Crystal and Molecular Structure of $(\pi\text{-}C_5H_5)Fe_3(CO)_7C_2C_6H_5$ Obtained from $(\pi\text{-}C_5H_5)Fe(CO)_2C{\equiv}CC_6H_5$ with $Fe_2(CO)_9$[1]

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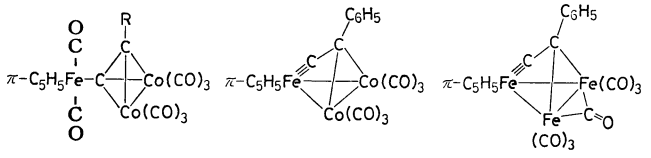
The crystal structure of $\pi\text{-}C_5H_5Fe_3(CO)_2(C_2C_6H_5)$ obtained from the reaction of $\pi\text{-}C_5H_5Fe(CO)_2C_2C_6H_5$ with $Fe_2(CO)_9$ has been determined from single crystal X-ray diffraction data. The space group is $P\bar{1}$ and the cell constants are $a=12.635$, $b=9.457$, $c=9.033$ Å, $\alpha=94.64$, $\beta=109.10$, and $\gamma=99.60$ °, and $Z=2$. The refinement was carried out using block-diagonal least-squares calculation including anisotropic thermal factors for the non-hydrogen atoms and isotropic thermal factors for the hydrogens. The final R value for 2488 reflections is 0.035. The molecular configuration consists of an isosceles triangle of the three iron atoms, each two of which bonds to three terminal carbonyl groups and one bonds to the cyclopentadienyl ring. The phenylethynyl group is disposed above the iron plane and is σ-bonded to one iron atom with three carbonyls and π-bonded symmetrically to the other two iron atoms. The seventh carbonyl group is bridged asymmetrically between these two iron atoms, below the iron plane. The characteristic shortening in the Fe-C σ-bond and in the acetylenic C–C bond was observed.

Some interesting reactions of transition metal acetylides with organic reagents are known.[2] However, reactions of these acetylides with organometallics have been little studied. Recently, the acetylides with organometallics have attracted attention from a viewpoint of metal cluster preparation. We have briefly reported[3] the reactions of some transition metal acetylides with metal carbonyls giving new mixed transition metal complexes. Also, Bruce *et al.*[4] have reported the reactions of cupper acetylides with halometal complexes to be an expedient route to clusters.

In a previous paper,[3] we reported the reaction of ethynyldicarbonyl-π-cyclopentadienyliron (**1**), $\pi\text{-}C_5H_5Fe(CO)_2C{\equiv}CR$, with octacarbonyldicobalt which gave $\pi\text{-}C_5H_5Fe(CO)_2(C_2R)Co_2(CO)_6$ (**2a**), when $R=CH_3$, but gave $\pi\text{-}C_5H_5Fe(C_2C_6H_5)Co_2(CO)_6$, when $R=C_6H_5$. A speculative structure **2b** was presented for the product, however later remeasurement of the mass spectra of the product with various conditions revealed that the composition was incorrect but should have been **2a**($R=C_6H_5$). Thus, the reaction of **1** with $Co_2(CO)_8$ gave unequivocally **2a** irrespective of the nature of R($R=CH_3$, CO_2CH_3, and C_6H_5).



2a **2b** **3a**

It is interesting to determine the structure of $\pi\text{-}C_5H_5Fe_3(CO)_7C_2C_6H_5$ (**3**) [which was obtained by us[3] from the reaction of **1** with $Fe_2(CO)_9$ and later also by Bruce[5] from the reaction of $[\pi\text{-}C_5H_5Fe(CO)_2C_2Ph\cdot CuCl]_2$ with $Fe_2(CO)_9$], because the structure **3a** proposed on the basis of an analogy with **2b** is now somewhat doubtful, although metal carbine complexes, $X(CO)_4M{\equiv}CR$, have been obtained by Fischer *et al.*,[6] recently.

Here we report the X-ray determination of the structure of **3**.

Experimental

Monoclinic and triclinic brown crystals were obtained from hexane solution. Preliminary examination of Weissenberg photographs showed that the triclinic crystals were more suitable for further examination than the monocilinic crystals because of large cell constant of the latter, $b\sim55$ Å. (The IR spectrum of the triclinic crystal was identical to that of **3** before growing the crystals.) The diffraction data for the triclinic crystal were collected on automated Phillips PW-100 Single Crystal Diffractometer using monochromatic Mo Kα radiation. The cell constants and the orientation matrix of the triclinic crystal were determined from least-squares refinements of the setting angles for high-angle reflections. These dimensions and other crystal data are given in Table 1. For collection of intensity data, the ω-2θ scan technique with a scan rate of 4.0 °/min was used and 2685 independent reflections up to a maximum 2θ value of 50 ° were measured.

TABLE 1. CRYSTAL DATA FOR $\pi\text{-}C_5H_5Fe_3(CO)_7C_2C_6H_5$

Formula wt 529.8	Triclinic $P\bar{1}$
$a=12.635$ Å	$\alpha=94.64°$
$b=9.457$ Å	$\beta=109.10°$
$c=9.033$ Å	$\gamma=99.60°$
$V=994.98$ Å^3	$Z=2$
Mo Kα radiation	$\mu=22.56$ cm^{-1}
$d_x=1.77$ g/cm^3	d_m[a] $=1.75$ g/cm^3

a) Measured by floatation in an aqueous zinc bromide solution

The intensities of three reflections were measured every 123 reflections as a check on crystal and electronic stability. A correction for Lorentz and polarization factors but no correction for absorption was applied to the data. In the structural refinement the 2488 reflections with $Fo>3\sigma(Fo)$ were used.

The approximate positions of the three Fe atoms were determined from a sharpened Patterson function. From a three-dimensional Fourier synthesis calculated with all terms phased by the Fe atoms, all non-hydrogen atoms of the molecule were located. At this stage, the value of R was 0.353. After five cycles of block-diagonal least-squares refinement with isotropic thermal parameters and five further cycles with anisotropic thermal parameters, (minimizing the function $[\sum w||F_o|-|F_c||^2/\sum w|F_o|^2]^{1/2}$) the R value decreased to 0.045. A weighting scheme, $w=1$, was used. Scattering factors were

TABLE 2. POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS OF THE NON-HYDROGEN ATOMS ($\times 10^4$) WITH THEIR STANDARD DEVIATIONS IN PARANTHESES

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	1406(1)	2208(1)	1197(1)	53(1)	95(1)	119(1)	17(1)	38(1)	−4(1)
Fe(2)	3420(1)	1827(1)	1162(1)	47(1)	96(1)	95(1)	16(1)	21(1)	8(1)
Fe(3)	2296(1)	3206(1)	−865(1)	50(1)	83(1)	115(1)	16(1)	23(1)	15(1)
C(1)	1762(6)	3896(7)	2467(8)	86(6)	131(10)	185(14)	28(7)	59(8)	−15(9)
C(2)	−36(5)	2330(7)	161(8)	72(6)	146(10)	186(14)	35(6)	52(7)	4(10)
C(3)	1124(5)	994(7)	2513(7)	60(5)	126(9)	140(11)	19(6)	37(6)	11(8)
C(4)	3891(6)	2667(7)	3216(7)	85(6)	141(10)	114(11)	23(7)	28(7)	6(8)
C(5)	4763(5)	1931(6)	823(7)	59(5)	113(9)	115(10)	16(5)	22(6)	28(8)
C(6)	3411(4)	35(6)	1679(6)	47(5)	121(9)	105(10)	20(5)	25(6)	9(7)
C(7)	3532(5)	4174(6)	735(7)	74(6)	95(8)	138(11)	14(5)	28(7)	1(8)
C(8)	1767(4)	1247(5)	−352(6)	42(4)	85(7)	98(9)	9(4)	16(5)	0(6)
C(9)	2410(4)	1095(5)	−1195(6)	51(4)	81(7)	93(9)	17(5)	23(5)	1(6)
C(10)	2583(4)	138(6)	−2412(6)	48(4)	100(8)	75(8)	26(5)	15(5)	11(6)
C(11)	1889(5)	−1236(6)	−2961(7)	62(5)	110(8)	109(9)	27(5)	36(6)	18(7)
C(12)	2066(5)	−2166(6)	−4095(7)	84(6)	100(9)	110(10)	24(6)	21(6)	−5(8)
C(13)	2927(6)	−1723(7)	−4676(7)	99(7)	144(10)	118(11)	59(7)	44(7)	−2(9)
C(14)	3612(5)	−372(7)	−4150(7)	69(6)	178(11)	118(11)	34(6)	50(7)	20(9)
C(15)	3445(5)	557(6)	−3016(7)	58(5)	124(10)	109(10)	16(6)	34(6)	−1(8)
C(16)	2689(6)	4590(7)	−2414(8)	92(7)	148(11)	187(14)	32(7)	47(8)	83(10)
C(17)	2125(6)	5259(7)	−1524(9)	101(7)	96(10)	215(15)	28(7)	38(8)	46(10)
C(18)	1063(6)	4433(8)	−1856(9)	89(7)	153(11)	261(17)	57(7)	64(9)	109(12)
C(19)	937(6)	3207(8)	−2927(9)	88(7)	146(12)	194(15)	−7(7)	−42(8)	80(11)
C(20)	1944(7)	3307(8)	−3277(8)	169(10)	175(13)	114(13)	90(10)	32(9)	49(10)
O(1)	1973(5)	4983(6)	3252(7)	170(7)	151(9)	307(15)	26(7)	80(9)	−88(9)
O(2)	−947(4)	2409(6)	−522(7)	63(4)	219(10)	280(13)	46(5)	42(6)	31(9)
O(3)	920(4)	222(5)	3330(6)	103(5)	188(9)	186(10)	23(5)	55(6)	64(8)
O(4)	4238(5)	3146(6)	4504(6)	141(6)	220(10)	118(9)	29(6)	16(6)	−31(8)
O(5)	5587(4)	1971(5)	568(6)	60(4)	202(9)	202(10)	32(5)	52(5)	52(7)
O(6)	3426(4)	−1104(5)	1991(5)	92(4)	119(7)	188(9)	29(4)	54(5)	42(6)
O(7)	4242(4)	5150(5)	1472(6)	102(5)	114(7)	209(11)	−15(5)	−4(6)	−3(7)

The β_{ij}'s are defined by: $\exp[-(h^2\beta_{11}+k^2\beta_{33}+l^2{}_{33}\beta+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$

TABLE 3. POSITIONAL ($\times 10^3$) AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS

	X	Y	Z	B
HC(11)	132(4)	−154(5)	−266(6)	3.60(1.04)
HC(12)	163(5)	−308(6)	−442(6)	4.16(1.04)
HC(13)	307(4)	−232(6)	−533(6)	3.71(1.04)
HC(14)	416(5)	−38(6)	−456(7)	4.34(1.04)
HC(15)	387(4)	154(6)	−263(6)	3.67(1.04)
HC(16)	339(6)	503(7)	−247(8)	7.14(1.04)
HC(17)	248(5)	618(7)	−88(7)	6.06(1.04)
HC(18)	57(6)	470(7)	−122(8)	6.47(1.04)
HC(19)	35(5)	241(7)	−321(8)	6.31(1.04)
HC(20)	211(5)	272(7)	−385(8)	6.43(1.04)

The B is defined by: $\exp[-B(\sin\theta/\lambda)^2]$.

taken from the International Tables.[7] The anomalous dispersion effect was included in the calculated structure factors for iron using $\Delta f'=0.4$ and $\Delta f''=1.0$.[8]

A difference Fourier map then revealed the positions of all the hydrogen atoms. Four cycles of refinement with isotropic thermal parameters for hydrogen and anisotropic thermal parameters for non-hydrogen atoms were carried out, giving a final R of 0.038. The atomic coordinates and anisotropic thermal parameters with estimated standard deviations (esd's) for the non-hydrogen atoms are given in Table 2. The coordinates and isothermal parameters for the hydrogens are given in Table 3.

Description of the Structure and Discussion

The bond distances (with esd's) are shown in Table 4 and the bond angles (with esd's) are listed in Table 5. Important least-squares planes and dihedral angles are shown in Table 6. Fig. 1 shows the packing of the two molecules of **3** in the unit cell. The shortest intermolecular contacts are 2.970(6) Å between O(2) and O(6) at (−x, −y, −z) and 3.082(6) Å between O(5)

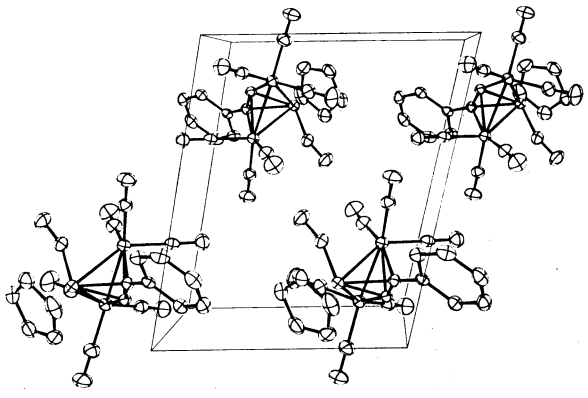


Fig. 1. View of the structure along the c axis showing crystal packing.

TABLE 4. SELECTED BOND LENGTHS (Å)

[Fe_3 Ring and Acetylene moiety]		[Fe–C≡O]	
Fe(1)–Fe(2)	2.639 (1)	Fe(1)–C(1)	1.787 (6)
Fe(1)–Fe(3)	2.632 (1)	Fe(1)–C(2)	1.783 (6)
Fe(2)–Fe(3)	2.524 (1)	Fe(1)–C(3)	1.829 (6)
Fe(1)–C(8)	1.829 (6)	Fe(2)–C(4)	1.819 (6)
Fe(2)–C(8)	2.040 (4)	Fe(2)–C(5)	1.810 (7)
Fe(3)–C(8)	2.006 (5)	Fe(2)–C(6)	1.793 (6)
Fe(2)–C(9)	2.081 (5)	Fe(2)–C(7)	2.273 (6)
Fe(3)–C(9)	2.031 (5)	Fe(3)–C(7)	1.788 (5)
C(8)–C(9)	1.299 (9)	C(1)–O(1)	1.138 (8)
[C_6H_5]		C(2)–O(2)	1.132 (8)
C(9)–C(10)	1.461 (8)	C(3)–O(3)	1.137 (9)
C(10)–C(11)	1.391 (7)	C(4)–O(4)	1.125 (7)
C(11)–C(12)	1.393 (9)	C(5)–O(5)	1.133 (8)
C(12)–C(13)	1.375 (10)	C(6)–O(6)	1.137 (7)
C(13)–C(14)	1.368 (8)	C(7)–O(7)	1.155 (6)
C(14)–C(15)	1.386 (9)		
C(15)–C(10)	1.387 (9)		
[C_5H_5]			
C(16)–C(17)	1.414 (12)		
C(17)–C(18)	1.360 (9)		
C(18)–C(19)	1.400 (11)		
C(19)–C(20)	1.399 (13)		
C(20)–C(16)	1.397 (9)		

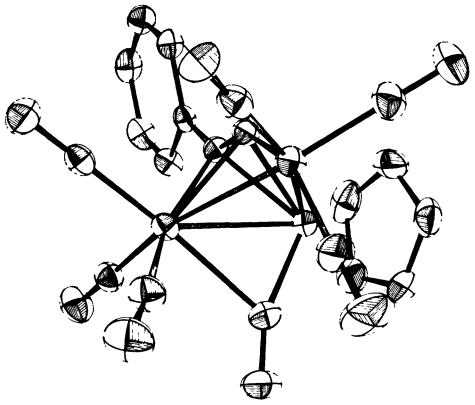


Fig. 2. Perspective view of π-$C_5H_5Fe_3(CO)_7C_2C_6H_5$ molecule.

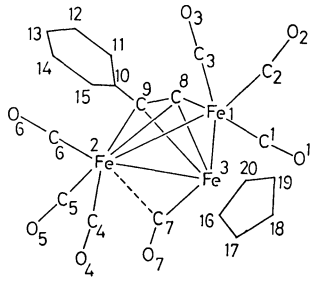


Fig. 3. Numbering scheme for the molecule.

and O(6) at (1−x, −y, −z). All other intermolecular contacts between non-hydrogen atoms are >3.34Å.

The perspective view of **3** without the hydrogens showing thermal vibration with 20% electron density is shown in Fig. 2 and the numbering scheme for the atoms in Fig. 3. The three iron atoms form a triangle in which the distance, Fe(2)–Fe(3)=2.524(1) Å, is slightly shorter than the other two Fe–Fe distances, Fe(1)–Fe(2)=2.639(1) and Fe(1)–Fe(3)=2.632(1) Å. The six carbonyls bond to the Fe(1) and Fe(2) atoms as terminal carbonyls: Two of the three carbonyls on Fe(1) and one of the three on Fe(2) are nearly in the plane of the iron atoms. The terminal carbonyl Fe–C bonds range from 1.738 to 1.829 Å (average 1.801 Å). The seventh carbonyl group is located between the Fe(2) and Fe(3) atoms as an asymmetric bridge[9] [Fe(2)–C(7)=2.273(6) Å and Fe(3)–C(7)=1.788(5) Å, ∠Fe(2)–C(7)–O(7)=126.35(46)° and ∠Fe(3)–C(7)–O(7)=157.63(56)°] below the iron plane. The dihedral angle between the iron plane and the Fe(2)C(7)Fe(3) plane is 106.95°. An IR band, $\nu_{C\equiv O}$= 1870 cm^{-1}, corresponds to this asymmetrically bridged CO. The cyclopentadienyl ring attached to Fe(3) is almost perpendicular to the iron plane: Fe(3) is 1.730 Å from the ring.

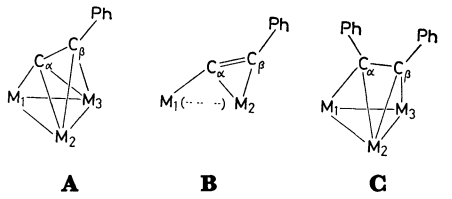


Fig. 4. Schematic geometry of the related σ,π-coordinated ethynyl complexes.

The phenylethynyl group is located above the iron plane: Fe(1)–C(8)=1.829(6), C(8)–C(9)=1.299(9), Fe(2)–C(8)=2.040(4), Fe(3)–C(8)=2.006(9), Fe(2)–C(9)=2.081(5), Fe(3)–C(9)=2.031(5) Å. The dihedral angle between the iron plane and the Fe(2)C(8)Fe(3) plane is 51.97° and that between the iron plane and the Fe(2)C(9)Fe(3) plane is 99.28°. These distances and angles show that the phenylethynyl group, originally σ-bonded to the Fe(3) atom, is now σ-bonded to the Fe(1) atom and π-bonded symmetrically to both the Fe(2) and Fe(3) atoms through the C(8)–C(9) triple bond. The configuration about the three iron atoms and the phenylethynyl group is shown in Fig. 4 (Type **A**) (in which C(α) and C(β) correspond to C(8) and C(9)). $Ru_3(CO)_9H(C_2Bu^t)$ (**4**) has been reported[10] to have a very similar configuration to **3**. Some complexes in which a σ-bonded acetylide is π-bonded to one metal (type **B**) have also been reported.[11,12] The geometries of these related complexes are summarized in Table 7.

A similarity around the C(α)–C(β) moiety in both **3** and **4** is evident when the difference (~0.1 Å) in the M–C distances for the terminal carbonyls (the average Fe–C in **3** is 1.801 and Ru–C in **4** is 1.91 Å), and in the M(1)–C(α) distances in [π-$C_5H_5Fe(CO)_2C_2Ph$·$CuCl]_2$[12] and π-$C_5H_5Ru(PPh_3)_2C_2Ph$·$CuCl$[5a] is assumed also to be due solely to the difference between Fe and Ru covalent radii.

The distance C(α)–C(β) in **3** is markedly shorter than the acetylenic C–C distances found in the usual dinuclear monoacetylene complexes, *e.g.* (π-$C_5H_5)_2Ni_2$-(PhC_2Ph)[13] 1.35(3), $Co_2(CO)_6(PhC_2Ph)$[14] 1.46, and (π-C_5H_5)$NiFe(CO)_3(Ph_3PC_2H)$[15] 1.37(3) Å. The C(α)–C(β) distance in the type **B** complexes are a little shorter than that in **3**, whereas the Fe(1)–C(α) distance

TABLE 5. SELECTED BOND ANGLES (deg)

Fe(2)–Fe(1)–Fe(3)	57.23 (3)	Fe(3)–Fe(1)–C(1)	96.00 (23)
Fe(1)–Fe(2)–Fe(3)	61.24 (3)	Fe(3)–Fe(1)–C(2)	97.47 (23)
Fe(1)–Fe(3)–Fe(2)	61.52 (3)	Fe(3)–Fe(1)–C(3)	156.94 (20)
C(8)–Fe(1)–Fe(2)	50.45 (17)	C(8)–Fe(1)–C(1)	142.88 (29)
C(8)–Fe(1)–Fe(3)	49.52 (17)	C(8)–Fe(1)–C(2)	101.71 (28)
C(8)–Fe(2)–Fe(1)	43.72 (15)	C(8)–Fe(1)–C(3)	110.18 (26)
C(8)–Fe(2)–Fe(3)	50.79 (15)	C(1)–Fe(1)–C(2)	95.43 (32)
C(8)–Fe(2)–C(9)	36.73 (21)	C(1)–Fe(1)–C(3)	99.61 (31)
C(8)–Fe(3)–Fe(1)	43.92 (15)	C(2)–Fe(1)–C(3)	97.83 (30)
C(8)–Fe(3)–Fe(2)	52.01 (15)		
C(8)–Fe(3)–C(9)	37.55 (21)	Fe(1)–Fe(2)–C(4)	82.66 (21)
C(9)–Fe(2)–Fe(3)	51.22 (15)	Fe(1)–Fe(2)–C(5)	165.26 (19)
C(9)–Fe(3)–Fe(2)	53.04 (15)	Fe(1)–Fe(2)–C(6)	101.05 (19)
C(9)–Fe(2)–C(7)	91.32 (22)	Fe(3)–Fe(2)–C(4)	115.95 (21)
C(9)–Fe(3)–C(7)	109.24 (25)	Fe(3)–Fe(2)–C(5)	104.52 (19)
		Fe(3)–Fe(2)–C(6)	141.39 (19)
Fe(1)–C(8)–Fe(2)	85.83 (22)	C(8)–Fe(2)–C(4)	126.02 (26)
Fe(1)–C(8)–Fe(3)	86.56 (22)	C(8)–Fe(2)–C(5)	131.43 (24)
Fe(2)–C(8)–Fe(3)	77.21 (19)	C(8)–Fe(2)–C(6)	92.01 (24)
C(9)–C(8)–Fe(1)	152.91 (45)	C(4)–Fe(2)–C(5)	101.93 (28)
C(9)–C(8)–Fe(2)	73.36 (33)	C(4)–Fe(2)–C(6)	93.10 (28)
C(9)–C(8)–Fe(3)	72.27 (33)	C(5)–Fe(2)–C(6)	92.74 (26)
Fe(2)–C(9)–Fe(3)	75.73 (18)	C(7)–Fe(2)–C(4)	82.05 (26)
C(8)–C(9)–Fe(2)	69.91 (33)	C(7)–Fe(2)–C(5)	86.57 (25)
C(8)–C(9)–Fe(3)	70.18 (33)	C(7)–Fe(2)–C(6)	174.90 (24)
C(10)–C(9)–Fe(2)	131.07 (39)	C(7)–Fe(2)–Fe(3)	43.38 (16)
C(10)–C(9)–Fe(3)	135.97 (39)	C(7)–Fe(3)–Fe(2)	60.80 (20)
C(8)–C(9)–C(10)	144.74 (52)	Fe(2)–C(7)–Fe(3)	75.82 (22)
Fe(2)–Fe(1)–C(1)	102.61 (23)	O(7)–C(7)–Fe(2)	126.35 (49)
Fe(2)–Fe(1)–C(2)	149.96 (23)	O(7)–C(7)–Fe(3)	157.63 (56)
Fe(2)–Fe(1)–C(3)	102.52 (20)		
Fe(1)–C(1)–O(1)	178.56 (66)	C(10)–C(11)–C(12)	120.20 (54)
Fe(1)–C(2)–O(2)	178.69 (64)	C(11)–C(12)–C(13)	119.91 (58)
Fe(1)–C(3)–O(3)	178.51 (58)	C(12)–C(13)–C(14)	120.48 (62)
Fe(2)–C(4)–O(4)	175.77 (61)	C(13)–C(14)–C(15)	119.97 (60)
Fe(2)–C(5)–O(5)	177.92 (55)	C(14)–C(15)–C(10)	120.76 (55)
Fe(2)–C(6)–O(6)	178.32 (52)	C(15)–C(10)–C(11)	118.68 (51)
C(16)–C(17)–C(18)	108.73 (65)		
C(17)–C(18)–C(19)	108.43 (67)		
C(18)–C(19)–C(20)	108.00 (67)		
C(19)–C(20)–C(16)	107.62 (68)		
C(20)–C(16)–C(17)	107.21 (65)		

TABLE 6. LEAST-SQUARE PLANES AND DIHEDRAL ANGLES

Plane	Atoms defining plane	Equation of mean plane
I	Fe(1) Fe(2) Fe(3)	$0.2705x+0.8548y+0.4429z=2.2267$
II	Fe(1) C(8) C(9)	$0.6420x-0.5081y+0.5742z=-0.0416$
III	Fe(2) Fe(3) C(7)	$-0.6115x+0.1302y+0.7804z=-2.4545$
IV	C(10) C(11) C(12) C(13) C(14) C(15)	$0.7250x-0.3684y+0.5819z=0.2739$
V	C(16) C(17) C(18) C(19) C(20)	$0.4864x-0.4957y+0.7195z=-3.5856$
VI	Fe(2) C(8) Fe(3)	$-0.4018x+0.4287y+0.8092z=-1.1836$
VII	Fe(2) C(9) Fe(3)	$0.7572x+0.2680y-0.5957z=3.5761$

Displacements of atoms from mean palne (Å)

Plane I		Plane II		Plane IV		Plane V	
Fe(1)	0.0000	Fe(1)	0.0000	C(10)	−0.0001	C(16)	−0.0050
Fe(2)	0.0000	C(8)	0.0000	C(11)	−0.0015	C(17)	0.0077
Fe(3)	0.0000	C(9)	0.0000	C(12)	0.0009	C(18)	−0.0074
C(8)	−1.2449	C(10)	0.0692	C(13)	0.0013	C(19)	0.0041
C(9)	−1.5989	Fe(2)	1.2907	C(14)	−0.0028	C(20)	0.0006
C(7)	1.4932	Fe(3)	−1.2335	C(15)	0.0022	Fe(3)	1.7297

Dihedral angles between planes (deg)

I—II	I—III	I—IV	I—V	II—IV	I—VI	I—VII
100.58	106.95	82.02	91.22	9.33	51.97	99.28

The planes are in cartesian coordinates with the z axis coinciding with c and the y axis coinciding with to b*.

TABLE 7. GEOMETRIES OF THE RELATED COMPLEXES

	Type[a]	Distances (Å)						Angles (deg)	
		M(1)–C(α)	C(α)–C(β)	C(α)–M(2 or 3)	C(β)–M(2 or 3)	M(1)–M(2 or 3)	M(2)–M(3)	∠M(1)-C(α) C(β)	∠C(α)-C(β)Ph
π-$C_5H_5Fe_3(CO)_7C_2Ph$[b]	A	1.829(6)	1.299(9)	2.040(4)	2.081(5)	2.639(1)	2.524(1)	152.91(45)	144.74(52)
				2.006(5)	2.031(5)	2.632(1)			
$Ru_3(CO)_9H(C_2Bu^t)$[c]	A	1.99(2)	1.29(3)	2.23(2)	2.25(3)	2.795(2)	2.790(2)	153(2)	138(2)[h]
				2.26(2)	2.18(2)	2.796(2)			
$Fe_2(CO)_6(PPh_2)(C_2Ph)$[d]	B	1.89(6)	1.232(10)	2.125(8)	2.304(7)	2.597(2)		160.3(6)	162.3(8)
[π-$C_5H_5Fe(CO)_2C_2Ph$·CuCl]$_2$[e]	B	1.89(2)	1.27(2)	1.99(2)	1.99(2)			162(2)[i]	162(2)
π-$C_5H_5Ru(PPh_3)_2C_2Ph$·CuCl[f]	B	2.016(9)	1.25(1)	2.01(1)	2.04(1)			172.76(8)[i]	165.0(1.0)
$Fe_3(CO)_9(PhC_2Ph)$[g]	C	2.048(16)	1.492(23)	2.098(15)	1.947(16)	2.480(10)	2.579(11)	126.9(1.0)	130.8(1.3)
				2.043(15)	1.945(15)	2.501(9)			

a) as shown in Fig. 4. b) This work, c) Ref. 10. d) Ref. 11, e) Ref. 12, f) Ref. 5a, g) Ref. 17, h) ∠C(α) C(β) C(of Bu^t), i) These two complexes have no M_1–M_2 bond and the M_1–C=C–Ph moiety has *cis* configuration.

in **3** is a little shorter than that in the type **B** compounds. The shorter distances, M(1)–C(α) and C(α)–C(β), in **3** may reflect an additional interaction between the Fe(1) and C(α) or among Fe(1), C(α), and C(β), although the decrease in the Fe(1)–C(α) distance is not so great as the decrease between carbene and carbin complexes: $(Co)_5CrC(OCH_3)C_6H_5$ 2.04(3) and $(CO)_4ICrCCH_3$ 1.69(1) Å.[16]

The shortening of the Fe(1)–C(α) and C(α)–C(β) bonds may be emphasized also by comparison with $Fe_3(CO)_9(PhC_2Ph)$[17] (**5**) (type **C**) in which the C(α) atom has more phenyls than the C(α) atom in **3**. Another difference between **3** and **5** is that the phenyl plane in **3** is almost parallel to the Fe(1)C(α)C(β) plane (dihedral angle=9.33°), whereas the phenyls in **5** are not.

The C(β)–(phenyl) distance and ∠C(α)–C(β)–(phenyl) are in good agreement with those in $(\pi$-$C_5H_5)_2Ni_2(PhC_2Ph)$,[13] average 1.45 Å and 140°, and in $Co_2(CO)_6(PhC_2Ph)$,[14] average 1.43 Å and 138°.

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