Structure of and Bonding in an Alkyne–Nonacarbonyltriiron Complex. A New Type of Iron–Acetylene Interaction

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Abstract: Complexes of the class $RC_2R'Fe_3(CO)_9$, isolated in small yields along with other organoiron carbonyl complexes from the reaction of diphenylacetylene with $Fe_2(CO)_9$ and methylphenylacetylene with $Fe_3(CO)_{12}$, have been characterized both by physical and chemical means including a three-dimensional single-crystal X-ray study of the diphenylacetylene derivative. Crystals of $C_6H_5C_2C_6H_5Fe_3(CO)_9$ are triclinic with two molecules in a unit cell of symmetry $P\bar{1}$ and of reduced cell parameters $a = 9.08$, $b = 9.16$, $c = 16.28$ Å., $\alpha = 80°\,15'$, $\beta = 75°\,57'$, $\gamma = 62°\,31'$. A full matrix isotropic least-squares refinement of the structure yielded discrepancy factors of $R_1 = 8.6\%$ and $R_2 = 9.2\%$. The idealized molecular configuration has C_s-m symmetry and consists of an isosceles triangle of iron atoms with three terminal carbonyl groups attached to each iron atom. The diphenylacetylene group is stereochemically disposed above the plane of iron atoms such that one acetylene carbon is coordinated to all three iron atoms while the other acetylene carbon is bonded to the two symmetry-related iron atoms. A qualitative bonding description of this new type of metal–acetylene interaction consistent with the molecular parameters and the diamagnetism of the compound is given in terms of the functioning of the acetylene as a metal-coordinating olefinic group by the formation of one two-center and two three-center bonds. The reactions and stereochemical implications of this triiron–alkyne complex, regarded as one of the intermediates in the formation of other organoiron carbonyls with more complicated ligands, are discussed.

Reactions of alkynes with $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ have yielded a wide variety of organoiron carbonyl complexes with unusual configurations and novel types of bonding.[2-11] One such complex, prepared in low yields from the reaction of diphenylacetylene with $Fe_2(CO)_9$ at room temperature for several days, is a diamagnetic compound of formula $C_6H_5C_2C_6H_5Fe_3(CO)_9$. The corresponding methylphenylacetyleneiron carbonyl complex, $CH_3C_2C_6H_5Fe_3(CO)_9$, previously was isolated[2] from the reaction of $Fe_3(CO)_{12}$ with methylphenylacetylene at 90° and incorrectly formulated at first[2] as $CH_3C_2C_6H_5Fe_2(CO)_{10}$ when no oxygen analysis was available. The infrared spectra of both the diphenyl- and methylphenylacetylene derivatives show absorption bands characteristic of terminal carbonyl groups only.

Since complexes of formula $RC_2R'Fe_3(CO)_9$ presumably are intermediates in the formation of organoiron carbonyls with more complicated ligands their stereochemistry is of prime significance. A three-dimensional X-ray analysis of $C_6H_5C_2C_6H_5Fe_3(CO)_9$, here described, has established the molecular character of the compound and has revealed the existence of a new type of interaction involving an acetylene coordinated with three metal atoms which cannot be simply described by the usual σ–π-bonding formulation.

Experimental Section

Preparation and Properties of $C_6H_5C_2C_6H_5Fe_3(CO)_9$. A suspension of 72 g. (0.2 mole) of $Fe_2(CO)_9$ in 0.5 l. of light petroleum ether was stirred at room temperature, and ten portions each of 1.78 g. (0.01 mole) of diphenylacetylene were added at intervals of 5 hr. The filtered reaction mixture was evaported to dryness under reduced pressure in order to eliminate the $Fe(CO)_5$ formed. The complex, $C_6H_5C_2C_6H_5Fe_3(CO)_9$, was extracted with petroleum ether from the residue consisting mainly of $[(C_6H_5C_2C_6H_5)_2CO]Fe_2(CO)_6$[3] and some $(C_6H_5C_2C_6H_5)_2Fe_2(CO)_6$[3], and the filtrate was chromatographed on silica gel. The complex together with some unreacted diphenylacetylene was eluted with petroleum ether. Recrystallization from petroleum ether or petroleum ether–benzene mixtures yielded 0.6 g. (1%) of black needles which decompose at 147° without melting.

Anal. Calcd. for $C_{23}H_{10}Fe_3O_9$: C, 46.20; H, 1.69; Fe, 28.02; O, 24.09. Found: C, 46.09; H, 1.69; Fe, 27.80; O, 24.26.

$C_6H_5C_2C_6H_5Fe_3(CO)_9$ is diamagnetic with $\chi_{\text{mole}}^{293°\text{K}} = (-131.5 \pm 3.0) \times 10^{-6}$ cm.^{3} mole^{-1}. The infrared spectrum in KBr shows bands at 2083 (m) and 2024 (s) with shoulders at 2000, 1976, and 1957 cm.$^{-1}$. Its n.m.r. spectrum (60 Mc.) in CS_2 consists of three groups of resonances for the phenyl protons centered at −7.3, −6.8, and −5.9 p.p.m. (relative to $Si(CH_3)_4$) with an intensity ratio of 5:3:2. The different chemical shifts of the *ortho* protons (−5.9 p.p.m.) and the *meta* and *para* protons (−6.8 p.p.m.) of one phenyl group from the five protons of the other phenyl group may perhaps be explained more readily by a diamagnetic shielding effect of an iron atom than by polarization.

Refluxing of $C_6H_5C_2C_6H_5Fe_3(CO)_9$ (0.12 g.) with an excess of iodine in CCl_4 (10 ml.) for 0.5 hr. led to the liberation of diphenylacetylene which could be isolated in a 66% yield (0.023 g.).

Reaction of $C_6H_5C_2C_6H_5Fe_3(CO)_9$ with $C_6H_5C_2C_6H_5$. $C_6H_5C_2C_6H_5Fe_3(CO)_9$ (0.12 g., 0.2 mmole) and diphenylacetylene (0.071 g., 0.4 mmole) were refluxed in 5 ml. of benzene for 2 hr. Chromatography on silica gel led to the isolation of 0.031 g. of recovered diphenylacetylene and 0.14 g. (93%) of the black isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$.[3]

Refluxing of 0.12 g. of $C_6H_5C_2C_6H_5Fe_3(CO)_9$ with 0.035 g. of diphenylacetylene in a mixture of 3 ml. of benzene and 4 ml. of methanol for 10 min. gave upon chromatographic separation 0.02 g. of diphenylacetylene, 0.03 g. of unreacted complex, and 0.007

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Table I. Final Atomic Parameters with Standard Deviations

Atom	x	$10^4\sigma_x$	y	$10^4\sigma_y$	z	$10^4\sigma_z$	B, Å.^{2}	$10^2\sigma_B$
Fe-1	0.5680	3	0.7328	2	0.1738	1	3.37	6
Fe-2	0.8608	3	0.5457	2	0.1944	1	3.02	6
Fe-3	0.7720	3	0.8548	2	0.1510	1	3.10	6
C-1	0.3851	26	0.9191	21	0.1900	10	4.81	38
O-1	0.2591	18	1.0397	15	0.2040	7	5.69	27
C-2	0.5130	28	0.6980	21	0.0830	12	5.84	44
O-2	0.4766	20	0.6840	16	0.0231	9	7.64	36
C-3	0.4954	28	0.5966	23	0.2372	12	6.20	45
O-3	0.4467	19	0.5063	16	0.2814	8	6.97	33
C-4	0.8481	24	0.4727	20	0.1042	10	4.58	37
O-4	0.8522	19	0.4190	16	0.0431	8	6.66	31
C-5	0.8573	24	0.3770	21	0.2618	11	4.93	39
O-5	0.8563	19	0.2649	17	0.3088	9	7.55	35
C-6	1.0789	27	0.4700	20	0.1710	10	4.89	39
O-6	1.2208	23	0.4249	17	0.1552	9	8.02	36
C-7	0.9665	28	0.8570	21	0.1118	11	5.36	41
O-7	1.0920	24	0.8615	17	0.0878	9	8.20	38
C-8	0.6663	25	1.0692	22	0.1624	10	5.20	41
O-8	0.6028	21	1.2120	18	0.1704	8	8.04	37
C-9	0.7257	27	0.8602	21	0.0505	12	5.56	42
O-9	0.7204	20	0.8626	16	−0.0202	9	7.44	34
C-10	0.6844	20	0.7526	16	0.2616	8	2.96	29
C-11	0.8551	20	0.7202	16	0.2507	8	3.22	30
C-12	0.9530	22	0.7219	19	0.3117	9	3.98	33
C-13	1.0243	26	0.5795	21	0.3634	11	5.37	41
C-14	1.1043	25	0.5865	21	0.4240	11	5.54	43
C-15	1.1189	26	0.7312	22	0.4318	11	5.53	43
C-16	1.0555	28	0.8714	23	0.3766	12	6.32	46
C-17	0.9713	24	0.8670	20	0.3155	10	4.98	39
C-18	0.5764	20	0.7934	16	0.3470	8	2.96	29
C-19	0.4619	22	0.9617	18	0.3604	10	4.16	34
C-20	0.3581	26	0.9950	21	0.4457	11	5.57	42
C-21	0.3744	29	0.8740	24	0.5082	12	6.26	45
C-22	0.4922	28	0.7116	23	0.4949	11	5.89	43
C-23	0.5940	24	0.6684	19	0.4120	10	4.57	36

g. (5%) of the violet isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[3] which was contaminated with some of the black isomer.

Reaction of $CH_3C_2C_6H_5Fe_3(CO)_9$ with $CH_3C_2C_6H_5$. $CH_3C_2C_6H_5Fe_3(CO)_9$ (0.12 g., 0.23 mmole) and $CH_3C_2C_6H_5$ (0.027 g., 0.23 mmole) were refluxed in 4 ml. of benzene for 7 hr. The following products were isolated by chromatography on silica gel: 0.051 g. (43%) of $(CH_3C_2C_2H_5)_2Fe_2(CO)_6$,[2] 0.037 g. (25%) and 0.009 g. (6%) of two black isomeric complexes of formula $(CH_3C_2C_6H_5)_2Fe_3(CO)_8$.[2]

X-Ray Data. Considerable difficulty in obtaining a suitable single crystal was encountered because of crystal twinning along the a axis, and X-ray patterns of a number of crystals were examined before a suitable crystal was found. A needle crystal of length 0.34 mm. and average width 0.08 mm. was used for the collection of intensity data. The crystal was mounted in a Lindemann glass capillary which then was evacuated, filled with argon, and sealed. Only slight decomposition of the crystal was noticed over the 3-month period required for the collection of the intensity data. The unit cell dimensions were obtained from NaCl-calibrated $h0l$ and $hk0$ precession photographs of the B-centered cell. The density of the crystal was determined by flotation in 2-iodopropane–carbon tetrachloride solutions.

Multiple-film equi-inclination Weissenberg photographs were taken for ten reciprocal levels ($0kl$ through $9kl$) with zirconium-filtered molybdenum Kα radiation. Since the crystals are triclinic, two sets of multiple films were taken for each of the nonzero levels in order to record all 360° of reciprocal space on the upper halves of the Weissenberg films and thereby avoid the problem of spot contraction on the lower halves of the films. Each level was later placed on a single scale by a weighted least-squares merging of reflections common to both sets of films. The intensities of 1528 independent reflections were estimated visually by comparison with a calibrated set of spots obtained from the same crystal and then corrected for Lorentz-polarization effects and for spot extension[12]; absorption corrections were neglected since the average estimated value of the absorption parameter μR was 0.15. The standard deviations of the structure factor amplitudes used in the least-squares refinement were assigned according to the scheme[13]

$$\sigma(F_o) = 0.05F_o \qquad \text{if } I_0 \geq \sqrt{10}I_{\min}$$

$$\sigma(F_o) = 0.05F_o[\sqrt{10}I_{\min}/I_0]^2 \qquad \text{if } I_0 < \sqrt{10}I_{\min}$$

Unit Cell and Space Group. Crystals of $C_6H_5C_2C_6H_5Fe_3(CO)_9$ (mol. wt. 597.9) are triclinic with reduced cell parameters a = 9.085 ± 0.025, b = 9.16 ± 0.025, c = 16.28 ± 0.05, α = 80° 15′ ± 10′, β = 75° 57′ ± 10′, γ = 62° 31′ ± 10′; the volume of the unit cell is 1163 Å.^{3}. The calculated density of 1.66 g. cm.$^{-3}$ for two molecules per unit cell agrees well with the observed density of 1.64 g. cm.$^{-3}$. The choice of the centric space group P$\bar{1}$ was confirmed by the structural determination. All atoms are in the general twofold set of positions (2i): $\pm(x, y, z)$.[14]

Structural Determination. The structural analysis of the compound required the location of three iron, twenty-three carbon, and nine oxygen atoms (and, ideally, ten hydrogen atoms) which correspond to one molecule.

The positions of the three independent iron atoms were found by an interpretation of the three-dimensional sharpened Patterson function based on the corrected intensities. A three-dimensional Fourier synthesis phased only on the three iron atoms was computed, and assignments were made of the coordinates of eight carbonyl groups (all except C-9–O-9), the two acetylene carbons, and one phenyl ring (C-12–C-17). A second Fourier synthesis phased on the positional parameters of these twenty-seven atoms was calculated, and the remaining eight carbon atoms were located. Finally, a full matrix isotropic least-squares refinement with individual atomic thermal parameters and with a variable scale factor per reciprocal layer was carried out for these thirty-five

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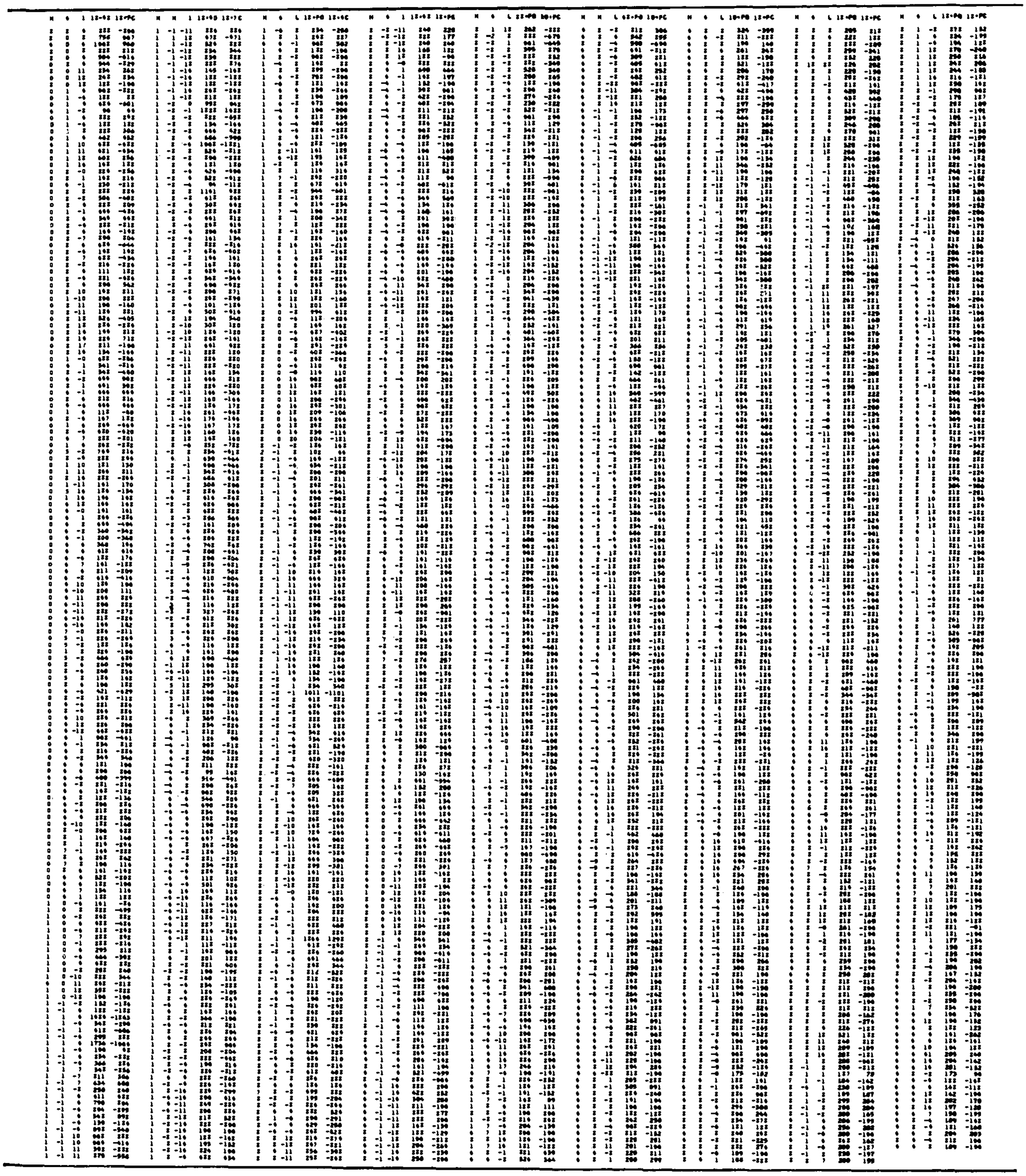
(12) D. C. Phillips, *Acta Cryst.*, 7, 746 (1954); *ibid.*, 9, 819 (1956).

(13) D. L. Smith, "DACOR—A Data Reduction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

(14) "International Tables for Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 75.

Table II. Comparison of Observed and Calculated Structure Factors



nonhydrogen atoms. After six cycles, all positional and thermal parameter shifts were less than one-half of their respective standard deviations. The final discrepancy values, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$, are 8.6 and 9.2%, respectively, for the 1528 independent, observed reflections. A three-dimensional difference synthesis showed only small anisotropy about the iron atoms (maximum peak height of 1.2 electrons/Å.^{3}); no other residual peak heights were greater than 0.8 electron/Å.^{3}. No attempt was made to identify any of these peaks as the phenyl hydrogen atoms.

The Patterson and Fourier syntheses were computed on a CDC 1604 computer with the Blount program.[15] The first two cycles of the full matrix least-squares refinement were performed on an IBM 704 computer with the Busing–Levy ORXLS program[16]; the last four cycles also were calculated on an IBM 704 but with the Busing–Martin–Levy ORFLS program.[17] In the calculation of structure

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(15) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(16) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory Report 59-4-37, 1959.

(17) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A

Table III. Intramolecular Distances (Å.) with Standard Deviations

Fe-1–Fe-2	2.480 ± 0.010	Fe-1–C-10	2.048 ± 0.016
Fe-1–Fe-3	2.501 ± 0.009	Fe-2–C-10	2.098 ± 0.015
Fe-2–Fe-3	2.579 ± 0.011	Fe-3–C-10	2.043 ± 0.015
Fe-1–C-1	1.751 ± 0.020	Fe-2–C-11	1.947 ± 0.016
Fe-1–C-2	1.790 ± 0.023	Fe-3–C-11	1.945 ± 0.015
Fe-1–C-3	1.746 ± 0.023	C-10–C-11	1.409 ± 0.022
Fe-2–C-4	1.761 ± 0.019	C-11–C-12	1.492 ± 0.023
Fe-2–C-5	1.745 ± 0.020	C-12–C-13	1.393 ± 0.021
Fe-2–C-6	1.734 ± 0.023	C-13–C-14	1.385 ± 0.026
Fe-3–C-7	1.735 ± 0.024	C-14–C-15	1.420 ± 0.024
Fe-3–C-8	1.763 ± 0.019	C-15–C-16	1.402 ± 0.024
Fe-3–C-9	1.772 ± 0.022	C-16–C-17	1.411 ± 0.027
C-1–O-1	1.172 ± 0.019	C-17–C-12	1.426 ± 0.024
C-2–O-2	1.146 ± 0.020	C-10–C-18	1.486 ± 0.019
C-3–O-3	1.174 ± 0.021	C-18–C-19	1.425 ± 0.020
C-4–O-4	1.168 ± 0.018	C-19–C-20	1.467 ± 0.022
C-5–O-5	1.174 ± 0.018	C-20–C-21	1.351 ± 0.022
C-6–O-6	1.132 ± 0.022	C-21–C-22	1.390 ± 0.024
C-7–O-7	1.130 ± 0.024	C-22–C-23	1.439 ± 0.023
C-8–O-8	1.177 ± 0.018	C-23–C-18	1.400 ± 0.020
C-9–O-9	1.160 ± 0.019		

factors, the atomic scattering factors of Freeman and Watson[18] were used for iron, those of Freeman[19] for carbon, and those of Berghuis, *et al.*,[20] for oxygen.

Table I gives the final positional and isotropic thermal parameters as obtained from the final least-squares cycle. A listing of the observed and calculated structure factors, based on the final parameters, is given in Table II. Intramolecular distances and bond angles together with estimated standard deviations are tabulated in Tables III and IV, respectively. The Busing–Martin–Levy function and error program ORFFE[21] was used for the distance and angle calculations in which the errors were obtained from the full inverse matrix. Finally, Table V presents the "best" planes and perpendicular distances of atoms from these planes for both the three iron atoms and the C-18–C-10–C-11–C-12 system computed *via* a least-squares method.[22] Since the correlation matrices show considerable interaction of the thermal and interlayer scale factor parameters (*i.e.*, as great as 0.5 for the iron atoms), no *physical meaning* in terms of root-mean-square displacements should be attached to the thermal parameters. However, the low correlations of the positional parameters with the thermal and scaling parameters support the premise that the atomic coordinates are essentially invariant to any systematic errors in the isotropic thermal coefficients.

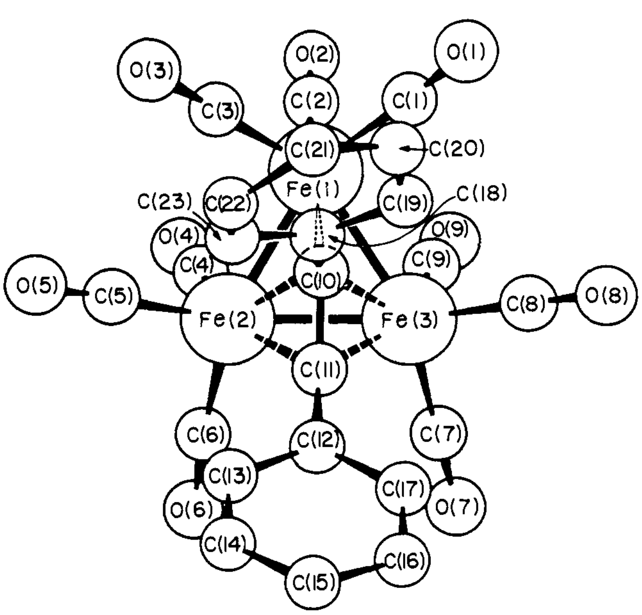

Figure 1. The configuration of $C_6H_5C_2C_6H_5Fe_3(CO)_9$.

Discussion

Description of the Structure. The crystal is composed of discrete molecules whose configuration is shown in Figure 1. The three iron atoms are located at the corners of an isosceles triangle with the diphenylacetylene fragment stereochemically disposed above the plane of the iron atoms such that one acetylene carbon, C-10, is coordinated to all three iron atoms while the other, C-11, is bonded to two iron atoms, Fe-2 and Fe-3. Three terminal carbonyl groups are attached to each iron; two (*viz.*, the equatorial carbonyls) are roughly positioned about the plane of the iron atoms with the third (*viz.*, the axial carbonyl) directed almost perpendicularly beneath the plane. The symmetrical orientation of the diphenylacetylene moiety relative to the three $Fe(CO)_3$ groups results in an approximate molecular symmetry of C_s-m. Figure 2, which gives the packing of the two molecules in the unit cell, shows no intramolecular interaction of the phenyl rings of the disubstituted acetylene with the iron atoms.[23] The closest intermolecular contacts of 3.07 Å. indicate no abnormal interactions between molecules.

A detailed examination of the geometry of the $Fe_3(CO)_9$ fragment (Figure 3) shows the noncrystallographic mirror plane to hold within experimental error for the given bond lengths and angles. Although the Fe-2–Fe-3 distance of 2.58 ± 0.01 Å. is significantly longer than the average (2.49 Å.) of the symmetry-equivalent Fe–Fe distances, all three distances are within the range of Fe–Fe distances in other carbonyl complexes with metal–metal bonds.[8] The mirror-related $Fe(CO)_3$ fragments possess C_{3v} localized symmetry with the average OC–Fe–CO angle being 95°; for the unique iron atom, however, the value of 100° for the equatorial–equatorial OC–Fe–CO angle is significantly larger than the average value of 92° for the two equatorial–axial OC–Fe–CO angles. These two types of OC–Fe–CO bond angles for the latter $Fe(CO)_3$ group compare well with the corresponding *average* angles found for *cis*-$M(CO)_4$ groups symmetrically bonded in a triangular array to two other metal atoms. Compounds with such groups include $[Ru(CO)_4]_3$ (103.3 and 90.1° with individual e.s.d. of 1.4° for the three *cis*-$Ru(CO)_4$)[25] and $HFe_3(CO)_{11}^-$ (102.3 and 91.8° with individual e.s.d. of 0.7° for the one *cis*-$Fe(CO)_4$),[26] for both of which a bent metal–metal bonding description involving octahedral metal valency of the *cis*-$M(CO)_4$ group has been

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Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(18) A. J. Freeman and R. E. Watson, *Acta Cryst.*, **14**, 231 (1961).

(19) A. J. Freeman, *ibid.*, **12**, 261 (1959).

(20) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(21) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(22) D. L. Smith, "A Least-Squares Planes Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

(23) The possibility for $RC_2C_6H_5Fe_3(CO)_9$ ($R = C_6H_5$ or CH_3) that a phenyl ring is coordinated to the iron atoms by two of its carbon atoms being part of a benzoferracyclopentadiene (or ferraindene) ring (*i.e.*, resulting from the migration of an *o*-phenyl hydrogen atom to the attached acetylene carbon atom), which forms delocalized μ bonds with the other two $Fe(CO)_3$ groups on both sides of the ring, is ruled out. Such speculation arose from an X-ray structural analysis[24] of $C_6H_5C_2C_6H_5Fe_2(CO)_6$ which revealed the formation of this type of complex with the benzoferracyclopentadiene ring coordinated to one $Fe(CO)_3$ group.

(24) *Cf.* M. Van Meerssche, *Ind. Chim. Belge*, **28**, 507 (1963).

(25) E. R. Corey, E. R. de Gil, and L. F. Dahl, to be published.

(26) J. F. Blount and L. F. Dahl, to be published.

Table IV. Bond Angles (Degrees) with Standard Deviations

Fe-1–Fe-2–Fe-3	59.2 ± 0.2	C-5–Fe-2–C-11	114.6 ± 0.7
Fe-1–Fe-3–Fe-2	58.4 ± 0.2	C-6–Fe-2–C-11	87.4 ± 0.8
Fe-2–Fe-1–Fe-3	62.4 ± 0.3	C-7–Fe-3–C-11	90.1 ± 0.8
Fe-1–C-1–O-1	176.7 ± 1.5	C-8–Fe-3–C-11	115.1 ± 0.7
Fe-1–C-2–O-2	176.4 ± 1.7	C-9–Fe-3–C-11	146.9 ± 0.7
Fe-1–C-3–O-3	178.6 ± 1.7	C-4–Fe-2–M[a]	143.0
Fe-2–C-4–O-4	175.2 ± 1.6	C-5–Fe-2–M	110.7
Fe-2–C-5–O-5	178.0 ± 1.7	C-6–Fe-2–M	108.4
Fe-2–C-6–O-6	178.1 ± 1.7	C-7–Fe-3–M	111.2
Fe-3–C-7–O-7	178.1 ± 1.8	C-8–Fe-3–M	111.2
Fe-3–C-8–O-8	176.9 ± 1.8	C-9–Fe-3–M	138.8
Fe-3–C-9–O-9	169.2 ± 1.9	Fe-1–C-10–C-11	126.9 ± 1.0
C-1–Fe-1–C-2	92.3 ± 0.9	Fe-1–C-10–C-18	114.6 ± 1.1
C-2–Fe-1–C-3	90.9 ± 1.0	C-18–C-10–C-11	118.3 ± 1.3
C-3–Fe-1–C-1	100.1 ± 1.0	Fe-2–Fe-1–C-10	54.2 ± 0.4
C-4–Fe-2–C-5	94.5 ± 0.8	Fe-3–Fe-1–C-10	52.2 ± 0.4
C-5–Fe-2–C-6	95.9 ± 0.8	Fe-1–C-10–Fe-2	73.5 ± 0.5
C-6–Fe-2–C-4	94.8 ± 0.8	Fe-1–C-10–Fe-3	75.4 ± 0.5
C-7–Fe-3–C-8	93.1 ± 0.9	C-10–C-11–C-12	130.8 ± 1.3
C-8–Fe-3–C-9	97.1 ± 0.8	Fe-2–C-10–Fe-3	77.0 ± 0.6
C-9–Fe-3–C-7	95.8 ± 1.0	Fe-2–M–Fe-3	86.5
C-1–Fe-1–Fe-2	150.8 ± 0.4	Fe-2–C-11–Fe-3	83.0 ± 0.6
C-1–Fe-1–Fe-3	96.0 ± 0.4	C-10–Fe-2–Fe-3	50.5 ± 0.4
C-2–Fe-1–Fe-2	114.8 ± 0.5	C-10–Fe-3–Fe-2	52.4 ± 0.4
C-2–Fe-1–Fe-3	118.6 ± 0.5	C-10–Fe-2–C-11	40.5 ± 0.6
C-3–Fe-1–Fe-2	90.5 ± 0.4	C-10–Fe-3–C-11	41.3 ± 0.6
C-3–Fe-1–Fe-3	145.7 ± 0.5	C-11–Fe-2–Fe-3	48.4 ± 0.5
C-4–Fe-2–Fe-1	77.4 ± 0.4	C-11–Fe-3–Fe-2	48.5 ± 0.4
C-4–Fe-2–Fe-3	102.4 ± 0.4	Fe-2–C-10–C-11	63.9 ± 0.8
C-5–Fe-2–Fe-1	108.3 ± 0.4	Fe-3–C-10–C-11	65.6 ± 0.8
C-5–Fe-2–Fe-3	155.3 ± 0.4	Fe-2–C-11–C-10	75.5 ± 0.9
C-6–Fe-2–Fe-1	155.0 ± 0.5	Fe-3–C-11–C-10	73.1 ± 0.9
C-6–Fe-2–Fe-3	100.4 ± 0.4	C-11–C-12–C-13	118.2 ± 1.4
C-7–Fe-3–Fe-1	153.8 ± 0.5	C-11–C-12–C-17	119.7 ± 1.4
C-7–Fe-3–Fe-2	101.6 ± 0.5	C-12–C-13–C-14	117.6 ± 1.6
C-8–Fe-3–Fe-1	111.4 ± 0.4	C-13–C-14–C-15	121.7 ± 1.7
C-8–Fe-3–Fe-2	157.4 ± 0.4	C-14–C-15–C-16	120.7 ± 1.7
C-9–Fe-3–Fe-1	73.0 ± 0.4	C-15–C-16–C-17	118.2 ± 1.7
C-9–Fe-3–Fe-2	98.4 ± 0.5	C-16–C-17–C-12	119.5 ± 1.5
C-1–Fe-1–C-10	97.4 ± 0.6	C-17–C-12–C-13	122.1 ± 1.6
C-2–Fe-1–C-10	167.2 ± 0.7	C-10–C-18–C-19	118.1 ± 1.2
C-3–Fe-1–C-10	95.5 ± 0.7	C-10–C-18–C-23	119.7 ± 1.3
C-4–Fe-2–C-10	129.5 ± 0.6	C-18–C-19–C-20	115.8 ± 1.4
C-5–Fe-2–C-10	104.7 ± 0.6	C-19–C-20–C-21	121.9 ± 1.7
C-6–Fe-2–C-10	127.9 ± 0.8	C-20–C-21–C-22	121.4 ± 1.8
C-7–Fe-3–C-10	131.3 ± 0.9	C-21–C-22–C-23	119.9 ± 1.6
C-8–Fe-3–C-10	105.0 ± 0.7	C-22–C-23–C-18	118.8 ± 1.5
C-9–Fe-3–C-10	125.2 ± 0.7	C-23–C-18–C-19	122.1 ± 1.4
C-4–Fe-2–C-11	150.5 ± 0.7		

[a] M refers to the midpoint of C-10–C-11.

utilized to rationalize the equatorial–equatorial OC–M–CO angles being significantly greater than 90°. The stereochemical considerations above suggest a similar octahedral valency for Fe-1 in $C_6H_5C_2C_6H_5Fe_3(CO)_9$ with the sixth coordination site being occupied by a σ-bonded acetylene carbon, C-10, instead of the fourth carbonyl group.

The three carbonyl groups attached to each iron are positioned (Table V) so as to direct the appropriate iron orbitals toward the diphenylacetylene. Figure 4 gives the perpendicular displacements of the oxygen atoms from the plane of the iron atoms and thereby indicates the orientations of the $Fe(CO)_3$ groups. The Fe-1 tricarbonyl group is tipped such that the axial Fe–CO vector points toward C-10 and intersects the plane which contains C-10 and C-11 and which is perpendicular to the mean plane of C-18, C-10, C-11, and C-12 at 0.5 Å. from C-10. Each of the other two iron tricarbonyl groups is oriented such that one Fe–CO vector points more nearly toward C-11; the points of intersection of these lines with the previously defined plane which encompasses the olefinic π orbitals (*vide infra*) are 1.0 Å. from C-11 and 1.6 Å. from C-10.

The dimensions and bond angles of the diphenylacetylene moiety coordinated to the three iron atoms are illustrated in Figure 5. The similar values (2.06 Å.(av.)) for the distances of C-10 to each of the three iron atoms certainly necessitates an interaction of this acetylene carbon to all three iron atoms; likewise, the identical bonding distances of 1.95 Å. from C-11 to Fe-2 and Fe-3 are not unlike the Fe–C distances for other organoiron complexes.[8,27] The acetylene interaction with the three iron atoms results in a lengthening of the C-10–C-11 bond to 1.41 ± 0.02 Å. This distance is similar to the olefinic C–C distance of 1.44 ± 0.02 Å. found in $C_2H_5C_2C_2H_5Co_4(CO)_{10}$[28] for the acetylene fragment which functions as an olefinic coordinating group by forming σ bonds with two cobalts and a delocalized three-center μ-type bond[29] with the other two

[27] R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, **3**, 274 (1965).

[28] L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **84**, 2450 (1962).

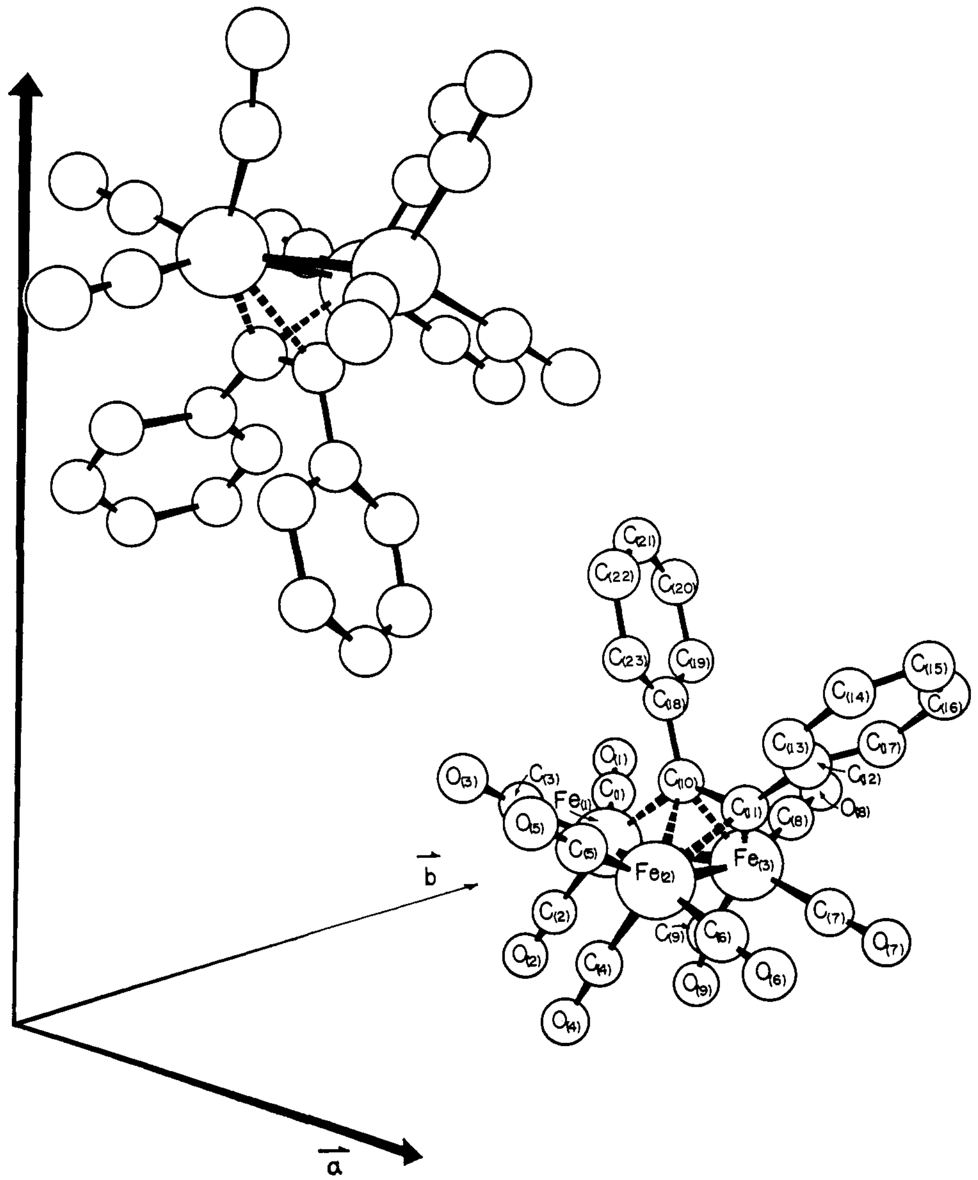

Figure 2. The packing of the two molecules of $C_6H_5C_2C_6H_5Fe_3(CO)_9$ in the unit cell.

cobalts. This distance also is comparable with the acetylene C–C distances in $C_6H_5C_2C_6H_5Co_2(CO)_6$ (1.37 Å.)[32,33] and $C_6H_5C_2C_6H_5Ni_2(C_5H_5)_2$ (1.35 Å.)[34] for which the diphenylacetylene is symmetrically linked to the two metal atoms *via* its two localized, orthogonal μ bonds. Another salient feature is the trigonal character of the three bond angles involving C-10 linked to Fe-1, C-11, and the phenyl carbon, C-18.

Discussion of Bonding. In order to obtain a suitable description of the bonding involved in this new type of triiron–acetylene interaction consistent with the molecular geometry and the observed diamagnetism of the compound, it first should be noted that the two bonding iron neighbors plus the three carbonyl groups can be considered as "effectively" donating eight electrons to each of the three zerovalent iron atoms leaving each iron two electrons short of the noble gas configuration. Hence, a qualitative explanation is required concerning the means by which $C_6H_5C_2C_6H_5$ can donate its electrons such that a closed-shell electronic ground state occurs.

A model based upon the diphenylacetylene forming a localized μ-type bond with each of the two symmetry-related $Fe(CO)_3$ groups (*i.e.*, analogous to the bonding in $C_6H_5C_2C_6H_5Co_2(CO)_6$[32,33]), in which the third $Fe(CO)_3$ group still formally possesses a 34-electron system by not interacting with any of the valence electrons of the acetylene, can be discarded. As stated previously, the equivalent bond distances from C-10 to the three iron atoms require a bonding scheme involving the coordination of this acetylene carbon to all three iron atoms.[35]

(29) A μ bond is defined[30] as the interaction by direct overlap of a σ orbital of a metal with an electron-donating π orbital of an unsaturated hydrocarbon. In a linear μ bond the metal orbital is perpendicular to the nodal plane of the π orbital. A delocalized three-center μ bond similarly involves a σ-type orbital for each of the two metals and the one π orbital for the olefinic moiety which contributes two electrons to the bonding MO combination. A compound with only the bonding three-center MO occupied is called electron deficient.[31]

(30) P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

(31) *Cf.* R. E. Rundle, *J. Phys. Chem.*, 61, 45 (1957).

(32) W. G. Sly, *J. Am. Chem. Soc.*, 81, 18 (1959).

(33) D. A. Brown, *J. Chem. Phys.*, 33, 1037 (1960).

(34) O. S. Mills, "Proceedings of the VIII International Conference on Coordination Chemistry," V. Gutmann, Ed., Springer-Verlag, Vienna, 1964, pp. 257–259.

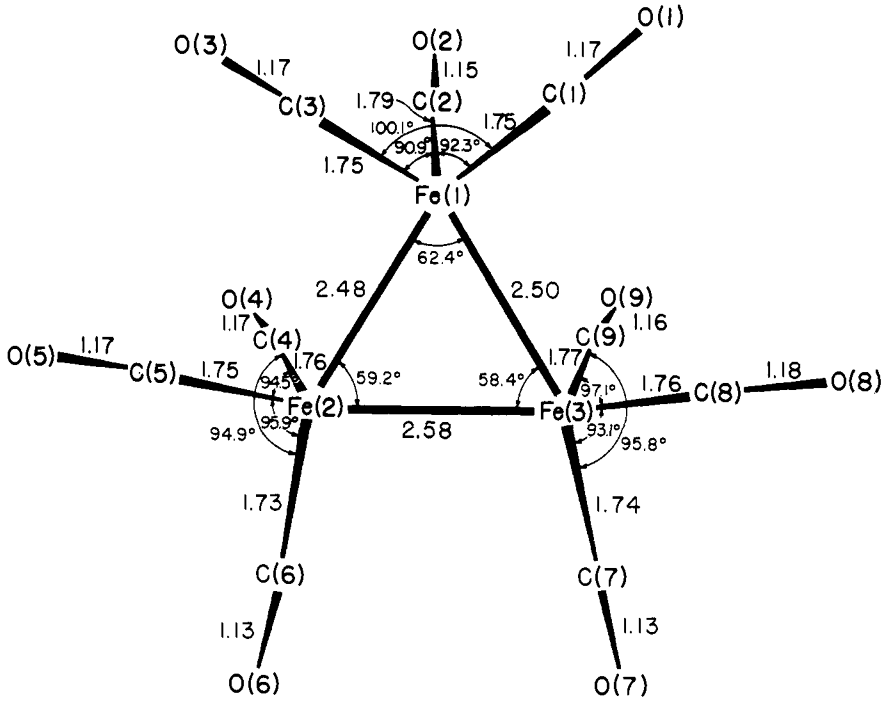

Figure 3. Intramolecular distances and angles in the $Fe_3(CO)_9$ fragment.

The use of an equivalent orbital representation allows the $C_6H_5C_2C_6H_5$ moiety to distribute four electrons among the three iron atoms but presents certain bonding difficulties not conveniently rationalized. Consider C-10 and C-11 each to be tetrahedrally hybridized with two orbitals utilized in σ bonding to a phenyl carbon and to the other acetylene carbon. The other two σ-type tetrahedral lobes then are directed from each of the acetylene carbons toward the plane of the iron atoms as indicated in Figure 6. Each iron is assumed to be seven-coordinated with two orbitals overlapping the orbitals of the other iron atoms as given in Figure 6. The Fe-2–C-11 and Fe-3–C-11 bonds may be considered as localized two-center bonds; the other two sets of three overlapping orbitals each form a three-center bonding orbital combination. (If C-10 and the three irons are viewed as occupying the four corners of a distorted tetrahedron, then the three orbitals of each three-center combination intersect above the corresponding face of the tetrahedron.) Consequently, two electrons from the acetylene fragment are distributed among each of the three iron atoms *via* one localized and one delocalized bond for Fe-2 and Fe-3 and *via* two delocalized bonds for Fe-1.

Table V. Equations of Best Planes, Distances (Å.) from These Planes, and Angles (Degrees) between Planes[a]

A. Plane through Fe-1, Fe-2, Fe-3			
$-0.041X - 0.262Y - 0.964Z + 4.617 = 0$			
Fe-1	0.000	O-9	−2.677
Fe-2	0.000	C-5	0.663
Fe-3	0.000	C-8	0.634
		O-5	1.140
C-1	0.614	O-8	1.064
C-3	0.651	C-6	−0.459
O-1	1.064	O-6	−0.535
O-3	1.114	C-7	−0.758
C-2	−1.520	O-7	−0.852
O-2	−2.502	C-10	1.462
C-4	−1.582	C-11	1.279
C-9	−1.575	C-12	2.273
O-4	−2.660	C-18	2.849
B. Plane through C-18, C-10, C-11, C-12			
$0.153X + 0.956Y - 0.251Z - 6.667 = 0$			
C-18	0.002	Fe-1	0.118
C-10	−0.005	Fe-2	1.333
C-11	0.005	Fe-3	−1.245
C-12	−0.003	C-21	−0.018
		C-15	−0.031
The dihedral angle between these two planes is 90.9°			

[a] The equations of the planes are given in an orthogonal Angström coordinate system (X, Y, Z) which is related to the fractional unit cell coordinate system (x, y, z) as follows: $Z = xa + yb \cos \gamma + zc \cos \beta$, $Y = yb \sin \gamma + zc \cos \mu$, $Z = zc \cos \sigma$, where $\cos \mu = (\cos \alpha - \cos \beta \cos \gamma)/\sin \gamma$ and $\cos \sigma = 1 - \cos^2 \beta - \cos^2 \mu$.

This representation of bonding suggests a single C-10–C-11 bond in the acetylene residue, a prediction incompatible with the observed distance of 1.41 ±

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(35) From the approximate molecular configuration it was postulated initially that the structure demanded two additional hydrogen atoms, one attached to C-11 and the other coordinated to Fe-1. In this way the resulting $C_6H_5C_2HC_6H_5$ fragment would be olefinic with its two π electrons distributed over both Fe-2 and Fe-3 *via* a three-center delocalized μ-type bond similar to that in $C_2H_5C_2C_2H_5Co_4(CO)_{10}$.[28] The carbon, C-10, of the olefin then would utilize an sp^2 orbital with one donating electron to form a σ-type bond with Fe-1, and consequently the second hydrogen attached to Fe-1 would be needed to account for the observed diamagnetism. This proposed bonding scheme was proved wrong both by additional chemical and physical evidence which became available later and by the least-squares refinement of the structure. Both the regeneration of diphenylacetylene from $C_6H_5C_2C_6H_5$-$Fe_3(CO)_9$ by refluxing with excess iodine in carbon tetrachloride and the formation of two isomers of formula $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[3] by the reaction of the complex with additional diphenylacetylene conclusively showed that there is no hydrogen bonded to C-11. In addition, an n.m.r. spectrum did not indicate a resonance at high-field strength characteristic of a hydrogen bonded to a transition metal.[36] After structural refinement, no significant differences between the nonbonding carbon–carbon distances in the Fe-1 tricarbonyl group and those in the Fe-2 and Fe-3 groups were found, thereby completely eliminating the possibility of a hydrogen directly attached to Fe-1.

(36) *Cf.* A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962); L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, 3, 22 (1964).

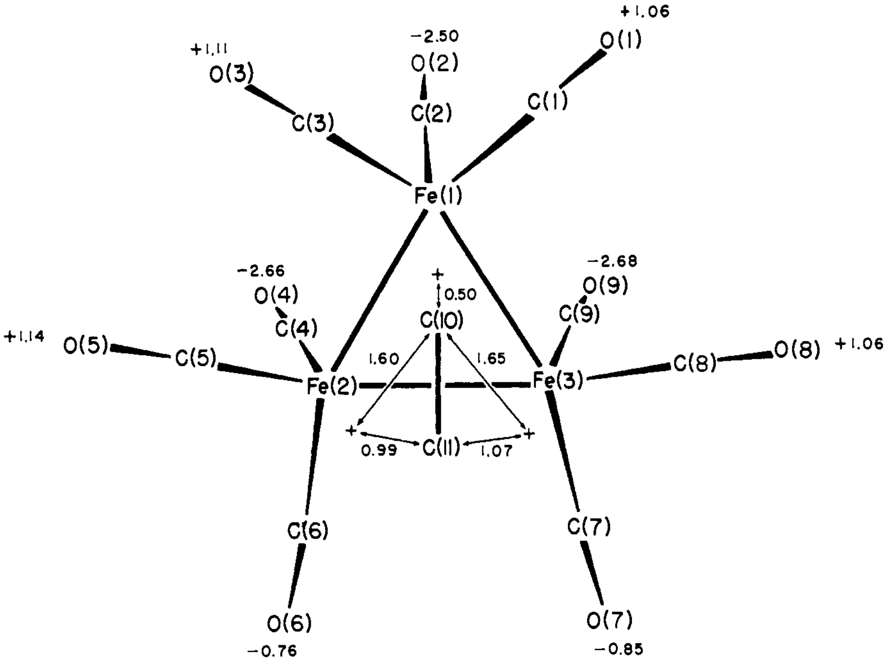

Figure 4. A projection of the carbonyl atoms along the normal to the plane of the three iron atoms, with the perpendicular displacements of the oxygen atoms from the plane given in Å. The intersections of the three axial Fe–CO vectors with the plane passing through the carbons C-10 and C-11 and encompassing their olefinic π-orbitals are given along with the distances from these atoms.

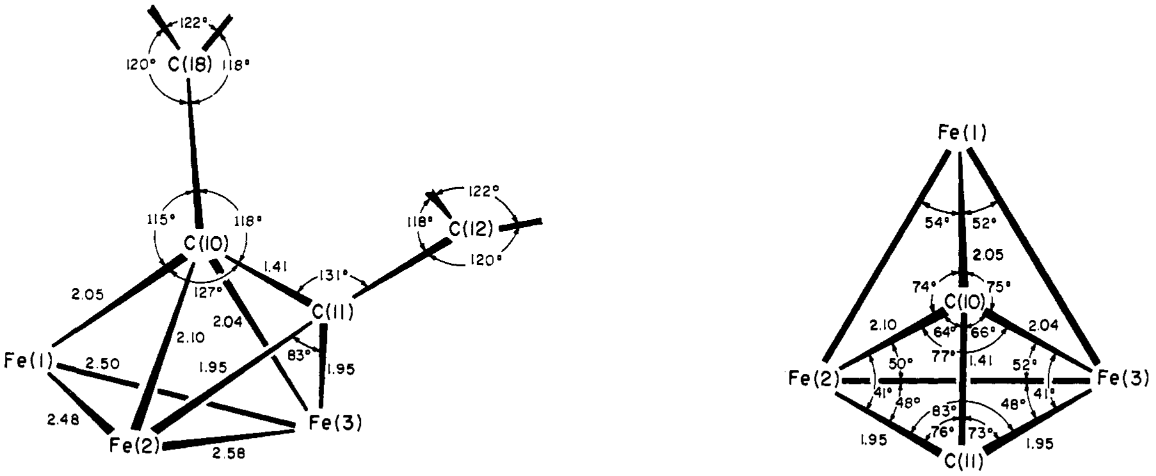

Figure 5. Intramolecular distances and angles of the diphenylacetylenetriiron moiety pertinent to a system of bonding in which the diphenylacetylene functions as an olefinic group (see text).

0.02 Å. Furthermore, the donation of one electron from the two involved iron atoms to fill each of the two bonding three-center orbital combinations leads to a violation of the noble gas configuration, and the resulting bonding description is not clear-cut. Of significance is that the combination of two- and three-center bonds necessary to describe the electronic configuration of other electron-deficient transition metal carbonyl complexes[22,28,37,38] in general is in accord with the noble gas rule which assumes participation of all the bonding MO's and none of the antibonding ones in bonding.[39]

The best representation of bonding for $C_6H_5C_2C_6H_5$-$Fe_3(CO)_9$ (Figure 7b), which completely conforms to the experimental molecular parameters, arises from regarding the acetylene fragment as an olefinic coordinating group with two normally π electrons placed in a σ-type sp^2 orbital on C-10 directed toward an octahedral-type orbital of Fe-1. This electron-pair interaction enables Fe-1 to possess octahedral valency in agreement with the environment of ligands about it (see earlier discussion) and also to achieve a closed-shell electronic configuration. The two olefinic π-electrons are distributed over both Fe-2 and Fe-3 *via* a three-center delocalized μ-type bond similar to that in $C_2H_5C_2C_2H_5Co_4(CO)_{10}$.[28] The empty sp^2 orbital on C-11 may be utilized as part of a three-center

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[37] R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

[38] H. D. Kaesz, W. Fellman, G. R. Wilkes, and L. F. Dahl, *ibid.*, **87**, 2753 (1965).

[39] The electronic configurations of compounds such as $(C_5H_5)_3Ni_3(CO)_2$[40] which do not have a closed-shell configuration usually can be understood at least qualitatively from MO considerations.[41]

[40] A. A. Hock and O. S. Mills, ref. 5, pp. 640–648.

[41] H. C. Longuet-Higgins and A. J. Stone, *Mol. Phys.*, **5**, 417 (1962).

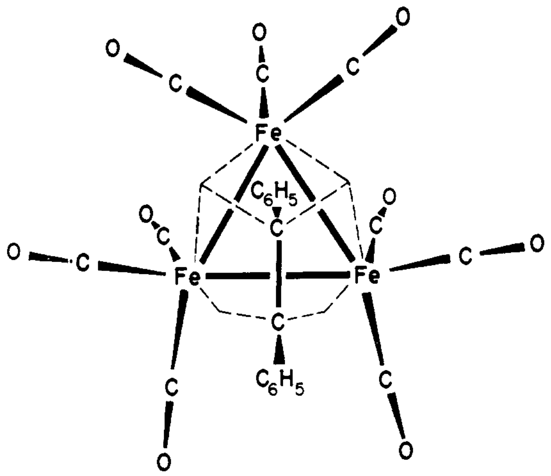

Figure 6. Equivalent orbital representation of the bonding in $C_6H_5C_2C_6H_5Fe_3(CO)_9$. This bonding description conforms neither to the molecular parameters nor to the noble gas configuration of iron atoms.

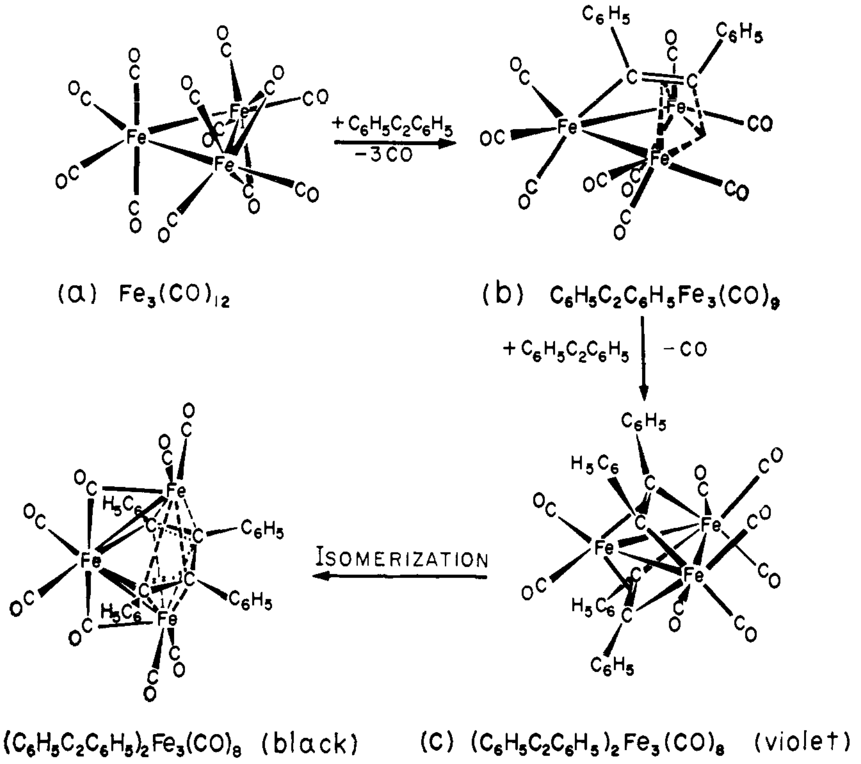

Figure 7. Configurations and indicated bonding of (a) $Fe_3(CO)_{12}$, (b) $C_6H_5C_2C_6H_5Fe_3(CO)_9$, (c) violet isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$, (d) black isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$.

bonding MO involving an electron-pair coupling of Fe-2 and Fe-3 with each other. This type of delocalized interaction, which presumably would lead to greater molecular stability than a direct Fe-2–Fe-3 bond, is formally analogous to the recently determined symmetrical, bent, delocalized metal–hydrogen–metal systems in $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$,[37] $HMn_3(CO)_{10}(BH_3)_2$,[38] and $HFe_3(CO)_{11}^-$,[26] by which each of the transition metals obtains a closed-shell configuration without the need for a separate metal–metal bond. One noteworthy feature of this pictorial bonding description is the justification of an olefinic C–C distance in $C_6H_5C_2C_6H_5Fe_3(CO)_9$ similar to that found in $C_2H_5C_2C_2H_5Co_4(CO)_{10}$.[28]

Discussion of the Reactions and Structural Implications. On refluxing $C_6H_5C_2C_6H_5Fe_3(CO)_9$ with more diphenylacetylene in benzene, the black isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$ was obtained in nearly quantitative yield. Milder reaction conditions also led to the isolation of the violet isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$ which previously was shown[3] to undergo rearrangement to the more stable black form on prolonged heating. The corresponding complex $CH_3C_2C_6H_5Fe_3(CO)_9$ is less readily attacked by alkynes than the diphenylacetylene derivative, but it also yields $(CH_3C_2C_6H_5)_2Fe_3(CO)_8$[2] besides $(CH_3C_2C_6H_5)_2Fe_2(CO)_6$[2] when refluxed with methylphenylacetylene in benzene for longer periods. The structures of both isomers of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$ (Figure 7c and d) were ascertained by Dodge and Schomaker[27] from three-dimensional X-ray analyses, which showed for the violet isomer each diphenylacetylene group, located on opposite sides of the isosceles triangle of iron atoms, to exist as a separate entity and to function as an olefinic group in being bonded to the two equivalent iron atoms *via* two σ bonds and symmetrically coordinated to the third iron *via* a μ-type bond. The average olefinic C–C distance of 1.38 Å. (individual e.s.d. 0.031 Å.) is not unlike the corresponding C–C distances in the metal–acetylene complexes previously discussed. In the black isomer, which represents the final stage in the stabilization of the alkyne–triironcarbonyl system before decomposition to binuclear and mononuclear organoiron complexes, the two diphenylacetylenes are joined as part of a ferracyclopentadiene ring in which the *cis*-butadiene fragment is coordinated to two symmetry-equivalent iron atoms on both sides of the ring.

The X-ray determination of the diphenylacetylene member of the class $RC_2R'Fe_3(CO)_9$, which may be regarded as an alkyne-substituted $Fe_3(CO)_{12}$,[42] thereby fills the missing structural link in observing the detailed stereochemical changes in trinuclear iron carbonyl–acetylene complexes on successive chemical replacement of carbonyl groups by alkynes. The sequence illustrated in Figure 7a–d demonstrates how the linkage of the alkynes can be achieved within the framework of the trinuclear organorion complexes. The given configuration of $Fe_3(CO)_{12}$ (Figure 7a) represents the probable structure[43] obtained from the structure of the trinuclear anion $HFe_3(CO)_{11}^-$ [26] by the substitution of a bridging carbonyl group in the regular coordination site occupied by a bridging hydrogen atom. The proposed structure, regarded as being formed by the insertion of a *cis*-$Fe(CO)_4$ group in place of one of the three bridging carbonyl positions of $Fe_2(CO)_9$, is in accord with the X-ray, reinterpreted Mössbauer, and *solid-state* infrared studies of $Fe_3(CO)_{12}$ and *no doubt* is correct.[43]

Figure 7 also shows the structural relation between $Fe_3(CO)_{12}$ (a) and $C_6H_5C_2C_6H_5Fe_3(CO)_9$ (b) to involve the substitution of the diphenylacetylene for the two bridging carbonyls and one of the carbonyls of the *cis*-$Fe(CO)_4$ fragment. Since one alkyne (with four π electrons available for bonding) has displaced three carbonyl groups (with six bonding σ-type electrons) to give $RC_2R'Fe_3(CO)_9$ complexes, an electron-deficient compound results with the electronic configuration involving two three-center bonds. The further addition of the second alkyne with the loss of only one carbonyl group to give the nonelectron-deficient violet isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$ (c) can be visualized in terms of the displacement of a terminal carbonyl from one of the equivalent iron atoms of $C_6H_5C_2C_6H_5Fe_3(CO)_9$ (b) with the more or less simultaneous attachment of the olefinic group to the other formerly equivalent iron along with the formation of new bonds from the addition of the second alkyne as an olefinic coordinating group. The isomerization of the violet compound to give the ferracyclopentadiene group of the black $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$ (d) involves the breaking of an iron–iron bond and formation of the butadiene bond and iron carbonyl (bridge) bonds.[27] Although the reaction mechanisms involving the bond-breaking and -making sequence with formation of the new complexes are not known, the above pictorial representation of structural change does illustrate the complexity of metal–alkyne reactions involving molecular reorganization of the carbonyls due to the stereochemical requirements of the alkyne groups in their distinctly different types of interaction with the three iron atoms.

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[42] Although the diphenyl derivative was isolated from the alkyne reaction with $Fe_2(CO)_9$, the methylphenyl derivative was obtained from $Fe_3(CO)_{12}$.

[43] L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

Lewis Basicity of Metals. II. The Interaction of Group VI and VII Transition Metal Cyclopentadienyl Derivatives with BF_3, BCl_3, and B_2H_6

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Abstract: The reaction of $(C_5H_5)_2MoH_2$, $(C_5H_5)_2WH_2$, and $(C_5H_5)_2ReH$ with Lewis acids leads to the following adducts: $(C_5H_5)_2WH_2 \cdot BF_3$, $(C_5H_5)_2WH_2 \cdot BCl_3$, $(C_5H_5)_2MoH_2 \cdot BF_3$, $(C_5H_5)_2ReH \cdot BF_3$, and $(C_5H_5)_2ReH \cdot BCl_3$. However, borane addition compounds do not form. Infrared spectra of the adducts indicate the presence of tetracoordinated boron and the most reasonable structures involve metal–BX_3 donor–acceptor bond formation. Attempts to add BF_3 to $(C_5H_5)_2Mo(CO)_3^-$ and $(C_5H_5)_2W(CO)_3^-$ resulted in their neutral dimers as the principal products.

In a recent communication, an example of the apparent basicity of a metal toward BF_3 was reported.[1] This report on $(C_5H_5)_2WH_2 \cdot BF_3$ was soon followed by Parshall's observation that some manganese and rhenium complexes are basic toward BH_3.[2] Very recently Brunner, Wailes, and Kaesz reported the stable adducts $(C_5H_5)_2WH_2 \cdot AlMe_3$ and $(C_5H_5)_2ReH \cdot AlMe_3$.[3] We are now aware of a system which appears analogous to those above—$Co_2(CO)_8 \cdot AlBr_3$—which was reported by Chini and Ercoli in 1958.[4]

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[1] D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 3509 (1963).

[2] G. W. Parshall, *ibid.*, **86**, 361 (1964).

[3] H. Brunner, P. C. Wailes, and H. D. Kaesz, Abstracts, Proceedings of the Second International Symposium on Organometallic Chemistry, Madison, Wis., 1965, p. 40.

[4] P. Chini and R. Ercoli, *Gazz. chim. ital.*, **88**, 1170 (1958).