8

Synthesis, Crystal Structure, and Stereochemical Non-rigidity of Octacarbonyl-μ_3-(1,3,6-trimethylhexa-1,3,5-triene-1,5-diyl)-*triangulo*-tri-iron

By **Enrico Sappa** * and **Luciano Milone,** Istituto di Chimica Generale ed Inorganica dell'Università, Torino, Italy
Antonio Tiripicchio, Istituto di Chimica Generale, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, Italy

Crystals of the title compound, obtained by reaction of [$Fe_3(CO)_{12}$] with methylacetylene, are monoclinic, space group $P2_1/c$, with $Z = 4$, in a unit cell of dimensions $a = 8.971(6)$, $b = 9.881(6)$, $c = 21.570(9)$ Å, $\beta = 93.8(1)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by block-diagonal least squares to R 0.038 for 2 590 observed reflections. The molecule consists of an unsymmetrical cluster of three iron atoms co-ordinated by eight carbonyls and a σ- and π-bonded organic ligand derived from three methylacetylene molecules. The organic moiety chelates to an iron atom *via* two σ bonds so a nearly planar six-atom heterocycle is formed. One of the carbonyl groups very unsymmetrically bridges two iron atoms. Hydrogen-1 and ^{13}C n.m.r. spectra show that the solid-state structure is maintained in solution, and that the complex is stereochemically non-rigid.

By allowing [$M_3(CO)_{12}$] (M = Fe, Ru, or Os) to react with symmetrically and unsymmetrically substituted acetylenes [1-3] several tri-, bi-, and mono-metallic acetylene–carbonyl complexes are formed. These show a variety of structural features, either in the different ways in which the acetylene molecules react to give more complex organic ligands, or in the different, and often unusual, bonding of these organic units, or the acetylenes themselves, with the metal atoms.

X-Ray analyses have been reported so far for mono-,[4-6] bi-,[7-11] and tri-acetylenic carbonyl complexes.[12-15] We now report the synthesis and structure determination of a new triacetylenic cluster, [$Fe_3(CO)_8$(tmhd)] obtained from the reaction of [$Fe_3(CO)_{12}$] and methylacetylene (tmhd = 1,3,6-trimethylhexa-1,3,5-triene-1,5-diyl), the first example, in metal carbonyl acetylene chemistry, of the formation of a nearly planar six-membered heterocyclic ring, formed by trimerization of the alkyne, and made up of one iron and five carbon atoms. The dynamic behaviour of the complex has been investigated by variable-temperature ^{13}C n.m.r. spectroscopy.

EXPERIMENTAL

Preparation of the Complex.—The title complex, a dark green crystalline solid, m.p. 135 °C (decomp.), was obtained (5%) by slowly bubbling gaseous methylacetylene (Merck-Schuchardt) for 0.75 h into [$Fe_3(CO)_{12}$] in n-heptane heated under reflux. The solvent was previously dried (molecular sieve) and the solution of the carbonyl initially kept under dry nitrogen. The reaction is reproducible, giving more than 14 products, among which [$Fe_3(CO)_8$(tmhd)] was isolated. Other major products were [$Fe_3(CO)_8\{(HC_2Me)_2\}$] (isomer with bridging CO), [$Fe_2(CO)_6\{(HC_2Me)_2\}$] (three isomers), [$Fe_2(CO)_7\{(HC_2Me)_2\}$] (three isomers), and [$Fe_3(CO)_8\{(HC_2Me)_4\}$].[16]

The reaction mixture was purified by t.l.c. (preparative plates, solid-phase Kieselgel P.F., eluant light petroleum–diethyl ether); [$Fe_3(CO)_8$(tmhd)] was further purified by crystallization from dry n-heptane (Found: C, 40.0; H, 2.50; Fe, 32.0; O, 25.5. $C_{17}H_{12}Fe_3O_8$ requires C, 39.9; H, 2.35; Fe, 32.75; O, 25.0%; *M* 511.79).

Physical Measurements.—I.r. spectra were obtained on a Beckmann IR 12 (KBr optics), mass spectra on a Hitachi-Perkin-Elmer RMU 6H spectrometer. Hydrogen-1 n.m.r. spectra were recorded on a Jeol JNM C60 HL, and ^{13}C n.m.r. spectra on a Jeol PS 100 FT spectrometer operating at 25.1 MHz in the Fourier-transform mode. Chemical shifts are reported as downfield positive, relative to tetramethylsilane as reference. Carbon tetrachloride solutions were sealed *in vacuo* in a 5-mm tube for ^1H n.m.r. spectra; $CDCl_3$ and CD_2Cl_2 solutions were sealed *in vacuo* in 10-mm tubes with the addition of 0.05 mol dm^{-3} [Cr(pd)$_3$] (pd = pentane-2,4-dionato) as an inert relaxation reagent for ^{13}C n.m.r. spectra. Deuteriated solvents (N.M.R. Ltd.) were used immediately after drying (molecular sieve).

Crystal Data.—$C_{17}H_{12}Fe_3O_8$, $M = 511.79$, Monoclinic, $a = 8.971(6)$, $b = 9.881(6)$, $c = 21.570(9)$ Å, $\beta = 93.8(1)°$, $U = 1\,908.1$ Å^3, $Z = 4$, $D_c = 1.78$, $F(000) = 1\,024$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 23.50 cm^{-1}. Space group $P2_1/c$ from systematic absences.

Preliminary unit-cell dimensions were determined from rotation and Weissenberg photographs, and accurate dimensions obtained by least-squares refinement of the diffractometer measurements of 13 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.* 0.200 × 0.190 × 0.300 mm was aligned with its *c* axis along the

---

[1] W. Hubel, in 'Organic Syntheses *via* Metal Carbonyls,' eds. I. Wender and P. Pino, vol. I, Interscience, New York, 1968, p. 273.

[2] G. Cetini, O. Gambino, E. Sappa, and M. Valle, *J. Organometallic Chem.*, 1969, **17**, 437.

[3] O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organometallic Chem.*, 1971, **30**, 381.

[4] J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Amer. Chem. Soc.*, 1966, **88**, 292.

[5] G. Gervasio and G. Ferraris, *Cryst. Struct. Comm.*, 1973, **2**, 447.

[6] S. Aime, O. Gambino, L. Milone, E. Sappa, and E. Rosenberg, *Inorg. Chim. Acta*, 1975, **15**, 53.

[7] G. Gervasio, *J.C.S. Chem. Comm.*, 1976, 25.

[8] R. P. Dodge and V. Shomaker, *J. Organometallic Chem.*, 1965, **3**, 274.

[9] G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1972 1057.

[10] A. A. Hock and O. S. Mills, *Acta Cryst.*, 1961, **14**, 139.

[11] J. Piron, P. Piret, J. Meunier-Piret, and Y. Degreve, *Bull. Soc. chim. belges*, 1969, **78**, 21.

[12] G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1973, 1933.

[13] E. Sappa, L. Milone, and G. D. Andreetti, *Inorg. Chim. Acta*, 1975, **13**, 67 and refs. therein.

[14] P. Piret, J. Meunier-Piret, M. Van Meerssche, and G. S. D. King, *Acta Cryst.*, 1965, **19**, 78.

[15] J. Meunier-Piret, P. Piret, and M. Van Meerssche, *Acta Cryst.*, 1965, **19**, 85.

[16] E. Sappa and A. Tiripicchio, unpublished work.

ϕ axis of the diffractometer and all the reflections with $2\theta < 50°$ were measured. Of 3 366 independent reflections, 2 590 having $I > 2\sigma(I)$ were considered observed and used in the analysis. Intensity data were corrected for Lorentz and polarization factors, but not for absorption, since maximum μR was only 0.25. The absolute scale was determined first by Wilson's method and then by correlation of observed and calculated values.

TABLE 1

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

	x/a	y/b	z/c
Fe(1)	1 219(1)	2 863(1)	1 492(1)
Fe(2)	3 431(1)	1 174(1)	1 555(1)
Fe(3)	3 172(1)	3 187(1)	703(1)
O(1)	362(4)	5 303(3)	780(2)
O(2)	1 934(4)	2 215(5)	1 538(2)
O(3)	1 836(5)	4 976(4)	2 435(2)
O(4)	5 266(4)	2 663(4)	2 476(2)
O(5)	5 968(4)	−597(4)	1 388(2)
O(6)	4 994(5)	4 986(5)	1 524(2)
O(7)	5 649(4)	1 721(5)	203(2)
O(8)	2 976(5)	5 141(5)	−306(2)
C(1)	849(5)	4 326(5)	999(2)
C(2)	708(5)	2 479(5)	1 527(2)
C(3)	1 602(5)	4 115(5)	2 099(2)
C(4)	4 542(5)	2 104(5)	2 104(2)
C(5)	4 986(5)	104(5)	1 439(2)
C(6)	4 291(6)	4 250(5)	1 220(3)
C(7)	4 673(5)	2 254(5)	420(2)
C(8)	3 036(6)	4 379(6)	96(3)
C(9)	1 356(5)	2 237(5)	169(2)
C(10)	1 479(4)	1 682(4)	777(2)
C(11)	1 949(5)	286(4)	841(2)
C(12)	1 939(5)	−520(4)	1 367(2)
C(13)	1 795(5)	−007(5)	1 970(2)
C(14)	1 684(4)	1 376(5)	2 112(2)
C(15)	1 632(6)	1 692(6)	2 804(2)
C(16)	2 264(6)	−2 026(5)	1 295(2)
C(17)	1 655(6)	1 438(6)	−416(2)
H(9)	71(4)	300(4)	4(2)
H(11)	234(5)	−5(5)	40(2)
H(13)	187(4)	−68(4)	233(2)
H(151)	191(5)	80(4)	303(2)
H(152)	228(4)	238(4)	297(2)
H(153)	61(5)	191(5)	290(2)
H(161)	134(5)	−211(5)	108(2)
H(162)	201(5)	−233(5)	166(2)
H(163)	306(5)	−230(5)	124(2)
H(171)	257(5)	89(4)	−38(2)
H(172)	188(5)	202(5)	−73(2)
H(173)	79(5)	77(4)	−46(2)

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares, first with isotropic, then with anisotropic thermal parameters.[*] Hydrogen atoms were located directly from a difference synthesis calculated after several cycles of least squares. Further least-squares cycles were computed including the hydrogen atoms with isotropic thermal parameters. Unit weights were chosen at every stage of the refinement by analyzing the variation of $|\Delta F|$ with respect to $|F|$. The final R was 0.038. Atomic scattering factors for non-hydrogen atoms were taken from ref. 17, and for hydrogen from ref. 18. Final atomic co-ordinates are given in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21783 (17 pp., 1 microfiche).[†] All the calculations were made on a CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) with programs of Immirzi.[19]

RESULTS AND DISCUSSION

I.r. Spectrum.—In CCl_4 solution the complex showed ν(CO) at 2 062s, 2 025vs, 2 001vs, 1 979m, and 1 870w cm^{-1}, the latter attributed to a bridging carbonyl.

Mass Spectrum.—The complex showed the parent ion, those due to the loss of eight CO groups, then those due to loss of H_2 and to partial destruction of the whole organic cluster moiety, as for previously reported acetylenic carbonyls.[20] While the trimetallic cluster shows intermediate stability to breakdown (abundance of trimetallic fragments 50.4%; no trimetallic doubly charged ions were observed), the organic moiety is more stable as indicated by the high abundance of ions such as $[Fe_2(CO)(tmhd)]^+$ and $[Fe(CO)(tmhd)]^+$.

X-*Ray Structure.*—The structure of $[Fe_3(CO)_8(tmhd)]$ is represented in Figure 1; bond distances and angles in the molecule are given in Table 2. The structure is characterized by a trinuclear cluster of iron atoms co-ordinated by eight carbonyls and by a σ- and π-bonded organic ligand derived from the trimerization of the alkyne.

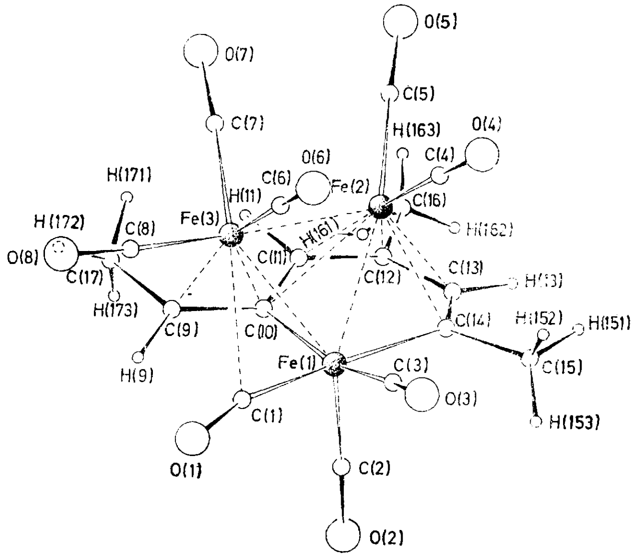

FIGURE 1 Molecular view of $[Fe_3(CO)_8(tmhd)]$ showing the atom-labelling system

Seven carbonyls are terminal [two attached to Fe(1), two to Fe(2), and three to Fe(3)], and one bridges Fe(1) and Fe(3) very unsymmetrically [Fe(1)–C(1) 1.812,

---

[*] The blocks in the matrix were 9 × 9 for the anisotropic atoms, 4 × 4 for the isotropic atoms, and 2 × 2 for scale factors and overall thermal parameters. Estimated standard deviations were deduced from the diagonal elements of the inverse matrix.

[†] For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[17] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[18] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[19] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

[20] O. Gambino and E. Sappa, *Atti Accad. Sci. Torino*, 1974, **108**, 305 and refs. therein.

TABLE 2

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

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

Fe(1)–Fe(2)	2.590(2)	Fe(2)–C(11)	2.154(5)
Fe(1)–Fe(3)	2.542(3)	Fe(2)–C(12)	2.165(4)
Fe(2)–Fe(3)	2.708(3)	Fe(2)–C(13)	2.119(5)
Fe(1)–C(1)	1.812(5)	Fe(2)–C(14)	2.047(5)
Fe(1)–C(2)	1.776(5)	Fe(3)–C(1)	2.489(5)
Fe(1)–C(3)	1.817(5)	Fe(3)–C(6)	1.791(6)
Fe(1)–C(10)	1.960(5)	Fe(3)–C(7)	1.773(5)
Fe(1)–C(14)	2.012(5)	Fe(3)–C(8)	1.759(7)
Fe(2)–C(4)	1.756(5)	Fe(3)–C(9)	2.148(5)
Fe(2)–C(5)	1.781(5)	Fe(3)–C(10)	2.139(4)
Fe(2)–C(10)	2.397(5)		

Fe(2)–Fe(1)–Fe(3)	63.7(1)	C(5)–Fe(2)–Fe(1)	168.4(2)
Fe(2)–Fe(1)–C(1)	130.9(2)	C(10)–Fe(2)–C(11)	36.6(1)
Fe(2)–Fe(1)–C(2)	127.2(2)	C(10)–Fe(2)–C(12)	67.5(2)
Fe(2)–Fe(1)–C(3)	107.1(2)	C(10)–Fe(2)–C(13)	85.2(2)
Fe(2)–Fe(1)–C(10)	61.8(1)	C(10)–Fe(2)–C(14)	80.7(2)
Fe(2)–Fe(1)–C(14)	51.0(1)	C(10)–Fe(2)–Fe(1)	46.1(1)
Fe(3)–Fe(1)–C(1)	67.3(1)	C(11)–Fe(2)–C(12)	37.5(2)
Fe(3)–Fe(1)–C(2)	140.5(2)	C(11)–Fe(2)–C(13)	70.5(2)
Fe(3)–Fe(1)–C(3)	106.9(2)	C(11)–Fe(2)–C(14)	89.9(2)
Fe(3)–Fe(1)–C(10)	54.9(1)	C(11)–Fe(2)–Fe(1)	77.9(1)
Fe(3)–Fe(1)–C(14)	114.5(1)	C(12)–Fe(2)–C(13)	38.4(2)
C(1)–Fe(1)–C(2)	93.1(2)	C(12)–Fe(2)–C(14)	72.4(2)
C(1)–Fe(1)–C(3)	84.2(2)	C(12)–Fe(2)–Fe(1)	91.5(1)
C(1)–Fe(1)–C(10)	92.3(2)	C(13)–Fe(2)–C(14)	39.4(2)
C(1)–Fe(1)–C(14)	174.0(2)	C(13)–Fe(2)–Fe(1)	80.1(1)
C(2)–Fe(1)–C(3)	104.6(2)	C(14)–Fe(2)–Fe(1)	49.8(1)
C(2)–Fe(1)–C(10)	94.2(2)	C(1)–Fe(3)–C(6)	91.1(2)
C(2)–Fe(1)–C(14)	88.6(2)	C(1)–Fe(3)–C(7)	172.4(2)
C(3)–Fe(1)–C(10)	161.0(2)	C(1)–Fe(3)–C(8)	82.5(2)
C(3)–Fe(1)–C(14)	89.8(2)	C(1)–Fe(3)–C(9)	73.6(2)
C(10)–Fe(1)–C(14)	93.3(2)	C(1)–Fe(3)–C(10)	71.6(2)
Fe(3)–Fe(2)–C(4)	95.3(2)	C(1)–Fe(3)–Fe(1)	42.2(1)
Fe(3)–Fe(2)–C(5)	111.9(2)	C(1)–Fe(3)–Fe(2)	101.2(1)
Fe(3)–Fe(2)–C(10)	49.1(1)	C(6)–Fe(3)–C(7)	96.4(2)
Fe(3)–Fe(2)–C(11)	78.0(1)	C(6)–Fe(3)–C(8)	94.5(3)
Fe(3)–Fe(2)–C(12)	114.6(1)	C(6)–Fe(3)–C(9)	164.7(2)
Fe(3)–Fe(2)–C(13)	131.3(1)	C(6)–Fe(3)–C(10)	137.1(3)
Fe(3)–Fe(2)–C(14)	107.0(1)	C(6)–Fe(3)–Fe(1)	92.3(2)
Fe(3)–Fe(2)–Fe(1)	57.3(1)	C(6)–Fe(3)–Fe(2)	89.4(2)
C(4)–Fe(2)–C(5)	89.5(2)	C(7)–Fe(3)–C(8)	96.2(3)
C(4)–Fe(2)–C(10)	135.9(2)	C(7)–Fe(3)–C(9)	98.9(2)
C(4)–Fe(2)–C(11)	172.5(2)	C(7)–Fe(3)–C(10)	102.9(2)
C(4)–Fe(2)–C(12)	147.9(2)	C(7)–Fe(3)–Fe(1)	137.5(2)
C(4)–Fe(2)–C(13)	112.4(2)	C(7)–Fe(3)–Fe(2)	79.6(2)
C(4)–Fe(2)–C(14)	88.6(2)	C(9)–Fe(3)–C(10)	38.7(2)
C(4)–Fe(2)–Fe(1)	95.6(2)	C(9)–Fe(3)–Fe(1)	76.8(1)
C(5)–Fe(2)–C(10)	124.6(2)	C(9)–Fe(3)–Fe(2)	94.1(1)
C(5)–Fe(2)–C(11)	96.3(2)	C(10)–Fe(3)–Fe(1)	48.6(1)
C(5)–Fe(2)–C(12)	89.7(2)	C(10)–Fe(3)–Fe(2)	57.9(1)
C(5)–Fe(2)–C(13)	107.7(2)	Fe(1)–Fe(3)–Fe(2)	59.0(1)
C(5)–Fe(2)–C(14)	141.0(2)		

TABLE 2 (*Continued*)

(*b*) In the carbonyl groups

O(1)–C(1)	1.148(6)	O(5)–C(5)	1.132(6)
O(2)–C(2)	1.132(6)	O(6)–C(6)	1.141(7)
O(3)–C(3)	1.128(6)	O(7)–C(7)	1.148(6)
O(4)–C(4)	1.141(6)	O(8)–C(8)	1.147(8)

Fe(1)–C(1)–Fe(3)	70.5(2)	Fe(2)–C(4)–O(4)	177.2(4)
Fe(1)–C(1)–O(1)	164.1(4)	Fe(2)–C(5)–O(5)	177.3(4)
Fe(3)–C(1)–O(1)	125.2(4)	Fe(3)–C(6)–O(6)	176.0(5)
Fe(1)–C(2)–O(2)	178.4(4)	Fe(3)–C(7)–O(7)	174.9(4)
Fe(1)–C(3)–O(3)	173.9(4)	Fe(3)–C(8)–O(8)	178.3(5)

(*c*) In the organic ligand

C(9)–C(10)	1.419(6)	C(13)–H(13)	1.02(4)
C(9)–C(17)	1.527(7)	C(15)–H(151)	1.03(4)
C(10)–C(11)	1.446(6)	C(15)–H(152)	0.95(4)
C(11)–C(12)	1.387(6)	C(15)–H(153)	0.98(5)
C(12)–C(13)	1.410(6)	C(16)–H(161)	0.93(4)
C(12)–C(16)	1.526(6)	C(16)–H(162)	0.89(5)
C(13)–C(14)	1.405(7)	C(16)–H(163)	0.78(5)
C(14)–C(15)	1.529(6)	C(17)–H(171)	0.98(4)
C(9)–H(9)	0.98(4)	C(17)–H(172)	0.92(5)
C(11)–H(11)	1.09(5)	C(17)–H(173)	1.02(4)

C(17)–C(9)–Fe(3)	120.0(3)	Fe(1)–C(14)–Fe(2)	79.3(2)
C(10)–C(9)–C(17)	123.8(4)	Fe(1)–C(14)–C(13)	125.4(3)
C(10)–C(9)–Fe(3)	70.3(2)	C(10)–C(9)–H(9)	125(3)
C(11)–C(10)–Fe(1)	122.8(3)	C(17)–C(9)–H(9)	107(3)
C(11)–C(10)–Fe(2)	62.5(2)	Fe(3)–C(9)–H(9)	103(2)
C(11)–C(10)–Fe(3)	117.8(3)	C(10)–C(11)–H(11)	109(3)
C(11)–C(10)–C(9)	117.5(4)	C(12)–C(11)–H(11)	124(3)
Fe(1)–C(10)–Fe(2)	72.1(1)	Fe(2)–C(11)–H(11)	122(2)
Fe(1)–C(10)–Fe(3)	76.5(2)	C(12)–C(13)–H(13)	118(2)
Fe(1)–C(10)–C(9)	119.4(3)	C(14)–C(13)–H(13)	118(2)
Fe(2)–C(10)–Fe(3)	73.0(1)	H(13)–C(13)–Fe(2)	132(2)
Fe(2)–C(10)–C(9)	137.4(3)	C(14)–C(15)–H(151)	105(2)
Fe(3)–C(10)–C(9)	71.0(3)	C(14)–C(15)–H(152)	117(3)
C(12)–C(11)–Fe(2)	71.7(3)	C(14)–C(15)–H(153)	110(3)
C(12)–C(11)–C(10)	127.5(4)	H(151)–C(15)–H(152)	108(4)
C(10)–C(11)–Fe(2)	80.9(2)	H(152)–C(15)–H(153)	109(4)
C(13)–C(12)–C(16)	118.3(4)	H(151)–C(15)–H(153)	107(4)
C(13)–C(12)–Fe(2)	69.1(3)	C(9)–C(17)–H(171)	114(3)
C(13)–C(12)–C(11)	123.7(4)	C(9)–C(17)–H(172)	110(3)
C(16)–C(12)–Fe(2)	130.8(3)	C(9)–C(17)–H(173)	104(2)
C(16)–C(12)–C(11)	117.7(4)	H(171)–C(17)–H(172)	100(4)
Fe(2)–C(12)–C(11)	70.8(3)	H(171)–C(17)–H(173)	106(3)
C(12)–C(13)–Fe(2)	72.5(3)	H(172)–C(17)–H(173)	123(4)
C(14)–C(13)–C(12)	124.3(4)	C(12)–C(16)–H(161)	88(3)
C(14)–C(13)–Fe(2)	67.5(2)	C(12)–C(16)–H(162)	100(3)
C(15)–C(14)–Fe(1)	118.8(4)	C(12)–C(16)–H(163)	123(4)
C(15)–C(14)–Fe(2)	131.9(3)	H(161)–C(16)–H(162)	98(4)
C(15)–C(14)–C(13)	114.7(4)	H(162)–C(16)–H(163)	108(5)
Fe(2)–C(14)–C(13)	73.1(3)	H(161)–C(16)–H(163)	134(4)

TABLE 3

Fe–C Distances (Å) and i.r. bands (cm^{-1}) in iron cluster compounds containing bridging CO groups

Complex	Fe–C		Ratio [a]	ν(CO)
$[Fe_3(CO)_9(PMe_2Ph)_3]$ [b]	1.97(2)	1.97(3)	1.00	1 745, 1 792
$[Fe_3(CO)_8\{(HC_2Me)_4\}]$ [c]	1.883	2.006	1.07	1 818, 1 865
	1.875	2.031	1.08	
$[Fe_3(CO)_{11}(PPh_3)]$ [d]	1.86(4)	2.07(4)	1.11	1 825
	1.85(5)	2.04(5)	1.10	
$[Fe_3(CO)_8(C_2Ph_2)_2]$ [e]	1.842(19)	1.991(19)	1.08	1 858, 1 869
	1.771(21)	1.988(21)	1.12	
$[Fe_3(CO)_{12}]$ [f]	1.93(2)	2.21(3)	1.15	1 830, 1 875
	1.96(4)	2.11(4)	1.08	
$[Fe_3(CO)_8(tmhd)]$ [g]	1.812(1)	2.489(1)	1.37	1 870
$[Fe_3(CO)_8(SC_4H_8)_2]$ [h]	1.76(1)	2.55(1)	1.45	1 903
$[Fe_4(CO)_{13}]^{2-}$	1.80(4)	2.24	1.24	
	1.85(3)	2.33	1.26	
	1.81(4)	2.28	1.26	

[a] Ratio of Fe–C distances. [b] G. Raper and W. S. McDonald, *J. Chem. Soc.* (*A*), 1971, 3430. [c] Ref. 16. [d] D. J. Dahm and R. A. Jacobson, *J. Amer. Chem. Soc.*, 1968, **90**, 5106. [e] Black form; refs. 2 and 8. [f] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4155. [g] This work. [h] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 5070. [i] R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 4847.

Fe(3)–C(1) 2.489 Å]. The presence of this bridging CO is confirmed by the angle Fe(1)–C(1)–O(1), 164.1°, which is narrower than those formed by the terminal carbonyls (mean 176.6°). In addition to the stretching bands for terminal CO in the i.r. spectrum, there was a band at 1 870 cm^{-1} which can be assigned to the bridging carbonyl. Table 3 shows the influence of asymmetry on i.r. frequency for carbonyl bridges in iron carbonyl clusters, with reference to the ratio of the Fe–C distances.

The Fe–Fe bond distances in the cluster, which fall in the range of those usually found in carbonyliron complexes, are of different lengths, with Fe(2)–Fe(3) > Fe(1)–Fe(2) > Fe(1)–Fe(3). The relative position of Fe(2) and Fe(3) with respect to Fe(1) can be accounted for by the π attraction exerted by the heterocycle Fe(1) and C(10)—(14) on Fe(2) and by the π interaction between C(9)–C(10) and Fe(3) together with the effect of the CO bridging. As the organic ligand is rather rigid, these attractions, together with the hindrance due to the terminal carbonyls at Fe(3) and Fe(2), are probably responsible for the observed differences in Fe–Fe distances.

The organic ligand, which is formed by two methylacetylenes linked head-to-tail and by a third linked tail-to-tail (the linkage requiring a hydrogen shift), has a conformation suitable for chelation to Fe(1) *via* two σ bonds, giving rise to a six-membered heterocyclic ring. This type of heterocycle is nearly planar, the equation of the best plane through it being: $-0.9758X - 0.2096Y - 0.0630Z = 1.6576$ [where X, Y, and Z are co-ordinates in Å, $X = x$, $Y = y$, and Z is perpendicular to (X,Y)]. Deviations from this plane are: Fe(1) 0.004, C(10) 0.018, C(11) −0.105, C(12) 0.073, C(13) 0.095, C(14) −0.093, C(9) 0.008, C(15) −0.111, C(16) 0.100, and C(17) −0.091 Å. The three double bonds in the ligand are completely delocalized on the six carbon atoms C(9)—(14) as shown by the C–C bond distances which are in the range 1.387—1.446 Å. It is the π-electron cloud along C(10) ··· C(14) which attracts Fe(2) so this atom is almost equidistant from the carbon atoms of the ring. As a further π-donor bond is formed with Fe(3) by the C(9)–C(10) bond, the ligand as a whole is a six-electron donor (through π co-ordination), while it forms two σ bonds to Fe(1) in agreement with the requirements of the noble-gas rule.

The non-equivalence of the three metal atoms [Fe(1) is only σ bonded to the organic ligand, Fe(2) and Fe(3) only π bonded, but in different ways] could explain the relatively low stability of the cluster with respect to its breakdown as observed by mass spectrometry. The σ- and π-bond lengths are fairly comparable to those found in other tri- and bi-nuclear iron–carbonyl acetylenes, containing either heterocyclic five-membered rings or homocyclic rings.[10,11,13-15]

N.m.r. Spectra.—Hydrogen-1 and ^{13}C n.m.r. data (Table 4) show that the solid-state structure is maintained in solution. The assignment of three CH resonances in the ^{1}H spectrum was based on double-resonance experiments and assumes that the lowest-field resonance (intensity 3) is to be associated with C(15).[21] In the room-temperature ^{13}C n.m.r. spectrum six resonances were observed in the carbonyl region with integrated

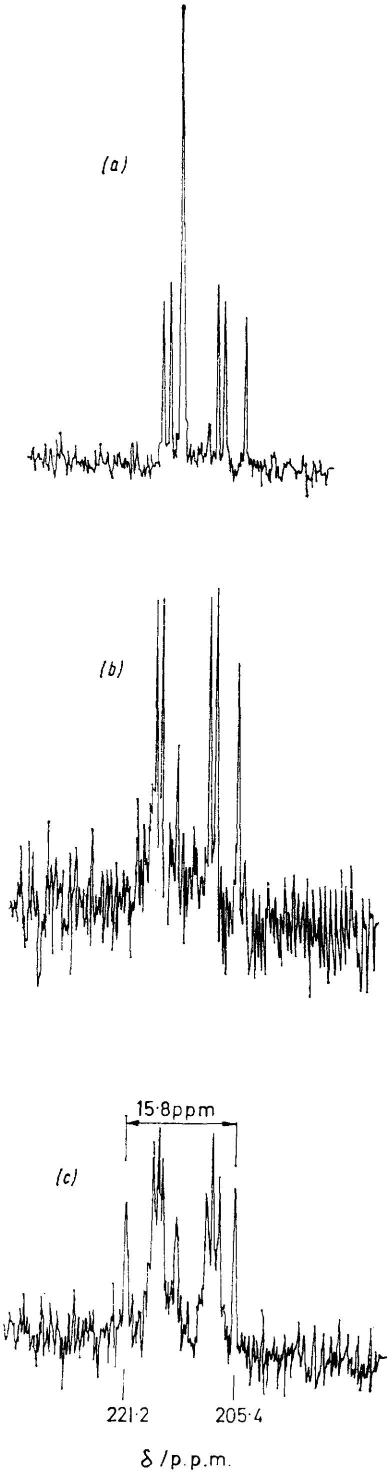

FIGURE 2 Variable-temperature ^{13}C n.m.r. spectra of $[Fe_3(CO)_8(tmhd)]$, with $CDCl_3$ and CD_2Cl_2 as solvents (*a*) 25, (*b*) −50, and (*c*) −73° C

---

[21] O. Gambino, M. Valle, S. Aime, and G. A. Vaglio, *Inorg. Chim. Acta*, 1974, **8**, 71.

TABLE 4

N.m.r. data for $[Fe_3(CO)_8(tmhd)]$

	CO	C(14)	C(10)	C(12)	C(11)	C(13)	C(9)	C(15)	C(16)	C(17)
$\delta(^1H)$ [a,b]					6.27 (q, 1) [e]	5.15 (q, 1) [c]	2.12 (d, 3) [c]	3.39 (d, 3) [c]	2.53 (d, 3) [c]	2.08 (d, 3) [d]
$\delta(^{13}C)$ [e]	217.4, 216.5, 214.7 209.5, 208.5, 205.4	*f*	152.4	121.7	99.6 (166)	76.5 (156)	61.9 (162)	42.5	30.3	24.6

[a] Hydrogen atoms numbered according to the carbons to which they are bonded (see Figure 1). [b] Multiplicity and integrated intensities are in parentheses. [c] *J ca.* 1 Hz. [d] *J ca.* 7 Hz. [e] $^1J(H-C)$ (±5 Hz) values are in parentheses. [f] Any of the values of the CO.

intensities 1 : 1 : 4 : 1 : 1 : 1, indicating that one resonance of the organic chain must fall in that region and that the molecule is stereochemically non-rigid. The former observation was confirmed by the presence of only eight resonances in addition to the low-field groups, and both observations by low-temperature runs.

At −73 °C the peak at 214.7 p.p.m. was maintained but its relative intensity was decreased to 1 and three new peaks appeared at 221.2, 216.0, and 207.6 p.p.m. (Figure 2). On raising the temperature, these three signals broadened, coalesced, and sharpened, superimposing on the peak at 214.7 p.p.m. The spectrum was unchanged at high temperature (up to 45 °C); at higher temperature, extensive decomposition of the sample occurred in the time required for the experiment (10 h). The observed interchange of the carbonyl groups is then localized at one of the two iron atoms bearing three carbonyls, but, on the basis of these data only, we have no way of distinguishing between scrambling localized on Fe(1) or on Fe(3). However, we assign the axial–equatorial interchange to the carbonyls on Fe(3), as non-participation in the stereochemical non-rigidity of the molecule in $[Fe_3(CO)_8(C_2Ph_2)_2]$ and in $[Fe_2(CO)_6(C_2Ph_2)_2]$ has been observed for the carbonyls bonded to the iron atom forming two σ bonds with the ligand,[22,23] whereas the scrambling is facile for carbonyls bonded to iron atoms π bonded to an olefin.[23,24]

The assignment of the other resonances was possible by registration of off-resonance and ^1H-coupled spectra. One resonance in the carbonyl region is ascribed to C(14), and that at 152.4 to C(10) on the grounds of the observed downfield shift for carbon atoms σ- and π-bonded to two metal atoms.[23,25]

We thank Professor M. Nardelli for helpful discussions.

[5/2548 *Received*, 30*th December*, 1975]

---

[22] S. Aime, L. Milone, and E. Sappa, *Inorg. Chim. Acta*, 1976, **16**, L7.

[23] S. Aime, L. Milone, and E. Sappa, *J.C.S. Dalton*, 1976, 838.

[24] L. Kruczynski, L. K. K. Li Shing Man, and J. Tabbots, *J. Amer. Chem. Soc.*, 1974, **96**, 4006; S. T. Wilson, N. J. Coville, J. R. Shapely, and J. A. Osborn, *ibid.*, p. 4040; L. Kruczynski, J. L. Martin, and J. Tabbots, *J. Organometallic Chem.*, 1974, **80**, C9.

[25] J. P. Hickey, J. R. Wilkinson, and L. J. Todd, *J. Organometallic Chem.*, 1975, **99**, 281.