characterization was not attempted.

Attempted Reaction of [CpWS(μ-S)]₂ with LiB(Et)₃H. [CpWS(μ-S)]₂ (0.5 g, 0.8 mmol) was slurried in 70 mL of THF in a 500-mL round-bottomed flask which was then degassed two times on the Schlenk line. To this, under N₂, was added LiEt₃BH (9 equiv). The initial brown color changed to a light green. The solution was stirred at 25 °C for 18 h and was then quenched with deaerated distilled water. The THF was removed by flash evaporation. Attempts to extract the resulting brown product into CH₂Cl₂ or CHCl₃ were unsuccessful.

Attempted Reaction of III with H₂. One atmosphere of hydrogen was added to a degassed CDCl₃ solution of III, and the NMR tube was sealed. The solution was heated at 60 °C for 7 days. The color of the solution changed to purple, and new NMR resonances were observed which corresponded to those of complex IV. Neither ethylene nor other molybdenum products were identified. A similar transformation of III was found to occur under a nitrogen atmosphere.

Reaction of V with H₂. In an NMR tube H₂ (1 atm) was added at –196 °C to a degassed solution of V (0.025 g, 0.03 mmol) in CDCl₃. The NMR tube was then sealed and kept at 38 °C. After 2 days new resonances in the spectrum could be assigned to IV and free ethylene. Conversion was >90% after 8 days. No intermediates were detected.

Catalytic Hydrogenations. The tungsten dimer II was dissolved in CHCl₃ and one of the following substrates was added: *cis*-azobenzene (3 equiv), diethyl azodicarboxylate, (5 equiv), N-benzylideneaniline (2.5 equiv). Each solution was degassed, and H₂ (1 atm) was added at –196 °C. The reaction tubes were sealed and stirred at 55 °C. The following turnover frequencies were determined by NMR analysis of products (mol/((mol of catalyst)h)): diphenylhydrazine (0.12), N-benzylaniline (0.08), diethyl hydrazodicarboxylate (1.3).

Attempted Reactions of [CpVSCH₂CHRS]₂ with Alkynes or Alkenes. The neutral dimer VIa or VIb (0.1 mmol) was dissolved in CHCl₃ (15 mL) in a 50-mL flask and the solution was twice freeze-thaw degassed. The alkyne or alkene was introduced

in the following amounts: acetylene (1 atm), 2-butyne (25 mmol), ethylene (3 atm), propene (3.2 atm), *cis*-2-butene (4.2 atm). The reaction mixture was stirred at 55–85 °C for 3–6 days. The gases were analyzed by gas chromatography, and the recovered solids were analyzed by mass spectrometry. No evidence for reaction was observed.

[CpVSCH₂CH(CH₃)S]₂ + NaH. VIb (0.08 g, 0.18 mmol) was dissolved in THF (25 mL) in a reaction vessel (100 mL) fitted with a Kontes Teflon high-vacuum stopcock. The solution was twice freeze-thaw degassed; NaH (0.06 g, 2.7 mmol) was added under N₂. After 48 h at 60 °C the solution was orange in color. Propene was detected in the gases by mass spectrometry. TLC of the solution on alumina showed two products in addition to the starting dimer. The solution was evaporated and redissolved in CDCl₃. (CpV)₂S₅ and [CpVS₂]₂ were identified by comparison of the NMR spectrum with those of authentic samples.

Iron Carbonyl Complexes of Dimethyl Cyclooctatetraene-1,8-dicarboxylate

Robert C. Kerber,* Dean Glasser, and Barbara Luck

Department of Chemistry, State University of New York at Stony Brook, Long Island, New York 11794

Received November 14, 1983

Reaction of dimethyl cyclooctatetraene-1,8-dicarboxylate with iron carbonyls yields, in addition to the known 3-6-η⁴-Fe(CO)₃ complex, two new Fe₂(CO)₆ complexes. One is a yellow 1-4-η⁴,5-8-η⁴-bis[Fe(CO)₃] complex, with the iron tricarbonyl groups probably trans. The other is a red compound with a 1,5,6-η³,2-4-η³-Fe₂(CO)₆(*Fe–Fe*) structure. The X-ray crystallographic structure of the latter compound shows an iron–iron distance of 2.771 Å and indicates a strong interaction of the Cl-bound ester group with the C–Fe σ-bond. The red Fe₂(CO)₆(*Fe–Fe*) complex is the most stable, probably as a consequence of that interaction. None of the compounds exhibits haptotropy at room temperature, in contrast to the parent hydrocarbon complexes.

Study of metal complexes of cyclooctatetraene and its derivatives has contributed immeasurably to our understanding of organometallic structure and reactivity. In the case of iron carbonyl derivatives of cyclooctatetraene, Scheme I summarizes the known compounds and their interconversions.[1] The variety of bonding modes observed

and the fluxional character of several of the products make derivatives of these compounds excellent choices for assessment of substituent effects on organometallic structure and reactivity. We report here the results of studies of the

(1) This scheme summarizes information from extensive reviews of (cyclooctatetraene)iron complexes, which appear in: (a) Kerber, R. C. "The Organic Chemistry of Iron"; Koerner von Gustorf, E. A., Grevels, F. W., Fischler, I., Eds.; Academic Press: New York, 1981; Vol. 2, Chapter 1. (b) Deganello, G. "Transition Metal Complexes of Cyclic Polyenes"; Academic Press: New York, 1979.

(2) Compound 4 was originally assigned a bis(allyl), 1-3-η³,4-6-η³ (*Fe–Fe*) structure (Keller, C. E.; Emerson, G. F.; Pettit, R. *J. Am. Chem. Soc.* 1965, *87*, 1388). Subsequent studies[1] of numerous cyclooctatriene and -tetraene complexes have shown the unsymmetrical 1,5,6-η³,2-4-η³ (*Fe–Fe*) structure to be preferred in eight-membered rings, and the latter structure is assigned here. The analogous diruthenium compound, with similar IR and NMR spectra (Cotton, F. A.; Musco, A. *J. Am. Chem. Soc.* 1968, *90*, 1444), has the unsymmetrical structure (Cotton, F. A.; Edwards, W. T. *J. Am. Chem. Soc.* 1968, *90*, 5412).

Scheme I. Iron Carbonyl Complexes of Cyclooctatetraene
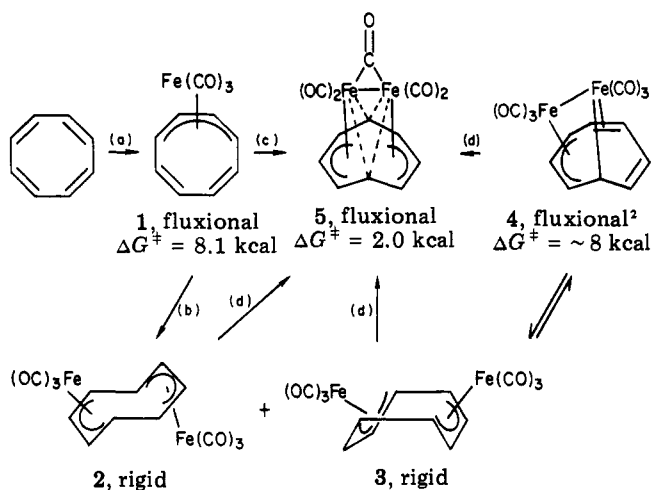
(a) $Fe(CO)_5$ and 120 °C; $Fe(CO)_5$ and $h\nu$, $Fe_2(CO)_9$ and C_6H_6, or $Fe_3(CO)_{12}$ at reflux; (b) $Fe_2(CO)_9$ or excess $Fe(CO)_5$, $h\nu$; (c) $h\nu$, hexane, 3 h; (d) $h\nu$, brief heating or prolonged standing in solution at room temperature
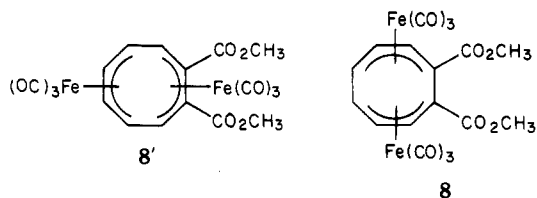
reaction of dimethyl cyclooctatetraene-1,8-dicarboxylate, **6**, with iron carbonyls, which cast light on the interactions of a typical electron-withdrawing group with C–Fe bonds.

Results and Discussion

The diester **6** is available from photocycloaddition of dimethyl acetylenedicarboxylate and benzene,[3] in yields of 15–20% per pass. Recycling of starting materials allows production of substantial **6** over a period of time and also leads to accumulation of a trace byproduct that is difficult to separate from **6**. We have been able to identify this byproduct as dimethyl anthracene-9,10-dicarboxylate, based on NMR and mass spectral results on an enriched sample from which most of the **6** had been removed by complexation with iron carbonyls.

Reaction of **6** with $Fe_3(CO)_{12}$ in refluxing benzene was first reported in 1967.[4] After an extensive isolation sequence, an $Fe(CO)_3$ complex, **7**, was obtained in 12% yield. NMR spectroscopy revealed the static 3-6-η^4 structure shown. We confirm both the formation and structure of **7** and in addition report the simultaneous formation of two additional iron carbonyl complexes of **6**, isolable by column chromatography.

Both of these are $Fe_2(CO)_6$ complexes of **6** as shown by analytical and mass spectral data. One, **8**, is a yellow compound that is very similar in polarity to the uncomplexed diester, **6**. The infrared spectrum (see Table I) showed a single ester stretching frequency (somewhat lower than that of **6**) and two metal carbonyl frequencies, suggesting a symmetrical structure. This was confirmed by the proton and carbon NMR spectra. Since the yellow color is not consistent with presence of an Fe–Fe bond, only two constitutional structures have the requisite symmetry, **8** and **8'**. The proton NMR spectrum, with only

8'

8

(3) Paquette, L. A.; Beckley, R. S. *Org. Photochem. Synth.* **1976**, *2*, 45.
(4) Grubbs, R.; Breslow, R.; Herber, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1967**, *89*, 6864.

Table I. Spectroscopic Data for 6 and Its Iron Carbonyl Complexes[a]

compd	IR (CH_2Cl_2)		^1H NMR ($CDCl_3$)						^{13}C NMR ($CDCl_3$, $Cr(acac)_3$)							
	$\nu_{CO}(CH_2Cl_2)$	$\nu_{CO_2CH_3}$	δ_2	δ_3	δ_4	δ_{CH_3}		δ_1	δ_2	δ_3	δ_4	$\delta_{CO_2CH_3}$	δ_{CH_3}		
6		1720	7.11 (d, $J_{23} = 3$)	5.97 (m)		3.65		132.0	143.0	130.2	132.8)	165.9	52.2		
7	2064, 2002 (br)	1730[4]	7.08 (d, $J_{23} = 9.6$)	3.83 (tt, $J = 9.6, 2.6$)	4.86 (dt, $J = 6.7, 2.6$)	3.55		57.6	(96.5	91.9)	58.5	178.6	51.8		
8	2054, 2000 (br)	1702	6.47 (d, $J = 5.2$)	5.32 (td, $J = 5.2, 2.4$)	3.27 (dd, $J = 5.3, 2.4$)	3.50		33.8	57.6	80.5	56.7		51.2		
9	2073 (vs), 2034 (vs), 2002 (vs), 1983	1685	4.69 (d, $J = 6.5$)	4.30 (m)	4.91 (t, $J = 5.6$)	3.57									

| | | | δ_7 | δ_6 | δ_5 | | | δ_8 | δ_7 | δ_6 | δ_5 | | | | |
| **9** | | 1705 | 6.87 (d, $J = 3.4$) | 3.23 (dd, $J = 9.2, 3.3$) | 4.17 (dd, $J = 5.7, 9.2$) | 3.65 | | 149.6 | 143.6 | (72.7 | 76.4) | 149.6 | 51.9 | | |

[a] Coupling constants in hertz.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B_{eq}{}^a$	atom	x	y	z	$B_{eq}{}^a$
Fe1	0.06316 (3)	0.12483 (2)	0.31213 (5)	3.08 (2)	C10	0.0848 (3)	0.4171 (2)	1.0217 (5)	5.1 (2)
Fe2	0.64954 (3)	0.67502 (2)	0.29514 (5)	3.20 (2)	C11	0.2913 (2)	0.0168 (1)	0.8614 (4)	3.7 (1)
					C12	0.4177 (4)	0.0947 (2)	0.9856 (6)	7.8 (2)
O9	0.3079 (2)	0.4287 (1)	0.0652 (2)	4.1 (1)	C13	0.2042 (3)	0.0917 (2)	0.3446 (4)	4.1 (1)
O10	0.1507 (2)	0.4172 (1)	0.8823 (3)	3.9 (1)	C14	0.0589 (3)	0.1335 (2)	0.5362 (4)	3.9 (1)
O11	0.2730 (2)	0.0487 (1)	0.7388 (3)	5.9 (1)	C15	0.1134 (3)	0.2024 (2)	0.2650 (4)	4.6 (1)
O12	0.3608 (2)	0.0339 (1)	0.9954 (3)	6.1 (1)	C16	0.3831 (3)	0.2459 (2)	0.6340 (5)	5.2 (2)
O13	0.2938 (2)	0.0727 (1)	0.3595 (3)	6.0 (1)	C17	0.3637 (3)	0.2972 (1)	0.9176 (4)	4.0 (1)
O14	0.0644 (2)	0.1378 (1)	0.6768 (3)	6.2 (1)	C18	0.2009 (3)	0.3109 (1)	0.6648 (4)	4.3 (1)
O15	0.1478 (2)	0.2513 (1)	0.2332 (4)	7.2 (1)					
O16	0.3978 (3)	0.1954 (1)	0.5872 (5)	8.7 (1)	H2	0.0488 (0)	0.9844 (0)	0.5918 (0)	5.0 (0)
O17	0.3645 (2)	0.2758 (1)	0.0488 (3)	5.8 (1)	H3	0.4238 (0)	0.5137 (0)	0.2949 (0)	5.0 (0)
O18	0.1065 (2)	0.2989 (1)	0.6399 (4)	6.8 (1)	H4	0.0996 (0)	0.0840 (0)	0.000 (0)	5.0 (0)
					H5	0.4746 (0)	0.3281 (0)	0.4434 (0)	5.0 (0)
C1	0.3248 (2)	0.4220 (1)	0.7705 (3)	2.8 (1)	H6	0.2988 (0)	0.3281 (0)	0.3691 (0)	5.0 (0)
C2	0.4396 (2)	0.4511 (1)	0.8057 (3)	3.0 (1)	H7	0.2246 (0)	0.4414 (0)	0.3691 (0)	5.0 (0)
C3	0.0139 (2)	0.0429 (1)	0.1824 (3)	3.3 (1)	H101	0.0060 (0)	0.4120 (0)	0.9842 (0)	5.0 (0)
C4	0.0266 (2)	0.0913 (1)	0.0640 (3)	3.5 (1)	H102	0.1075 (0)	0.3818 (0)	1.0971 (0)	5.0 (0)
C5	0.4437 (3)	0.3604 (1)	0.4997 (4)	3.7 (1)	H103	0.0956 (0)	0.4558 (0)	1.0846 (0)	5.0 (0)
C6	0.3258 (3)	0.3660 (1)	0.4558 (4)	3.8 (1)	H121	0.4650 (0)	0.1037 (0)	1.0896 (0)	5.0 (0)
C7	0.2632 (2)	0.4261 (1)	0.4675 (3)	3.5 (1)	H122	0.4627 (0)	0.0957 (0)	0.8965 (0)	5.0 (0)
C8	0.2606 (2)	0.4532 (1)	0.6164 (3)	3.0 (1)	H123	0.3620 (0)	0.1288 (0)	0.9700 (0)	5.0 (0)
C9	0.2646 (2)	0.4238 (1)	0.9220 (4)	3.1 (1)					

a Isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

a single high field resonance, requires **8** as the correct structure; this is consonant with observation of only two metal carbonyl stretching bands in the IR. Comparison of the chemical shifts of H₃ and H₄ (relatively unaffected by the ester groups) with those of **2** (δ 5.6 and 3.1)[5] and **3** (δ 5.0 and 4.0)[2] leads us to assign the trans stereochemistry to the Fe(CO)₃ groups of **8**; this is supported by the low polarity of **8**. Compound **8** was obtained in low yields in all cases.

The principal product of reaction of **6** with iron carbonyls, especially from reactions involving excess iron carbonyl reagent, high temperatures, and long reaction times, was a red Fe₂(CO)₆ complex, **9**. **9** is the most polar of the products, and, in contrast to **7** and **8**, lacks any element of molecular symmetry, as indicated by the presence of nonequivalent ester groups in IR and NMR spectra and the complexity of the NMR spectra. The presence of four metal carbonyl stretching frequencies and the deep color of **9** bespoke a Fe–Fe bonded structure analogous to **4**. The presence of the two vicinal ester groups in **9** would lead to eight regioisomers derived from the basic skeleton of **4**. An unusually low ester C=O stretching frequency in **9** and the presence of a proton resonance (H₇) relatively unperturbed from **6** favored the structure shown in Table I for **9** over its alternative isomers. Proton NMR assignments were based on the observed couplings and on consistency with normal organometallic shifts. The averaged chemical shifts of H₂ and H₅ (δ 4.43) and H₃ and H₄ (δ 4.60) agreed satisfactorily with the average values observed for the fluxional analogue **4** (δ 4.1 and 4.6).[2a] The assignments were further supported by studies using the shift reagent, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III), Eu(fod)₃. At shift saturation, the methyl resonances shifted downfield by 1.0 and 0.7 ppm, H₂ by 0.75 ppm, H₇ by 1.0 ppm, and H₆ by 0.1 ppm. All other shifts were negligible. The carbon-13 NMR assignments were based on peak intensities and consistency with normally observed organometallic data. They agree well with the low-temperature limiting spectrum reported for (cyclooctatriene)diiron hexacarbonyl,[6] **10**.
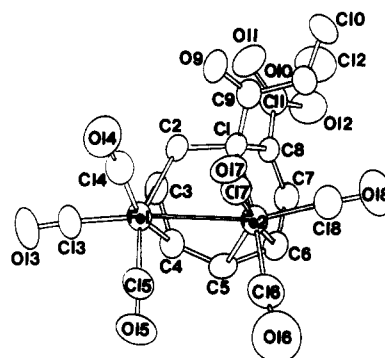
(5) Fritz, H. P.; Keller, H. *Chem. Ber.* **1962**, *95*, 158.
(6) Cotton, F. A.; Hunter, B. L.; Lahuerta, P. *J. Am. Chem. Soc.* **1975**, *97*, 1046.

Figure 1. X-ray crystallographic structure of **9**, showing the labeling scheme. Hydrogens are omitted for clarity.

Although the spectra were consistent with the assigned structure for **9**, their complexity left the structural assignment not quite certain. Accordingly, an X-ray crystallographic structure determination was carried out on **9**.

The molecular structure and labeling scheme are shown in Figures 1 and 2; atomic coordinates are given in Table II, and lists of bond distances and angles are presented in Tables III and IV. The compound is confirmed to be a derivative of **4**, with the ester groups positioned on the σ-bonded carbon and the free double bond as postulated from the spectroscopic results. Fe1 is attached to the ring through a π-allyl linkage to C2–C4 and to Fe2 by a single bond of length 2.771 Å. Fe2 is attached to C1 through a 2.121 Å σ-bond and to the C5–C6 double bond. The Fe₂(CO)₆ unit is in the now familiar sawhorse arrangement, with the cyclooctatetraene ring severely bent to accommodate the bonding needs of the Fe₂(CO)₆ group. Some distances and angles in **9** are compared to those in some previously studied 1,5,6-η³,2-4-η³-Fe₂(CO)₆ complexes of cyclooctatriene derivatives in Table IV. The overall pattern of C–Fe distances is very similar in these four compounds, as is the pattern of C–C distances (other than C7–C8).

The bond angles about C1 are all within the range 106–114°, consistent with sp³ hybridization of that carbon. The ester group at C1 adopts a rotational orientation that optimizes overlap of the π^*_{CO} orbital with the C1–Fe2

Table III. Selected Bond Distances (A) and Angles (deg) in 9

Distances[a]

Fe1–C13	1.798 (3)	C1–C2	1.486 (3)	C13–O13	1.126 (3)
Fe1–C14	1.808 (3)	C2–C3	1.401 (3)	C14–O14	1.123 (3)
Fe1–C15	1.779 (3)	C3–C4	1.404 (4)	C15–O15	1.138 (4)
Fe2–C16	1.800 (3)	C4–C5	1.457 (3)	C16–O16	1.137 (4)
Fe2–C17	1.788 (3)	C5–C6	1.405 (4)	C17–O17	1.139 (3)
Fe2–C18	1.787 (3)	C6–C7	1.463 (3)	C18–O18	1.141 (3)
		C7–C8	1.321 (3)		
		C8–C1	1.517 (3)		
C1–C9	1.477 (3)			C8–C11	1.482 (3)
C9–O9	1.204 (3)			C11–O11	1.184 (3)
C9–O10	1.356 (3)			C11–O12	1.322 (3)
O10–C10	1.434 (3)			O12–C12	1.442 (4)

Angles

|					
C8–C1–C2	109.9 (2)	C1–C8–C11	117.4 (2)	C1–C9–O9	126.2 (2)
C1–C2–C3	122.6 (2)	C7–C8–C11	123.0 (2)	C1–C9–O10	111.5 (2)
C2–C3–C4	122.5 (2)			O9–C9–O10	122.2 (2)
C3–C4–C5	127.8 (2)	C13–Fe1–Fe2	170.3 (1)	C9–O10–C10	115.8 (2)
C4–C5–C6	129.8 (2)	C13–Fe1–C14	91.6 (1)		
C5–C6–C7	123.5 (2)	C13–Fe1–C15	93.0 (1)	C8–C11–O11	124.3 (2)
C6–C7–C8	119.3 (2)	C14–Fe1–C15	99.7 (1)	C8–C11–O12	111.8 (2)
C7–C8–C1	119.2 (2)	C14–Fe1–Fe2	98.1 (1)	O11–C11–O12	123.9 (2)
C8–C1–C9	114.4 (2)	C15–Fe1–Fe2	84.6 (1)	C11–O12–C12	116.3 (3)
C2–C1–C9	110.7 (2)	Fe1–C13–O13	177.0 (3)	Fe1–Fe2–C1	73.4 (1)
Fe2–C1–C8	106.2 (1)	Fe1–C14–O14	175.1 (3)	Fe1–Fe2–C18	164.6 (1)
Fe2–C1–C9	108.9 (2)	Fe1–C15–O15	178.2 (3)	C16–Fe2–C18	92.1 (1)
Fe2–C1–C2	106.4 (2)	Fe2–C16–O16	176.5 (3)	C17–Fe2–C18	95.3 (1)
		Fe2–C17–O17	174.0 (3)	C16–Fe2–C17	90.3 (1)
		Fe2–C18–O18	176.8 (3)	C17–Fe2–Fe1	81.5 (1)
				C16–Fe2–Fe1	102.9 (1)
				C1–Fe2–C16	173.7 (1)
				C1–Fe2–C17	94.2 (1)
				C1–Fe2–C18	91.9 (1)

[a] Fe–Fe and Fe–ring, see Table IV.
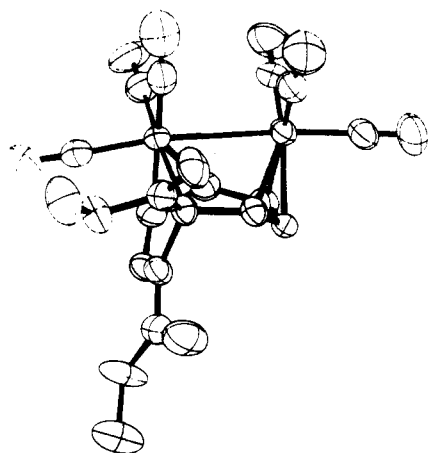
Figure 2. Structure of 9, emphasizing the conformation of the eight-membered ring and the orientation of the C1-bound ester group.

σ-bond, allowing σ → π* transfer of electron density.[7] That this is more extensive than the π → π* conjugation of the ester group at C8 with the C7–C8 double bond is indicated by the longer C=O and shorter C—O bonds of the former ester group. The effects of this interaction are

(7) A reviewer has suggested that the orientation of this ester group may be sterically determined. While conceding the steric congeniality of its environment in this conformation, we continue to believe that the accumulated evidence (thermodynamic, spectroscopic, and structural) favors the electronic interaction as the principal determinant favoring this conformation.
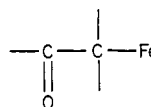
(8) Cotton, F. A.; Edwards, W. T. *J. Am. Chem. Soc.* **1969**, *91*, 843.

(9) Takats, J. *J. Organomet. Chem.* **1975**, *90*, 211.

(10) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

also evident in the spectroscopic data (Table I). This stabilizing

interaction accounts in part for the observed structure of 9. Only two of the eight possible regioisomers of 9 can have such an interaction. The preference for 9 may reflect intrinsic preference of the second ester group for attachment to the free double bond (C8) rather than the π-allyl unit (C2). More likely, it arises from better avoidance in 9 of intramolecular contact of the two ester groups, as a consequence of the folding of the ring about C1 and C6.

None of the three iron carbonyl complexes of 6 shows haptotropy at room temperature. In the case of the bis-[Fe(CO)₃] complex 8 this is consistent with its unfunctionalized analogue 2. However, the analogues (1 and 4) of 7 and 9 are fluxional at room temperature. The facile interconversion of equivalent isomers of 1 and 4 at room temperature makes it probable that the nonequivalent regioisomers of 7 and 9 can interconvert at least under the more vigorous reaction conditions, by analogous mechanisms, and that consequently the specific isomers formed resulted from thermodynamic control, as already implied in the discussion of the structure of 9.

The obtention of single regioisomers of each type of complex implies significant stabilization of the observed isomer over its unobserved regioisomers. This stabilization must arise by donation of electron density from the various organometallic moieties into the π^*_{CO} orbital of the ester groups. The observed structures of 7–9 therefore suggest the following ordering of organoiron moieties as sources of electron density for such interactions: $\sigma_{C-Fe} > \pi_{C=C} >$

Table IV. Comparison of Selected Distances (Å) and Angles (deg) in 9 with (Cyclooctatriene)Fe₂(CO)₆ Derivatives
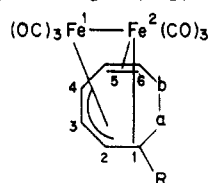
$(OC)_3 Fe^1$——$Fe^2 (CO)_3$

compd	R	\a—b/	Fe1-Fe2	Fe2-C1	Fe2-C2	Fe1-C1	Fe1-C2	Fe1-C3	Fe1-C4	Fe1-C5
9	CO₂CH₃	C=C (CO₂CH₃, H)	2.771 (1)	2.121	2.913	2.970	2.153	2.047	2.101	2.743
10	H	CH₂—CH₂	2.764 (3)	2.08	2.91	2.91	2.17	2.06	2.12	2.82
11	H	CH—CH / CH₂	2.773 (1)	2.108	2.884		2.154	2.047	2.129	2.821
12	H	CH—CH / CH₂—CH₂	2.786 (2)	2.099	2.883	2.960	2.140	2.042	2.120	2.745

compd	Fe2-C5	Fe2-C6	Fe-C esd's	∠I-II[a,b]	∠II-III[b,c]	∠I-III[a,c]	ref
9	2.209	2.157	0.002	142	133	97	this work
10	2.22	2.18	0.01	135	135	93	8
11	2.223	2.179	0.003	142	130	95	9
12	2.214	2.199	0.004	139	136	96	10

[a] I is the mean plane through atoms C1-C5. [b] II is the mean plane through atoms C1, C5, and C6. [c] III is the mean plane through atoms C1, C6, C7, and C8.

(η^3-allyl)Fe(CO)₃ or (η^4-diene)Fe(CO)₃. This ordering derived from 6-8 is consistent with previous observations.[1a]

It is also notable that the structures of 7-9 derive directly from the 1,8-diester 6 rather than from its 1,2-diester isomer.[11] Evidently the factors that destabilize the latter continue to function on complexation, despite the electronic and conformational changes which attend complexation.

Lastly, we would like to point out that the static structures of 9-12 lead to easy visualization of the established "twitch" mechanism for haptotropy in 10-12,[1] in which two new Fe–C bonds (Fe2–C2 and Fe1–C5) form as two existing Fe–C bonds (Fe2–C5 and Fe1–C2) break. In each case, the bonds to be broken are the longest ones formed by the respective iron, and the bonds to be formed are prefigured by short nonbonded distances of 2.913 and especially 2.742 Å (Fe1–C5). The length of the latter appears in fact to correlate with the activation energy for the "twitch".

The absence of haptotropy in 9 does not exclude all fluxionality, since the room-temperature ¹³C NMR spectrum in the metal carbonyl region shows a sharp three-carbon resonance at δ 210.0 and three single-carbon resonances at δ 212.1, 211.7, and 204.7. By comparison with previous studies on 10-12,[12] we interpret these data as showing rapid pseudorotation of the carbonyl groups on the allyl-bonded iron Fe1 and rigidity of the three carbonyls on Fe2. The NMR coalescence temperatures for Fe1 and Fe2 carbonyl pseudorotation in 10 are –35 and 60 °C, respectively.[12]

The Fe(CO)₃ complex 7 is best obtained by the published method[4] or by reaction of 6 with Fe₂(CO)₉ in tetrahydrofuran at room temperature; yields in either case are about 12%. The bis[Fe(CO)₃] complex 8 is best ob-

tained by reaction of 6 with Fe₃(CO)₁₂ in refluxing benzene; our best yield was 9%. The Fe₂(CO)₆ complex 9 could be obtained in good yield by use of excess Fe(CO)₅ in refluxing toluene. Refluxing the bis[Fe(CO)₃] complex 8 with Fe(CO)₅ in toluene led to its conversion to the Fe₂(CO)₆ complex 9 in 79% yield. Refluxing 8 with Fe₃(CO)₁₂ in benzene also led to 9 (22%); the rest was Fe(CO)₃ complex 7. Attempts to convert 8 or 9 to 7 or an isomer by treatment with 1 equiv of ceric ammonium nitrate were not successful; only mixtures of uncomplexed 6 and unreacted Fe₂(CO)₆ complex were obtained.

In contrast to its unsubstituted analogue 4, 9 showed no tendency under any conditions to lose CO to form an Fe₂(CO)₅ complex analogous to 5 (Scheme I).

Experimental Section

Infrared data were recorded on a Perkin-Elmer 567 spectrophotometer, using the 5× scale expansion. NMR spectra were recorded on a Varian EM-360 or CFT-20 or a Nicolet NT-300 spectrometer, in CDCl₃ solutions.

Solvents used were reagent grade or were bulk grades and were distilled and degassed with nitrogen before use. Fe(CO)₅ and Fe₃(CO)₁₂ were used as obtained from Alfa Products. All reactions were run under a nitrogen atmosphere. Column chromatography was done in neutral alumina, unless otherwise stated, and TLC on Eastman Chromagram silica plates treated with a fluorescent indicator. Mass spectra were obtained on a H-P 5980A spectrometer using 70-V ionizing voltage and a direct inlet.

The diester 6 was prepared by photolysis of solutions of dimethyl acetylenedicarboxylate in benzene.[3]

Reaction of 6 with Fe₂(CO)₉ in THF. 6 (1.546 g, 7.02 mmol) and nonacarbonyldiiron (2.50 g, 6.79 mmol) were stirred in 50 mL of freshly distilled THF at room temperature. After 18.5 h, no Fe₂(CO)₉ remained. The mixture was filtered and rotary evaporated, leaving 2.33 g of residue. This was chromatographed on silica gel. Elution with hexane–methylene chloride gave (a) a deep green band, presumably Fe₃(CO)₁₂, (b) unreacted 6 (1.08 g, 71% recovery), (c) bis[Fe(CO)₃] complex 8 (0.059 g, 2% yield), (d) dimethyl anthracene-9,10-dicarboxylate (0.089 g, 4%), and (e) Fe(CO)₃ complex 7 (0.292 g, 12% yield). Intermediate fractions

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Table V. Crystal Data and Collection Procedures for 9

formula: $C_{18}H_{12}Fe_2O_{10}$
mol wt: 499.98
space group: $P2_1/n$ (monoclinic, No. 1014)
$a = 11.845$ (2) A
$b = 20.845$ (8) A
$c = 8.000$ (1) A
$\beta = 96.67$ (1)°
$V = 1961.9$ (1.3) A³
$Z = 4$
$\rho_{calcd} = 1.693$ g cm⁻³
$\rho_{obsd} = 1.69$ (2) g cm⁻³
radiation: Mo Kα ($\lambda = 0.710\ 73$ A) with a graphite
    monochromator
linear abs coeff (μ): 15.743 cm⁻¹; no correction made
temp: ca. 22 °C
takeoff angle: 6.0°
2θ range: $0 < 2\theta < 54°$
scan type: θ-2θ
scan speed: 1.8-20°/min
scan range: symmetrical [2θ(Mo Kα₁) − 1.0°] to
    [2θ(Mo Kα₁) + 1.0°] extended 25% on
    each end for background counts
reflctns measd: 4263
reflctns collected: 3108, 2879 unique with $F_o^2 >$
    $3\sigma(F_o^2)$ std reflctns intensity
    variations within counting statistics
P: 0.04

that were mixtures were assayed by NMR, using the ester CH₃ resonances, to determine total yields.

The anthracene derivative was not obtained in pure form but was identified based on NMR and mass spectra of samples also containing some 6: NMR δ 7.43 (A₂′B₂′ multiplet, 4 H), 3.70 (s, 3 H); MS; m/e (relative intensity) 295 (10.4%, P + 1), 294 (52.1%, P), 263 (100.0%, P − OCH₃), 176 (34.8%, P − 2 CO₂CH₃), 164 (27.3%). The mass spectrum was similar to that of dimethyl terephthalate,[13] with the masses incremented by 100 amu because of the two annulated benzo rings.

Reaction of 6 with Fe₃(CO)₁₂ in Refluxing Benzene. 6 (3.30 g, 15 mmol) and dodecacarbonyltriiron (9.50 g, 18.8 mmol) were refluxed in 60 mL of benzene for 24 h. After being cooled, the mixture was filtered through Celite and evaporated, leaving 5.5 g of crude product. Rapid passage through neutral alumina using 2:1 toluene/methylene chloride gave a preliminary separation into a fast-moving and a slower moving material. Careful rechromatography of these materials, eluting with 10-75% methylene chloride/hexane gave 0.76 g of recovered 6 (23%), 0.65 g of bis[Fe(CO)₃] complex 8 (9%), 0.16 g (1%) of Fe(CO)₃ complex 7, and an undetermined amount of 9.

Pure 8 was obtained by room temperature diffusion of hexane into an ether solution, as amber prisms; mp 154 °C dec. The mass spectrum showed a trace parent peak at m/e 500 (0.2%), with a complete sequence for $C_{12}H_{12}O_4Fe_2(CO)_n$, $n = 0$-5; the largest four peaks were at m/e (relative intensity) 360 (100%), 112, (Fe₂⁺, 90%), 332 (86%), and 102 (C₈H₆⁺, 83%). Anal. Calcd for $C_{18}H_{12}Fe_2O_{10}$: C, 43.24; H, 2.42; Fe, 22.34. Found: C, 43.06; H, 2.51; Fe, 22.13.

In another run, 2.20 g (10.0 mmol) of 6 and 6.35 g (12.5 mmol) of Fe₃(CO)₁₂ were refluxed in 30 mL of benzene for 45 h. The residue from filtration and evaporation (4.3 g) gave, upon column chromatography, 1.20 g of recovered 6 (55%), 0.121 g of 8 (2%), 0.488 g of Fe(CO)₃ complex 7 (13%), and 0.357 g of 9 (7%).

Reaction of 6 with Fe(CO)₅ in Refluxing Toluene. 6 (2.20 g, 10.0 mmol) and Fe(CO)₅ (10.0 mL, 14.6 g, 74 mmol) in 150 mL of toluene were refluxed for 50 h. After being cooled to room temperature, the mixture was filtered through Celite and evaporated, leaving 3.28 g of (mostly crystalline) residue, predominantly 9, 66% crude yield. Chromatography gave 0.61 g of recovered 6 (28%), which eluted with 25% methylene chloride/hexane, and 2.41 g of 9, which eluted with methylene chloride.

Pure 9 was obtained by recrystallization from a hexane/methylene chloride mixture as deep red prisms, mp 175 °C dec. The mass spectrum showed no parent peak but showed a sequence for $C_{12}H_{12}O_4Fe_2(CO)_n$, $n = 0$-4. The four largest peaks were at m/e (relative intensity) 160 ($C_{10}H_8O_2^+$, 100%), 102 (C₈H₆⁺, 90%), 112 (Fe₂⁺, 82%), and 158 (C₈H₆Fe⁺, 77%). Anal. Found: C, 42.26; H, 2.54; Fe, 21.85.

Reactions of 8 with Iron Carbonyls. Refluxing 8 (0.027 g, 0.054 mmol) in benzene containing excess Fe₃(CO)₁₂, for 48 h, followed by cooling, filtration, and evaporation gave a product whose NMR spectrum showed 78% Fe(CO)₃ complex 7 and 22% Fe₂(CO)₆ complex 9. Refluxing 0.175 g of 8 (0.35 mmol) in toluene containing 3 mL of Fe(CO)₅ (22 mmol) for 48 h, followed by cooling, filtration, and evaporation, gave a residue whose NMR spectrum showed only 9. Chromatography led to isolation of 9 in 79% yield.

X-ray Data Collection and Reduction. Crystals of 9 were grown by vapor diffusion of hexane into a methylene chloride solution. A deep red prism of approximate dimensions 0.22 mm × 0.40 mm × 0.45 mm was mounted on a glass fiber in air. All X-ray measurements were carried out with an Enraf-Nonius CAD4A diffractometer controlled by a PDP 11/45 computer system. Important features of the data collection are summarized in Table V.

Computing was carried out on the PDP 11/45 using the Enraf-Nonius structure determination package developed principally by Okaya and Frenz.[14] The two iron atoms were located from a Patterson map. After three cycles of isotropic refinement, a difference Fourier revealed 17 of the 18 carbon atoms and 9 of the 10 oxygens; the remaining ones were located with one additional refinement cycle. These atoms were refined isotropically (three cycles), then for two cycles with the irons anisotropic and two more with all heavy atoms anisotropic. At this point the ring-bound hydrogens were located from a difference Fourier map, and the methyl hydrogens were introduced assuming staggered, tetrahedral orientations for the methyl groups and 0.95-A bond lengths. Three further cycles of anisotropic refinement of the heavy atoms converged to values of R and R_w of 0.035 and 0.048, respectively, and to an error in an observation of unit weight of 1.587 electrons for the 271 variables and 2879 observations. Final positional and thermal parameters are given in Table II. A table of observed and calculated structure factors (Table VI) is included in the supplementary material, as is a table of general temperature factor expressions (Table VII).

Registry No. 6, 15956-91-9; 7, 89596-86-1; 8, 89618-29-1; 9, 89655-88-9; Fe₂(CO)₉, 15321-51-4; Fe₃(CO)₁₂, 17685-52-8; Fe(CO)₅, 13463-40-6; Fe, 7439-89-6; dimethyl anthracene-9,10-dicarboxylate, 73016-10-1.

Supplementary Material Available: Tables of observed and calculated structure factors and temperature factor expressions (14 pages). Ordering information is given on any current masthead page.

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