

Carbon Compounds of the Transition Metals. Part XXVII.¹ Crystal and Molecular Structure of [Bis(biphenylidene)butatriene]hexacarbonyldi-iron, a Binuclear Metal Cumulene Complex

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The crystal structure of the title complex has been determined from 1351 visually estimated X-ray intensities and refined by least-squares methods to R 6.9%. The unit-cell parameters are $a = 16.36$, $b = 10.83$, $c = 16.47$ Å, $\beta = 110.13^\circ$, $Z = 4$, space group $P2_1/n$. The butatriene chain is bent into a zig-zag in which the bond angles at the central chain atoms are 128° and the iron atoms may be regarded as bonded to the chain *via* σ bonds to the central carbons and *via* π bonds to the terminal double bonds. The three C–C(chain) distances are equal. Distances are: Fe–Fe (2.596(4)), mean Fe–CO 1.77(1), mean Fe–C(chain) 2.39 and 2.04 (π), 1.94 (σ), mean C–C(chain) 1.39 Å.

THE synthesis of a series of butatriene(hexacarbonyl)di-iron complexes² and of a butatriene(tetracarbonyl)iron complex³ was recently reported. Some of the same di-iron complexes were isolated independently and initially formulated as being pentacarbonyl complexes,⁴ although later it was recognised, in accord with our own crystallographic determination, that there were six carbonyl groups per molecule.⁵ In an earlier paper we reported the structure of the mononuclear tetracarbonyl complex.⁶ We present here the structure of one of the

di-iron complexes: [bis(biphenylidene)butatriene]hexacarbonyldi-iron (1).

EXPERIMENTAL

Several crystalline complexes of variously substituted butatrienes were examined.

(1) Butatrienehexacarbonyldi-iron, $C_{10}H_4O_6Fe_2$, $M = 331.8$, Orthorhombic, $a = 12.03(5)$, $b = 8.12(3)$, $c = 12.25(5)$ Å, $U = 1197$ Å³, $D_m = 1.79$, $D_c = 1.84$, $Z = 4$, systematic absences $0kl$ for $k + l$ odd, $h0l$ for h odd, space group $Pna2_1$ or $Pnam$.

³ K. K. Joshi, *J. Chem. Soc. (A)*, 1966, 598.

⁴ A. Nakamura, P.-J. Kim, and N. Hagihara, *J. Organometallic Chem.*, 1965, **3**, 7.

⁵ A. Nakamura, P.-J. Kim, and N. Hagihara, *J. Organometallic Chem.*, 1966, **6**, 420.

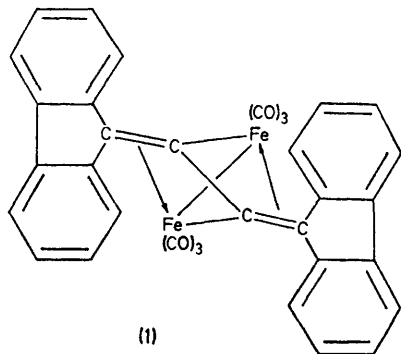
⁶ D. Bright and O. S. Mills, *J. Chem. Soc. (A)*, 1971, 1979.

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¹ Part XXVI, R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 2141.

² K. K. Joshi, *J. Chem. Soc. (A)*, 1966, 594.

(2) Tetramethylbutatrienehexacarbonyldi-iron, $C_{14}H_{12}O_6Fe_2$, $M = 387.9$, Monoclinic, $a = 15.17(6)$, $b = 14.87(6)$, $c = 15.56(6)$ Å, $\beta = 114.63(5)^\circ$, $U = 3190$ Å³, $D_m = 1.62$, $D_c = 1.62$, $Z = 8$, space group $P2_1/n$ by systematic absences.



(1)

(3) Tetraphenylbutatrienehexacarbonyldi-iron, $C_{34}H_{20}O_6Fe_2$, $M = 636.0$ Monoclinic, $a = 17.27(6)$, $b = 10.18(5)$, $c = 17.29(6)$ Å, $\beta = 110.67(5)^\circ$, $U = 2844$ Å³, $D_m = 1.48$, $D_c = 1.49$, $Z = 4$, space group $P2_1/n$ by systematic absences.

(4) Bis(biphenylidene)butatrienehexacarbonyldi-iron, $C_{34}H_{16}Fe_2O_6$, $M = 632.0$, Monoclinic, $a = 16.36(6)$, $b = 10.83(5)$, $c = 16.47(6)$ Å, $\beta = 110.13(5)^\circ$, $U = 2740$ Å³, $D_m = 1.51$, $Z = 4$, $D_c = 1.49$. Space group $P2_1/n$ by systematic absences. $Mo-K\alpha$ radiation, $\lambda = 0.7107$ Å; $\mu(Mo-K\alpha) = 11.36$ cm⁻¹.

The unsubstituted complex was unstable to X-rays, the tetramethyl complex has the disadvantage of having two molecules per asymmetric unit, and the crystals of the tetraphenyl complex were rather poorly formed. The bis(biphenylidene) complex was chosen for the structure determination and the intensities of 1351 reflexions, of which 95 were too weak to be recorded, were measured visually from precession photographs taken with $Mo-K\alpha$ radiation. No correction was made for absorption. A crystal of maximum dimension 0.3 mm was used.

Structure Solution and Refinement.—The structure was solved by conventional Patterson and Fourier techniques and refined by least-squares methods. The function minimised was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = 1 + a \cdot F_o^2$. The constant a was chosen to maintain values of the mean $w(|F_o| - |F_c|)^2$ approximately equal for ranges of F_o and $\sin \theta/\lambda$, and was 6×10^{-5} . The unobserved reflexions were given zero weight if $|F_c| < F_{min}$, the smallest value of $|F_o|$ listed, otherwise $w(|F_o| - |F_c|)$ was set equal to $0.5(F_{min} - |F_c|)$.

Atomic scattering factors were taken from ref. 7 and a correction of 0.42 electrons was added over the whole of the curve for iron to allow for the effects of anomalous dispersion. A difference-Fourier synthesis calculated at the stage R 9.4% showed peaks of approximately 0.3 eÅ⁻³ in the regions where hydrogen atoms were to be expected. In the subsequent refinement cycles the hydrogen atoms were included at fixed positions 1.08 Å from the carbon atoms. The iron atoms were refined with anisotropic temperature factors and the remaining non-hydrogen atoms with isotropic temperature factors. The final value of R was 6.9% for the observed reflexions and 7.8% for all 1351 reflexions. A list

⁷ 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

⁸ A. A. Hock and O. S. Mills, *Acta Cryst.*, 1961, **14**, 139.

of final observed and calculated structure factors is available from the authors.

RESULTS AND DISCUSSION

The structure comprises discrete molecules of $[(C_{12}H_8)_2C_4]Fe_2(CO)_6$ with no intermolecular contact < 3.2 Å, save $H \cdots H$ contacts. Projections of the structure along two of the crystallographic axes are shown in Figures 1 and 2. Figures 3 and 4 show two views of the molecule. Atomic parameters are listed in Table 1 and selected interatomic distances and angles in Tables 2 and 3; details of the best least-squares planes through some atomic groupings are given in Table 4.

Within experimental error, the molecule possesses a non-crystallographic two-fold axis which passes through the mid-points of the $Fe \cdots Fe$ vector and the central C-C bond of the butatriene chain. The iron atoms are thus in essentially identical environments.

The central atoms of the butatriene chain occupy slightly asymmetric bridging positions with respect to the $Fe \cdots Fe$ vector and the chain, although linear in the uncomplexed species, takes up a zig-zag configuration in the complex with bond angles of $128(2)$ and $129(2)^\circ$ at the central atoms. The mean Fe-C bridging distances are 1.94(1) and 2.04(1) Å. The shorter of these is similar to the value 1.94 Å found⁸ in the ferrapentadienyl ring and this, coupled with the observation that the iron

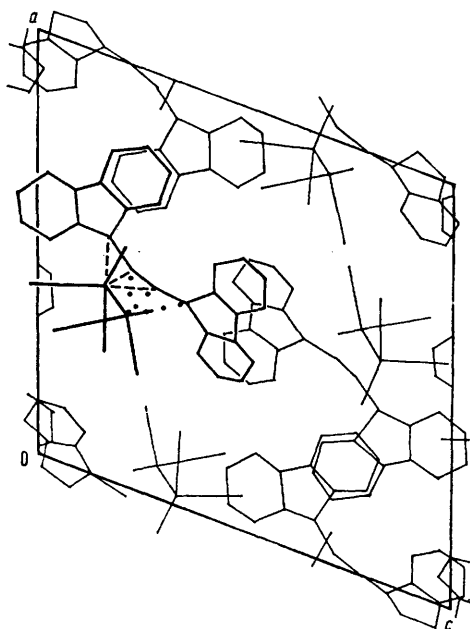


FIGURE 1 The structure of bis(biphenylidene)butatrienehexacarbonyldi-iron projected along the b axis

atoms are each almost coplanar with one of the biphenylidene groups (see Table 4), strongly suggests that the terminal double bonds of the butatriene system have remained essentially intact on complex formation and that each of the central carbon atoms are largely σ bonded to one iron atom. A valence-bond description

may then be completed by assuming olefinic π bonds from the terminal C-C double bonds to the nearer iron

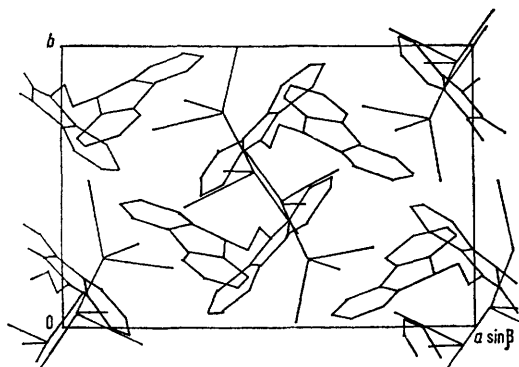


FIGURE 2 The structure projected along the c axis

TABLE 1
Atomic parameters

Atom	x	y	z	$B/\text{\AA}^2$
Fe(1)	0.0362(1)	0.0576(2)	0.3350(2)	*
Fe(2)	0.0907(1)	0.2626(3)	0.2904(2)	*
C(1)	0.1317(11)	-0.0156(19)	0.2275(11)	3.3(4)
O(1)	0.1948(8)	-0.0651(15)	0.3417(8)	4.4(3)
C(2)	0.0714(10)	0.0608(20)	0.4520(10)	2.5(3)
O(2)	0.0954(8)	0.0628(15)	0.5268(9)	4.6(3)
C(3)	-0.0281(12)	-0.0781(22)	0.3092(13)	4.1(4)
O(3)	-0.0677(10)	-0.1667(18)	0.2919(11)	6.8(4)
C(4)	0.1903(11)	0.2342(21)	0.2709(11)	3.5(4)
O(4)	0.2553(9)	0.2149(14)	0.2582(9)	4.8(3)
C(5)	0.1442(11)	0.2900(19)	0.4024(11)	3.2(4)
O(5)	0.1826(7)	0.3113(13)	0.4746(8)	3.8(3)
C(6)	0.0754(12)	0.4188(22)	0.2604(12)	4.1(4)
O(6)	0.0621(9)	0.5219(17)	0.2448(10)	5.4(4)
C(7)	-0.0835(8)	0.1913(16)	0.3257(9)	1.3(3)
C(8)	-0.0273(9)	0.2177(16)	0.2821(10)	2.0(3)
C(9)	-0.0055(10)	0.1422(18)	0.2248(11)	2.7(4)
C(10)	-0.0139(9)	0.1744(16)	0.1514(9)	1.8(3)
C(11)	-0.0906(8)	0.2427(17)	0.4046(9)	1.7(3)
C(12)	-0.0319(9)	0.3152(17)	0.4669(9)	2.0(3)
C(13)	-0.0548(10)	0.3539(17)	0.5403(11)	2.7(3)
C(14)	-0.1337(10)	0.3162(20)	0.5442(11)	3.1(3)
C(15)	-0.1912(9)	0.2442(17)	0.4844(9)	2.9(3)
C(16)	-0.1689(9)	0.2086(17)	0.4123(10)	2.3(3)
C(17)	-0.2171(9)	0.1376(16)	0.3377(10)	2.2(3)
C(18)	-0.3011(10)	0.0877(18)	0.3093(10)	2.6(3)
C(19)	-0.3357(10)	0.0314(17)	0.2298(10)	2.3(3)
C(20)	-0.2864(10)	0.0205(19)	0.1729(11)	3.1(4)
C(21)	-0.2026(9)	0.0715(17)	0.1998(10)	2.2(3)
C(22)	-0.1701(9)	0.1246(17)	0.2801(10)	2.0(3)
C(23)	-0.0369(9)	0.2751(17)	0.0906(9)	1.9(3)
C(24)	-0.1034(10)	0.3490(18)	0.0881(11)	2.8(4)
C(25)	-0.1417(12)	0.4284(22)	0.0175(12)	4.0(4)
C(26)	-0.1115(12)	0.4275(23)	-0.0487(13)	4.5(4)
C(27)	-0.0462(11)	0.3495(19)	-0.0491(12)	3.1(4)
C(28)	-0.0081(9)	0.2672(18)	0.0181(10)	2.4(3)
C(29)	0.0532(9)	0.1744(18)	0.0289(10)	2.2(3)
C(30)	0.0996(11)	0.1283(20)	-0.0245(11)	3.3(4)
C(31)	0.1504(10)	0.0295(18)	0.0008(11)	2.7(3)
C(32)	0.1569(9)	-0.0363(18)	0.0756(10)	2.4(3)
C(33)	0.1117(11)	0.0033(21)	0.1287(12)	3.7(4)
C(34)	0.0631(6)	0.1113(14)	0.1055(7)	1.5(2)

* Anisotropic thermal parameters ($\times 10^4$) for the iron atoms:

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe(1)	29(1)	45(3)	23(1)	-1(2)	14(1)	7(2)
Fe(2)	27(1)	49(3)	19(1)	-6(2)	13(1)	2(2)

The form of the anisotropic thermal ellipsoid is given by:

$$\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$$

atom with a metal-metal bond. The bonding scheme shown in (1) leads to an inert gas configuration of 36

electrons on each iron atom and accounts for the diamagnetism of the complex. The compound can be regarded as a double π -allyl-metal bonded arrangement in which one of the valence-bond forms predominates and in which the central bond participates in both organometallic links.

Subsequently, other examples of asymmetric π -allyl bonding have been described and in these cases the

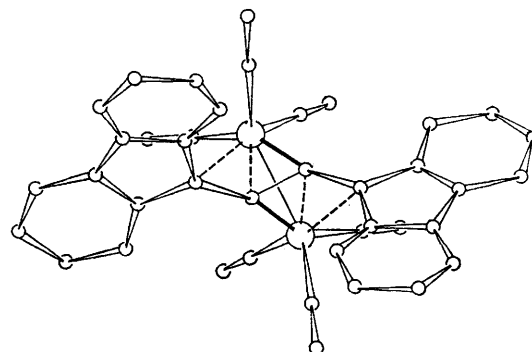


FIGURE 3 The molecule viewed along the molecular two-fold axis

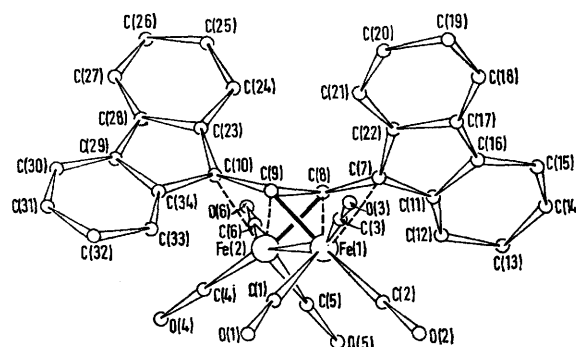


FIGURE 4 The molecule viewed perpendicular to the molecular two-fold axis showing the atom numbering system used in the analysis

TABLE 2
Selected interatomic distances (\AA)

Fe(1)-Fe(2)	2.596(4)	C(14)-C(15)	1.34(2)
Fe(1)-C(8)	2.05(2)	C(15)-C(16)	1.42(2)
Fe(2)-C(9)	2.03(2)	C(16)-C(17)	1.42(2)
Fe(1)-C(7)	2.40(2)	C(17)-C(18)	1.39(2)
Fe(2)-C(10)	2.38(2)	C(17)-C(22)	1.43(2)
Fe(1)-C(9)	1.93(2)	C(18)-C(19)	1.37(2)
Fe(2)-C(8)	1.95(2)	C(19)-C(20)	1.44(2)
Fe(1)-C(1)	1.74(2)	C(20)-C(21)	1.40(2)
Fe(1)-C(2)	1.80(2)	C(21)-C(22)	1.36(2)
Fe(1)-C(3)	1.77(2)	C(22)-C(7)	1.53(2)
Fe(2)-C(4)	1.80(2)	C(11)-C(7)	1.46(2)
Fe(2)-C(5)	1.76(2)	C(10)-C(23)	1.51(2)
Fe(2)-C(6)	1.75(2)	C(10)-C(34)	1.46(2)
C(1)-O(1)	1.14(2)	C(23)-C(24)	1.34(2)
C(2)-C(2)	1.15(2)	C(23)-C(28)	1.44(2)
C(3)-O(3)	1.14(2)	C(24)-C(25)	1.40(2)
C(4)-O(4)	1.17(2)	C(25)-C(26)	1.35(2)
C(5)-O(5)	1.15(2)	C(26)-C(27)	1.36(2)
C(6)-O(6)	1.15(2)	C(27)-C(28)	1.38(2)
C(7)-C(8)	1.39(2)	C(28)-C(29)	1.39(2)
C(8)-C(9)	1.39(2)	C(29)-C(30)	1.44(2)
C(9)-C(10)	1.40(2)	C(29)-C(34)	1.39(2)
C(11)-C(12)	1.37(2)	C(30)-C(31)	1.33(2)
C(11)-C(16)	1.38(2)	C(31)-C(32)	1.39(2)
C(12)-C(13)	1.45(2)	C(32)-C(33)	1.40(2)
C(13)-C(14)	1.38(2)	C(33)-C(34)	1.39(2)

TABLE 3
Selected interatomic angles (deg.)

C(1)-Fe(1)-C(2)	92.6(8)	C(14)-C(15)-C(16)	117(2)
C(1)-Fe(1)-C(3)	94.5(9)	C(15)-C(16)-C(11)	122(2)
C(1)-Fe(1)-C(7)	169.6(8)	C(17)-C(16)-C(11)	108(2)
C(1)-Fe(1)-C(8)	135.1(8)	C(15)-C(16)-C(17)	130(1)
C(1)-Fe(1)-C(9)	104.4(8)	C(16)-C(17)-C(18)	132(1)
C(2)-Fe(1)-C(3)	102.0(9)	C(16)-C(17)-C(22)	111(1)
C(2)-Fe(1)-C(7)	89.8(7)	C(18)-C(17)-C(22)	116(1)
C(2)-Fe(1)-C(8)	110.9(8)	C(17)-C(18)-C(19)	121(1)
C(2)-Fe(1)-C(9)	150.1(9)	C(18)-C(19)-C(20)	122(1)
C(3)-Fe(1)-C(7)	94.7(9)	C(19)-C(20)-C(21)	118(1)
C(3)-Fe(1)-C(8)	115.8(7)	C(20)-C(21)-C(22)	118(1)
C(3)-Fe(1)-C(9)	101.0(8)	C(17)-C(22)-C(21)	125(1)
C(7)-Fe(1)-C(8)	35.2(5)	C(17)-C(22)-C(7)	105(1)
C(7)-Fe(1)-C(9)	69.4(6)	C(21)-C(22)-C(7)	130(1)
C(8)-Fe(1)-C(9)	40.8(6)	C(11)-C(7)-C(22)	105(1)
C(4)-Fe(2)-C(5)	94.3(8)	C(11)-C(7)-C(8)	132(1)
C(4)-Fe(2)-C(6)	99.3(9)	C(22)-C(7)-C(8)	121(1)
C(4)-Fe(2)-C(8)	152.2(8)	C(7)-C(8)-C(9)	128(2)
C(4)-Fe(2)-C(9)	112.0(8)	C(8)-C(9)-C(10)	129(2)
C(4)-Fe(2)-C(10)	87.6(7)	C(9)-C(10)-C(34)	132(2)
C(5)-Fe(2)-C(6)	95.7(10)	C(9)-C(10)-C(23)	121(1)
C(5)-Fe(2)-C(8)	102.8(7)	C(23)-C(10)-C(34)	106(1)
C(5)-Fe(2)-C(9)	131.6(8)	C(10)-C(23)-C(24)	134(1)
C(5)-Fe(2)-C(10)	165.4(8)	C(10)-C(23)-C(28)	104(1)
C(6)-Fe(2)-C(8)	100.6(8)	C(24)-C(23)-C(28)	121(2)
C(6)-Fe(2)-C(9)	117.7(8)	C(23)-C(24)-C(25)	121(2)
C(6)-Fe(2)-C(10)	98.3(8)	C(24)-C(25)-C(26)	119(2)
C(8)-Fe(2)-C(9)	40.8(6)	C(25)-C(26)-C(27)	122(2)
C(8)-Fe(2)-C(10)	70.5(6)	C(26)-C(27)-C(28)	122(2)
C(9)-Fe(2)-C(10)	35.9(6)	C(27)-C(28)-C(29)	132(1)
Fe(1)-C(1)-O(1)	178(2)	C(23)-C(28)-C(29)	112(2)
Fe(1)-C(2)-O(2)	179(1)	C(23)-C(28)-C(27)	116(2)
Fe(1)-C(3)-O(3)	178(2)	C(28)-C(29)-C(30)	134(2)
Fe(2)-C(4)-O(4)	180(2)	C(28)-C(29)-C(34)	108(1)
Fe(2)-C(5)-O(5)	176(2)	C(30)-C(29)-C(34)	118(1)
Fe(2)-C(6)-O(6)	175(2)	C(27)-C(30)-C(31)	120(2)
C(12)-C(11)-C(16)	120(1)	C(30)-C(31)-C(32)	122(2)
C(12)-C(11)-C(7)	129(1)	C(31)-C(32)-C(33)	120(2)
C(16)-C(11)-C(7)	111(1)	C(32)-C(33)-C(34)	118(2)
C(11)-C(12)-C(13)	118(1)	C(33)-C(34)-C(28)	128(1)
C(12)-C(13)-C(14)	119(2)	C(28)-C(34)-C(29)	110(1)
C(13)-C(14)-C(15)	124(2)	C(29)-C(34)-C(33)	122(1)
Fe(1)-C(8)-Fe(2)	80.6(5)	Fe(1)-C(9)-Fe(2)	81.2(5)

asymmetry has been ascribed to the differing electron donating properties of groups *trans* to the terminal allylic carbon atoms. In these compounds the expected lengthening of the 'single' C-C bonds is found. Thus in Pd(C₄H₇)(PPh₃)Cl⁹ the 'double' bond and 'single' bond lengths are 1.40 and 1.47 Å respectively. In [Rh(C₃H₅)Cl]₂,¹⁰ where the effect is found twice, the corresponding values are 1.40 and 1.41, on the one hand, and 1.45 and 1.48 Å on the other. Although the differences in the individual cases are scarcely significant when the estimated standard deviations are considered, a trend is nevertheless apparent. In the butatriene complex we find no comparable effect. Although one might expect the central bond to be longer than the terminal ones on the basis of the scheme shown in (1), the three C-C bonds of the butatriene are equal in length, mean 1.39 Å. This seems to indicate that there remains considerable electron delocalisation in the complexed butatriene system even though there is a torsion angle of 34° about the central bond. Such delocalisation is not unexpected since the valence-bond description is clearly an oversimplification. The orbital symmetry of the central bond in butatriene is similar to that in acetylene and small rotations about it should not therefore have a great effect on the orbital overlap. Extended Hückel

calculations carried out for an isolated butatriene molecule indicate that in the complexed configuration the total overlap populations in the terminal and central bonds are 0.57 and 0.67 e⁻ respectively. These values

TABLE 4

Equations of best least-squares planes defined by atomic positions, where X, Y, Z are atomic co-ordinates, in Å, with respect to orthogonal axes parallel with *a*, *b*, and *a* × *b*. Deviations (Å) of atoms from the planes are given in square brackets

Plane (1): C(11)—(22), C(7)

$$-0.2524X + 0.8494Y - 0.4635Z - 0.3024 = 0$$

[C(7) -0.066, C(11) -0.017, C(12) 0.050, C(13) 0.080, C(14) 0.036, C(15) -0.045, C(16) -0.051, C(17) -0.077, C(18) -0.026, C(19) 0.054, C(20) 0.077, C(21) 0.046, C(22) -0.061, Fe(2) 0.073]

Plane (2): C(10), C(23)—(34)

$$0.6187X + 0.6403Y + 0.4552Z - 1.7453 = 0$$

C(10) 0.139, C(23) 0.109, C(24) -0.061, C(25) -0.147, C(26) -0.081, C(27) 0.037, C(28) 0.090, C(29) 0.104, C(30) 0.066, C(31) -0.016, C(32) -0.142, C(33) -0.137, C(34) 0.038, Fe(1) 0.204]

Plane (3): C(11)—(16)

$$-0.2809X + 0.8223Y - 0.4950Z - 0.1268 = 0$$

[C(11) -0.002, C(12) -0.003, C(13) 0.002, C(14) 0.005, C(15) -0.010, C(16) 0.008]

Plane (4): C(17)—(22)

$$-0.2387X + 0.8786Y - 0.4135Z - 0.4503 = 0$$

[C(17) 0.005, C(18) 0.001, C(19) 0.001, C(20) -0.008, C(21) 0.014, C(22) -0.012]

Plane (5): C(7), C(11), C(16), C(17), C(22)

$$-0.2609X + 0.8395Y - 0.4766Z - 0.1947 = 0$$

[C(7) -0.018, C(11) 0.015, C(16) -0.006, C(17) -0.006, C(22) 0.014]

Plane (6): C(23)—(28)

$$0.5546X + 0.7065Y + 0.4397Z - 2.0675 = 0$$

[C(23) 0.034, C(24) -0.013, C(25) -0.011, C(26) 0.014, C(27) 0.008, C(28) -0.030]

Plane (7): C(29)—(34)

$$0.6509X + 0.5661Y + 0.5058Z - 1.7632 = 0$$

[C(29) -0.008, C(30) -0.017, C(31) 0.022, C(32) -0.003, C(33) -0.022, C(34) 0.027]

Plane (8): C(10), C(23), C(28), C(29), C(34)

$$0.6353X + 0.6286Y + 0.4486Z - 1.8052 = 0$$

[C(10) 0.032, C(23) -0.014, C(28) -0.010, C(29) 0.031, C(34) -0.040]

are to be compared with 0.60 and 0.80 e⁻ for the corresponding bonds when butatriene is in the uncomplexed configuration. When the interactions of the iron atoms with the chain are taken into account, this should lead to reduced values for the estimated total overlap population in both kinds of bond, but the reduction should be greater for the central bond. Thus from a molecular orbital standpoint it is not unreasonable that the three bonds should have been found to be equal in length.

The angles subtended by the iron atoms at the bridging carbons are 80.6(5) and 81.2(5)°. These lie within the range 80—87° noted as the limiting values for such angles.¹¹

⁹ R. Mason and D. R. Russell, *Chem. Comm.*, 1966, 26.

¹⁰ M. McPartlin and R. Mason, *Chem. Comm.*, 1967, 16.

¹¹ O. S. Mills and A. D. Redhouse, *Chem. Comm.*, 1966, 444.

Iron-iron bonds have been found to vary considerably in length. Values from 2.37¹² to 2.63 Å¹¹ have been reported for neutral binuclear complexes. The distance in this butatriene complex lies close to the upper end of this range, *viz.* 2.596(4) Å.

Although the torsion angle about the central bond is only 34°, this twist increases through the molecule until the angle between the biphenylylidene groups, as measured by the least-squares planes defined by the constituent atoms, becomes 80°. Additionally, neither of the biphenylylidene groups is planar. The atoms of each group deviate systematically from the best least-

squares plane by up to 0.08 Å in one case and up to 0.15 Å in the other. However, all the five- and six-membered rings are planar to within 0.03 Å. The six-membered rings are tilted with respect to the five-membered rings through angles which range from 2 to 6°.

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¹² P. E. Baikie and O. S. Mills, *Chem. Comm.*, 1966, 707.
