–H}_{trans})$ 18.7, and $J(\text{H–H}_{gem})$ 2.2 Hz] are typical of a vinyl group.[15] The low field resonance at δ 345.6 p.p.m. in the ^{13}C spectrum (Table 4) is assigned to the apical carbon of the Fe_3C cluster, since values in a similar range have been observed for a series of $[Co_3(CY)(CO)_9]$ derivatives; the relevance of this chemical shift to the understanding of the nature of this kind of carbon atom has been discussed.[16] The assignment of resonances other than CO has been confirmed by off-resonance and ^{1}H-coupled spectra.

In the carbonyl region four resonances with integrated intensities 1 : 1 : 1 : 1 were observed in the limiting spectrum (−74 °C) (Figure 4). Throughout the range −74 to −18 °C the three upfield resonances broadened and merged to give a simple peak, whereas the downfield resonance remained sharp. As the temperature was increased further, the broad average signal did not sharpen completely and the resonance of the CO bridges began to broaden. Decomposition of the sample prevented runs at higher that 50 °C at which further broadening of the two resonances present in the −10 °C spectrum was observed.

The first stage of the stereochemical non-rigidity of the compound is interchange of the terminal carbonyls, for which two mechanisms are possible: one involves an intermediate with bridging carbonyls between Fe(1) and Fe(3) and the second does not. In the second stage, the bridging carbonyls also participate. The dynamic behaviour of this compound represents the first example in polynuclear carbonyls of scrambling of terminal carbonyls prior to exchange of bridging carbonyls.

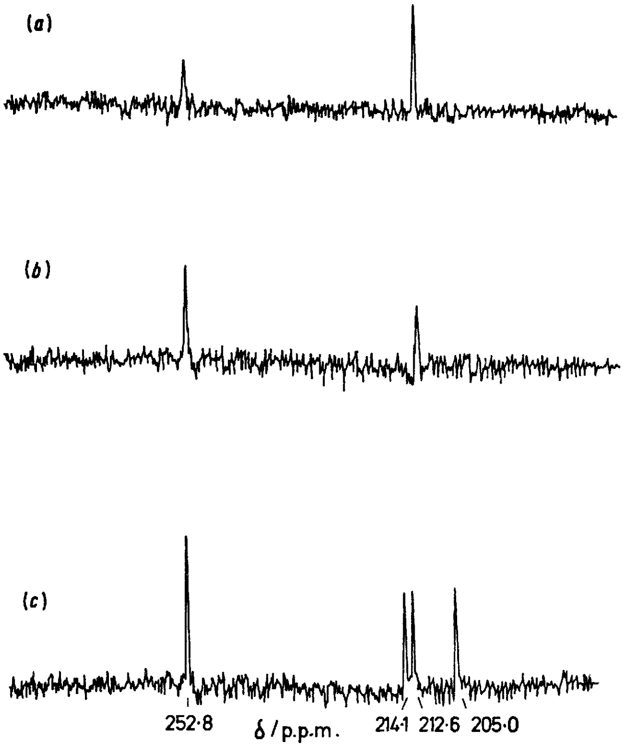

FIGURE 4 Variable-temperature ^{13}C n.m.r. spectra of the title compound in the carbonyl region in CD_2Cl_2 at (*a*) −10, (*b*) −18, and (*c*) −74 °C

Expectations based on the geometry of the molecule would predict two resonances for the bridging carbonyls, in the limiting spectrum, providing casual superpositions are avoided. The observation of only one resonance can be attributed to the fluxionality of the cyclopentadienyl unit.

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