THE MOLECULAR STRUCTURES OF TWO ISOMERS OF $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$*

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INTRODUCTION

Complexes of iron carbonyl having more than one iron atom are readily obtained by reactions involving iron tetracarbonyl, $Fe_3(CO)_{12}$. The reaction with diphenylacetylene in methanol yields a violet form of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$[1]. In boiling benzene or petroleum ether, however, the violet complex undergoes rearrangement to a more stable black isomer.

These new three-center complexes were submitted to this laboratory for structure determination by W. Hübel of Union Carbide European Research Associates. It was known that the black isomer has C–O absorption bands in the infrared at about 5.40 μ, in the region of carbonyl-bridge stretching frequencies, while the violet form does not. Also, the black isomer decomposes at 150° to the yellow complex $Fe_2(CO)_6(C_6H_5C_2C_6H_5)_2$, a compound thought to have the same basic structure as $Fe_2C_{12}O_8H_8$ as determined by Hock and Mills[2]. The black isomer was therefore presumed to be structurally similar to the Hock and Mills compound, but for the violet isomer no structural inference was available other than the absence of bridge carbonyls.

EXPERIMENTAL

The unit cell data for both isomers (Table 1) were measured by use of a single crystal orienter mounted on a General Electric XRD-5 diffractometer. The accuracy of the cell parameters is about the same as is obtained by the more usual film methods.

The crystal of the black isomer chosen for the diffraction study was close to a rectangular parallelopiped of dimensions 0.18 mm × 0.11 mm × 0.06 mm. The violet crystal was of about the same size but somewhat less regular in shape.

The data for both compounds were obtained with Zr-filtered Mo radiation and a G.E. scintillation counter. The stationary-crystal, stationary-counter method was used with particular care to meet the various criteria for collecting accurate integrated intensities[3]. A good source profile proved to be the most important requisite for a smooth-topped diffraction curve. The take-off angle was 3 degrees, allowing a negligible separation of the α_1–α_2 doublet at the maximum value of 2θ used. The corresponding errors should not exceed 5 % in the intensity[4] and should affect mainly the temperature factor.

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All reflections were counted for a constant time, which results in poorly determined weak intensities. Also, several hundred counted intensities (Table 1) for both crystals were found to be no stronger than background. The background was estimated in two different ways as described below.

TABLE 1

UNIT CELL DATA FOR THE ISOMERS OF $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$

	Violet form	*Black form*
a_0	38.49	9.39
b_0	8.31	18.45
c_0	21.75	18.29
β	115.1°	96.8°
V	6304 Å^3	3148 Å^3
Z	8	4
Space group	$C2/c$	$P2_1/c$
Observed density	1.575	1.578
X-ray density	1.576	1.57
No. of reflections	1969	1811
No. with $F^2 > 0$	1649	1510

STRUCTURE DETERMINATION AND REFINEMENT

For the black form, the three-dimensional Patterson function was first calculated with a general IBM-7090 program written by A. Zalkin. The symmetry was assumed to be $P2_1/c$, so that in general the three iron atoms of the molecule would lead to 21 heavy-atom–heavy-atom peaks, excluding the origin, in the asymmetric unit. It was then possible to account for the major features of the Patterson by assigning the three heavy-atom positions. The heavy-atom–light-atom interactions amounted to only a tolerable noise background.

The light atoms of the black isomer were located by several cycles of Fourier refinement. Several of the carbon atoms were not well defined and the discrepancy index $R = \Sigma||F_{obs}| - |F_{calcd}||/\Sigma|F_{obs}|$ would not improve beyond 0.27. Two cycles of least squares, in which only the parameters for the iron atoms were varied, resulted in an improvement of R to 0.18. Full-matrix least squares was then applied to a trial structure including all of the atoms, and this resulted in successful convergence to a final R value of 0.087 for the 1510 reflections of non-zero weight.

During the refinement it was discovered that 18 of the original measurements were seriously affected by streaks from nearby strong reflections. These measurements were given zero weight in the final refinements. The final position parameters and temperature factors along with the estimated standard deviations are given in Table 2.

The same general approach was made to the structure determination of the violet isomer. However, greater difficulty was encountered in obtaining the correct heavy-atom positions. An assignment of the iron-atom parameters was made which seemed to give a good fit to the Patterson, but repeated attempts at Fourier refinement met with no success. Without abandoning the space group assignment of $C2/c$, a new set of heavy-atom positions was arrived at that soon proved to be correct. The cause of difficulty was that the y parameters of the correct assignment are close to either

TABLE 2

ATOMIC PARAMETERS FOR BLACK ISOMER

Atom	*x*	σ_x	*y*	σ_y	*z*	σ_z	*B*	σ_B
Fe_1	.0843	.0003	.1747	.0001	.2939	.0001	2.64	.06
Fe_2	.3026	.0003	.0891	.0001	.1887	.0001	3.01	.07
Fe_3	.3421	.0003	.1574	.0001	.3032	.0001	2.86	.07
O_1	.3687	.0015	—.0604	.0008	.1546	.0007	6.88	.37
O_2	.3912	.0013	.1170	.0007	.0451	.0007	5.77	.33
O_3	.6030	.0015	.1054	.0007	.2439	.0007	6.57	.35
O_4	.5332	.0015	.2793	.0008	.3228	.0007	7.12	.38
O_5	.5103	.0014	.0884	.0008	.4292	.0007	6.27	.34
O_6	.2326	.0012	.2405	.0007	.4249	.0007	5.28	.32
O_7	—.0845	.0013	.3057	.0007	.2889	.0006	5.62	.34
O_8	—.1292	.0013	.1278	.0007	.3858	.0007	5.41	.32
C_1	.3385	.0022	.0004	.0012	.1679	.0011	6.13	.54
C_2	.3532	.0019	.1047	.0010	.1022	.0011	4.98	.48
C_3	.4707	.0023	.1105	.0012	.2384	.0011	6.44	.57
C_4	.4543	.0022	.2296	.0012	.3147	.0011	5.88	.54
C_5	.4378	.0019	.1167	.0010	.3820	.0010	4.27	.46
C_6	.2180	.0019	.2081	.0010	.3680	.0011	4.65	.48
C_7	—.0148	.0018	.2551	.0010	.2876	.0009	3.37	.42
C_8	—.0406	.0020	.1454	.0010	.3497	.0010	4.76	.48
C_9	.0998	.0016	.1489	.0008	.1798	.0008	2.46	.38
C_{10}	.2204	.0016	.1913	.0008	.2103	.0008	2.42	.38
C_{11}	.1911	.0016	.0762	.0008	.2852	.0008	2.29	.37
C_{12}	.0874	.0016	.0811	.0009	.2194	.0008	2.68	.38
C_{13}	—.0112	.0017	.1671	.0009	.1167	.0008	3.05	.39
C_{14}	.2523	.0017	.2624	.0009	.1719	.0009	3.37	.42
C_{15}	.1924	.0016	.0133	.0009	.3372	.0009	3.00	.41
C_{16}	—.0206	.0016	.0239	.0009	.1936	.0009	2.48	.38
C_{17}	—.1540	.0019	.1689	.0010	.1281	.0009	3.97	.43
C_{18}	—.2585	.0018	.1832	.0010	.0645	.0010	4.21	.44
C_{19}	—.2125	.0019	.1968	.0010	—.0034	.0010	4.11	.45
C_{20}	—.0705	.0020	.1982	.0010	—.0134	.0009	4.41	.47
C_{21}	.0386	.0018	.1845	.0009	.0484	.0009	3.56	.41
C_{22}	.1495	.0018	.3164	.0010	.1507	.0009	3.77	.42
C_{23}	.1826	.0019	.3774	.0010	.1127	.0009	4.29	.46
C_{24}	.3185	.0019	.3858	.0010	.0935	.0009	4.26	.45
C_{25}	.4226	.0019	.3351	.0011	.1094	.0009	5.12	.47
C_{26}	.3940	.0018	.2722	.0009	.1524	.0009	4.17	.45
C_{27}	.2074	.0017	—.0595	.0008	.3118	.0009	2.58	.37
C_{28}	.2034	.0017	—.1147	.0009	.3634	.0010	3.71	.43
C_{29}	.1949	.0017	—.1034	.0010	.4369	.0009	3.52	.41
C_{30}	.1819	.0017	—.0318	.0010	.4609	.0009	3.70	.43
C_{31}	.1826	.0017	.0270	.0010	.4123	.0009	3.55	.42
C_{32}	—.1191	.0018	.0006	.0009	.2398	.0009	3.33	.42
C_{33}	—.2288	.0019	—.0482	.0010	.2112	.0010	4.43	.46
C_{34}	—.2290	.0020	—.0741	.0011	.1408	.0011	5.37	.51
C_{35}	—.1319	.0020	—.0519	.0010	.0948	.0010	4.75	.47
C_{36}	—.0235	.0019	—.0015	.0010	.1218	.0010	4.36	.46

one-quarter or zero, and that the *z* parameters are all about equal (Table 3). This fact causes the Patterson peaks to be grouped together in a way that is not easy to unfold.

A refinement of the heavy-atom parameters was carried out by least squares before any light atoms were located. After this calculation, all of the light atoms of the structure were located easily by Fourier refinement. Full-matrix least-squares re-

TABLE 3

ATOMIC PARAMETERS FOR VIOLET ISOMER

Atom	*x*	σ_x	*y*	σ_y	*z*	σ_z	*B*	σ_B
Fe_1	.1308	.0001	.2598	.0004	.1568	.0002	2.36	.08
Fe_2	.1551	.0001	−.0176	.0005	.1641	.0002	3.03	.09
Fe_3	.0845	.0001	.0422	.0005	.1405	.0002	2.94	.09
O_1	.0905	.0005	.5554	.0025	.1458	.0009	5.62	.47
O_2	.1983	.0006	.4406	.0025	.1785	.0009	6.59	.51
O_3	.1369	.0005	−.2749	.0026	.0601	.0009	6.53	.50
O_4	.2360	.0005	.0489	.0023	.1921	.0008	6.18	.48
O_5	.1609	.0005	−.2731	.0025	.2619	.0009	6.30	.46
O_6	.0782	.0005	−.1723	.0021	.2407	.0008	5.16	.45
O_7	.0126	.0005	.1946	.0022	.1163	.0008	5.62	.46
O_8	.0501	.0006	−.1927	.0027	.0302	.0011	8.17	.60
C_1	.1068	.0007	.4385	.0035	.1496	.0012	4.32	.65
C_2	.1710	.0008	.3679	.0033	.1715	.0013	4.48	.69
C_3	.1459	.0007	−.1680	.0035	.0994	.0014	5.02	.69
C_4	.2042	.0008	.0113	.0034	.1805	.0012	4.61	.66
C_5	.1639	.0006	−.1689	.0030	.2254	.0012	3.33	.59
C_6	.0827	.0008	−.0901	.0036	.2017	.0015	6.10	.79
C_7	.0417	.0009	.1393	.0039	.1254	.0015	6.86	.85
C_8	.0639	.0008	−.0997	.0039	.0720	.0015	6.59	.84
C_9	.1568	.0006	.1256	.0025	.2389	.0010	1.55	.48
C_{10}	.1192	.0005	.1592	.0024	.2285	.0009	1.40	.46
C_{11}	.0960	.0005	.1636	.0024	.0693	.0009	1.09	.46
C_{12}	.1339	.0006	.1345	.0025	.0833	.0010	1.77	.50
C_{13}	.1902	.0006	.1632	.0026	.3039	.0010	1.85	.50
C_{14}	.1053	.0006	.2134	.0027	.2782	.0010	2.45	.50
C_{15}	.0674	.0006	.2151	.0028	.0022	.0010	2.32	.50
C_{16}	.1525	.0005	.1787	.0025	.0377	.0009	1.41	.47
C_{17}	.2208	.0006	.0499	.0028	.3357	.0010	2.62	.52
C_{18}	.2520	.0007	.0866	.0030	.3974	.0012	3.82	.61
C_{19}	.2552	.0006	.2363	.0032	.4254	.0010	3.19	.54
C_{20}	.2264	.0008	.3516	.0035	.3970	.0013	5.37	.72
C_{21}	.1948	.0006	.3152	.0027	.3366	.0010	2.26	.51
C_{22}	.1222	.0006	.1386	.0028	.3434	.0011	2.76	.55
C_{23}	.1103	.0006	.1900	.0028	.3926	.0011	3.30	.56
C_{24}	.0825	.0007	.3124	.0031	.3811	.0012	4.07	.61
C_{25}	.0643	.0008	.3921	.0034	.3170	.0013	5.61	.72
C_{26}	.0767	.0007	.3350	.0030	.2648	.0012	4.36	.62
C_{27}	.0427	.0006	.3483	.0028	−.0032	.0011	2.94	.56
C_{28}	.0156	.0007	.4037	.0030	−.0709	.0013	4.03	.62
C_{29}	.0088	.0008	.3120	.0039	−.1264	.0014	6.32	.77
C_{30}	.0303	.0007	.1849	.0033	−.1206	.0012	4.36	.64
C_{31}	.0598	.0007	.1226	.0030	−.0571	.0012	3.67	.60
C_{32}	.1421	.0006	.3297	.0026	.0018	.0010	2.05	.50
C_{33}	.1583	.0007	.3709	.0030	−.0427	.0012	3.96	.62
C_{34}	.1829	.0006	.2593	.0030	−.0548	.0010	2.92	.52
C_{35}	.1929	.0006	.1120	.0027	−.0213	.0011	2.90	.55
C_{36}	.1777	.0006	.0713	.0025	.0219	.0010	1.85	.49

finement for the complete structure brought the *R* index to 0.127 for 1649 reflections of non-zero weight. Again, a few reflections that were badly overlapped or missed were given zero weight in the refinement. The final position parameters and standard deviations for the violet isomer are given in Table 3.

The least-squares weight assigned to each reflection from the violet compound was proportional to the expression $[C - B]/[C + (B/2)]$, where *C* was the count observed at the peak position and B was the average of counts made for the same time as C at two opposite nearby points along the 2Θ streak. (A more exact treatment would of course take account of the variation of the Lorentz and polarization factors with 2Θ.) Reflections that counted no higher than background were given zero weight. For the black compound, B was estimated from a general survey and used in the same weight expression.

Part of the difference between the two final R values (0.127 for violet as against 0.087 for black) is surely due to difference in accuracy of the two methods of estimating the background, but other differences between the two structures and sets of data are clearly considerably more important. If the least-squares refinement had been properly made on the essential observations—the counts of peaks and background levels—the two structure determinations of isomeric substances with identical atomic compositions of the primitive unit cells (*and* asymmetric units) would probably have afforded an interesting practical test of the two methods; the actual refinement on F, unfortunately still rather conventional, leaves the effect of the various differences hopelessly mixed. We can only mention some of the advantages of the general survey while indicating how it was made and how its drawbacks were overcome. Background counts twice as long as the peak counts were made at suitable, usually varying intervals in 2Θ and the goniostat angles Φ and χ, such that routine linear interpolation on the computer would preserve good accuracy. The necessary spacings in Φ and χ were very broad, in 2Θ less so. Care had to be taken to avoid Bragg peaks and the associated streaks, and to allow for significant streaks underlying the peak counts especially for some of the inner reflections, but this was not so difficult as might be expected. The twofold advantage of the survey is that a great overall saving in time is realized while the resulting background counting accuracy is easily made as high as could be desired. Actually, the separate background counts for the violet compound were longer than optimal relative to the peak counts (hardly any time could in fact have been saved by making them shorter); even so, the counting precision of the survey background was always at least as good and would generally have justified weights for the weak nonzero reflections about a third higher than were used.

DISCUSSION OF THE TWO STRUCTURES

The central feature of the structure of the black form of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ (Fig. 1) is the ferracyclopentadiene ring with the unique aspect of π-bond formation to iron atoms on both sides of the ring. This arrangement is absent in the violet form (Fig. 3) and, in a sense, represents a final stage in the stabilization of the original iron-carbonyl–acetylene system.

The estimates of the errors in the bond distances and bond angles of both isomers (Tables 4, 5, 6, and 7) were made assuming that the errors are isotropic. An inspection of the least squares results confirmed that this was a reasonable assumption.

Aside from the twisting of the phenyl groups out of the plane of the five-membered ring, the symmetry of the molecule of the black form is close to C_{2v}. One mirror plane is defined by the five-membered ring and the other by the iron atoms. The twists of the phenyl groups, all by about 55° (Table 8) and all in the same sense, upset this symmetry. Nearly octahedral bonding of the carbon atoms to Fe_3 prevails (Fig. 2), the 77° angle in the five-membered ring representing the greatest deviation.

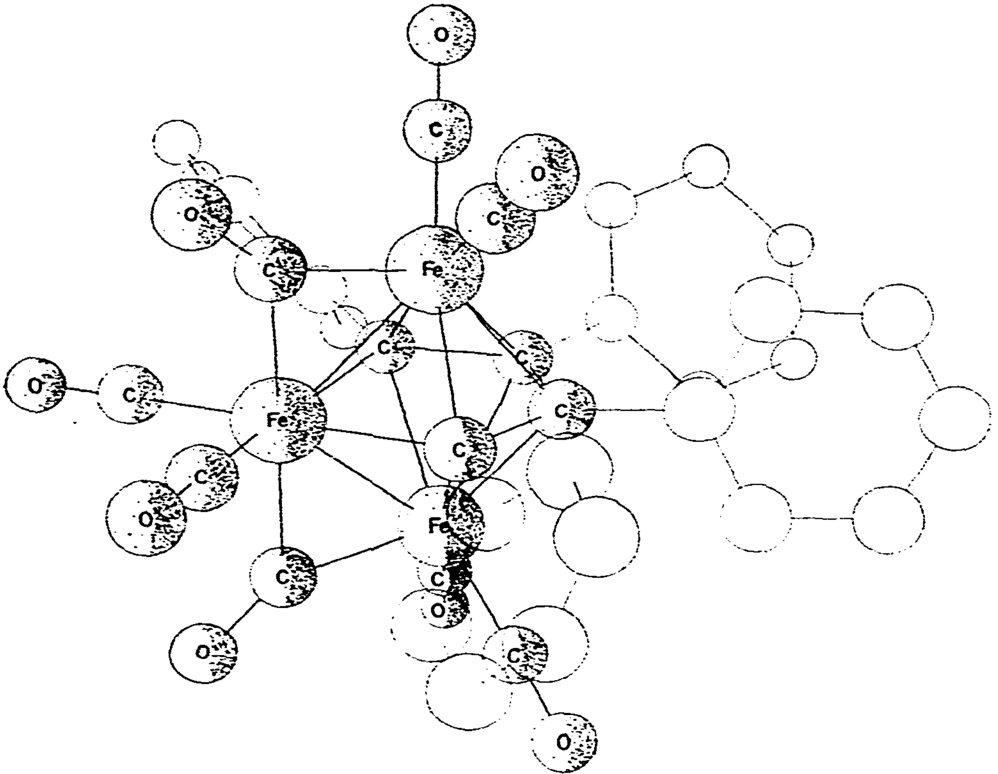

Fig. 1. A molecule of the black isomer of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$. The projection is perpendicular to the *b* axis.

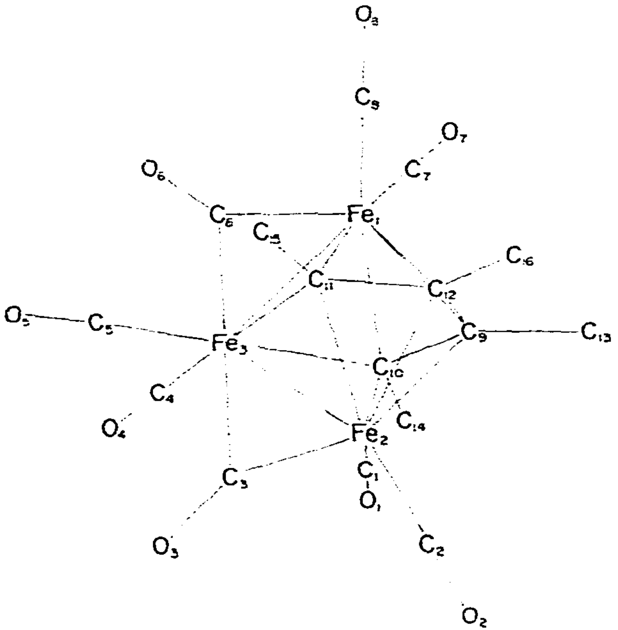

Fig. 2. Numbering system for the black isomer.

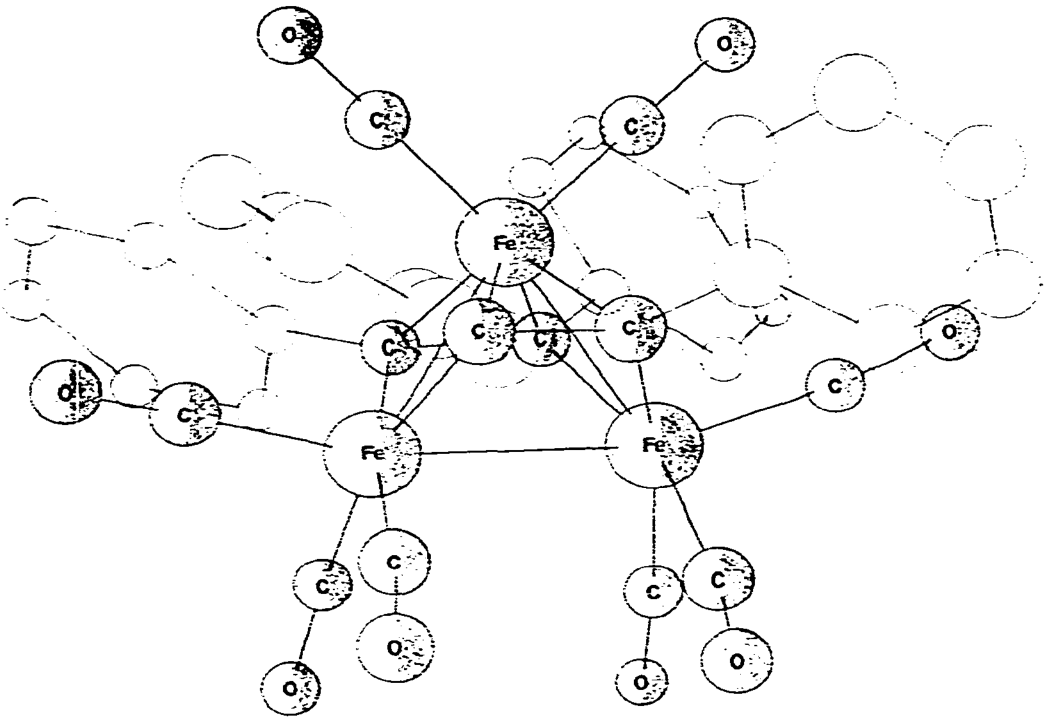

Fig. 3. A molecule of the violet form of $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$. The projection is perpendicular to the c axis.

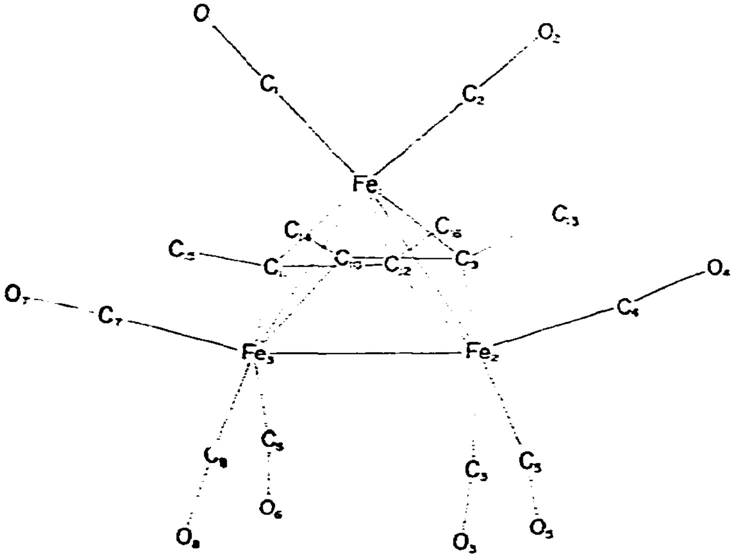

Fig. 4. Numbering system for the violet isomer.

TABLE 4

BOND DISTANCES IN THE BLACK ISOMER

Bond	Distance (Å)	σ	Bond	Distance (Å)	σ
Fe_1–Fe_3	2.428	.003	C_1–O_1	1.189	.026
Fe_2–Fe_3	2.435	.003	C_2–O_2	1.165	.023
Fe_1–C_6	1.842	.019	C_3–O_3	1.238	.025
Fe_1–C_7	1.747	.017	C_4–O_4	1.178	.025
Fe_1–C_8	1.729	.019	C_5–O_5	1.159	.023
Fe_1–C_9	2.162	.015	C_6–O_6	1.194	.022
Fe_1–C_{10}	2.128	.015	C_7–O_7	1.142	.021
Fe_1–C_{11}	2.091	.015	C_8–O_8	1.168	.022
Fe_1–C_{12}	2.202	.016	C_9–C_{10}	1.435	.021
Fe_2–C_1	1.723	.022	C_9–C_{12}	1.456	.022
Fe_2–C_2	1.731	.019	C_{11}–C_{12}	1.459	.021
Fe_2–C_3	1.771	.021	C_9–C_{13}	1.500	.022
Fe_2–C_9	2.191	.015	C_{10}–C_{14}	1.536	.022
Fe_2–C_{10}	2.093	.015	C_{11}–C_{15}	1.499	.022
Fe_2–C_{11}	2.169	.015	C_{12}–C_{16}	1.502	.022
Fe_2–C_{12}	2.165	.016			
Fe_3–C_3	1.988	.021			
Fe_3–C_4	1.696	.021			
Fe_3–C_5	1.774	.018			
Fe_3–C_6	1.991	.019			
Fe_3–C_{10}	2.031	.015			
Fe_3–C_{11}	2.063	.015			

TABLE 5

BOND ANGLES IN THE BLACK ISOMER

Angle	Degrees	σ	Angle	Degrees	σ
Fe_1–Fe_3–Fe_2	87.6	0.1	Fe_3–C_{10}–C_{14}	126.0	1.1
C_7–Fe_1–C_8	84.9	0.8	Fe_3–C_{10}–C_9	119.9	1.1
C_1–Fe_2–C_2	82.8	1.0	C_9–C_{10}–C_{14}	118.4	1.3
C_{10}–Fe_3–C_{11}	77.4	0.6	Fe_3–C_{11}–C_{15}	129.2	1.1
Fe_2–C_1–O_1	177.4	1.9	Fe_3–C_{11}–C_{12}	117.8	1.0
Fe_2–C_2–O_2	177.5	1.7	C_{12}–C_{11}–C_{15}	121.7	1.3
Fe_2–C_3–O_3	148.2	1.7	C_{10}–C_9–C_{13}	128.5	1.4
Fe_2–C_3–O_3	131.2	1.6	C_{10}–C_9–C_{12}	112.3	1.3
Fe_3–C_4–O_4	179.5	1.9	C_{12}–C_9–C_{13}	119.1	1.3
Fe_3–C_5–O_5	173.4	1.6	C_9–C_{12}–C_{11}	112.3	1.3
Fe_2–C_6–O_6	137.7	1.5	C_9–C_{12}–C_{16}	122.5	1.4
Fe_1–C_6–O_6	143.8	1.5	C_{11}–C_{12}–C_{16}	125.2	1.4
Fe_1–C_7–O_7	174.1	1.6			
Fe_1–C_8–O_8	176.9	1.6			
Fe_2–C_3–Fe_3	80.5	0.8			
Fe_1–C_6–Fe_3	78.5	0.7			
C_4–Fe_2–C_5	89.1	0.9			
C_3–Fe_3–C_6	177.6	0.8			

TABLE 6

BOND DISTANCES IN THE VIOLET ISOMER

Bond	*Distance* (Å)	σ	*Bond*	*Distance* (Å)	σ
Fe_1–Fe_2	2.469	.005	C_1–O_1	1.142	.034
Fe_1–Fe_3	2.457	.005	C_2–O_2	1.167	.035
Fe_2–Fe_3	2.592	.005	C_3–O_3	1.179	.036
Fe_1–C_1	1.720	.028	C_4–O_4	1.183	.034
Fe_1–C_2	1.699	.028	C_5–O_5	1.214	.032
Fe_2–C_3	1.801	.030	C_6–O_6	1.159	.035
Fe_2–C_4	1.786	.028	C_7–O_7	1.150	.038
Fe_2–C_5	1.760	.025	C_8–O_8	1.139	.040
Fe_3–C_6	1.750	.031	C_9–C_{10}	1.395	.030
Fe_3–C_7	1.733	.033	C_9–C_{12}	3.117	.031
Fe_3–C_8	1.800	.033	C_{10}–C_{11}	3.191	.028
Fe_1–C_9	1.980	.022	C_{11}–C_{12}	1.375	.030
Fe_1–C_{10}	1.980	.021	C_9–C_{13}	1.488	.031
Fe_1–C_{11}	1.975	.020	C_{10}–C_{14}	1.464	.030
Fe_1–C_{12}	1.954	.022	C_{11}–C_{15}	1.473	.030
Fe_2–C_9	1.995	.022	C_{12}–C_{16}	1.493	.030
Fe_2–C_{12}	2.036	.022			
Fe_3–C_{10}	2.057	.021			
Fe_3–C_{11}	2.049	.020			

TABLE 7

BOND ANGLES IN THE VIOLET ISOMER

Angle	*Degrees*	σ	*Angle*	*Degrees*	σ
Fe_2–Fe_1–Fe_3	63.5	0.2	Fe_1–C_1–O_1	178.2	2.5
Fe_1–Fe_2–Fe_3	58.0	0.1	Fe_1–C_2–O_2	176.8	2.5
Fe_1–Fe_3–Fe_2	58.5	0.1	Fe_2–C_3–O_3	171.7	2.6
C_1–Fe_1–C_2	88.3	1.3	Fe_2–C_4–O_4	172.3	2.5
C_3–Fe_2–C_4	95.2	1.3	Fe_2–C_5–O_5	164.9	2.2
C_3–Fe_2–C_5	90.4	1.3	Fe_3–C_6–O_6	173.9	2.7
C_4–Fe_2–C_5	95.5	1.2	Fe_3–C_7–O_7	175.6	2.9
C_6–Fe_3–C_7	95.0	1.5	Fe_3–C_8–O_8	177.1	2.9
C_6–Fe_3–C_8	94.1	1.5	C_{10}–C_9–C_{13}	122.0	1.9
C_7–Fe_3–C_8	95.6	1.5	C_9–C_{10}–C_{14}	128.3	1.9
C_9–Fe_1–C_{10}	41.3	0.9	C_{12}–C_{11}–C_{15}	123.3	1.0
C_{10}–Fe_1–C_{11}	107.6	0.8	C_{11}–C_{12}–C_{16}	124.8	1.9
C_{11}–Fe_1–C_{12}	41.0	0.9			
C_9–Fe_1–C_{12}	104.8	0.9			
C_9–Fe_2–C_{12}	101.3	0.9			
C_{10}–Fe_3–C_{11}	102.0	0.8			

The triangular structure for $Fe_3(CO)_{12}$ proposed by Dahl and Rundle[5]*, suggests a simple picture of the reactions leading up to the formation of the ferracyclopentadiene ring. The structure of the violet compound (Fig. 3) is then closely related to the individual structures of both reactants and can be viewed as simply a double substitution of $Fe_3(CO)_{12}$ by diphenylacetylene. The two diphenylacetylene groups remain

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* The structure of $Fe_3(CO)_{12}$ is not entirely certain: the quadrupole splitting and chemical shift in the Mössbauer effect[6,7] seems to demand a linear structure, but the X-ray evidence[5] rules out this possibility.

TABLE 8

INFORMATION ON THE PHENYL GROUPS OF BOTH ISOMERS

Phenyl group at	*Average C–C distance (Å)*	*Average deviation*	*R. m. s. dev. from best l.s. plane (Å)*	*Av. dev. of C–C–C angle from mean*	*Angle of twist*	*Angle of bend**
Black isomer						
C_{13}	1.411	.033	.018	2.1°	55°	5°
C_{14}	1.399	.029	.016	1.4°	54°	−2°
C_{15}	1.402	.014	.012	2.0°	57°	2°
C_{16}	1.396	.018	.011	1.6°	55°	−5°
Violet isomer						
C_{13}	1.404	.018	.015	1.7°	62°	19°
C_{14}	1.431	.017	.006	2.6°	36°	12°
C_{15}	1.409	.049	.041	2.1°	46°	10°
C_{16}	1.418	.016	.011	0.8°	57°	20°

* Positive toward Fe_1 and negative away from Fe_1.

clearly separate (note the interatomic distances in Table 6), and it is the rearrangement to the black compound that represents the synthesis of the butadiene unit as well as the ferracyclopentadiene ring.

The twists of the phenyl groups given in Table 8 are actually interplanar angles between phenyl group and a reference plane, and must be regarded as resultants of both bending and twisting motions. The bendings are negligibly small for the black isomer but not for the violet isomer. For the black isomer the reference plane is the least-squares plane of the ferracyclopentadiene ring; for the violet it is the least-squares plane of the four acetylene carbon atoms. The bend angle in each case is the angle between the reference plane and the C–C bond line to the phenyl group. In the black isomer, as in tetraphenylcyclobutadiene iron tricarbonyl[8], the twists in any molecule are all of the same sense, but not so for the violet isomer. Two phenyls on any one diphenylacetylene group are twisted in the same sense to avoid an obvious steric hindrance. The separation of the two diphenylacetylene groups clearly allows adjacent phenyl groups on opposite sides of the iron plane (on C_{10} and C_{11}, for instance) to have opposite rotations without incurring steric hindrance, but it is not clear why that arrangement is adopted in preference to the other. Goodness of intermolecular packing is very probably decisive, but the deviations on the bends and twists (Table 7) from C_{2v} symmetry and the retention of approximate C_s symmetry suggest that relative ease of intramolecular distortion may be important too. We have not followed up this point in detail. As for the individual angles of twist, inspection of all of the interatomic distances in the molecule reveals that the actual angle of twist for each of the phenyls is such as to equalize as much as possible the distances to the carbonyl groups in the same molecule. The shortest intermolecular contacts in both forms are between oxygen atoms; however, a few carbonyl–phenyl contacts may be close enough to affect the balance of forces on the phenyl groups.

The further information on the phenyl groups, in Table 8, shows that they are all regular planar hexagons to the accuracy of the determination. The best least-squares plane was calculated in each case to determine the degree of non-planarity.

The average angle at each carbon atom is within 0.04° of 120° except for the phenyl group at C_{15} in the violet isomer, for which it is 119.78°. The average deviations from the means are about those expected from the least-squares estimates of the standard deviations.

The isomerization of the violet compound results in the formation of a butadiene unit, a recurrent theme in the chemistry of the acetylene–iron-carbonyl complexes[9,10]. With the help of the present structure determinations it is easy to visualize the rearrangement in terms of more or less simultaneous breaking of an iron–iron bond, formation of the butadiene bond, and formation of new iron–carbonyl (bridge) bonds, but neither the exact sequence nor the necessary amount of thermal activation energy is clear. More interesting than further speculation, in fact, would be a determination of whether the rearrangement is indeed an uncatalyzed, first-order reaction or not.

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SUMMARY

The reaction between $Fe_3(CO)_{12}$ and diphenylacetylene produces a violet compound $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$ which readily transforms to a more stable black isomer. The present X-ray structure determinations have revealed the nature of the bonding in these new three-center complexes. The diphenylacetylene molecules in the violet isomer remain separate, being located on opposite sides of the triangle of iron atoms, while they unite to form a ferracyclopentadiene ring in the black isomer.

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