Reaction of $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ with $(CH_3)_3N$. A dark orange solution of $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ (38.5 mg, 0.0612 mmol) in $(CH_3)_3N$ (76.0 mg, 1.29 mmol) was stirred for 1 hr in a reaction vessel at room temperature. The volatile material, $(CH_3)_3N$ (75.1 mg; 1.27 mmol; 98.4% recovery; mol wt calcd, 59.13; found, 59.2; confirmed by infrared spectrum[35]), was distilled from the solid, unchanged $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ (39.0 mg, 0.0620 mmol, 101.3% recovery, identified by infrared spectrum).

Reaction of $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ with $(CH_3)_3P$. An orange solution of $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ (175.3 mg, 0.2789 mmol) in $(CH_3)_3P$ (83.9 mg, 1.10 mmol) was stirred for 1 hour at room temperature. The volatile material, $(CH_3)_3P$ (83.6 mg; 1.10 mmol; 100.0% recovery; mol wt calcd, 76.09; found, 76.5; confirmed by infrared spectrum[39]) was distilled from the solid, unchanged $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ (174.9 mg, 0.2782 mmol, 99.7% recovery, identified by infrared spectrum).

Reaction of $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ with $[(n\text{-}C_4H_9)_4N]Cl$. A yellow solution of $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ (101.4 mg, 0.1613 mmol) and $[(n\text{-}C_4H_9)_4N]Cl$ (105.8 mg, 0.3806 mmol) in $(C_2H_5)_2O$ (270.7 mg) was stirred for 1 hr at room temperature in a reaction vessel. Some of the $[(n\text{-}C_4H_9)_4N]Cl$ did not dissolve. After distilling off the ether, the residue (207.1 mg, 99.9% recovery) was shown by its infrared spectrum to consist of a mixture of the two starting materials. Pure $[(CH_3)_3SiFe[COSi(CH_3)_3](CO)_3]_2$ (77.1 mg, 0.123 mmol, 76.0% recovery, identified by infrared spectrum) was extracted with hexane.

Structure of the Unsymmetrical 12-Oxa[4.4.3]propella-2,4,7,9-tetraene Bis(iron tricarbonyl). An Example of an Oxygen–Diene Interaction through Space

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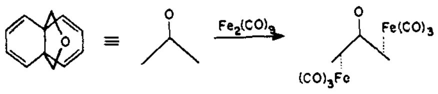
Abstract: The three-dimensional structure of the unsymmetrical 12-oxa[4.4.3]propella-2,4,7,9-tetraene–bis(iron tricarbonyl) complex, $(C_{12}H_{12}O)Fe_2(CO)_6$, was determined by X-ray crystallography. The substance crystallizes in the triclinic space group $P\bar{1}$ with two molecules of the complex in a unit cell of dimensions $a = 6.823 \pm 0.006$, $b = 11.480 \pm 0.004$, $c = 11.706 \pm 0.004$ Å; $\alpha = 89.19 \pm 0.04$, $\beta = 94.09 \pm 0.04$, $\gamma = 107.03 \pm 0.04°$. The intensities were measured with a diffractometer and the structure was solved by the heavy-atom method. Refinement by the least-squares method converged at $R = 3.5\%$ for 3288 observed reflections. The positions of all hydrogen atoms were found and refined. Each iron tricarbonyl group is coordinated to a cyclic diene system, one of the systems being perturbed by an interaction with a pair of electrons on the oxygen atom of the propellane. In view of the presence of an internal calibration, the effects of this interaction can be assessed. They include an enhanced back-donation of d_π electrons to the propellane ligand. In both diene systems the central bonds are significantly shorter than the "outer" ones.

Following their studies of the electrocyclic reactions of tetraenic propellanes,[1] Ginsburg and his colleagues turned their attention to an investigation of the behavior upon irradiation of the corresponding bis(iron tricarbonyl) derivatives as well as their thermal behavior.[2] Three such derivatives were prepared by treating 12-oxa[4.4.3]propella-2,4,7,9-tetraene (**1**) with diiron nonacarbonyl,[3] and the structure of one of them was recently reported.[4] This report deals with the structure of another isomer (**2**), one in which the two iron tricarbonyl groups are complexed unsymmetrically.



1 **2**

The structures of various diene complexes with iron tricarbonyl were recently reviewed.[5,6] Three such structures have been reported[7–9] in which the diene group was part of a six-membered ring, but only one of them was described in detail.[8] Although some general features have emerged, the nature of the bond between the iron atom and the diene system is not yet fully understood, partly, at least, because many previous X-ray structure determinations of such complexes have failed to reveal sufficient geometrical details from which theoretical conclusions could be drawn.[10] It was hoped, therefore, that a more accurate X-ray analysis would shed additional light on this subject.

Experimental Section

Crystal Data. 12-Oxa[4.4.3]propella-2,4,7,9-tetraene Bis(iron tricarbonyl), $(C_{12}H_{12}O)Fe_2(CO)_6$; Formula Weight 451.98. The material was one of the products obtained by refluxing a solution of the propellane ligand with $Fe_2(CO)_9$ in dry benzene for 24 hr in a nitrogen atmosphere.[3] It was crystallized from CH_2Cl_2–petroleum ether (120–160°) to give yellow prisms, mp 135–138°. Precession photographs indicated a triclinic cell. The lattice constants of a centered (nonprimitive) cell were measured at room temperature on a four-circle diffractometer fitted with a Cu target at a 1° takeoff angle with a 0.02° slit. Several reflections were scanned along each

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[1] J. Altman, E. Babad, D. Ginsburg, and M. B. Rubin, *Israel J. Chem.*, 7, 435 (1969).

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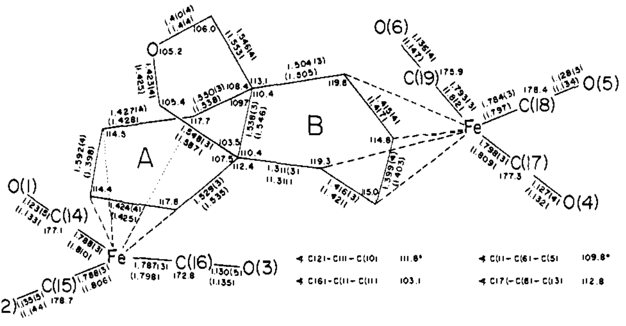

Figure 1. Bond lengths (with esd's) and bond angles (esd's are 0.2° in the organic ligand and 0.3° in the carbonyl groups).

axis and both Cu Kα_1 (λ 1.54051 Å) and Cu Kα_2 (λ 1.54433 Å) radiations were used. The average deviations were doubled in order to account for the error in the β angle of the centered cell. From these measurements the following parameters of a reduced primitive cell were calculated: $a = 6.823 \pm 0.006$, $b = 11.480 \pm 0.004$, $c = 11.706 \pm 0.004$ Å, $\alpha = 89.19 \pm 0.04$, $\beta = 94.09 \pm 0.04$, $\gamma = 107.03 \pm 0.04°$; $V = 874.5$ Å^3, $D_x = 1.716$, $D_m = 1.71$ g cm^{-3} (by flotation in aqueous KI solution), $Z = 2$, $F(000) = 456$, μ(Mo Kα) = 17.3 cm^{-1}; no systematic absences, space group $P1$ or $P\bar{1}$.

Data Collection. A crystal was cut to give a fragment with dimensions 0.4–0.5 mm. This was mounted along the B axis of the centered cell ($A = a$, $B = a + 2b$, $C = c$). The data were collected on an automated Picker four-circle diffractometer using Mo Kα radiation, and monochromatization was achieved by a niobium filter and a pulse-height analyzer. The moving-crystal–moving-counter (θ–2θ scan) method was employed with 2° scans for $0 < 2\theta \leq 35°$ and 2.8° scans for $35 < 2\theta \leq 55°$. The rate of scans was 2°/min and backgrounds were counted for 20 sec on both ends of each scan. When the count rate exceeded 20,000 cps the current was reduced and, if necessary, brass attenuators were used. A standard reflection was monitored at approximately hourly intervals and its intensity was used for scaling the data. There was no indication of any deterioration of the crystal during the data collection. Of the 4026 reflections with $2\theta \leq 55°$, 3288 (81%) were considered observed. A net count of 150 or 10% of the background, whichever was higher, was determined to be threshold intensities. Later on it was discovered that the shutter had been accidentally closed during the scan of $53\bar{8}$ and this reflection was therefore not used in the refinement.

Structure Determination. Lorentz and polarization corrections were applied to the intensities. Absorption corrections were not applied. If the crystal had a cylindrical shape of similar dimensions, the maximum and minimum absorption correction factors (A^*) would have been 1.95 and 1.92, respectively. There was no evidence of the intensities being affected by extinction. The space group was determined from the three-dimensional Patterson synthesis. The density of the crystals indicated two molecules of the complex in the unit cell and if the space group was $P1$, the four Fe atoms would give rise to six interaction peaks. Instead, only four peaks were observed, two of them about twice as high as the other two. This configuration is precisely what was to be expected in space group $P\bar{1}$.

A three-dimensional Fourier map, phased on the positions of the two Fe atoms, revealed all 27 nonhydrogen atoms. After five cycles of isotropic, block-diagonal least-squares refinement, in which $\Sigma w(F_o - F_c)^2$ was minimized, the value of conventional R converged at 10.1%. Anisotropic temperature parameters were then introduced for all atoms, and after two more cycles of refinement a difference Fourier map was calculated which clearly showed the positions of all 12 hydrogen atoms. The coordinates and isotropic temperature parameters of these atoms were refined in the subsequent cycles. The following weighting scheme was used during the final stages of the refinement: $\sqrt{w} = \sqrt{w_1}\sqrt{w_2}$, where $\sqrt{w_1} = |F_o|/p_1$ if $|F_o| \leq p_1$, $\sqrt{w_1} = p_1/|F_o|$ if $|F_o| > p_1$; and $\sqrt{w_2} = \sqrt{\sin^2\theta/p_2}$ if $\sin^2\theta \leq p_2$, $\sqrt{w_2} = 1$ if $\sin^2\theta > p_2$. The values of the weighting parameters were adjusted so as to give uniform distribution of $w\Delta F$ with respect to $|F_o|$ and $\sin^2\theta$. The final values were $p_1 = 12.0$, $p_2 = 0.1$. There were no unusual coordinate shifts following the introduction of this weighting scheme. The refinement converged to a conventional agreement index R = 3.49% and a weighted factor $R' = (\Sigma w(\Delta F)^2/\Sigma wF_o^2)^{1/2} = 3.63\%$ for the 3288 observed reflections. Of the 737 unobserved reflections 57 had $|F_c|$ values in the range $1.0|F_{th}| < |F_c| \leq 1.5|F_{th}|$ and 2 had $|F_c|$ values in the range $1.5|F_{th}| < |F_c| \leq 2.0|F_{th}|$. All other F_c values were below the threshold. A shift factor of 0.8 was used throughout the refinement. At the end of the last cycle the average coordinate shift was 0.1σ and the maximum shift equalled 0.38σ. A difference Fourier map calculated at this stage showed no significant features except for peaks of 0.6 e Å^{-3} in the vicinity of the Fe atoms. The atomic scattering factors of Fe^0 were those given by Cromer and Waber.[11] They were corrected for anomalous scattering with $f' = 0.37$ and $f'' = 0.92$.[12] The scattering factors of Hanson, *et al.*,[13] were used for C, N, and O and those of Stewart, *et al.*,[14] for bonded H. A table of the final observed and calculated structure factors is available.[15] The final atomic coordinates and temperature parameters are listed in Table I. The estimated standard deviations (shown everywhere in parentheses and referring always to the last digit) were derived from the inverse of the least-squares matrix.

Thermal Vibration Analysis. The whole complex as well as its three individual components were subjected to a rigid-body analysis in terms of translation (**T**), libration (**L**), and screw motion (**S**) tensors.[16] The average values of $\sigma(U^{ij}_{\text{obsd}})$ were 0.0017, 0.0015, 0.0020, and 0.0018 Å^2 for the complex, the organic ligand, and the two iron tricarbonyl groups, respectively. The values of $\sigma(U_{\text{calcd}}) = [\Sigma(\Delta U^{ij})^2/(n - s)]^{1/2}$ were 0.0092, 0.0016, 0.0051, and 0.0053 Å^2 for the same groups. This shows that while the rigid-body model is inappropriate for the whole complex it is very good for the propellane ligand. The assumption of a rigid body is not quite correct for the iron tricarbonyl groups. Nevertheless, it was used to correct the bond lengths within these groups as well, since the rigid-body model accounts for most of their thermal vibration. The corrected bond lengths are shown in parentheses in Figure 1. The bond angles remained unchanged by these corrections.

Discussion of the Structure

A stereoscopic diagram of the structure is shown in Figure 2.[17] Each iron tricarbonyl group is coordinated to a cyclic diene system. The organic ligand contains two six-membered rings in boat conformations which, as indicated by the torsional angles (Figure 3), are flatter than an ideal cyclohexane boat in which the torsional angles are 0 and ±54°.[18] The third "blade" of the propellane consists of an envelope-shaped five-membered ring whose flap is tilted toward ring A. The structure analysis of the related symmetrical complex[4,19] revealed that the dihedral angles between the three planes constituting the blades were approximately 120°. There are significant deviations from such symmetry in the present structure, the heterocyclic ring and ring A being bent toward each other (Figure 4). The standard deviations for the dihedral and torsional angles are 0.2–0.3°. Details of the least-squares planes are given in Table II. The χ^2 values indicate that in planes 1–5 the relevant atoms are coplanar, while in

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(11) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(12) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(13) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *ibid.* **17**, 1040 (1964).

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) A table of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(16) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968). A computer program written by these authors was used in these calculations.

(17) The drawing was made with the help of the ORTEP program of C. K. Johnson.

(18) R. Bucourt and D. Hainaut, *Bull. Soc. Chim. Fr.*, 1366 (1965).

(19) K. B. Birnbaum, *Acta Crystallogr., Sect. B*, **28**, 161 (1972).

Table I. Final Fractional Coordinates and Thermal Parameters (Å^2)

(a) Nonhydrogen Atoms^a

	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U^{11}	10^3U^{22}	10^3U^{33}	$10^3(2U^{23})$	$10^3(2U^{13})$	$10^3(2U^{12})$
C(1)	1112 (3)	2330 (2)	7784 (2)	28 (1)	32 (1)	42 (1)	10 (2)	10 (2)	21 (2)
C(2)	290 (3)	1005 (2)	7373 (2)	27 (1)	37 (1)	53 (1)	6 (2)	1 (2)	12 (2)
C(3)	149 (4)	72 (2)	8208 (3)	38 (1)	34 (1)	65 (2)	16 (2)	34 (2)	8 (2)
C(4)	1916 (4)	222 (2)	8932 (2)	53 (1)	37 (1)	41 (1)	30 (2)	28 (2)	33 (2)
C(5)	3557 (4)	1277 (2)	8707 (2)	37 (1)	38 (1)	32 (1)	13 (2)	6 (2)	29 (2)
C(6)	3067 (3)	2492 (2)	8580 (2)	33 (1)	33 (1)	27 (1)	8 (1)	11 (2)	25 (2)
C(7)	4831 (3)	3490 (2)	8144 (2)	30 (1)	31 (1)	36 (1)	−2 (2)	0 (2)	18 (2)
C(8)	5148 (4)	3542 (2)	6960 (2)	39 (1)	30 (1)	42 (1)	3 (2)	32 (2)	16 (2)
C(9)	3371 (4)	3384 (2)	6232 (2)	60 (1)	28 (1)	28 (1)	2 (2)	14 (2)	22 (2)
C(10)	1541 (4)	3202 (2)	6798 (2)	41 (1)	34 (1)	38 (1)	7 (2)	−14 (2)	26 (2)
C(11)	−423 (4)	2584 (3)	8586 (3)	38 (1)	50 (1)	78 (2)	16 (3)	46 (3)	37 (2)
O(12)	252 (4)	2329 (2)	9702 (2)	73 (1)	61 (1)	62 (1)	31 (2)	86 (2)	55 (2)
C(13)	2431 (5)	2808 (3)	9753 (2)	68 (2)	47 (1)	33 (1)	15 (2)	31 (2)	50 (3)
Fe(1)	2557.2 (5)	111.8 (3)	7265.5 (3)	39.5 (2)	26.8 (1)	40.4 (1)	7.3 (3)	10.0 (3)	19.9 (3)
C(14)	941 (5)	−937 (3)	6235 (3)	70 (2)	42 (1)	50 (2)	4 (2)	−1 (3)	24 (3)
O(1)	−127 (6)	−1565 (3)	5583 (3)	116 (2)	74 (2)	68 (2)	−36 (3)	−48 (3)	0 (3)
C(15)	4035 (5)	−906 (3)	7652 (3)	55 (2)	39 (1)	69 (2)	−4 (2)	−1 (3)	35 (2)
O(2)	4940 (5)	−1568 (3)	7904 (3)	93 (2)	66 (2)	134 (3)	6 (3)	−28 (3)	100 (3)
C(16)	4257 (5)	956 (2)	6254 (3)	70 (2)	31 (1)	65 (2)	−1 (2)	58 (3)	34 (2)
O(3)	5356 (6)	1377 (2)	5582 (3)	134 (3)	50 (1)	112 (2)	19 (3)	176 (4)	49 (3)
Fe(2)	3787.6 (5)	4857.3 (3)	7271.9 (3)	45.9 (2)	27.0 (1)	31.9 (1)	4.7 (2)	12.3 (2)	23.2 (3)
C(17)	6270 (5)	5976 (2)	7390 (3)	65 (2)	34 (1)	48 (1)	−2 (2)	27 (2)	11 (2)
O(4)	7860 (5)	6641 (3)	7469 (3)	75 (2)	64 (1)	96 (2)	−23 (3)	38 (3)	−34 (3)
C(18)	2767 (5)	5669 (3)	6188 (3)	71 (2)	37 (1)	51 (1)	20 (2)	16 (3)	37 (2)
O(5)	2077 (6)	6161 (3)	5503 (3)	115 (2)	79 (2)	74 (2)	71 (3)	−3 (3)	89 (3)
C(19)	2707 (5)	5377 (2)	8446 (2)	62 (2)	39 (1)	48 (1)	8 (2)	19 (2)	43 (2)
O(6)	2087 (5)	5777 (3)	9174 (2)	104 (2)	77 (2)	63 (1)	−20 (2)	51 (3)	91 (3)

(b) Hydrogen Atoms

	$10^3x/a$	$10^3y/b$	$10^3z/c$	10^3U_{iso}		$10^3x/a$	$10^3y/b$	$10^3z/c$	10^3U_{iso}
H(21)	−84 (5)	88 (3)	678 (3)	47 (8)	H(91)	347 (5)	351 (3)	547 (3)	51 (8)
H(31)	−96 (6)	−63 (3)	821 (3)	55 (9)	H(101)	41 (5)	320 (3)	639 (3)	44 (8)
H(41)	198 (5)	−37 (3)	939 (3)	39 (7)	H(111)	−179 (6)	208 (3)	837 (3)	57 (9)
H(51)	491 (4)	134 (3)	908 (2)	29 (6)	H(112)	−43 (6)	345 (3)	854 (3)	51 (9)
H(71)	603 (5)	377 (3)	866 (3)	41 (7)	H(131)	304 (5)	244 (3)	1037 (3)	49 (8)
H(81)	648 (4)	379 (3)	666 (3)	35 (7)	H(132)	283 (5)	372 (3)	987 (3)	48 (8)

[a] The thermal vibration parameters are expressed as $\exp[-2\pi^2(U^{11}h^2a^{*2} + U^{22}k^2b^{*2} + U^{33}l^2c^{*2} + 2U^{23}klb^*c^* + 2U^{13}hla^*c^* + 2U^{12}\cdot hka^*b^*)]$.

planes 8 and 9 they deviate significantly from coplanarity.

Most bond lengths and angles, apart from those in ring A, agree with the ones found in the symmetrical complex.[19] The very good agreement between equivalent bond lengths and angles within each ring suggests that the esd's are realistic. This, therefore, appears to be the most accurate X-ray analysis of a "butadiene"

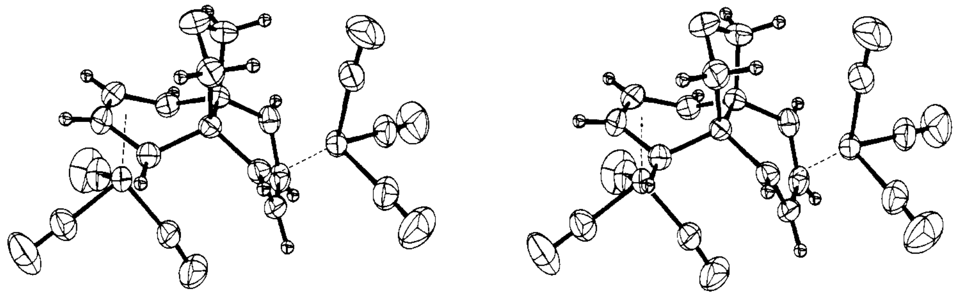

Figure 2. Stereoscopic view of the structure; the ellipscids include 50% probability. The hydrogen atoms are represented by spheres with an arbitrary radius.

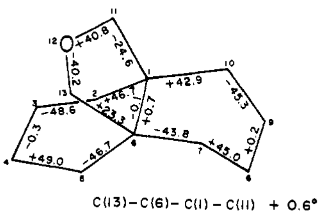

Figure 3. Torsional angles in the three rings (esd's are 0.2–0.3°). For a definition of these angles, see W. Klyne and V. Prelog, *Experientia*, 16, 521 (1960).

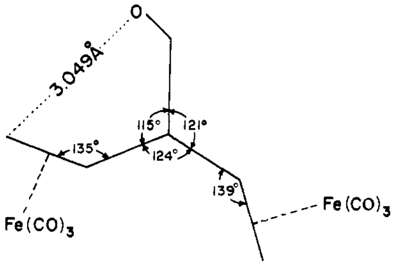

Figure 4. Selected dihedral angles between planes. Schematic representation of the view along the C(6)–C(1) bond.

Table II. Least-Squares Planes[a]

Plane 1	Δ, Å	Plane 2	Δ, Å	Plane 3	Δ, Å	Plane 4	Δ, Å	Plane 5	Δ, Å	Plane 6	Δ, Å	Plane 7	Δ, Å	Plane 8	Δ, Å	Plane 9	Δ, Å
C(1)	−0.001	C(2)	−0.001	C(1)	−0.004	C(1)	−0.004	C(7)	+0.001	C(14)	0.0	C(17)	0.0	C(2)	−0.063	C(7)	−0.053
C(2)	+0.001	C(3)	+0.002	C(11)	+0.002	C(6)	+0.004	C(8)	−0.001	C(15)	0.0	C(18)	0.0	C(5)	+0.059	C(10)	+0.054
C(5)	−0.001	C(4)	−0.002	C(13)	−0.002	C(7)	−0.002	C(9)	+0.001	C(16)	0.0	C(19)	0.0	C(14)	+0.062	C(17)	+0.052
C(6)	+0.001	C(5)	+0.001	C(6)	+0.004	C(10)	+0.002	C(10)	−0.001	Fe(1)[b]	−0.949	Fe(2)[b]	+0.920	C(15)	−0.059	C(18)	−0.054
H(21)[b]	+0.13	H(21)[b]	+0.13	O(12)[b]	−0.553	H(71)[b]	−0.18	H(71)[b]	−0.20					Fe(1)[b]	+0.293	Fe(2)[b]	−0.290
H(51)[b]	+0.17	H(31)[b]	+0.11	H(111)[b]	−0.51	H(101)[b]	−0.12	H(81)[b]	−0.13					C(16)[b]	+2.069	C(19)[b]	−2.080
		H(41)[b]	+0.11	H(112)[b]	+0.93			H(91)[b]	−0.11					M(3,4)[b]	−1.212	M(8,9)[b]	+1.201
		H(51)[b]	+0.18	H(131)[b]	−0.55			H(101)[b]	−0.11					$\chi^2 = 1982$		$\chi^2 = 1596$	
		Fe(1)[b]	+1.641	H(132)[b]	+0.94			Fe(2)[b]	−1.649								
$\chi^2 = 0.3$		$\chi^2 = 0.8$		$\chi^2 = 6.7$		$\chi^2 = 8.4$		$\chi^2 = 0.7$									

Dihedral Angles (deg) between Planes[c]

1, 2	1, 3	1, 4	2, 4	2, 6	2, 8	3, 4	4, 5	5, 7	5, 9
45.0	65.1	55.9	10.9	5.4	69.1	59.0	41.2	6.8	69.3

[a] Plane 1: $0.5729X + 0.2275Y - 0.7874Z + 6.9744 = 0$; plane 2: $0.5654X - 0.5234Y - 0.6374Z + 6.4593 = 0$; plane 3: $0.0405X + 0.9736Y - 0.2247Z - 0.3618 = 0$; plane 4: $0.5110X - 0.6736Y - 0.5339Z + 6.8725 = 0$; plane 5: $0.1584X - 0.9873Y - 0.0125Z + 3.6069 = 0$; plane 6: $0.5772X - 0.4439Y - 0.6854Z + 4.2580 = 0$; plane 7: $0.2179X - 0.9694Y - 0.1135Z + 6.9187 = 0$; plane 8: $0.4684X + 0.6064Y - 0.6426Z + 5.1909 = 0$; plane 9: $0.5820X - 0.2549Y - 0.7722Z + 7.4097 = 0$. The orthogonalized coordinates refer to a system of axes in which X is along the a axis, Y in the (a, b) plane, and Z along the c^* axis. [b] Not included in the calculation of the plane. [c] The esd's are 0.2–0.3°.

complex with iron tricarbonyl to date. Consequently, it is of great value to examine the geometry in the light of previously made observations. It has sometimes been noted that the "inner" bond of the complexed diene is shorter than the two "outer" bonds. In most cases, however, the difference was statistically not significant.[5] In this structure the differences, although numerically small, are definitely real. The C(1)–C(10) and C(6)–C(7) bond lengths are the same as a normal C(sp^2)–C(sp^3) single-bond distance (1.510 ± 0.005 Å).[20] However, it seems inappropriate to call such bonds C(sp^2)–C(sp^3) bonds[21] in view of the undeniable partial sp^3 character of the outer atoms C(7) and C(10). This is made evident by the displacement of the substituent atoms from the diene plane and by the bond angles involving hydrogen atoms, their average value (116 (1)°) being between tetrahedral and trigonal angles (Table III).

Table III. Bond Lengths and Angles Involving Hydrogen Atoms

Bond Lengths, Å			
C(2)–H(21)	0.98 (4)	C(7)–H(71)	0.96 (3)
C(3)–H(31)	0.93 (4)	C(8)–H(81)	0.96 (3)
C(4)–H(41)	0.87 (3)	C(9)–H(91)	0.90 (4)
C(5)–H(51)	0.97 (3)	C(10)–H(101)	0.88 (4)
C(11)–H(111)	0.96 (4)	C(13)–H(131)	0.97 (4)
C(11)–H(112)	1.00 (4)	C(13)–H(132)	1.01 (3)
Bond Angles, deg			
C(1)–C(2)–H(21)	113 (2)	C(6)–C(7)–H(71)	116 (2)
C(3)–C(2)–H(21)	117 (2)	C(8)–C(7)–H(71)	117 (2)
C(2)–C(3)–H(31)	123 (2)	C(7)–C(8)–H(81)	124 (2)
C(4)–C(3)–H(31)	122 (2)	C(9)–C(8)–H(81)	120 (2)
C(3)–C(4)–H(41)	118 (2)	C(8)–C(9)–H(91)	120 (2)
C(5)–C(4)–H(41)	127 (2)	C(10)–C(9)–H(91)	125 (2)
C(4)–C(5)–H(51)	118 (2)	C(9)–C(10)–H(101)	119 (2)
C(6)–C(5)–H(51)	114 (2)	C(1)–C(10)–H(101)	111 (2)
C(1)–C(11)–H(111)	110 (2)	C(6)–C(13)–H(131)	111 (2)
O(12)–C(11)–H(111)	112 (2)	O(12)–C(13)–H(131)	110 (2)
C(1)–C(11)–H(112)	111 (2)	C(6)–C(13)–H(132)	110 (2)
O(12)–C(11)–H(112)	110 (2)	O(12)–C(13)–H(132)	109 (2)
H(111)–C(11)–H(112)	108 (3)	H(131)–C(13)–H(132)	110 (3)

The geometry of ring A differs from that of ring B, particularly in the vicinity of the outer atoms. The bond angles at C(2) and C(5) are significantly smaller and the bond distances between these atoms and their neighbors are longer than in ring B. Furthermore, the outer atoms in ring A are closer to the coordinating Fe atom than the corresponding ones in ring B. The difference between the two average distances (0.012 Å) is statistically highly significant, being five times the standard deviation. Details of the bonding between the iron atoms and their ligands can be obtained from the distances and angles listed in Table IV.

The differences between the geometries of rings A and B may be interpreted by postulating an interaction between O(12) and the center of the diene system in ring A. The tilt of the flap of the envelope-shaped heterocyclic ring allows an overlap between a lone pair of electrons of the oxygen atom and the diene group which became electron deficient by donating π electrons to the iron atom.[22] The interaction is further facilitated by bending the two rings toward each other (see Figure

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(20) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, S15s (1965).

(21) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 8, 1941 (1969).

(22) For a recent discussion of interactions of orbitals through space, see R. Hoffmann, *Accounts Chem. Res.*, 4, 1 (1971).

Table IV. Distances and Angles Involving the Iron Atoms

(a) Distances, Å			
Fe(1)···C(2)	2.103 (3)	Fe(2)···C(7)	2.125 (2)
Fe(1)···C(3)	2.032 (3)	Fe(2)···C(8)	2.039 (2)
Fe(1)···C(4)	2.043 (3)	Fe(2)···C(9)	2.037 (2)
Fe(1)···C(5)	2.114 (2)	Fe(2)···C(10)	2.115 (2)
Fe(1)···M(2, 3)	1.941 (3)	Fe(2)···M(7, 8)	1.959 (2)
Fe(1)···M(3, 4)	1.915 (3)	Fe(2)···M(8, 9)	1.914 (2)
Fe(1)···M(4, 5)	1.953 (2)	Fe(2)···M(9, 10)	1.952 (2)
(b) Angles, deg			
C(2)–Fe(1)–C(3)	40.3 (1)	C(7)–Fe(2)–C(8)	39.7 (1)
C(3)–Fe(1)–C(4)	40.0 (1)	C(8)–Fe(2)–C(9)	40.1 (1)
C(4)–Fe(1)–C(5)	40.0 (1)	C(9)–Fe(2)–C(10)	39.8 (1)
C(2)–Fe(1)–C(5)	75.2 (1)	C(7)–Fe(2)–C(10)	75.3 (1)
Fe(1)–C(2)–C(3)	67.2 (2)	Fe(2)–C(7)–C(8)	66.9 (1)
Fe(1)–C(3)–C(2)	72.5 (2)	Fe(2)–C(8)–C(7)	73.4 (1)
Fe(1)–C(3)–C(4)	70.4 (2)	Fe(2)–C(8)–C(9)	69.9 (1)
Fe(1)–C(4)–C(3)	69.6 (3)	Fe(2)–C(9)–C(8)	70.0 (1)
Fe(1)–C(4)–C(5)	72.7 (1)	Fe(2)–C(9)–C(10)	73.1 (1)
Fe(1)–C(5)–C(4)	67.3 (1)	Fe(2)–C(10)–C(9)	67.1 (1)
Fe(1)–C(2)–H(21)	120 (2)	Fe(2)–C(7)–H(71)	116 (2)
Fe(1)–C(3)–H(31)	119 (2)	Fe(2)–C(8)–H(81)	118 (2)
Fe(1)–C(4)–H(41)	119 (2)	Fe(2)–C(9)–H(91)	118 (2)
Fe(1)–C(5)–H(51)	118 (2)	Fe(2)–C(10)–H(101)	121 (2)
C(14)–Fe(1)–C(15)	92.5 (1)	C(17)–Fe(2)–C(18)	93.9 (1)
C(14)–Fe(1)–C(16)	95.1 (1)	C(17)–Fe(2)–C(19)	97.9 (1)
C(15)–Fe(1)–C(16)	95.7 (1)	C(18)–Fe(2)–C(19)	96.2 (1)

4). The distance of 3.049 (4) Å between O(12) and M(3, 4), the midpoint between C(3) and C(4), may be compared with the sum of the van der Waals radius of oxygen (1.4 Å) and the half-thickness of aromatic molecules (1.7 Å).

One may predict several consequences of the proposed interaction. One of them would be an enhanced localization of electrons in the center of the diene system in ring A and a concomitant increase in the sp^3 character of the outer atoms C(2) and C(5). The decreased bond angles at these two atoms and the increased lengths of the outer bonds C(2)–C(3) and C(4)–C(5) agree with this prediction. Furthermore, the outer atoms being more electron deficient, one might expect their antibonding orbitals to receive more π electrons from the iron atom. Although $d_\pi \rightarrow \pi^*$ back-donation of electrons from a transition metal to an organic ligand is an acknowledged structural feature of such complexes, its extent has been difficult to assess.[10] From a recent nmr and infrared study of transition metal–aryl complexes, Stewart and Treichel[23] concluded that very little back-bonding to the aryl ligand occurs compared with the charge delocalization to the carbonyls in the complex. In the present structure, an enhancement in back-donation from Fe(1) to C(2) and C(5) would result in decreased Fe···C distances compared to the corresponding ones in ring B. As mentioned above, this was indeed observed. An increased accumulation of electrons in the antibonding orbitals of C(2) and C(5) would tend to weaken the bonds between these atoms and their neighbors. These bonds are, in fact, longer than the corresponding ones in ring B, although the difference is statistically significant only in the bonds involving C(1) and C(6). One may, therefore, conclude that back-bonding to diene ligands is sufficiently extensive to allow variations therein to be detected by an accurate X-ray analysis.

The differences in back-bonding in the complex appear to affect its reactivity. It was reported[4] that removal of only one $Fe(CO)_3$ group from **2** by means of ceric ammonium nitrate in methanolic solution yielded a single product, *viz.*, that in which the remaining $Fe(CO)_3$ was coordinated to ring A. This selectivity can now be interpreted on the basis of increased back-bonding in that moiety of **2** which includes ring A.

The iron tricarbonyl groups have the usual approximate C_{3v} symmetry. None of the corrected Fe–CO bond lengths deviates significantly from the average value of 1.805 (1) Å. This situation appears to be normal, although a substantially shorter Fe–CO bond length was reported for an axial carbonyl group.[5] The average of the corrected C–O bond lengths in the carbonyl group is 1.138 (2) Å. Both of these averages agree very well with the values obtained from the structure analysis of the related symmetrical complex[19] in which the iron tricarbonyl groups were found to vibrate as rigid bodies.

There are no intermolecular contacts shorter than the sum of van der Waals radii.

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(23) R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, **92**, 2710 (1970).