Structural Characterization of a Rearranged Trinuclear Iron Complex with a Bridging Ferracyclobutene Ligand

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The title compound (VII) crystallizes in the monoclinic space group $P2_1/c$, with $a = 12{\cdot}325(4)$, $b = 21.075(4)$, $c = 19.701(9)$ Å, $\beta = 133.54(1)°$, and $Z = 4$. The structure was solved by direct methods from 2 921 observed reflexions measured on a diffractometer, and refined by block-diagonal least-squares techniques to R 0.053. The analysis has shown that the conversion of another trinuclear complex $[Fe_3(CO)_8\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$ (III) into (VII) involves CO elimination, metal–metal bond formation, and structural changes in the diphenylphosphide bridge. The principal structural features of (VII) are the presence of a dimerized phosphinoacetylene in the form of a *trans*-butadiene [mean C–C 1.49(1), C=C 1.39(1) Å] co-ordinated simultaneously to three iron atoms [mean Fe–C (π-bonded) 2.14(8) and (σ-bonded) 2.02(3) Å], a bridging diphenylphosphide group [Fe–P 2.170(6), 2.288(3) Å] formed by cleavage of a P–C(*sp*) bond of one phosphinoacetylene, and two iron–iron bonds [2.662(7) (PPh_2-bridged) and 2.531(10) Å)]. The $Ph_2PC_4(CF_3)_2$ ligand remains bonded to iron *via* an Fe–P bond [2.238(3) Å]; mean Fe–C(carbonyl) 1.79(3) and C–O 1.14(2) Å.

THE reactions of acetylenes with the iron carbonyl complexes, $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$, generally give many diversified oligomerization products; intermediates are difficult to isolate and the reaction mechanisms are not generally known.[1-3] However, Carty and his co-workers have employed phosphinoacetylenes $R^1_2PC{:}CR^2$ and have managed to isolate an initial reaction intermediate {*i.e.* the π-co-ordinated acetylene complex $[Fe_2(CO)_6(Ph_2PC_2Ph)_2]$ (I)[4] in small quantities from the reaction of $[Fe_2(CO)_9]$ with $Ph_2PC{:}CPh$ as well as the σ,π-acetylide complex $[Fe_2(CO)_6(C_2Ph)(PPh_2)]$ (II)[5] as the major product}. They have also modified the oligomerization mechanism and hence the product structure by using phosphorus substituents on the acetylene. In this regard, the formation of linearly dimerized acetylene products, the trinuclear ferracyclobutene complex $[Fe_3(CO)_8\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$ (III)[6] (as opposed to cyclization to give ferracyclopentadienes, cyclopentadienones, or cyclobutadienes) as well as $[Fe_3(CO)_7\{Ph_2PC_4(CF_3)_2(H)(CO_2Me)\}(PPh_2)]$ (IV),[7] have been accomplished.

In the synthesis of the trinuclear complexes derived from $[Fe_3(CO)_{12}]$ and $Ph_2PC{:}CCF_3$, the key complex is $[Fe_3(CO)_{10}(Ph_2PC_2CF_3)_2]$ (V).[6] On warming, the unco-ordinated acetylenes in this complex dimerize, giving

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[1] W. Hübel, ' Organic Syntheses *via* Metal Carbonyls,' vol. I, eds. I. Wender and P. Pino, Interscience, New York, 1968, pp. 273—342.

[2] F. L. Bowden and A. B. P. Lever, *Organometallic Chem. Rev.*, 1968, **3**, 227.

[3] R. D. W. Kemmitt, *M.T.P. Int. Rev. Sci. Inorg. Chem. Ser.* 1, 1972, **6**, 221.

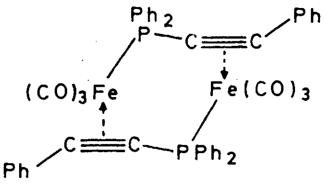
[4] T. O'Connor, A. J. Carty, M. Mathew, and G. J. Palenik, *J. Organometallic Chem.*, 1974, **70**, C17.

[5] H. A. Patel, R. G. Fischer, A. J. Carty, D. V. Naik, and G. J. Palenik, *J. Organometallic Chem.*, 1973, **60**, C49.

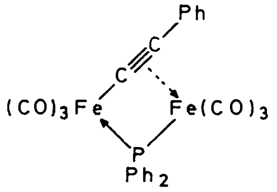
[6] M. Mathew, G. J. Palenik, A. J. Carty, and H. N. Paik, *J.C.S. Chem. Comm.*, 1974, 25.

[7] H. N. Paik, A. J. Carty, M. Mathew, and G. J. Palenik, *J.C.S. Chem. Comm.*, 1974, 946.

products $[Fe_3(CO)_8\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$ (VI),[8] containing a ferracyclopentadiene ring system and $[Fe_3(CO)_8\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$ (III),[6] containing a ferracyclobutene ring. Compound (III) [6] is then heated under



(I)



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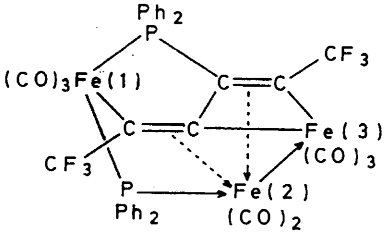
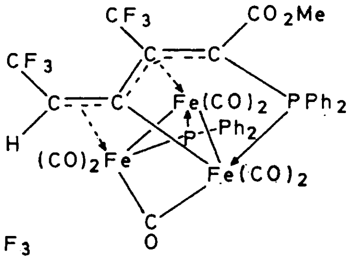
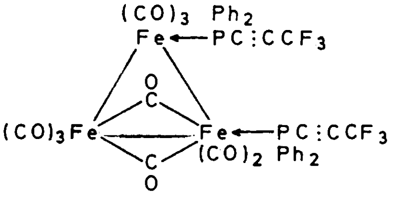


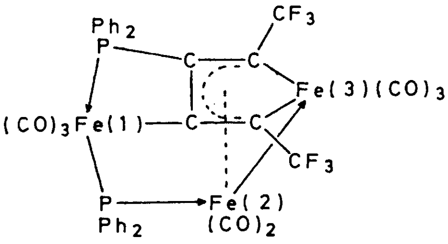
(III)



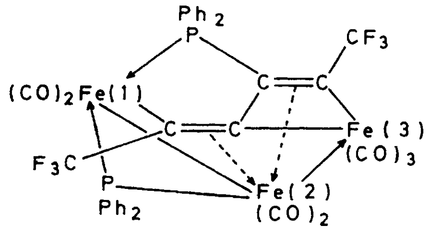
(IV)



(V)



(VI)



(VII)

reflux in light petroleum (b.p. 80—100 °C) for 1 h and the reaction mixture chromatographed on alumina. As reported in a preliminary communication,[9] the major product of this reaction is a red complex which analyzed as $[Fe_3(CO)_7\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$ (VII). We report here the results of the single-crystal *X*-ray structural determination of this rearrangement product.

EXPERIMENTAL

A dark red crystal *ca.* 0.40 × 0.20 mm square cross-section was cut to a cube and mounted parallel to the *a* axis. Accurate cell parameters were obtained by a least-squares fit of twelve reflexions on a Hilger and Watts Y 290 automated diffractometer.

Crystal Data.—$C_{37}H_{20}F_6Fe_3O_7P_2$, $M = 920$, Monoclinic, $a = 12.325(4)$, $b = 21.075(4)$, $c = 19.701(9)$ Å, $\beta = 133.54(1)°$, $U = 3\,709.5$ Å^3, $D_c = 1.647$, $Z = 4$, $D_m = 1.64(1)$, $F(000) = 1\,840$. Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 13.6$ cm^{-1}. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$.

Crystallographic Measurements.—Data were collected * on a Hilger and Watts diffractometer equipped with a scintillation counter and pulse-height analyzer by use of graphite-monochromated Mo-K_α radiation and a θ—2θ scanning technique to $\theta_{max.}$ 23°. The intensity of two standard reflexions, measured every 100 reflexions, dropped by *ca.* 12% during data collection, and this was corrected for by application of linear scale factors. Of 4 545 intensity maxima collected and corrected for Lorentz and polarization effects, 2 921 with $I > 3\sigma(I)$ were considered observed and used throughout the structural solution and refinement. Because of the small value of μ and the size of the crystal used in data collection, an absorption correction was not considered necessary.

Data were placed on an absolute scale by use of Wilson's method,[10] and normalized structure amplitudes *E* were derived. Approximate co-ordinates for the three unique iron atoms were obtained by direct methods using the Σ_2 and phase routines of the '*X*-Ray' system of crystallographic programs.[11] A Fourier synthesis based on the iron phases revealed the positions of all non-hydrogen atoms.

Isotropic refinement by full-matrix least-squares was initiated with unit weights and the scattering factors of the neutral species.[12] Both real and imaginary parts of the anomalous dispersion correction were applied to iron [13] and three cycles of refinement reduced *R* to 0.089.

A weighting scheme was then chosen such that $\sqrt{w} = 1/[\sigma^2(F) + 10^{-3}F^2]^{1/2}$, and an analysis of variance indicated that $\Sigma w\Delta^2$ was independent of $|F_o|$ and $\sin\theta/\lambda$. Two cycles of refinement by block-diagonal least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms reduced *R* to 0.063 and the weighted factor, *R'*, to 0.098 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}\}$. A difference-Fourier map, computed at this stage, revealed electron-density maxima in chemically reasonable positions for all hydrogen atoms; these were then allowed for (in chemically

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* For details of experimental procedure, see *e.g. J.C.S. Perkin I*, 1975, 496.

[8] T. O'Connor, A. J. Carty, M. Mathew, and G. J. Palenik, *J. Organometallic Chem.*, 1972, **38**, C15.

[9] A. J. Carty, G. Ferguson, H. N. Paik, and R. Restivo, *J. Organometallic Chem.*, 1974, **74**, C14.

[10] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

[11] '*X*-Ray' System of Computing Programs, 1972, Computing Science Center, University of Maryland, College Park, Maryland, U.S.A., Report TR-192.

[12] D. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

expected positions with isotropic U values of 0.063 Å^2 and scattering factors from ref. 14) but not refined in subsequent calculations. Two additional refinement cycles converged to R 0.053 and R' 0.074. The standard deviation of an observation of unit weight is 0.61 and a final difference-Fourier showed no significant features.

TABLE 1

Positional [a] (Fe × 10^5, others × 10^4) parameters for non-hydrogen atoms

Atom	x	y	z
Fe(1)	53 794(14)	29 656(6)	56 028(8)
Fe(2)	62 136(14)	24 281(6)	47 997(8)
Fe(3)	50 967(15)	14 142(6)	38 514(9)
P(1)	6 007(3)	3 484(1)	4 965(2)
P(2)	5 604(3)	1 998(1)	6 156(2)
F(51)	7 875(8)	0 531(3)	6 060(5)
F(52)	8 959(7)	1 095(3)	5 774(4)
F(53)	8 977(7)	1 392(3)	6 805(4)
F(61)	2 022(6)	3 277(3)	3 440(4)
F(62)	1 474(6)	2 308(3)	3 092(4)
F(63)	2 546(7)	2 805(3)	2 741(4)
O(11)	3 110(7)	3 678(4)	5 365(6)
O(12)	7 584(9)	3 563(4)	7 439(5)
O(21)	9 400(8)	2 565(4)	5 832(6)
O(22)	5 754(10)	2 601(3)	3 139(5)
O(31)	4 071(9)	0 177(4)	3 883(5)
O(32)	7 089(11)	0 905(5)	3 653(7)
O(33)	2 554(9)	1 634(4)	1 835(5)
C(1)	6 672(9)	1 455(4)	5 242(6)
C(2)	5 792(9)	1 719(4)	5 363(6)
C(3)	4 443(10)	1 912(4)	4 386(6)
C(4)	3 980(9)	2 528(4)	4 345(6)
C(5)	8 127(11)	1 126(5)	5 967(7)
C(6)	2 556(10)	2 733(4)	3 416(6)
C(11)	4 009(12)	3 386(4)	5 460(7)
C(12)	6 762(11)	3 324(4)	6 727(6)
C(21)	8 144(12)	2 524(4)	5 453(7)
C(22)	5 836(12)	2 469(5)	3 737(7)
C(31)	4 446(12)	0 668(5)	3 851(7)
C(32)	6 346(12)	1 111(5)	3 729(7)
C(33)	3 501(12)	1 159(5)	2 605(7)
C(111)	4 679(10)	3 987(4)	3 946(6)
C(112)	3 807(11)	4 403(4)	3 943(7)
C(113)	2 848(14)	4 823(5)	3 198(8)
C(114)	2 745(13)	4 814(5)	2 452(7)
C(115)	3 565(13)	4 395(5)	2 431(7)
C(116)	4 556(13)	3 996(5)	3 181(7)
C(121)	7 670(11)	3 963(4)	5 661(7)
C(122)	9 016(10)	3 777(4)	6 570(6)
C(123)	10 245(11)	4 157(5)	7 127(5)
C(124)	10 260(11)	4 729(5)	6 808(7)
C(125)	9 023(13)	4 929(5)	5 929(8)
C(126)	7 688(12)	4 560(4)	5 327(7)
C(211)	7 085(10)	1 717(4)	7 341(6)
C(212)	8 440(12)	2 025(5)	7 958(7)
C(213)	9 559(13)	1 839(6)	8 902(8)
C(214)	9 310(15)	1 335(6)	9 197(7)
C(215)	7 997(14)	1 001(6)	8 597(8)
C(216)	6 849(12)	1 186(5)	7 639(7)
C(221)	3 861(10)	1 637(4)	5 724(6)
C(222)	3 279(11)	1 083(5)	5 208(7)
C(223)	1 920(15)	0 864(6)	4 837(8)
C(224)	1 117(14)	1 183(6)	5 007(9)
C(225)	1 760(13)	1 720(6)	5 536(9)
C(226)	3 093(11)	1 954(5)	5 885(7)

[a] The estimated standard deviations of the last digit are in parentheses.

Final positional parameters for non-hydrogen atoms are in Table 1, calculated hydrogen-atom positions are in Table 2. Structure-factor data and thermal parameters are listed in Supplementary Publication No. SUP 21604 (34 pp., 1 microfiche).*

DISCUSSION

Interatomic distances and angles with their estimated standard deviations are shown in Table 3. The structure

TABLE 2

Positional parameters (× 10^3) for hydrogen atoms

Atom	x	y	z
H(112)	386	440	449
H(113)	222	515	322
H(114)	208	515	192
H(115)	338	437	184
H(116)	520	369	317
H(122)	908	333	684
H(123)	1 100	384	767
H(124)	1 121	501	723
H(125)	909	536	571
H(126)	824	412	564
H(212)	864	241	773
H(213)	1 059	208	937
H(214)	1 013	120	989
H(215)	782	061	883
H(216)	588	092	718
H(222)	385	084	509
H(223)	149	046	444
H(224)	009	102	474
H(225)	118	197	565
H(226)	352	237	628

TABLE 3

Principal intramolecular bond distances (Å) and bond angles (°), with estimated standard deviations in parentheses

(*a*) Distances involving iron and carbonyl groups

C(11)–O(11)	1.16(2)	Fe(1)–C(4)	2.02(2)
C(12)–O(12)	1.13(2)	Fe(2)–C(1)	2.15(1)
C(21)–O(21)	1.17(2)	Fe(2)–C(2)	2.13(1)
C(22)–O(22)	1.15(2)	Fe(2)–C(3)	2.04(1)
C(31)–O(31)	1.15(2)	Fe(2)–C(4)	2.24(2)
C(32)–O(32)	1.11(2)	Fe(3)–C(1)	1.99(3)
C(33)–O(33)	1.12(2)	Fe(3)–C(3)	2.01(1)
		Fe(1)–C(11)	1.75(2)
Fe(1)–Fe(2)	2.662(7)	Fe(1)–C(12)	1.78(2)
Fe(2)–Fe(3)	2.531(10)	Fe(2)–C(21)	1.77(2)
		Fe(2)–C(22)	1.81(2)
Fe(1)–P(1)	2.170(6)	Fe(3)–C(31)	1.77(1)
Fe(1)–P(2)	2.238(3)	Fe(3)–C(32)	1.83(2)
Fe(2)–P(1)	2.288(3)	Fe(3)–C(33)	1.83(3)

(*b*) Distances in $PC_4(CF_3)_2$ group

P(2)–C(2)	1.83(1)	C(4)–C(6)	1.48(2)
		C(5)–F(51)	1.33(1)
C(1)–C(2)	1.38(2)	C(5)–F(52)	1.32(2)
C(3)–C(4)	1.40(1)	C(5)–F(53)	1.33(2)
		C(6)–F(61)	1.34(1)
C(2)–C(3)	1.49(2)	C(6)–F(62)	1.35(1)
C(1)–C(5)	1.49(2)	C(6)–F(63)	1.33(2)

(*c*) Distances in diphenylphosphine groups

P(1)–C(111)	1.82(2)	C(125)–C(126)	1.42(2)
P(1)–C(121)	1.80(2)	C(121)–C(126)	1.43(2)
P(2)–C(211)	1.81(2)	C(211)–C(212)	1.37(2)
P(2)–C(221)	1.84(2)	C(212)–C(213)	1.41(2)
		C(213)–C(214)	1.34(2)
C(111)–C(112)	1.38(2)	C(214)–C(215)	1.37(2)
C(112)–C(113)	1.39(2)	C(215)–C(216)	1.43(2)
C(113)–C(114)	1.38(3)	C(211)–C(216)	1.43(2)
C(114)–C(115)	1.37(2)		
C(115)–C(116)	1.38(2)	C(221)–C(222)	1.38(2)
C(111)–C(116)	1.41(2)	C(222)–C(223)	1.37(2)
		C(223)–C(224)	1.41(3)
C(121)–C(122)	1.42(2)	C(224)–C(225)	1.36(2)
C(122)–C(123)	1.36(2)	C(225)–C(226)	1.36(2)
C(123)–C(124)	1.37(2)	C(221)–C(226)	1.36(2)
C(124)–C(125)	1.36(2)		

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975 Index, issue.

[14] R. F. Stewart, F. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1964, **42**, 3175.

TABLE 3 (*Continued*)

(*d*) Angles involving iron and carbonyl groups

Fe(1)–C(11)–O(11)	178.6(11)	P(1)–Fe(1)–C(4)	82.1(4)
Fe(1)–C(12)–O(12)	176.4(16)	P(1)–Fe(1)–C(11)	109.9(4)
Fe(2)–C(21)–O(21)	175.1(13)	P(1)–Fe(1)–C(12)	95.1(5)
Fe(2)–C(22)–O(22)	166.8(8)	P(2)–Fe(1)–C(4)	84.0(3)
Fe(3)–C(31)–O(31)	177.5(6)	P(2)–Fe(1)–C(11)	108.8(4)
Fe(3)–C(32)–O(32)	177.6(11)	P(2)–Fe(1)–C(12)	95.1(3)
Fe(3)–C(33)–O(33)	177.3(16)	C(4)–Fe(1)–C(11)	96.9(4)
Fe(1)–Fe(2)–C(21)	113.3(5)		
P(1)–Fe(1)–P(2)	140.1(2)	C(11)–Fe(1)–C(12)	88.6(5)
Fe(2)–Fe(1)–P(1)	55.4(1)	Fe(2)–Fe(1)–C(11)	147.7(3)
Fe(2)–Fe(1)–P(2)	86.1(1)	C(4)–Fe(1)–C(12)	174.4(5)
P(1)–Fe(2)–C(21)	90.7(3)	Fe(1)–Fe(2)–C(22)	140.5(4)
P(1)–Fe(2)–C(22)	98.8(3)	Fe(1)–Fe(2)–Fe(3)	124.2(1)
P(1)–Fe(2)–Fe(1)	51.3(1)	Fe(3)–Fe(2)–C(21)	114.1(4)
P(1)–Fe(2)–Fe(3)	150.3(1)	Fe(3)–Fe(2)–C(22)	67.1(3)
Fe(1)–Fe(2)–C(21)	113.3(5)	C(21)–Fe(2)–C(22)	89.0(6)
Fe(2)–Fe(1)–C(4)	55.2(4)	C(1)–Fe(3)–C(3)	67.6(4)
Fe(2)–Fe(1)–C(12)	119.3(5)		

(*e*) Angles in $PC_4(CF_3)_2$ group

Fe(3)–C(1)–Fe(2)	75.4(3)	Fe(1)–C(4)–C(3)	112.5(5)
Fe(3)–C(1)–C(2)	96.8(5)	Fe(2)–C(4)–C(3)	63.3(7)
C(2)–C(1)–C(5)	126.5(11)	Fe(2)–C(4)–C(6)	131.9(7)
Fe(3)–C(1)–C(5)	133.7(9)	Fe(2)–C(4)–C(6)	127.2(10)
P(2)–C(2)–C(1)	148.9(5)	C(3)–C(4)–C(6)	115.6(8)
Fe(2)–C(2)–C(1)	71.9(7)	C(1)–C(5)–F(51)	109.2(9)
C(1)–C(2)–C(3)	101.4(10)	C(1)–C(5)–F(52)	114.2(11)
Fe(2)–C(2)–P(2)	116.2(4)	C(1)–C(5)–F(53)	113.2(10)
Fe(2)–C(2)–C(3)	65.9(6)	F(51)–C(5)–F(52)	107.1(10)
Fe(2)–C(2)–Fe(3)	75.4(3)		
P(2)–C(2)–C(3)	109.3(8)	F(51)–C(5)–F(53)	106.6(10
Fe(2)–C(3)–Fe(3)	77.4(5)	F(52)–C(5)–F(53)	106.1(9)
Fe(2)–C(3)–C(2)	72.2(6)	C(4)–C(6)–F(61)	113.5(9)
Fe(3)–C(3)–C(2)	92.3(7)	C(4)–C(6)–F(62)	109.6(9)
Fe(2)–C(3)–C(4)	79.0(6)	C(4)–C(6)–F(63)	117.2(11)
Fe(3)–C(3)–C(4)	138.6(10)	F(61)–C(6)–F(62)	103.6(10)
C(2)–C(3)–C(4)	112.1(8)	F(61)–C(6)–F(63)	105.7(8)
Fe(1)–C(4)–Fe(2)	77.1(3)	F(62)–C(6)–F(63)	106.2(8)

(*f*) Angles in diphenylphosphine groups

Fe(1)–P(1)–Fe(2)	73.3(1)	C(121)–C(122)–C(123)	123.5(9)
Fe(1)–P(1)–C(111)	121.6(5)	C(122)–C(123)–C(124)	120.6(8)
Fe(1)–P(1)–C(121)	121.0(5)	C(123)–C(124)–C(125)	119.9(9)
Fe(2)–P(1)–C(111)	120.9(3)	C(124)–C(125)–C(126)	121.8(12)
Fe(2)–P(1)–C(121)	118.4(4)	C(125)–C(126)–C(121)	118.3(8)
C(111)–P(1)–C(121)	101.6(4)	C(126)–C(121)–C(122)	116.7(9)
Fe(1)–P(2)–C(2)	85.5(3)	C(211)–C(212)–C(213)	121.6(13)
Fe(1)–P(2)–C(211)	127.1(3)	C(212)–C(213)–C(214)	118.9(10)
Fe(1)–P(2)–C(221)	115.9(3)	C(213)–C(214)–C(215)	121.3(10)
C(2)–P(2)–C(211)	112.9(5)	C(214)–C(215)–C(216)	120.5(14)
C(2)–P(2)–C(221)	105.5(5)	C(215)–C(216)–C(211)	118.4(10)
C(211)–P(2)–C(221)	106.3(5)	C(216)–C(211)–C(212)	119.2(8)
C(111)–C(112)–C(113)	120.0(15)	C(221)–C(222)–C(223)	120.2(15)
C(112)–C(113)–C(114)	120.0(14)	C(222)–C(223)–C(224)	120.9(12)
C(113)–C(114)–C(115)	120.8(10)	C(223)–C(224)–C(225)	116.3(15)
C(114)–C(115)–C(116)	119.4(15)	C(224)–C(225)–C(226)	123.4(18)
C(115)–C(116)–C(111)	121.2(14)	C(225)–C(226)–C(221)	119.6(11)
C(116)–C(111)–C(112)	118.5(7)	C(226)–C(221)–C(222)	119.6(11)

consists of monomeric units of the $[Fe_3(CO)_7\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$ (VIII) complex separated by normal van der Waals distances (Figure 1); there are no abnormally close contacts.

A view of the molecule together with the atom numbering scheme (excluding the phenyl ring numbering) is illustrated in Figure 2; the iron atoms in the rearranged trinuclear iron species (VII) remain σ- and π-bonded to a dimerized phosphinoacetylene in the form of a butadiene unit which is similar to that present in reactant (III). In addition, complex (VII) retains the ferracyclobutene ring system [Fe(3), C(1)—(3)] and the Fe–Fe bond [Fe(2)–Fe(3) 2.531(10) Å] which were present in complex (III). However, there is a change in the geometry of the bridging diphenylphosphide PPh_2 group between Fe(1) and Fe(2), a carbonyl group has been eliminated and another Fe–Fe bond formed [Fe(1)–Fe(2) 2.662(7) Å]. All these structural changes may be general in this type of rearrangement.

The bridging PPh_2 group in complex (III) was initially formed by cleavage of a P–C(*sp*) bond of one phosphinoacetylene $Ph_2PC_2{\cdot}CF_3$ ligand; P–C bond cleavage occurs in many of these metal carbonyl phosphinoacetylene reactions [*cf*. formation of (II)].[5] Structural differences between (VII) and (III) include the fact that Fe(2)–P(1) [2.288(3) Å] is longer than Fe(1)–P(1) [2.170(6) Å], while the reverse is true in (III) [Fe(1)–P(1) 2.330(3), and Fe(2)–P(1) 2.277(4) Å].[6] This trend agrees with the prediction of a two-electron donor capacity for P(1) towards Fe(1) in (VII) whereas P(1) in (III) would behave as a one-electron donor to Fe(1), in order for all three iron atoms, in these two complexes, to achieve the krypton configuration. There is a notable decrease in the Fe(1)–P(1)–Fe(2) angle from 98.0(1)° in (III) to 73.3(1)° in (VII), along with Fe–Fe bond formation. These features of the Fe–PPh_2–Fe bridge are similar to those detailed in ref. 15 for phosphido-bridged binuclear complexes; namely, significant angular deformation of the bridged system to a more acute bridging angle occurs with metal–metal interaction. The elimination of a CO group required little change in the overall $Ph_2PC_4(CF_3)_2$ ligand geometry and this would imply that there must be considerable flexibility in the diphosphide bridge. From these observations it would seem reasonable to expect similar rearrangements for other polynuclear complexes having nonbonded metal atoms bridged by M_2R (R = N, P, or As).

The iron atom Fe(1) is bonded *via* a normal two-electron iron–phosphine bond [Fe(1)–P(2) 2.238(3) Å] to the diphenylphosphino-group of the organic ligand. The *trans*-butadiene portion of the ligand [mean C–C 1.49(1), and mean C=C 1.39(1) Å] is co-ordinated in π-diene fashion to Fe(2) [mean Fe(2)–C 2.14(8) Å] and to Fe(1) and Fe(3) *via* σ bonds to the chain atoms [Fe(1)–C(4) 2.02(2), Fe(3)–C(1) 1.99(3), Fe(3)–C(3) 2.01(1) Å].

The dimensions of the ferracyclobutene FeC_4 ring systems in (VII) and (III) [*cf*. Fe(3)–C(1) 1.959(12), and Fe(3)–C(3) 2.021(13) Å][6] are almost identical. However, it should be noted that in the formation of complex (VI), the two phosphinoacetylenes have dimerized in a different fashion to yield a ferracyclopentadiene ring with Fe(3)–C (mean 1.964 Å) and C–C (mean 1.43 Å)[8] having values similar to those in other ferracyclopentadiene structures.[16] Both systems are markedly different from that in complex (IV), which contains an

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[15] L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 1969, **91**, 1653; J. M. Coleman and L. F. Dahl, *ibid.*, 1967, **89**, 542.

[16] A. A. Hock and O. S. Mills, *Acta Cryst.*, 1961, **13**, 139; Y. Degrève, J. Meunier-Piret, M. Van Meerssche, and P. Piret, *ibid.*, 1967, **23**, 119; J. T. Mague, *Inorg. Chem.*, 1970, **9**, 1610; J. T. Mague, *J. Amer. Chem. Soc.*, 1971, **93**, 3550.

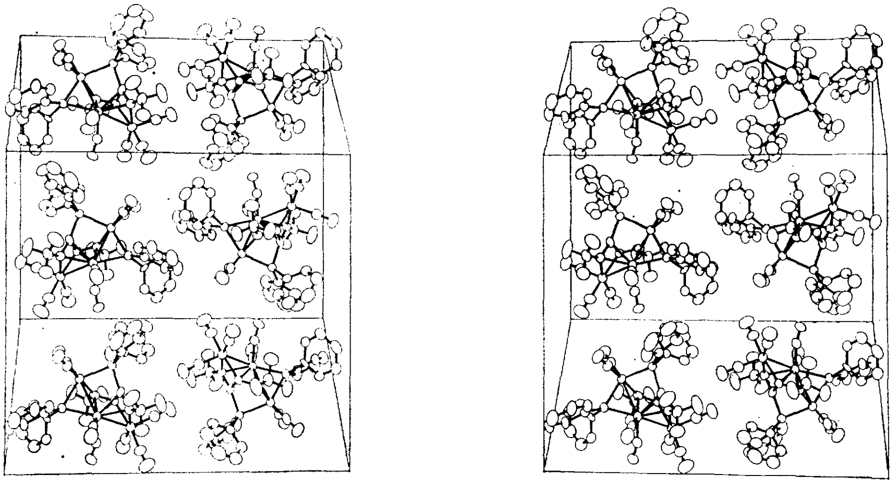

FIGURE 1 A stereoview of the molecular packing of $[Fe_3(CO)_7\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$

iron atom either weakly σ or asymmetrically bonded *via* π-allyl-type linkages to the carbon chain.

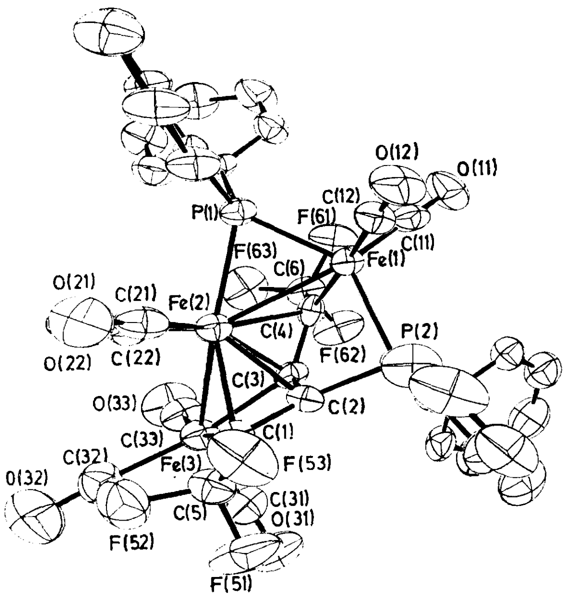

FIGURE 2 A perspective view with 50% probability ellipsoids of $[Fe_3(CO)_7\{Ph_2PC_4(CF_3)_2\}(PPh_2)]$ showing the molecular geometry and the atom numbering scheme

The non-bridged Fe(2)-Fe(3) distance [2.531(10) Å] in (VII) is comparable with those [2.514(3) (ref. 6) and 2.554 Å (ref. 8)] in complexes (III) and (VI) as well as in *cis*- (2.531 Å) and *trans*-$[(\pi\text{-}C_5H_5)_2Fe_2(CO)_4]$ (2.534 Å).[17] There is also a close resemblance between the PPh_2-bridged Fe(1)-Fe(2) distance [2.662(7) Å] in (VII) and the corresponding PPh_2-bridged Fe-Fe distance [7] [2.683(2) Å] in (IV). The mean Fe-C(carbonyl) [1.79(3) Å] and mean C-O lengths [1.14(2) Å] are similar to values quoted for terminal iron-carbonyl and C-O bond lengths in $[Fe_3(CO)_{12}]$.[18]

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[17] R. F. Bryan and P. T. Greene, *J. Chem. Soc.* (*A*), 1970, 3064; R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *ibid.*, p. 3068.

[18] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4155.

[19] C. K. Johnson, ORTEP, Technical Report ORNL 3794, 1965, Oak Ridge National Laboratory, Oak Ridge, Tennessee.