2770 *Inorg. Chem.* **1980**, *19*, 2770–2773

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Crystal and and Molecular Structure of Bis[dicarbonyl(π-pentamethylcyclopentadienyl)iron], (η^5-C_5Me_5)$_2$$Fe_2(CO)_4$, and Structural Comparisons with the Nonmethylated Analogue[1]

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Received February 14, 1980

The molecular structure of (η^5-C_5Me_5)$_2$$Fe_2(CO)_4$ has been determined via X-ray diffraction. The dimer has a monoclinic unit cell of space group $P2_1/n$ with a = 8.372 (4) Å, b = 9.864 (5) Å, c = 13.872 (5) Å, β = 93.13 (1)°, V = 1144 (1) Å^3, d_{calcd} = 1.43 g/cm^3, d_{obsd} = 1.46 g/cm^3, and Z = 2. The molecule contains two terminal and two bridging carbonyl ligands with a normal Fe–Fe single bond separation of 2.560 (1) Å. The most unusual finding in this study is that, unlike the case for the unsubstituted analogue (η^5-C_5H_5)$_2$$Fe_2(CO)_4$, no significant variations in the cyclopentadienyl ligand C–C bond lengths are observed. This result may bear directly on the catalytic activity, or lack of it, observed in certain permethylated-cyclopentadienyl complexes.

Introduction

Because of their nonlabile nature, cyclopentadienyl (Cp) ligands are commonly used in organometallic synthesis, an example being the extensive studies of chiral iron complexes of the type $CpFe(CO)(PPh_3)R$ and the reactions they undergo.[2] Kinetic and thermodynamic stabilities are necessary prerequisites for these studies. The stability this ligand imparts to a complex originates in the match in number, energies, and symmetries between the molecular orbitals of the Cp moiety and transition-metal d orbitals.[3,4]

The addition of five methyl groups to the Cp ring [$(Me_5C_5)^-$ = Mp] bestows subtle chemical changes on the chemistry of the corresponding complexes, which bears directly on the catalytic nature of some Mp-containing materials. Three examples serve to illustrate this point: (i) the existence of $[MpRhCl_2]_2$ as opposed to $[CpRhCl_2]_n$, an amorphous, polymeric reactive complex; (ii) the ease with which $[MpCr(CO)_2]_2$ can be synthesized,[5] in contrast to the Cp complex; and (iii) the stability of Mp_2Fe to hydrogenation as compared to that of the corresponding reaction[6] of Cp_2Fe under hydroformylation conditions. The stability of the Mp ligand to hydrogenation is a key factor in the ability of $(MpMCl)_2(\mu\text{-}Cl)(\mu\text{-}H)$ (M = Rh, Ir) complexes to catalyze the hydrogenation of olefins.[7]

Therefore, it is important to initiate a series of structural studies in order to compare the molecular structures of Cp and Mp complexes which will almost certainly lead to a better understanding of these materials. In this study we report the structure of $[MpFe(CO)_2]_2$, as determined by single-crystal X-ray diffractometry, and compare the important structural features with those derived for the nonmethylated derivative.

Experimental Section

Suitable crystals of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ for the X-ray experiment were grown by slow cooling from the boiling point of a saturated solution of the complex in CH_2Cl_2/hexane.

The crystal chosen for data collection exhibited the faces {011}, {0$\bar{1}\bar{1}$}, {$\bar{2}$10}, {2$\bar{1}$0}, {121}, and {$\bar{1}\bar{2}\bar{1}$} and had approximate dimensions 0.017 × 0.017 × 0.016 cm. Preliminary crystallographic investigations, followed by normal data collection, were performed by using a Syntex $P2_1$ diffractometer, with the crystal mounted in an arbitrary orientation.

Table I. Details of Data Collection and Least-Squares Refinement

crystal system	monoclinic, $P2_1/n$, Z = 2, T = 298 K
unit cell constants	a = 8.372 (4) Å b = 9.864 (5) Å c = 13.872 (5) Å β = 93.13 (1)° V = 1144 (1) Å^3
d_{obsd}	1.46 g/cm^3
d_{calcd}	1.43 g/cm^3
abs coeff	13.28 cm^{-1} (Mo Kα, λ = 0.710 69 Å)
min and max transmission factors	0.783–0.831
bkgd/scan time	1.00
data collection limit	0.595 Å^{-1}
data collected	3227 reflections (h,±k,±l); averaged to yield 1956 unique reflections; R(av) = 0.024
final agreement factors (1956 reflections, none rejected)	$R(F_o)$ = 0.038 $R(F_o^2)$ = 0.042 $R_w(F_o^2)$ = 0.063
goodness of fit	1.31
observation to parameter ratio	10:1

Autoindexing of ten accurately centered reflections, which had been observed photographically, suggested a monoclinic unit cell, and an axial photograph of the suspected b^* axis confirmed the presence of a mirror plane. A least-squares fit of 22 accurately centered reflections led to the unit cell constants, in addition to related details of data collection and refinement, which are given in Table I.

A full hemisphere of data (3227 reflections) were collected in the θ–2θ scan mode to $(\sin\theta)/\lambda$ = 0.595 Å^{-1} with a variable scan rate and monochromatized Mo Kα radiation (λ = 0.710 69 Å). During data collection three intense reflections were periodically monitored, and a small (<6%) steady decline was noted in the intensities of these standards. No data were rejected during data collection, and systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, were noted. These absences uniquely establish the space group as $P2_1/n$. Data were corrected for Lorentz, polarization, decay, and absorption effects, and equivalent reflections were averaged, yielding 1956 independent data for structure solution and refinement. The agreement factor upon averaging equivalent reflections was 0.024 ($R(\text{av}) = \sum(F_o^2 - F_o^2(\text{av}))/\sum(F_o^2)$). The iron atom coordinates were determined from a Patterson synthesis, and the remainder of the nonhydrogen atom positional parameters were determined from a difference-Fourier synthesis phased by using the iron atom coordinates.[8] The structural parameters were refined by using the full-matrix least-squares

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(1) This work was performed under the auspices of the Office of Basic Energy Sciences of the United States Department of Energy.

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(9) $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|^2/\sum w_i F_o^4]^{1/2}$. The function minimized in the least-squaring process was $\sum w_i|F_o^2 - S^2F_c^2|$ where S is the scale factor.

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Table II. Bond Lengths (Å) and Angles (Deg)

	Bond Lengths		
Fe-Fe'	2.560 (1)	Fe-C(11)	2.115 (2)
Fe-C(1)	1.753 (3)	Fe-C(12)	2.143 (2)
Fe-C(2)	1.922 (2)	Fe-C(13)	2.160 (2)
Fe-C(2)'	1.936 (2)	Fe-C(14)	2.162 (2)
C(1)-O(1)	1.154 (3)	Fe-C(15)	2.130 (2)
C(2)-O(2)	1.172 (3)		
C(11)-C(12)	1.422 (3)	C(11)-CM(11)	1.505 (4)
C(12)-C(13)	1.431 (3)	C(12)-CM(12)	1.491 (3)
C(13)-C(14)	1.430 (3)	C(13)-CM(13)	1.494 (4)
C(14)-C(15)	1.422 (3)	C(14)-CM(14)	1.501 (4)
C(15)-C(11)	1.429 (3)	C(15)-CM(15)	1.500 (4)
CM(11)-H(111)	0.94 (4)	CM(13)-H(133)	0.95 (5)
CM(11)-H(112)	0.90 (4)	CM(14)-H(141)	0.95 (5)
CM(11)-H(113)	1.10 (4)	CM(14)-H(142)	0.90 (5)
CM(12)-H(121)	0.96 (4)	CM(14)-H(143)	0.99 (5)
CM(12)-H(122)	1.01 (4)	CM(15)-H(151)	0.96 (6)
CM(12)-H(123)	0.93 (4)	CM(15)-H(152)	0.85 (5)
CM(13)-H(131)	0.86 (4)	CM(15)-H(153)	0.82 (5)
CM(13)-H(132)	0.92 (5)		
	Bond Angles		
C(2)-Fe-C(2)'	96.8 (1)	Fe-C(1)-O(1)	175.8 (2)
C(1)-Fe-C(2)	95.2 (1)	Fe-C(2)-O(2)	139.0 (2)
C(1)-Fe-C(2)'	93.8 (1)	Fe'-C(2)-O(2)	137.8 (2)
C(1)-Fe-Fe'	96.8 (1)	Fe-C(2)-Fe'	83.1 (1)
C(15)-C(11)-C(12)	108.5 (2)	CM(11)-C(11)-C(12)	125.3 (2)
C(11)-C(12)-C(13)	107.6 (2)	CM(12)-C(12)-C(13)	125.2 (2)
C(12)-C(13)-C(14)	108.1 (2)	CM(13)-C(13)-C(14)	127.5 (2)
C(13)-C(14)-C(15)	108.0 (2)	CM(14)-C(14)-C(15)	126.3 (3)
C(14)-C(15)-C(11)	107.8 (2)	CM(15)-C(15)-C(11)	125.6 (3)
C(11)-CM(11)-H(111)	114 (2)	C(13)-CM(13)-H(133)	112 (3)
C(11)-CM(11)-H(112)	109 (3)	C(14)-CM(14)-H(141)	108 (3)
C(11)-CM(11)-H(113)	108 (2)	C(14)-CM(14)-H(142)	110 (2)
C(12)-CM(12)-H(121)	110 (2)	C(14)-CM(14)-H(143)	118 (3)
C(12)-CM(12)-H(122)	113 (2)	C(15)-CM(15)-H(151)	112 (4)
C(12)-CM(12)-H(123)	113 (2)	C(15)-CM(15)-H(152)	115 (3)
C(13)-CM(13)-H(131)	113 (2)	C(15)-CM(15)-H(153)	108 (3)
C(13)-CM(13)-H(132)	113 (3)		

technique to an agreement factor of $R(F_o) = 0.049$.[11] In the least-squaring process all positional and anisotropic thermal parameters, and the scale factor, were varied. An unexpected result was that after the phase-angle determination, with use of the nonhydrogen atom positional parameters, the highest peaks in a difference-Fourier synthesis corresponded to positions expected for methyl group protons and therefore these atom parameters were included in four additional cycles of least-squares refinement. The refinement converged (shift/esd < 0.1) to $R(F_o) = 0.038$, $R(F_o^2) = 0.042$, and $R_w(F_o^2) = 0.063$[11] for all 1956 unique reflections. The location and refinement of all 15 methyl group protons were an unexpected and pleasing dividend to the structure solution. It appears likely that the lack of methyl group disorder is almost certainly due to crystal-packing forces. The importance of these hydrogen atoms in the structure analysis is illustrated by the following observation. Structural refinement without hydrogen atoms, followed by a calculation of interatomic distances, showed the C_5 ring C–C distances to vary from 1.415 (4) to 1.442 (4) Å. Inclusion of the methyl hydrogen atoms in the calculated model reduced this range of distances to 1.422 (3)–1.430 (3) Å and significantly decreased the agreement factor $R(F_o^2)$ by 0.029. Therefore, it appears that when small effects on the structural model of the light atom positions are examined, the inclusion of the hydrogen atoms, whenever possible, is a necessity even though C-H distances may not be precisely determined.

Scattering factor tables were taken from the "International Tables of X-ray Crystallography", and a correction for anomalous scattering was made for the iron atom. Interatomic distances and angles are listed in Table II. Final atomic parameters are given in Table III. A listing of observed and calculated structure factors is available as supplementary material.

Description of the Structure

An ORTEP plot of the molecule is presented in Figure 1. As expected, the structure consists of discrete molecules of the dimer $[(C_5Me_5)Fe(CO)_2]_2$ with no unusually short intermolecular contacts. The pentamethylcyclopentadienyl fragment is bound in a η^5 manner, and there are two terminal and two symmetrically bridging carbonyl ligands. The Cp rings are "trans" with respect to each other. There is a crystallographic center of symmetry midway between the Fe atoms which are separated by a distance of 2.560 (1) Å. This distance is identical with the Fe–Fe bond bridged by two carbonyl ligands in $Fe_3(CO)_9$,[10] 2.560 (6) Å, and can therefore be considered formally as a metal–metal single bond. The Fe–C(O) bond

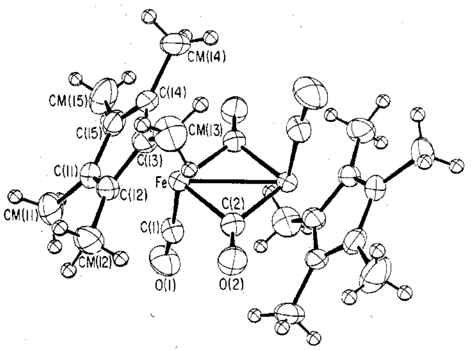

Figure 1. Drawing of the molecular configuration of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ as determined by X-ray diffraction showing the atom-labeling scheme. There is a center of symmetry at the midpoint of the Fe–Fe single bond (2.560 (1) Å). With the exception of the hydrogen atoms, which are drawn with isotropic temperature factors of 1.0 Å^2, the ellipsoids of thermal motion are scaled to enclose 50% probability.

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Table III. Final Positional[a] and Thermal[b,c] Parameters for $[(\eta^5\text{-Me}_5C_5)Fe(CO)_2]_2$

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.40691 (3)	0.47518 (3)	0.56803 (2)	0.0249 (2)	0.0305 (2)	0.0275 (2)	0.0022 (1)	0.0014 (1)	0.0009 (1)
C(1)	0.6657 (3)	0.3593 (3)	0.4204 (2)	0.036 (1)	0.041 (1)	0.041 (1)	−0.000 (1)	0.007 (1)	−0.001 (1)
C(2)	0.3716 (3)	0.4680 (2)	0.4301 (2)	0.032 (1)	0.036 (1)	0.033 (1)	0.000 (1)	0.001 (1)	0.002 (1)
O(1)	0.7182 (2)	0.2530 (2)	0.4079 (1)	0.062 (1)	0.042 (1)	0.032 (1)	0.015 (1)	0.018 (1)	−0.007 (1)
O(2)	0.2690 (2)	0.4409 (2)	0.3724 (1)	0.037 (1)	0.069 (1)	0.037 (1)	−0.013 (1)	−0.009 (1)	0.001 (1)
C(11)	0.2583 (3)	0.4157 (2)	0.6790 (2)	0.038 (1)	0.046 (1)	0.033 (1)	0.002 (1)	0.011 (1)	0.006 (1)
C(12)	0.2197 (3)	0.3349 (2)	0.5962 (2)	0.028 (1)	0.036 (1)	0.041 (1)	−0.002 (1)	0.004 (1)	0.008 (1)
C(13)	0.3600 (3)	0.2602 (2)	0.5750 (2)	0.034 (1)	0.029 (1)	0.045 (1)	0.002 (1)	0.005 (1)	0.006 (1)
C(14)	0.4840 (3)	0.2946 (2)	0.6457 (2)	0.030 (1)	0.043 (1)	0.046 (1)	0.005 (1)	0.006 (1)	0.020 (1)
C(15)	0.4215 (3)	0.3913 (3)	0.7097 (2)	0.040 (1)	0.056 (2)	0.029 (1)	−0.008 (1)	−0.000 (1)	0.011 (1)
CM(11)	0.1418 (4)	0.5015 (4)	0.7311 (2)	0.060 (2)	0.069 (2)	0.051 (2)	0.013 (2)	0.027 (2)	0.002 (2)
CM(12)	0.0597 (3)	0.3198 (3)	0.5446 (2)	0.033 (1)	0.058 (2)	0.063 (2)	−0.005 (1)	−0.003 (1)	0.008 (1)
CM(13)	0.3640 (5)	0.1533 (3)	0.4989 (3)	0.063 (2)	0.037 (2)	0.072 (2)	−0.003 (1)	0.012 (2)	−0.005 (1)
CM(14)	0.6460 (3)	0.2293 (4)	0.6556 (3)	0.037 (2)	0.069 (2)	0.079 (2)	0.012 (1)	0.001 (2)	0.036 (2)
CM(15)	0.5068 (5)	0.4500 (5)	0.7979 (2)	0.070 (2)	0.108 (3)	0.035 (2)	−0.028 (2)	−0.008 (1)	0.012 (2)

atom	*x*	*y*	*z*	*U*, Å^2	atom	*x*	*y*	*z*	*U*, Å^2
H(111)	0.067 (5)	0.548 (4)	0.690 (3)	5.1 (9)	H(133)	0.316 (5)	0.183 (4)	0.439 (3)	6.0 (11)
H(112)	0.097 (5)	0.451 (4)	0.776 (3)	5.0 (9)	H(141)	0.719 (6)	0.293 (4)	0.685 (3)	6.6 (11)
H(113)	0.209 (5)	0.582 (5)	0.771 (3)	5.9 (9)	H(142)	0.648 (4)	0.167 (4)	0.703 (3)	3.9 (8)
H(121)	0.015 (4)	0.234 (4)	0.560 (2)	4.6 (8)	H(143)	0.695 (6)	0.196 (4)	0.597 (4)	7.1 (12)
H(122)	−0.020 (5)	0.391 (4)	0.563 (2)	4.8 (8)	H(151)	0.490 (7)	0.546 (6)	0.803 (4)	9.7 (18)
H(123)	0.063 (4)	0.323 (3)	0.478 (3)	3.6 (7)	H(152)	0.607 (7)	0.461 (4)	0.794 (3)	6.0 (12)
H(131)	0.313 (4)	0.081 (4)	0.514 (2)	3.3 (7)	H(153)	0.488 (5)	0.402 (4)	0.844 (3)	5.3 (10)
H(132)	0.466 (7)	0.129 (5)	0.485 (3)	7.9 (13)					

[a] The fractional coordinates are *x*, *y*, and *z*. [b] Anisotropic temperature factors are of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2a^*b^*U_{12}hk + \ldots)]$. [c] Isotropic thermal parameters were refined for the hydrogen atoms.

lengths are shorter by ~0.1 Å (terminal) and ~0.3 Å (bridging) in $[MpFe(CO)_2]_2$ than in $Fe_3(CO)_{12}$. Conversely, the Fe–C(Mp) average distance is 0.1 Å longer than the average Fe–C distance reported for ferrocene.[11] This result is not unexpected[12] and reflects the ability of carbonyl ligands to bond more strongly to transition metals than that of Cp or Mp ligands. The average C(ring)–C(ring) bond length, 1.427 (2) Å, agrees favorably with that reported for ferrocene[11] (1.43 (5) Å) but is significantly shorter than the average C–Me bond length (1.498 (2) Å), reflecting the difference between an sp^2–sp^2 and an sp^2–sp^3 bond. As expected, the C–H bonds are systematically short (C–H(av) = 0.94 (2) Å), illustrating the influence of the C–H bond electron density on the observed hydrogen positions.

Except for the methyl group constituents $[MpFe(CO)_2]_2$ is isostructural with its unsubstituted analogue $[CpFe(CO)_2]_2$. A comparison of the structural geometry of the title compound with that derived from a recent high-precision low-temperature X-ray and neutron diffraction study[14] on the unsubstituted complex shows striking similarities (vide infra).

The addition of five methyl groups to each Cp ring might be expected to noticeably influence interatomic distances in the remainder of the molecule. Presumably the inductive effect of these groups could increase the electron density on the metal atom, thereby altering metal–carbonyl and C–O distances by changing the magnitude of back-donation to carbonyl antibonding orbitals. In fact this effect is not observed, and the Fe–CO and C–O distances are identical within limits of error to those found in $[CpFe(CO)_2]_2$. The metal–metal distance is larger by 0.019 (1) Å in the pentamethyl complex, but this is hardly structurally significant since the two studies were conducted at different temperatures. A small difference is also observed in the distances between the cyclopentadienyl ring center (Ω) and the Fe atom. The average Fe–C (2.144 (9) Å) and Fe–Ω (1.764 (1) Å) distances, respectively, are only very slightly longer than the corresponding distances in $[CpFe(CO)_2]_2$ (2.131 (8) and 1.753 (1) Å). Although some of this marginally significant difference may be due to the different temperatures at which the two data sets were collected, it may also reflect a subtle chemical difference between the two complexes. The five methyl carbon atoms of the Me_5C_5 moiety are not coplanar with the five-membered ring. This is often observed in permethylated-Cp ring complexes.[15] The perpendicular distance between the methyl group carbon atoms plane and the Fe atom is 1.878 (1) Å (see Table IV).

Table IV. Equations of "Best" Least-Squares Planes and Perpendicular Distances (Å) from These Planes[a]

(A) Plane I, through the Five Ring Carbon Atoms

$$0.3204x + 0.7435y - 0.5870z + 1.9447 = 0$$

C(11)	0.000 (2)	C(14)	−0.003 (2)
C(12)	−0.002 (2)	C(15)	0.002 (2)
C(13)	0.003 (2)	Fe[b]	1.764 (1)

(B) Plane II, through the Five Methyl Group Carbon Atoms

$$0.3206x + 0.7390y - 0.5925z + 2.1217 = 0$$

CM(11)	−0.019 (3)	CM(14)	−0.013 (4)
CM(12)	0.011 (3)	CM(15)	0.020 (4)
CM(13)	0.001 (3)	Fe[b]	1.878 (1)

(C)[c] Plane III, through C(1), O(1), Fe, C(1)′, O(1)′, Fe′

$$-0.7085x - 0.1977y - 0.6774z + 8.3644 = 0$$

C(1)	−0.004 (2)	C(1)′	0.004 (2)
O(1)	0.002 (2)	O(1)′	−0.002 (2)
Fe	−0.001 (1)	Fe′	0.001 (1)

[a] The equations of these planes are expressed in the triclinic fractional coordinates *x*, *y*, and *z*. [b] Assigned a weight of zero. [c] Primed atoms are related by a center of symmetry.

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(15) After submission of this paper Byers and Dahl (Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 1) reported the crystal structure of $Co[\eta^5\text{-}C_5(CH_3)_5](CO)_2$. It was noted that the methyl substituents effectively anchor the carbon atoms of the cyclopentadienyl ring, allowing their accurate locations. The salient feature of this structure determination is the observation of an allyl–ene geometry of the C_5 ring, consistent with the domination of the e$^-$ molecular orbital.

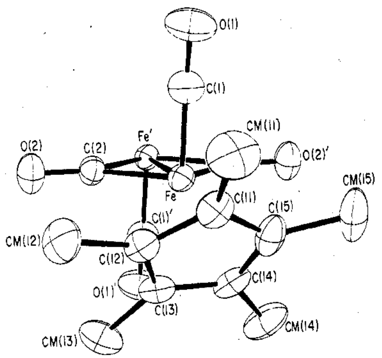

Figure 2. The (η^5-C_5C_5)$Fe_2(CO)_4$ fragment of [(η^5-C_5Me_5)$Fe(CO)_2]_2$ as viewed along the Fe–Fe bond. Note that the Fe–C(1) and C(11)–Ω (Ω = Cp ring centroid) vectors are eclipsed (dihedral angle = 4.2°). The ellipsoids of thermal motion are scaled to enclose 50% probability.

As in other Mp complexes one hydrogen atom of each methyl group is exo to the metal atom.[14]

The orientations of the cyclopentadienyl rings are very similar in the two complexes. The centroids of the C_5 rings, the iron atoms, and the terminal carbonyl carbon atoms are planar, and the angle between this plane and the C_5 plane of the Mp group is 91.4 (2)° in $[MpFe(CO)_2]_2$. One important difference between the two structures is that in the title compound the terminal carbonyl ligand is eclipsed with respect to C(11) (the C(11)–Ω–Fe–CO dihedral angle is 4.6 (2)°) rather than staggered (see Figure 2). There is an approximate mirror plane through C(11), the midpoint of C(13)–C(14), and the metal atom just as is observed in $[CpFe(CO)_2]_2$. In the above-mentioned low-temperature study[12] of the unsubstituted dimer a variation in bond lengths in the cyclopentadienyl fragment was attributed to the dominance of the e^+ molecular orbital (antisymmetric with respect to the mirror plane) because the observed variations were consistent with the symmetry of this molecular orbital. This pattern of bond lengths in the Cp fragment is consistent with a "diolefin" ring geometry. In the permethylated dimer the presence of the methyl groups, and likely differences in stuctural packing effects, has apparently reduced the thermal motion of the ring carbon atoms. The result is much the same as if the temperature were lowered, thus enabling us to examine small variations in C(ring)–C(ring) bond lengths.[15] (In this case 3σ = 0.013 Å for a C(ring)–C(ring) bond comparisons.) We do not observe any such variation, however. The range of C–C distances within the ring is quite small (1.422 (3)–1.431 (3) Å), and even the small fluctuations present do not reflect the symmetry of the molecular mirror plane and hence are not consistent with dominance of the e^+ (or e^-) molecular orbital. We therefore conclude that if the fluctuations noted in the structure of $[CpFe(CO)_2]_2$ do indeed stem from electronic effects, the presence of methyl groups in the titular complex has altered these effects. It is equally probable, however, that the methyl groups have effectively "masked" the fivefold symmetry of the C_5 ring and have mainly altered the packing forces within the lattice.[16]

The issue of distortions in cyclopentadienyl ligands remains an open question. While it is unquestionably true that electron localization within the π-network can cause distortions, the magnitude and observability of these distortions remains unknown.[17] It may be that the energies associated with these distortions are small compared to packing forces or other subtle electronic effects.

Acknowledgment. We wish to thank H. M. Feder and J. W. Rathke of the Argonne Chemical Engineering Division for helpful discussions and D. Slocum, J. Bencini, and S. Diviaj of Southern Illinois University, Carbondale, IL, for supplying the compound.

Registry No. $[MpFe(CO)_2]_2$, 12132-03-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(16) It was suggested by one reviewer that the eclipsed orientation of the terminal Fe–CO with respect to the Mp ring has removed any preference toward the e^+, or e^-, molecular orbital.

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Vibrational Study of Layered MPX_3 Compounds and of Some Intercalates with $Co(\eta^5\text{-}C_5H_5)_2^+$ or $Cr(\eta^6\text{-}C_6H_6)_2^+$

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Received November 28, 1979

Raman (10–800 cm^{-1}) and IR (10–4000 cm^{-1}) spectra of layered compounds represented by the general formula MPX_3 where M = Mn, Cd, or Zn and X = S or Se have been recorded in the 300–10 K temperature range. $MnPS_3$ and $CdPS_3$ compounds intercalated with $Co(\eta^5\text{-}C_5H_5)_2^+$ and $Cr(\eta^6\text{-}C_6H_6)_2^+$ cations, corresponding to formula $MPS_3{\cdot}0.33(\pi\text{-}R)_2\mathcal{M}$, were investigated under the same conditions. Host lattice vibrations give rise to a pattern characteristic of the PS_3 entity and are not strongly perturbed by intercalated molecules. New low-frequency bands observed for the Mn compounds can be interpreted in terms of a different unit cell multiplicity. Guest ion frequencies are practically the same as those of their iodide salts, which indicates weak interactions between cations and host lattices. Finally, polarized infrared spectra of platelets show that $(\pi\text{-}R)_2\mathcal{M}^+$ ion rings are oriented perpendicular to (00*l*) host lattice layer planes.

Introduction

This work has been undertaken as a part of a general vibrational study of layered compounds able to intercalate guest molecules or ions. It has been shown for different superionic conductors of the β-alumina type that infrared and Raman spectroscopies yield a wealth of information concerning structures and dynamics of guest ions such as H_3O^+, NH_4^+, Na^+, Ag^+, ...[1-3] Most of the compounds represented by the

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0020-1669/80/1319-2773$01.00/0