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Crystal Structure and Molecular Configuration of (3,5-Dimethylaceheptylene)octacarbonyltriiron(*Fe–Fe*), $(C_{14}H_8Me_2)Fe_3(CO)_8$

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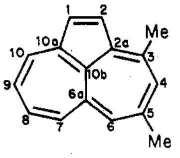
The species (3,5-dimethylaceheptylene)octacarbonyltriiron(*Fe–Fe*), $(C_{14}H_8Me_2)Fe_3(CO)_8$, has been identified and characterized by means of an X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 22.580\ (4)$ Å, $b = 7.299\ (1)$ Å, $c = 14.520\ (2)$ Å, $\beta = 104.62\ (1)°$, $V = 2315.3\ (7)$ Å^3, ρ(obsd) = 1.717 (8) g cm^{-3}, and ρ(calcd) = 1.715 g cm^{-3} for mol wt 597.92 and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer. The structure was solved via the multiple tangent formula method and refined using difference-Fourier and full-matrix least-squares refinement techniques. Final discrepancy indices are $R_F = 5.6\%$ and $R_{wF} = 4.6\%$ for 1930 independent reflections with $|F_o| > \sigma(|F_o|)$ and in the range $4 < 2\theta < 40°$ (Mo Kα radiation). All atoms other than the methyl hydrogens were located and refined. The molecule has an $Fe(CO)_2$ group bonded via a η^5-cyclopentadienyl→iron linkage to the five-membered ring and an $Fe(CO)_3$ group bound via an η^3-allylic linkage to atoms C(8)–C(9)–C(10) of the nonmethylated seven-membered ring; the associated $(OC)_2Fe–Fe(CO)_3$ linkage is 2.793 (2) Å. A further $Fe(CO)_3$ group is bound to the opposite face of the polycyclic aceheptylene system and is involved in an η^4-*cis*-diene linkage to atoms C(3)–C(4)–C(5)–C(6) of the methylated seven-membered ring. The C(6A)–C(7) distance is 1.350 (11) Å, as expected for a noncoordinated ethylenic linkage.

Introduction

Reactions of the nonalternant aromatic hydrocarbon 3,5-dimethylaceheptylene (I) with various transition-metal carbonyls have been carried out by King and Harmon.[1,2] The reaction of I with excess $Fe_3(CO)_{12}$ or with excess $Fe(CO)_5$



I

produces a red-brown material with $\nu_{C–O}$ at 2060, 1990, and 1972 cm^{-1}. The present structural analysis was carried out in order to determine unambiguously the stoichiometry of this new compound and to elucidate the nature of the various aceheptylene–iron linkages. (Elemental analysis suggested the formulas $(C_{14}H_8Me_2)Fe_3(CO)_7$ or $(C_{14}H_8Me_2)Fe_3(CO)_8$; other physical techniques had failed to distinguish between these possibilities.)

A brief account of this study has appeared previously.[2]

Collection of X-Ray Diffraction Data

Red-brown crystals of the complex, later shown to be $(C_{14}H_8Me_2)Fe_3(CO)_8$, were supplied by Professor R. B. King of the University of Georgia. The complex appears to be stable indefinitely in the presence of air and is not significantly disrupted upon exposure to Mo Kα radiation.

The crystal selected for the X-ray diffraction experiment was a fragment of approximate dimensions 0.35 × 0.25 × 0.25 mm. It was mounted along its extended dimension on a thin glass fiber, which was then sealed (with beeswax) into a brass pin and mounted on a eucentric goniometer. The crystal was centered in a random orientation (later found to be with [213] offset by approximately 4.8° from coincidence with the ϕ axis) on a Syntex $P2_1$ four-circle diffractometer under the control of a NOVA 1200 computer.

Measurement of unit cell parameters, determination of the orientation matrix, checks (via both θ–2θ and ω scans) on peak profiles, and data collection were carried out as described previously.[3] Details of the present study are listed in Table I.

An examination of the complete data set revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the space group $P2_1/c$ is thereby determined uniquely.

Table I. Details of Data Collection for $(C_{14}H_8Me_2)Fe_3(CO)_8$

(A) Crystal Data

Crystal system: monoclinic	$V = 2315.3\ (7)$ Å^3
Space group: $P2_1/c$ [No. 14; C_{2h}^5]	Temp 24 °C
$a = 22.5798\ (43)$ Å^a	Mol wt = 597.92
$b = 7.2985\ (12)$ Å^a	ρ(obsd)^b = 1.717 (8) g cm^{-3}
$c = 14.5197\ (22)$ Å^a	$Z = 4$
$\beta = 104.624\ (14)°^a$	ρ(calcd) = 1.715 g cm^{-3}

(B) Collection of Intensity Data

Diffractometer	Syntex $P\underline{2}_1$
Radiation	Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
Monochromator	Highly oriented graphite; equatorial mounting; $2\theta_M = 12.2°$
Reflections measd	$-h, +k, \pm l$
Scan type	Coupled θ(crystal)–2θ(counter)
2θ range	4.0–40.0°
Scan speed	2.0°/min in 2θ
Scan range	[2θ(Mo Kα_1) − 1.1]° → [2θ(Mo Kα_2) + 1.1]°
Bkgd measurement	Stationary; at beginning and end of each scan; each for half of the total scan time
Standards	Three measured after each batch of 97 data; no significant deviations from their mean values
Reflections collected	2914 total, yielding 2148 independent data (277 systematic absences; 90 check reflections)
Absorption coeff	19.01 cm^{-1}
Reflections used for empirical abs cor (hkl, 2θ, T_{max}/T_{min})	$21\bar{3}$, 10.20°, 1.15; $62\bar{6}$, 21.38°, 1.12; $83\bar{6}$, 26.13°, 1.12

[a] Based on a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections of the form $\{62\bar{6}\}$, $\{63\bar{4}\}$, $\{13,0,\bar{4}\}$, $\{242\}$, $\{22\bar{6}\}$, $\{10,0,2\}$, and $\{317\}$, all with 2θ in the range 20–25°. [b] The density was measured by neutral buoyancy in a methanolic solution of barium mercuric iodide (Rohrbach's solution).

The net intensity (I) and its standard deviation ($\sigma(I)$) were calculated from the scan count (SC) and background counts (B1 and B2) as shown in eq 1 and 2. The value of τ (the ratio of scan time to background counting time) was unity.

$$I = SC - \tau(B1 + B2) \tag{1}$$

$$\sigma(I) = [SC + \tau^2(B1 + B2)]^{1/2} \tag{2}$$

Data were now corrected for absorption by an empirical method based upon a set of ψ scans (see Table I and ref 4); systematic absences and check reflections were eliminated at this stage. The remaining data were corrected for Lorentz and polarization effects, the form of the Lp factor being that given in eq 3 and applied to the ab-

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sorption-correction intensities (I_{Abscor}) as shown in eq 4. Equation

$$Lp = \frac{0.5}{\sin 2\theta}\left[\left(\frac{1+\cos^2 2\theta_{\text{M}}\cos^2 2\theta}{1+\cos^2 2\theta_{\text{M}}}\right) + \left(\frac{1+|\cos 2\theta_{\text{M}}|\cos^2 2\theta}{1+|\cos 2\theta_{\text{M}}|}\right)\right] \tag{3}$$

$$|F_{\text{o}}| = (I_{\text{Abscor}}/Lp)^{1/2} \tag{4}$$

3 assumes that the equatorially mounted graphite monochromator is 50% mosaic and 50% perfect; $2\theta_{\text{M}}$, the monochromator angle, is 12.2° for Mo $K\bar{\alpha}$ radiation.

A total of 10 reflections with $I \leq -400$ counts was rejected from the analysis. Those reflections with $0 > I > -400$ counts were assigned a value of $|F_{\text{o}}| = 0$ and were retained.

Solution of the Structure

Crystallographic calculations were performed using the Syntex XTL system. This consists of (a) a Data General NOVA 1200 computer with 24K of 16-bit word memory and with a parallel floating-point processor for 32- or 64-bit arithmetic, (b) a Diablo moving-head disk unit with 1.2 million 16-bit words, (c) a Versatec electrostatic printer/plotter, and (d) a locally modified version of the XTL interactive (conversational) crystallographic program package.

The function $w(|F_{\text{o}}| - |F_{\text{c}}|)^2$ was minimized during least-squares refinement. The weights, w, are defined in eq 5; here $\sigma_{\text{c}}(|F_{\text{o}}|)$ is

$$w = \{[\sigma_{\text{c}}(|F_{\text{o}}|)]^2 + [p|F_{\text{o}}|]^2\}^{-1} \tag{5}$$

propagated from $\sigma(I)$ and is based solely on counting statistics. The "ignorance factor" (p) was set at a value of 0.01.

The analytical scattering factors of Cromer and Mann[5a] for *neutral* atoms were used throughout the analysis; both the real and imaginary components of anomalous dispersion[5b] were applied to all nonhydrogen atoms. Discrepancy indices used below are defined in eq 6 and 7.

$$R_F = \left[\frac{\Sigma||F_{\text{o}}| - |F_{\text{c}}||}{\Sigma|F_{\text{o}}|}\right] \times 100\,(\%) \tag{6}$$

$$R_{\text{w}F} = \left[\frac{\Sigma w(|F_{\text{o}}| - |F_{\text{c}}|)^2}{\Sigma w|F_{\text{o}}|^2}\right]^{1/2} \times 100\,(\%) \tag{7}$$

The "goodness-of-fit" (GOF) is defined in eq 8. Here NO is the

$$\text{GOF} = \left[\frac{\Sigma w(|F_{\text{o}}| - |F_{\text{c}}|)^2}{\text{NO} - \text{NV}}\right]^{1/2} \tag{8}$$

number of observations and NV is the number of variables.

Data were placed on an approximate absolute scale by means of a Wilson plot. The structure was solved via the multiple tangent formula method using the program MULTAN by Germain, Main, and Woolfson.[6]

A total of 306 reflections with $|E| > 1.50$ was chosen for the phase-determining process. The reflection 404 ($|E| = 2.98$) was recognized as having a phase angle (ϕ) of 0° by means of a "Σ_1 relationship". The origin of the unit cell was defined by assigning phase angles of 0° to three strong reflections of appropriate parity (70$\bar{6}$, $|E| = 2.68$; 10,4,$\bar{5}$, $|E| = 2.23$; 10,5,4, $|E| = 2.98$). All eight possible sets of starting phases for the reflections 24$\bar{2}$ ($|E| = 2.85$), 32$\bar{2}$ ($|E| = 2.49$), and 10,0,6 ($|E| = 4.20$) were investigated. The "best solution" [$\phi(24\bar{2}) = 0°$, $\phi(32\bar{2}) = 180°$, $\phi(10,0,6) = 180°$] had the highest "absolute figure of merit" (1.352), the lowest "ψ_0 value" (0.1075×10^4), the lowest "R index" (12.80), and the highest "combined figure of merit" (3.000) of the eight permutations. An "E map" based upon this solution contained three large peaks, consistent with the presence of three independent iron atoms.

Using all data, a structure factor calculation based on the contributions of the three iron atoms had discrepancy indices of R_F = 36.2% and $R_{\text{w}F}$ = 39.6%. A difference-Fourier map led to the location of all nonhydrogen atoms. Full-matrix least-squares refinement of positional and thermal parameters of all atoms (anisotropic thermal parameters for atoms in the $\text{Fe}_3(\text{CO})_8$ portion of the molecule and isotropic thermal parameters for carbon atoms of the 3,5-dimethylaceheptylene moiety) led to convergence with R_F = 6.5%, $R_{\text{w}F}$ = 5.8%, and GOF = 2.58. A second difference-Fourier map now led to the unambiguous location of the eight "ring hydrogens" of the aceheptylene system. Refinement of their positional parameters (with their isotropic thermal parameters set at B = 5.0 Å^2), along with all other previously refined parameters, led to final convergence [$(\Delta/\sigma)_{\text{max}}$ = 0.02 for a nonhydrogenic parameter and 0.07 for a hydrogenic positional parameter] with R_F = 5.6%, $R_{\text{w}F}$ = 4.6%, and GOF = 2.05 for the 1930 reflections with $|F_{\text{o}}| > 1.0\sigma(|F_{\text{o}}|)$. (Discrepancy indices for all 2148 reflections were R_F = 6.8% and $R_{\text{w}F}$ = 4.8%.)

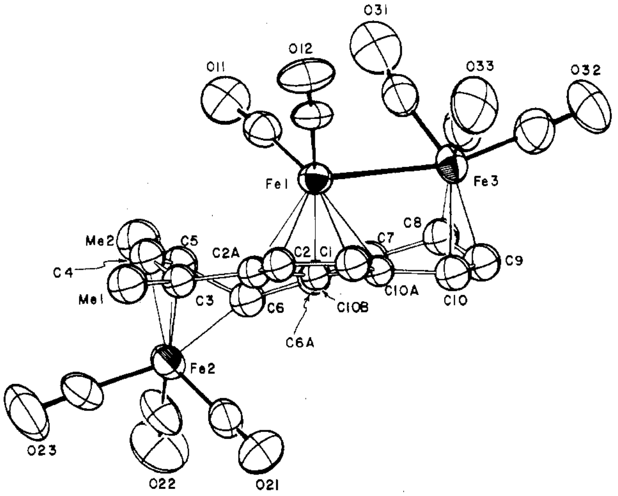


Figure 1. The $(\text{C}_{14}\text{H}_8\text{Me}_2)\text{Fe}_3(\text{CO})_8$ molecule, viewed from the side and showing the distortions within the aceheptylene system (ORTEP-II diagram).

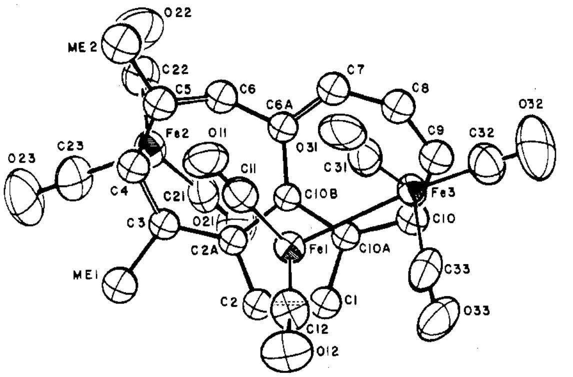


Figure 2. The $(\text{C}_{14}\text{H}_8\text{Me}_2)\text{Fe}_3(\text{CO})_8$ molecule, projected onto its η^5-cyclopentadienyl ring (ORTEP-II diagram).

The strongest feature on a final difference-Fourier synthesis was a peak of height 0.60 e Å^{-3} at (0.40, 0.90, 0.43); this and the three other peaks with $\rho > 0.4$ e Å^{-3} are possible hydrogen atoms of the methyl groups. However, neither CH_3 system was uniquely defined, and methyl hydrogens were therefore not included in the analysis. There were no indications of significant anisotropic motion for carbon atoms of the 3,5-dimethylaceheptylene ligand; the final model contains only isotropic thermal parameters for these atoms. The final NO:NV ratio was 1930:260 or approximately 7.42:1.

There was no evidence for secondary extinction. The average value of $\Sigma w(|F_{\text{o}}| - |F_{\text{c}}|)^2$ showed no significant variations as a function of $|F_{\text{o}}|$, $(\sin\theta)/\lambda$, identity or parity of Miller indices, or sequence number. The weighting scheme was therefore declared to be satisfactory.

Final positional and thermal parameters are collected in Tables II and III.

Discussion

The scheme used for labeling atoms is illustrated in Figures 1 and 2. A stereoscopic view of the molecule (with hydrogen atoms omitted for the sake of clarity) is given in Figure 3. Interatomic distances and angles are compiled in Tables IV and V; least-squares planes, and atomic deviations therefrom, are defined in Table VI.

The molecule contains an $\text{Fe}_2(\text{CO})_5$ system bonded to one face of a 3,5-dimethylaceheptylene system and an $\text{Fe}(\text{CO})_3$

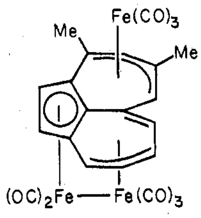
Table II. Final Positional Parameters for $(C_{14}H_8Me_2)Fe_3(CO)_8$

Atom	*x*	*y*	*z*	*B*, Å^2
Fe(1)	0.20006 (5)	0.34599 (6)	0.07448 (7)	*a*
Fe(2)	0.38198 (5)	0.73792 (17)	0.11685 (8)	*a*
Fe(3)	0.10036 (5)	0.45622 (17)	−0.07154 (8)	*a*
O(11)	0.2776 (3)	0.1506 (9)	−0.0263 (5)	*a*
O(12)	0.1601 (3)	0.0201 (9)	0.1554 (5)	*a*
O(21)	0.3076 (3)	0.9713 (9)	0.2071 (5)	*a*
O(22)	0.4358 (3)	1.0154 (12)	0.0163 (6)	*a*
O(23)	0.4937 (3)	0.7164 (11)	0.2700 (6)	*a*
O(31)	0.1508 (3)	0.1604 (11)	−0.1623 (5)	*a*
O(32)	−0.0127 (4)	0.4549 (11)	−0.2207 (6)	*a*
O(33)	0.0381 (3)	0.2430 (11)	0.0457 (5)	*a*
C(11)	0.2454 (4)	0.2242 (12)	0.0117 (6)	*a*
C(12)	0.1740 (4)	0.1488 (13)	0.1211 (6)	*a*
C(21)	0.3367 (4)	0.8857 (13)	0.1703 (6)	*a*
C(22)	0.4160 (4)	0.9046 (15)	0.0552 (7)	*a*
C(23)	0.4496 (4)	0.7215 (13)	0.2089 (7)	*a*
C(31)	0.1356 (4)	0.2761 (14)	−0.1210 (7)	*a*
C(32)	0.0326 (5)	0.4596 (13)	−0.1621 (7)	*a*
C(33)	0.0646 (4)	0.3261 (15)	0.0038 (7)	*a*
C(1)	0.1742 (4)	0.5387 (12)	0.1643 (6)	3.26 (18)
C(2)	0.2341 (4)	0.4829 (11)	0.2041 (5)	3.03 (18)
C(2A)	0.2713 (3)	0.5270 (10)	0.1418 (5)	2.76 (16)
C(3)	0.3377 (3)	0.5015 (10)	0.1639 (5)	3.02 (17)
C(4)	0.3720 (4)	0.4592 (12)	0.0963 (6)	3.48 (18)
C(5)	0.3634 (4)	0.5471 (11)	0.0077 (6)	3.63 (18)
C(6)	0.3175 (4)	0.6868 (12)	−0.0175 (6)	3.47 (20)
C(6A)	0.2517 (3)	0.6675 (10)	−0.0237 (5)	2.90 (16)
C(7)	0.2109 (4)	0.6896 (12)	−0.1087 (6)	3.43 (19)
C(8)	0.1450 (4)	0.6796 (12)	−0.1333 (6)	3.66 (18)
C(9)	0.1054 (4)	0.7360 (12)	−0.0792 (6)	3.81 (19)
C(10)	0.1159 (4)	0.6965 (11)	0.0157 (6)	3.52 (19)
C(10A)	0.1713 (3)	0.6220 (10)	0.0736 (5)	2.60 (15)
C(10B)	0.2324 (3)	0.6122 (10)	0.0595 (5)	2.39 (15)
Me(1)	0.3652 (4)	0.4266 (11)	0.2655 (6)	4.11 (19)
Me(2)	0.4057 (4)	0.5012 (13)	−0.0572 (7)	5.26 (22)
H(1)	0.139 (3)	0.527 (10)	0.180 (5)	5.0[b]
H(2)	0.248 (3)	0.431 (10)	0.250 (6)	5.0[b]
H(4)	0.408 (3)	0.378 (10)	0.123 (5)	5.0[b]
H(6)	0.319 (3)	0.754 (10)	−0.059 (6)	5.0[b]
H(7)	0.228 (3)	0.687 (10)	−0.150 (5)	5.0[b]
H(8)	0.131 (3)	0.668 (10)	−0.201 (5)	5.0[b]
H(9)	0.068 (3)	0.791 (10)	−0.112 (5)	5.0[b]
H(10)	0.086 (3)	0.704 (10)	0.043 (5)	5.0[b]

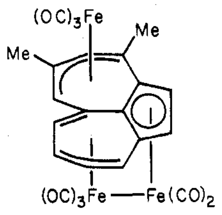
[a] See Table III for anisotropic thermal parameters. [b] Hydrogen atoms were assigned isotropic thermal parameters of 5.0 Å^2. These were not refined.

system bonded to the other face of this nonalternant polycyclic aromatic ligand. The $Fe_2(CO)_5$ moiety consists of an $Fe(CO)_2$ and an $Fe(CO)_3$ group linked via an iron–iron linkage [Fe(1)–Fe(3)] of length 2.793 (2) Å; the $Fe(CO)_2$ group interacts with all five atoms of the five-membered ring via an η^5-cyclopentadienyl→iron linkage, while the $Fe(CO)_3$ group is bonded to three carbon atoms of the non-methyl-substituted seven-membered ring via an η^3-allyl→iron linkage. The isolated $Fe(CO)_3$ group, which is centered on Fe(2), is bonded to four adjacent carbon atoms of the dimethylated seven-membered ring via an η^4-diene linkage.

The complex crystallizes in the centrosymmetric space group $P2_1/c$; the crystals thus contain an ordered racemic mixture of the enantiomeric forms II and III, in which the isolated

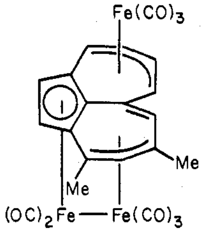


II

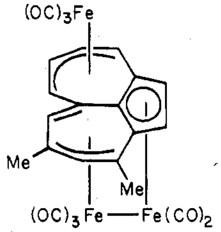


III

$Fe(CO)_3$ group is associated with the dimethyl-substituted seven-membered ring. There is no evidence for the formation of the other possible enantiomeric pair of isomers (IV and V)



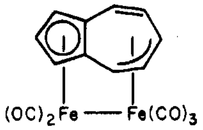
IV



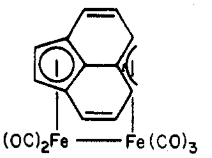
V

from the reaction of 3,5-dimethylaceheptylene with iron carbonyl.

The bonding of the $Fe_2(CO)_5$ fragment to the aceheptylene skeleton is precisely analogous to the metal–ligand bonding found in the complex $(azulene)Fe_2(CO)_5$[7] (VI) and closely related to that found in $(acenaphthylene)Fe_2(CO)_5$[8] (VII).



VI



VII

Table III. Anisotropic Thermal Parameters (in Å^2) for $(C_{14}H_8Me_2)Fe_3(CO)_8$[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	3.23 (6)	2.65 (6)	2.76 (5)	−0.09 (5)	0.61 (4)	−0.15 (5)
Fe(2)	3.05 (6)	3.67 (6)	3.87 (6)	−0.54 (5)	0.20 (5)	−0.05 (5)
Fe(3)	2.82 (6)	3.93 (7)	3.19 (6)	−0.12 (5)	0.29 (4)	0.63 (5)
O(11)	6.1 (4)	5.6 (4)	5.9 (4)	−0.7 (3)	2.8 (3)	1.2 (3)
O(12)	8.5 (5)	2.7 (3)	7.0 (4)	−1.1 (3)	3.2 (3)	0.0 (3)
O(21)	6.1 (4)	5.5 (4)	7.4 (4)	1.2 (3)	1.7 (3)	−1.3 (3)
O(22)	7.4 (5)	8.4 (5)	9.0 (5)	−3.1 (4)	3.3 (4)	1.0 (4)
O(23)	4.9 (4)	9.3 (5)	9.0 (5)	−1.9 (4)	−2.0 (4)	1.1 (4)
O(31)	7.0 (4)	6.8 (4)	5.9 (4)	−1.4 (4)	1.9 (3)	2.8 (4)
O(32)	5.9 (4)	10.4 (6)	8.2 (5)	0.3 (4)	−2.7 (4)	−2.7 (4)
O(33)	4.6 (4)	8.4 (5)	9.1 (5)	−0.4 (4)	3.5 (3)	1.4 (4)
C(11)	4.0 (5)	3.6 (5)	3.8 (5)	−0.4 (4)	0.7 (4)	0.2 (4)
C(12)	4.7 (5)	2.2 (4)	4.8 (5)	−0.5 (4)	0.7 (4)	−0.5 (4)
C(21)	3.3 (5)	4.2 (6)	4.4 (6)	−0.1 (4)	0.1 (4)	0.4 (4)
C(22)	3.6 (5)	6.8 (7)	5.3 (6)	−1.9 (5)	0.5 (4)	0.3 (5)
C(23)	4.0 (5)	4.5 (5)	6.3 (6)	−1.5 (4)	0.4 (5)	−0.4 (5)
C(31)	3.6 (5)	4.7 (6)	4.8 (5)	−0.3 (4)	0.5 (4)	0.7 (4)
C(32)	4.8 (5)	4.9 (5)	5.6 (6)	0.3 (5)	0.8 (5)	1.2 (5)
C(33)	3.1 (5)	6.0 (6)	5.6 (6)	−0.0 (5)	1.2 (4)	−1.4 (5)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

Table IV. Intramolecular Distances (in Å) with Esd's for $(C_{14}H_8Me_2)Fe_3(CO)_8$

(A) Iron-Iron Bond Length			
Fe(1)-Fe(3)	2.793 (2)		
(B) Iron-Aceheptylene Distances			
Fe(1)-C(1)	2.098 (8)	Fe(2)-C(4)	2.060 (9)
Fe(1)-C(2)	2.098 (8)	Fe(2)-C(5)	2.071 (8)
Fe(1)-C(2A)	2.120 (7)	Fe(2)-C(6)	2.151 (8)
Fe(1)-C(10B)	2.106 (7)	Fe(3)-C(8)	2.222 (9)
Fe(1)-C(10A)	2.116 (7)	Fe(3)-C(9)	2.050 (9)
Fe(2)-C(3)	2.188 (7)	Fe(3)-C(10)	2.140 (8)
(C) Distances Involving Carbonyl Ligands			
Fe(1)-C(11)	1.771 (9)	C(11)-O(11)	1.152 (11)
Fe(1)-C(12)	1.754 (9)	C(12)-O(12)	1.143 (11)
Fe(2)-C(21)	1.792 (9)	C(21)-O(21)	1.134 (12)
Fe(2)-C(22)	1.793 (10)	C(22)-O(22)	1.142 (13)
Fe(2)-C(23)	1.762 (10)	C(23)-O(23)	1.154 (13)
Fe(3)-C(31)	1.778 (10)	C(31)-O(31)	1.139 (12)
Fe(3)-C(32)	1.747 (10)	C(32)-O(32)	1.155 (13)
Fe(3)-C(33)	1.788 (10)	C(33)-O(33)	1.132 (12)
(D) Carbon-Carbon Distances within the Aceheptylene Ligand			
C(1)-C(2)	1.390 (12)	C(5)-Me(2)	1.539 (12)
C(1)-C(10A)	1.437 (11)	C(6)-C(6A)	1.472 (12)
C(2)-C(2A)	1.419 (11)	C(6A)-C(7)	1.350 (11)
C(2A)-C(3)	1.463 (11)	C(6A)-C(10B)	1.442 (10)
C(2A)-C(10B)	1.434 (10)	C(7)-C(8)	1.442 (12)
C(3)-C(4)	1.430 (11)	C(8)-C(9)	1.393 (12)
C(3)-Me(1)	1.548 (11)	C(9)-C(10)	1.369 (12)
C(4)-C(5)	1.407 (11)	C(10)-C(10A)	1.428 (11)
C(5)-C(6)	1.434 (12)	C(10A)-C(10B)	1.445 (10)
(E) Carbon-Hydrogen Distances			
C(1)-H(1)	0.88 (8)	C(7)-H(7)	0.79 (8)
C(2)-H(2)	0.76 (8)	C(8)-H(8)	0.96 (8)
C(4)-H(4)	1.00 (7)	C(9)-H(9)	0.94 (8)
C(6)-H(6)	0.78 (8)	C(10)-H(10)	0.87 (8)

The five-membered ring within the $(C_{14}H_8Me_2)Fe_3(CO)_8$ molecule has a root-mean-square deviation from planarity of 0.005 Å—i.e., it is strictly planar within the limits of experimental error. (We note here that, in the related species $(C_{14}H_8Me_2)Mn_2(CO)_6$,[9] there appears to be a slight bending of the five-membered ring about its C(2A)···C(10A) axis.)

Fe(1)–C(ring) bonding distances are (cyclically) Fe(1)–C(1) = 2.098 (8) Å, Fe(1)–C(2) = 2.098 (8) Å, Fe(1)–C(2A) = 2.120 (7) Å, Fe(1)–C(10B) = 2.106 (7) Å, and Fe(1)–C(10A) = 2.116 (7) Å; the average value is 2.108 Å as compared to average Fe–C(cyclopentadienyl) distances of 2.093 Å in VI and 2.112 Å in VII.

Individual carbon–carbon distances within the five-membered ring are C(1)–C(2) = 1.390 (12) Å, C(2)–C(2A) = 1.419 (11) Å, C(2A)–C(10B) = 1.434 (10) Å, C(10B)–C(10A) = 1.445 (10) Å, and C(10A)–C(1) = 1.437 (11) Å; the average value of 1.425 Å is close to that expected for a rigidly held nonlibrating η^5-cyclopentadienyl system (cf. ref 10). The iron atom (Fe(1)) lies +1.724 (1) Å from the least-squares plane defined by the five-membered ring. Of the carbon-atom substituents around the pentaatomic carbocyclic ring, C(6A) is displaced toward Fe(1) (by +0.088 (7) Å) and C(3) and C(10) are displaced away from Fe(1), their deviations from coplanarity with the cyclopentadienyl system being −0.114 (7) Å and −0.030 (8) Å, respectively.

Atom Fe(3) is linked to three carbon atoms of the nonmethylated seven-membered ring, the individual iron–carbon distances showing rather wide variations—Fe(3)–C(8) = 2.222 (9) Å, Fe(3)–C(9) = 2.050 (9) Å, and Fe(3)–C(10) = 2.140 (8) Å. These essentially duplicate the distances found in (azulene)$Fe_2(CO)_5$, where the corresponding values are (respectively) 2.200 (8), 2.050 (8), and 2.142 (8) Å. These variations in Fe–C(allyl) distances are probably best explained as part of a general pattern of strain within these molecular species, being the net result of simultaneous optimization of Fe(1)–(η^5-cyclopentadienyl) bonding, Fe(3)–(η^3-allyl) bonding, and Fe(1)–Fe(3) metal–metal bonding. The apical angle in the η^3-allyl group is C(8)–C(9)–C(10) = 122.3 (8)°. (This is significantly lower than the average internal angle of 128.57° expected for a planar heptagon, it is close to the ideal sp^2-hybridized angle of 120°, and it is indistinguishable from the value of 122.8° found for the corresponding angle in (azulene)$Fe_2(CO)_5$, VI.) Carbon–carbon distances within the η^3-allyl system are C(8)–C(9) = 1.393 (12) Å and C(9)–C(10) = 1.369 (12) Å. The η^3-allyl plane and the η^5-cyclopentadienyl system are displaced from coplanarity by 25.31°.

As might be expected, the shortest carbon–carbon bond in the entire aceheptylene system is that which is associated with

Table V. Interatomic Angles (deg) with Esd's for $(C_{14}H_8Me_2)Fe_3(CO)_8$

(A) Angles Involving the Iron Atoms			
C(11)-Fe(1)-C(12)	94.6 (4)	C(31)-Fe(3)-C(32)	95.9 (5)
C(21)-Fe(2)-C(22)	99.8 (4)	C(32)-Fe(3)-C(33)	91.4 (5)
C(22)-Fe(2)-C(23)	91.5 (5)	C(33)-Fe(3)-C(31)	99.9 (5)
C(23)-Fe(2)-C(21)	101.1 (4)		
(B) Iron-Carbon-Oxygen Angles			
Fe(1)-C(11)-O(11)	176.1 (8)	Fe(2)-C(23)-O(23)	177.8 (9)
Fe(1)-C(12)-O(12)	176.1 (8)	Fe(3)-C(31)-O(31)	170.6 (9)
Fe(2)-C(21)-O(21)	176.3 (8)	Fe(3)-C(32)-O(32)	177.2 (9)
Fe(2)-C(22)-O(22)	177.3 (9)	Fe(3)-C(33)-O(33)	174.6 (9)
(C) Angles within Five-Membered Ring			
C(10A)-C(1)-C(2)	108.6 (7)	C(2A)-C(10B)-C(10A)	108.0 (6)
C(1)-C(2)-C(2A)	109.8 (7)	C(10B)-C(10A)-C(1)	106.5 (6)
C(2)-C(2A)-C(10B)	107.0 (6)		
(D) Angles within Seven-Membered Rings			
C(10B)-C(2A)-C(3)	128.1 (7)	C(10B)-C(10A)-C(10)	131.4 (7)
C(2A)-C(3)-C(4)	125.4 (7)	C(10A)-C(10)-C(9)	125.1 (8)
C(3)-C(4)-C(5)	123.7 (7)	C(10)-C(9)-C(8)	122.3 (8)
C(4)-C(5)-C(6)	118.8 (7)	C(9)-C(8)-C(7)	127.9 (8)
C(5)-C(6)-C(6A)	127.0 (7)	C(8)-C(7)-C(6A)	130.1 (8)
C(6)-C(6A)-C(10B)	119.3 (7)	C(7)-C(6A)-C(10B)	121.2 (7)
C(6A)-C(10B)-C(2A)	124.6 (6)	C(6A)-C(10B)-C(10A)	127.3 (6)
(E) "External" Angles Involving Methyl Groups etc.			
C(2A)-C(3)-Me(1)	113.3 (6)	C(4)-C(5)-Me(2)	119.8 (7)
C(4)-C(3)-Me(1)	114.9 (7)	C(6)-C(5)-Me(2)	121.3 (7)
C(2)-C(2A)-C(3)	124.7 (7)	C(1)-C(10A)-C(10)	122.1 (7)
C(6)-C(6A)-C(7)	119.3 (7)		

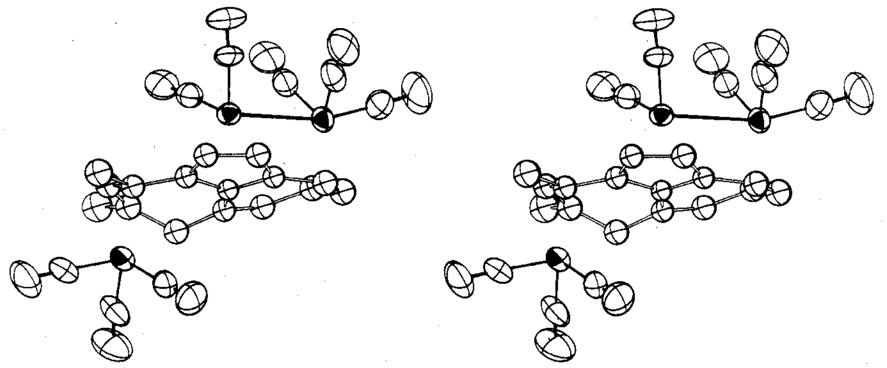


Figure 3. A stereoscopic view of the $(C_{14}H_8Me_2)Fe_3(CO)_8$ molecule (ORTEP-II diagram).

Table VI. Least-Squares Planes and Atomic Deviations (in Å) for $(C_{14}H_8Me_2)Fe_3(CO)_8$[a,b]

Atom	Dev	Atom	Dev
Plane 1: Five-membered Ring ($\chi^2 = 1.90$) ($-0.0978X - 0.8924Y - 0.4404Z = -4.8538$)			
C(1)*	0.003 (8)	Fe(1)	1.724 (1)
C(2)*	0.001 (8)	Fe(3)	2.078 (1)
C(2A)*	−0.005 (7)	C(3)	−0.114 (7)
C(10B)*	−0.005 (7)	C(6A)	0.088 (7)
C(10A)*	0.006 (7)	C(10)	−0.030 (8)
Plane 2: η^4-*cis*-Diene System ($\chi^2 = 0.09$) ($-0.5919X - 0.6906Y - 0.4156Z = -7.6418$)			
C(3)*	−0.001 (7)	C(2A)	0.839 (7)
C(4)*	0.002 (8)	Me(1)	−0.363 (8)
C(5)*	−0.002 (8)	Me(2)	−0.097 (9)
C(6)*	0.001 (9)	C(6A)	1.000 (8)
Fe(2)	−1.612 (1)		
Plane 3: η^3-Allyl System ($\chi^2 = 0$) ($-0.4765X - 0.8502Y - 0.2241Z = -5.5902$)			
C(8)*	0.000	C(7)	−0.806 (9)
C(9)*	0.000	C(10A)	−0.216 (7)
C(10)*	0.000		
Fe(3)	1.780 (1)		

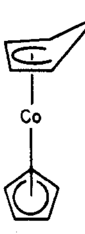
Dihedral Angles
Plane 1/plane 2 = 149.01° (30.99°)
Plane 1/plane 3 = 154.69° (25.31°)
Plane 2/plane 3 = 164.21° (15.79°)

[a] Those atoms indicated by an asterisk were used for calculating the least-squares planes. [b] Equations are in orthonormal coordinates.

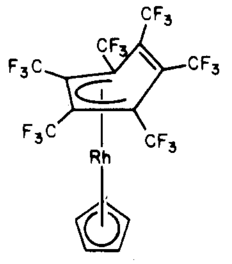
the single remaining uncoordinated ethylenic linkage, C(6A)–C(7) = 1.350 (11) Å.

The isolated $Fe(CO)_3$ group, centered on Fe(2), is bonded (via an η^4-*cis*-diene→metal linkage) to four atoms of the dimethyl-substituted seven-membered ring. The individual Fe(2)–C(diene) distances, cyclically, are Fe(2)–C(3) = 2.188 (7) Å, Fe(2)–C(4) = 2.060 (9) Å, Fe(2)–C(5) = 2.071 (8) Å, and Fe(2)–C(6) = 2.151 (8) Å; the central carbon atoms of the diene system are thus significantly closer to the iron atom than are the terminal carbon atoms. Bond lengths around the coordinated *cis*-diene system (taken cyclically) are C(3)–C(4) = 1.430 (11) Å, C(4)–C(5) = 1.407 (11) Å, and C(5)–C(6) = 1.434 (12) Å. This pattern of bond lengths (i.e., with the central carbon–carbon bond shorter than the outer carbon–carbon bonds) is appreciably different from that found in a free (uncoordinated) 1,3-diene system but is common to all (1,3-diene)$Fe(CO)_3$ species that have been structurally characterized. Compilations of these data have been presented previously by Churchill and Bird (in 1969)[11] and by Cotton et al. (in 1973).[12]

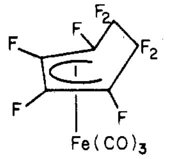
The η^4-*cis*-diene system is planar (the root-mean-square deviation from planarity being only 0.002 Å) and atom Fe(2) lies −1.612 (1) Å from this plane. As shown clearly in Figure 1, the aceheptylene ligand is bent severely about the C(3)···C(6) axis (i.e., about the ends of the *cis*-1,3-diene system) such that the diene system lies 30.99° from coplanarity with the η^5-cyclopentadienyl system. We note here that the bending about the ends of those coordinated η^4-*cis*-diene systems present in cyclic systems is always substantial.[13] Characteristic "bend angles" are 36.5° in $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5Ph)$[14] (VIII), 47.9° in $(\eta^5\text{-}C_5H_5)Rh(\eta^4\text{-}C_6(CF_3)_6)$[15] (IX), and 47.3° in $(\eta^4\text{-}C_6F_8)Fe(CO)_3$[16] (X).



VIII



IX



X

The $Fe(CO)_3$ group associated with the diene system has the expected conformation—i.e., with one carbonyl group [C(21)–O(21)] lying below and between the termini of the 1,3-diene system. The (1,3-diene)$Fe(CO)_3$ system has approximate C_s symmetry. The three OC–Fe–CO angles are not all equivalent; that opposite to C(21)–O(21) is some 8–10° less obtuse than the remaining two angles (i.e., C(22)–Fe(2)–C(23) = 91.5 (5)° vs. C(21)–Fe(2)–C(22) = 99.8 (4)° and C(23)–Fe(2)–C(21) = 101.1 (4)°).

All Fe–CO distances (overall range 1.747 (10)–1.793 (10) Å) and C–O distances (1.132 (12)–1.155 (13) Å) are normal and are internally consistent. The system Fe(3)–C(31)–O(31), with an angle of 170.6 (9)°, is significantly distorted from linearity (due to close intermolecular contacts). The other seven carbonyl ligands are closer to linearity, with Fe–C–O angles in the range of 174.6 (9)–177.8 (9)°. However, as pointed out by Kettle,[17] none of these M–C–O systems is required electronically to be *strictly* linear, since none of them belongs to an $M(CO)_x$ fragment of C_{3v} (or higher) symmetry.

Finally we note that reaction of 3,5-dimethylaceheptylene with iron carbonyl essentially destroys its aromaticity. Complexation results overall in the factoring of the 14 π electrons of the aceheptylene system into isolated η^5-cyclopentadienyl, η^4-diene, η^3-allyl, and simple noncoordinated ethylenic systems.

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Registry No. $(C_{14}H_8Me_2)Fe_3(CO)_8$, 66255-75-2.

Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Dimethyl Compounds of Platinum. 3. Oxidative-Addition and Methyl-Transfer Reactions with Mercury Compounds

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Novel binuclear compounds $PtMe_2X(HgX)(N\text{-}N)$ (N-N = Ph_2Me_2phen, X = Cl, Br, I, O_2CCH_3, O_2CCF_3; N-N = bpy, X = O_2CCH_3, O_2CCF_3) were obtained by reaction of equimolar amounts of $PtMe_2(N\text{-}N)$ and HgX_2. The compounds were formed by cis oxidative addition of HgX_2 to platinum. Reaction of $Hg(O_2CCF_3)_2$ with $PtMe_2(N\text{-}N)$ in a ratio 1:2 resulted in the formation of trinuclear compounds $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$ and $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$. Reaction with $PtMe_2(bpy)$ in a ratio 1:4 afforded a pentanuclear compound $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4$ which had a metallic appearance. The formation of $MeHgO_2CCF_3$ by a methyl-transfer reaction from $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(N\text{-}N)$ to $Hg(O_2CCF_3)_2$ was evidenced by ^1H NMR. Reaction of $MeHgO_2CCF_3$ with $PtMe_2(N\text{-}N)$ first gave Me_2Hg which reacted further (N-N = bpy) to form $PtMe_3(O_2CCF_3)(bpy)$. Similar reactions were observed with MeHgCl, $PhHgO_2CCF_3$, and $PhHgO_2CCH_3$.

Introduction

Many reactions of divalent mercury compounds with d^8 transition metals have been reported[1–5] and it has been shown that these reactions proceed differently. Reaction of Vaska's compound $IrCl(CO)(PPh_3)_2$ with HgX_2 (X = Cl, Br, I, O_2CCH_3, O_2CCF_3)[1,2] proceeded via a trans oxidative addition and $IrClX(HgX)(CO)(PPh_3)_2$ was formed. Reactions of mercury–triazenido compounds with $MCl(CO)(PPh_3)_2$ (M = Rh, Ir) resulted either in oxidative addition with the formation of a bimetallic five-membered ring or in oxidative addition followed by elimination of mercury.[2] Reaction of mercuric halides with dihalide compounds of palladium(II) and platinum(II) resulted in the formation of compounds with halides bridging between the mercury and palladium or platinum atom.[3] Reaction of $HgCl_2$ and $Hg(O_2CCH_3)_2$ with $PtMe_2(PPhMe_2)_2$ resulted in methyl transfer from platinum to mercury,[4,5] whereas reaction of $Hg(O_2CR)_2$ (R = CH_3, CF_3) with $[PtMe_2(Et_2S)]_2$ afforded binuclear compounds of platinum(III).[5] Both reactions possibly involved the formation of an intermediate platinum–mercury bonded compound.

In two previous papers[6,7] reactions of $PtMe_2(N\text{-}N)$ (N-N = bipyridine, phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) with carbon, silicon, germanium, tin, and lead compounds have been reported. Trans oxidative addition involving the metal–halogen bond was observed in the case of the germanium, tin, and lead compounds, and the substituents on the metals had a large effect on the stabilities of the product. In this paper reactions of divalent mercury compounds with $PtMe_2(N\text{-}N)$ are reported and it is shown that oxidative addition and/or methyl transfer can occur, depending upon the starting materials and the reaction conditions.

In addition, our interest in highly conducting compounds with linear chains of platinum atoms such as $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$[15] led us to investigate the possibility of partial oxidation of $PtMe_2(bpy)$. The first indication, that "one-dimensional" compounds with methyl substituents on platinum can exist, is presented in this paper.

Experimental Section

General Information. All compounds prepared in this study were stable in air. ^1H NMR spectra were recorded on a Varian HA100 NMR spectrometer, and for solubility reasons CH_2Cl_2 (ppm relative to CH_2Cl_2) was used as a solvent. Decomposition points were recorded on a DTA apparatus, du Pont Model 900, and were checked visually. Elemental analyses were performed by Childers Laboratories, Milford, N.J., and Chemical Analytical Services, University of California, Berkeley, Calif., and are summarized in Table I.

Chemicals. Reagent grade solvents were distilled prior to use. The mercury compounds HgX_2 (X = Cl, Br, I, O_2CCH_3, O_2CCF_3), MeHgCl, and $PhHgO_2CCH_3$ were commercially available. $PtMe_2(bpy)$[6,8] and $PtMe_2(Ph_2Me_2phen)$[6] (bpy = 2,2′-bipyridine, Ph_2Me_2phen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) were prepared according to the literature procedures.

Preparation of $RHgO_2CCF_3$ (R = Me, Ph). RHgCl (5.00 mol) and AgO_2CCF_3 (5.00 mmol) were added to a mixture of 10 mL of benzene and 10 mL of dichloromethane. The mixture was refluxed with stirring for 10 min and AgCl was removed by filtration. Evaporation of the solvent under vacuum gave $RHgO_2CCF_3$ as a white solid in quantitative yield.

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