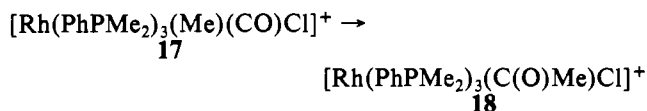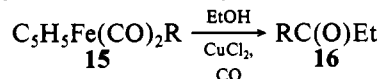rapid alkyl–acyl interconversion of the cationic Rh(III) complexes **17** → **18**,[34] and the facile acyl formation of **1** observed in this study indicate that the formal charge on the metal also plays an important role in methyl migration.

$$C_5H_5Fe(CO)_2R \xrightarrow[\substack{CuCl_2, \\ CO}]{EtOH} RC(O)Et$$
$$\quad\quad\mathbf{15} \quad\quad\quad\quad\quad\quad \mathbf{16}$$

$$[Rh(PhPMe_2)_3(Me)(CO)Cl]^+ \rightarrow$$
$$\mathbf{17}$$
$$\quad\quad\quad\quad [Rh(PhPMe_2)_3(C(O)Me)Cl]^+$$
$$\quad\quad\quad\quad\quad\quad \mathbf{18}$$

Steric Control of the Site Preference in Five-Coordinate Iron Carbonyl Derivatives: Molecular Structures of (η^2-Diethyl fumarate)(triphenylphosphine)tricarbonyliron, Fe(CO)$_3$(PPh$_3$)(DEF), and (η^2-Diethyl maleate)(triphenylphosphine)tricarbonyliron, Fe(CO)$_3$(PPh$_3$)(DEM)

MATTHEW V. R. STAINER and JOSEF TAKATS*

The structures of Fe(CO)$_3$(PPh$_3$)(DEF) and Fe(CO)$_3$(PPH$_3$)(DEM) (Ph = C$_6$H$_5$, DEF = diethyl fumarate, DEM = diethyl maleate) have been determined by single-crystal X-ray diffraction techniques. The crystals of Fe(CO)$_3$(PPh$_3$)(DEF) are monoclinic, space group C2/c, with unit cell constants a = 17.674 (4) Å, b = 16.551 (4) Å, c = 19.491 (6) Å, β = 91.98 (2)°, and Z = 8. Fe(CO)$_3$(PPh$_3$)(DEM) crystallizes in triclinic space group P$\bar{1}$ with unit cell constants a = 14.792 (21) Å, b = 10.420 (1) Å, c = 10.807 (2) Å, α = 112.41 (1)°, β = 65.89 (1)°, γ = 90.51 (1)°, and Z = 2. Full-matrix least-squares refinement of the structures with 3541 and 3119 unique reflections $(F_o^2 \geq 3(\sigma F_o))^2)$ led to final discrepancy indexes of R = 0.056, R_w = 0.073 and R = 0.053, R_w = 0.064 for Fe(CO)$_3$(PPh$_3$)(DEF) and Fe(CO)$_3$(PPh$_3$)(DEM), respectively. Both molecular structures are based on the trigonal bipyramid with the olefin bonded in an equatorial position, as is expected from electronic considerations. The PPh$_3$ ligand occupies an axial site in the maleate complex, while in the fumarate derivative it coordinates in the electronically less favored equatorial site. The unexpected equatorial disposition of the phosphine ligand in Fe(CO)$_3$(PPh$_3$)(DEF) is assigned to the steric hindrance caused by the trans substituents of the DEF moiety at the axial sites of the trigonal bipyramid. The Fe–CO and Fe–C(olefin) distances appear to reflect the relative π acidity of the coordinated olefins. This is also borne out by the degree of deformation of the olefinic ligands. Noteworthy is the fact that, whereas in the DEF moiety both substituents are almost coplanar with the plane of the olefin, in the DEM ligand only one substituent is oriented in this fashion; the other is approximately perpendicular to this. The resulting asymmetric nature of this olefin is reflected in the M–C(olefin) distances; the bond to the carbon bearing the π-acceptor substituent is longer.

Introduction

The elucidation of the coordination geometry of five-coordinate transition-metal complexes and the distribution of ligands on the coordination sphere have formed the basis of several theoretical studies[1,2] and a multitude of physical, mainly X-ray diffraction, investigations.[3] It is now well established that, for d^8 metal complexes containing nominally monodentate ligands, the geometry is based overwhelmingly on the trigonal bipyramid. In a very broad treatment, Hoffmann and Rossi[1] have established the electronic site preference of ligands and their influence on the metal–ligand bond distances in five-coordinate molecules. However, these authors readily recognized that the geometry of metal complexes is influenced not only by electronic factors but by steric effects as well.

During our studies on the fluxional behavior of Fe(CO)$_4$-(olefin) derivatives[4a] we prepared a series of complexes of the

type Fe(CO)$_3$(PR$_3$)(olefin)[4b] (PR$_3$ = PPh$_3$, PMe$_2$Ph, P-(OMe)$_3$; olefin = diethyl fumarate, diethyl maleate). Since the compounds contain significantly different ligands, their structures could in principle shed light on the relative importance of steric and electronic factors in determining the positioning of ligands on pentacoordinate, trigonal-bipyramidal molecules. Furthermore, infrared spectroscopy seemed to indicate that the fumarate and maleate complexes belonged to different isomeric classes, and this gave added impetus to determine the solid-state structure of a member of each class. Here we report the single-crystal X-ray structure determination of Fe(CO)$_3$(PPh$_3$)(DEF) and Fe(CO)$_3$(PPh$_3$)(DEM).

Experimental Section

(Diethyl fumarate)- and (diethyl maleate)(triphenylphosphine)-tricarbonyliron, Fe(CO)$_3$(PPh$_3$)(DEF) and Fe(CO)$_3$(PPh$_3$)(DEM), were prepared by prolonged photolysis of Fe(CO)$_4$(PPh$_3$) in the presence of excess olefin. Chromatography on alumina followed by crystallization from CH$_2$Cl$_2$/pentane affords the pure complexes as yellow crystals suitable for single-crystal X-ray diffraction studies.[4b]

Crystals of the complexes were sealed in thin-walled glass capillaries and aligned on a Picker FACS-1 automated diffractometer. A summary of the data collection is given in Table I.

The intensity data were processed in the usual manner, but because of the regular crystal shapes and small linear absorption coefficients,

(1) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.
(2) Demuynck, J.; Strich, A.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 217.
(3) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227.
(4) (a) Kruczynski, L.; LiShing Man, L. K. K.; Takats, J. *J. Am. Chem. Soc.* **1974**, *96*, 4006. (b) Gittawong, S.; LiShing Man, L. K. K.; Takats, J., unpublished results.
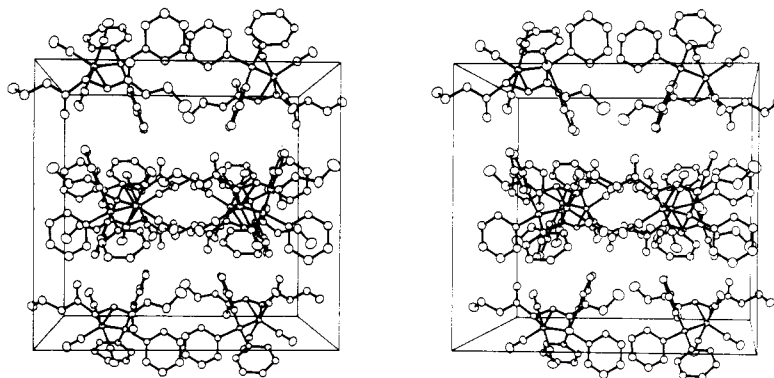(5) Dodens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

Figure 1. Stereoview (ORTEP) of the molecular packing in Fe(CO)₃(PPh₃)(DEF), 20% probability ellipsoids. The *a* axis is horizontal from left to right, the *b* axis runs top to bottom, and the *c* axis goes into the page.

Figure 2. Stereoview (ORTEP) of the molecular packing in Fe(CO)₃(PPh₃)(DEM), 20% probability ellipsoids. The *a* axis is horizontal from left to right, the *b* axis runs top to bottom, and the *c* axis goes into the page.
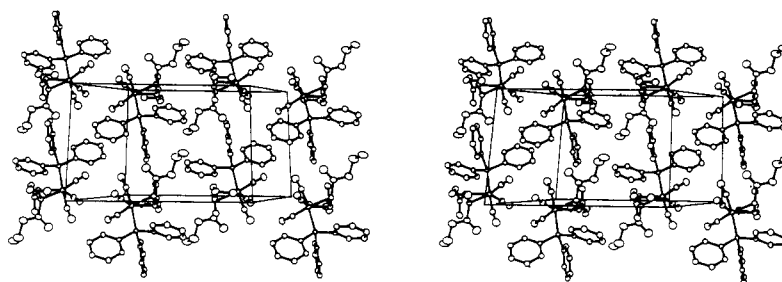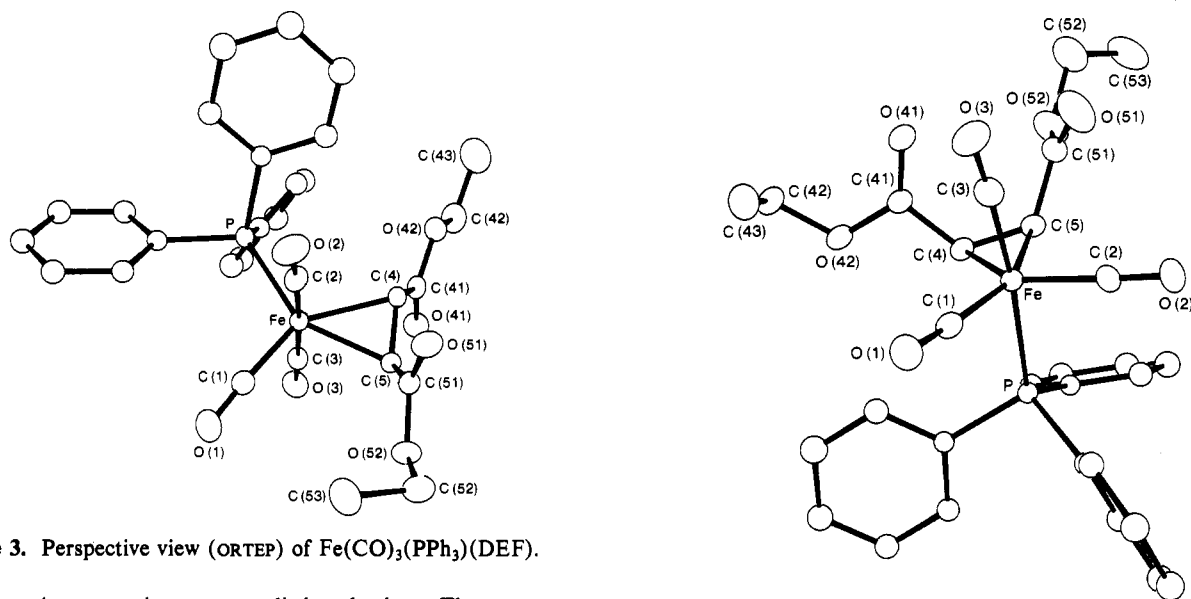

Figure 3. Perspective view (ORTEP) of Fe(CO)₃(PPh₃)(DEF).

Figure 4. Perspective view (ORTEP) of Fe(CO)₃(PPh₃)(DEM).

no absorption corrections were applied to the data. The structures were solved by a combination of Patterson and difference-Fourier syntheses and full-matrix least-squares refinement.[6] Atomic scattering factors were taken from Cromer and Waber's tabulations[7] for all atoms except hydrogen for which the values of Stewart et al.[8] were used. Anomalous dispersion terms were included for the iron atom.[9] The carbon atoms of the phenyl rings of the phosphine ligand were refined

as rigid bodies under D_{6h} symmetry with C–C distances of 1.392 Å and individually assigned isotropic temperature factors. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The olefinic hydrogen atoms were located from a difference-Fourier map and were refined isotropically. The remaining hydrogen atoms, with the exception of the methyl hydrogens, were included at their idealized positions. The final models converged to $R = 0.056$ and $R_w = 0.073$[10] for the fumarate complex and $R = 0.053$ and $R_w = 0.064$ for the maleate complex.

The final positional parameters of the refined nongroup atoms for the fumarate and maleate complexes are given in Tables II and III, respectively. The anisotropic thermal parameters, positional and thermal parameters of the rigid phenyl groups and the remaining

(6) Besides locally written programs, the following were used in solution and refinement of the structure: FORDAP, Fourier summation program by A. Zalkin; SFLS-5, structure factor and least-squares refinement by C. J. Prewit; ORFFE, calculation of bond lengths and angles by W. Busing and H. A. Levy; ORTEP, thermal ellipsoid plotting program by C. K. Johnson.

(7) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

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

(9) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(10) $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and $w = 1/\sigma^2(F_o^2)$.

Table I. Summary of Crystal Data and Intensity Data Collection for Fe(CO)₃(PPh₃)(olefin) (olefin = DEF, DEM)

compd	$Fe(CO)_3(PPh_3)(DEF)$	$Fe(CO)_3(PPh_3)(DEM)$
formula	$FePO_7C_{29}H_{27}$	$FePO_7C_{29}H_{27}$
space group	$C2/c$ (C_{2h}^6, No. 15)	$P\bar{1}$ (C_i^1, No. 2)
cell parameters^a		
a, Å	17.674 (4)	14.792 (2)
b, Å	16.551 (4)	10.420 (1)
c, Å	19.491 (6)	10.807 (2)
α, deg	90.0	112.41 (1)
β, deg	91.98 (2)	65.89 (1)
γ, deg	90.0	90.51 (1)
Z	8	2
temp, °C	22	22
radiation	Mo Kα, graphite monochromated	Mo Kα, Zr filtered
receiving aperture	6 mm × 6 mm, 30 cm from cryst	5.5 mm × 5.5 mm, 30 cm from cryst
takeoff angle, deg	2.45	2.4
scan speed, deg min⁻¹	2	2 (2.5° ≤ 2θ ≤ 40°); 1 (40° < 2θ ≤ 49°)
scan range	1.0° below Kα₁ to 1.0° above Kα₂	1.0° below Kα₁ to 1.0° above Kα₂
bkgd counting at each scan limit, s	10 (2.5° < 2θ < 40°); 20 (40° < 2θ < 51°)	10 (2.5° ≤ 2θ ≤ 36°); 20 (36° < 2θ ≤ 49°)
2θ limits, deg	2.5–51.0	2.5–49.0
p factor^5	0.05	0.05
μ, cm⁻¹	6.24	5.86
unique data collected	5486	4926
unique data used ($F_o^2 \geq 3(\sigma(F_o))^2$)	3541	3119
final no. of parameters varied	225	226
error in observn of unit wt^b	1.852	1.513
R	0.056	0.053
R_w	0.073	0.064

^{a} Unit cell parameters were obtained by least-squares analysis of the setting angles of 12 carefully centered reflections chosen from diverse regions of reciprocal space. ^{b} Error in observation of unit weight $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v is the number of variable parameters.

Table II. Final Positional Parameters for Nongroup Atoms of Fe(CO)₃(PPh₃)(DEF)

atom	x^a	y	z	B, Å²
Fe	0.18188 (3)	0.00122 (4)	-0.14563 (3)	
P	0.26807 (7)	-0.02345 (6)	-0.22702 (6)	
C(1)	0.0985 (3)	-0.0549 (3)	-0.1635 (3)	
C(2)	0.1464 (3)	0.0823 (3)	-0.1992 (2)	
C(3)	0.2167 (3)	-0.0834 (3)	-0.0954 (3)	
O(1)	0.0432 (2)	-0.0896 (3)	-0.1719 (2)	
O(2)	0.1234 (3)	0.1312 (3)	-0.2353 (2)	
O(3)	0.2331 (3)	-0.1389 (2)	-0.0636 (2)	
C(4)	0.2315 (3)	0.0862 (3)	-0.0788 (2)	
C(5)	0.1608 (3)	0.0594 (3)	-0.0543 (2)	
C(41)	0.3013 (3)	0.0612 (3)	-0.0418 (2)	
C(51)	0.0944 (3)	0.1121 (3)	-0.0580 (2)	
O(41)	0.3078 (2)	0.0075 (2)	-0.0007 (2)	
O(42)	0.3601 (2)	0.1076 (2)	-0.0593 (2)	
O(51)	0.0896 (2)	0.1772 (2)	-0.0851 (2)	
O(52)	0.0373 (2)	0.0778 (2)	-0.0248 (2)	
C(42)	0.4328 (3)	0.0885 (4)	-0.0252 (3)	
C(43)	0.4880 (4)	0.1494 (6)	-0.0486 (5)	
C(52)	-0.0357 (3)	0.1180 (4)	-0.0282 (3)	
C(53)	-0.0808 (4)	0.0882 (4)	-0.0900 (4)	
H(4)	0.235 (2)	0.137 (2)	-0.094 (2)	3.0 (8)
H(5)	0.161 (2)	0.026 (2)	-0.016 (2)	2.7 (8)

^{a} Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

hydrogen atoms, and a listing of the observed and calculated structure factor amplitudes are available as supplementary material.

Table III. Positional Parameters for Nongroup Atoms of Fe(CO)₃(PPh₃)(DEM)

atom	x	y	z	B, Å²
Fe	0.20929 (6)	0.06026 (7)	0.45766 (8)	
P	0.24286 (9)	0.2710 (1)	0.4462 (1)	
C(1)	0.0870 (4)	0.1501 (5)	0.6004 (6)	
C(2)	0.2069 (4)	-0.0072 (5)	0.2802 (6)	
C(3)	0.1673 (4)	-0.0919 (6)	0.4884 (7)	
O(1)	0.0056 (3)	0.1994 (5)	0.6911 (5)	
O(2)	0.2076 (4)	-0.0535 (5)	0.1658 (5)	
O(3)	0.1299 (4)	-0.1796 (5)	0.5150 (6)	
C(4)	0.3190 (4)	0.0630 (6)	0.5315 (6)	
C(5)	0.3573 (4)	-0.0246 (6)	0.3776 (7)	
C(41)	0.2940 (4)	0.0088 (6)	0.6476 (7)	
C(51)	0.3877 (5)	-0.1806 (6)	0.3122 (7)	
O(41)	0.2938 (3)	-0.1142 (4)	0.6267 (5)	
O(42)	0.2665 (3)	0.1153 (4)	0.7816 (5)	
O(51)	0.3416 (4)	-0.2696 (5)	0.2736 (7)	
O(52)	0.4796 (4)	-0.2124 (5)	0.2937 (6)	
C(42)	0.2223 (6)	0.0821 (7)	0.9117 (8)	
C(43)	0.1132 (6)	0.0744 (8)	0.9580 (9)	
C(52)	0.5244 (8)	-0.3650 (8)	0.228 (1)	
C(53)	0.6026 (8)	-0.4032 (9)	0.088 (1)	
H(4)	0.339 (4)	0.149 (6)	0.554 (6)	4 (1)
H(5)	0.402 (4)	0.007 (6)	0.325 (7)	3 (2)

Description of the Structures

The crystal-packing diagrams for the two structures are shown in Figures 1 and 2. The crystal structures of Fe-(CO)₃(PPh₃)(DEF) and Fe(CO)₃(PPh₃)(DEM) consist of discrete molecular units with no unusual intermolecular contacts. The molecular structures of the two complexes are shown in Figures 3 and 4 and are based on the expected trigonal-bipyramidal coordination geometry about the central iron atom. In both compounds the olefin is coordinated in an equatorial position and is tilted such that the carbon–carbon double bond makes an angle of 7.3 and 6.0° for the maleate and fumarate, respectively, with the plane formed by the remaining equatorial ligands and the iron atom. Similar tilting of the olefinic ligand is commonly found in structures of metal olefin complexes (for references see Table VIII).

The most interesting feature of the two molecular structures is the site occupied by the triphenylphosphine ligand. The maleate complex has the phosphine in an axial position while in the fumarate complex it is coordinated in an equatorial site.

The bond lengths and interbond angles for the two complexes are listed in Tables IV and V.

Discussion

Primarily on the basis of symmetry and overlap arguments, Rossi and Hoffmann[1] have shown that, for d⁸ trigonal-bipyramidal transition-metal complexes, the stronger σ-donor ligand would preferentially occupy an axial site while the stronger π-acceptor ligand would be found in an equatorial position. These conclusions have received ample experimental verification mainly from X-ray crystallographic studies on numerous five-coordinate molecules. Thus in Fe(CO)₄L complexes where L is a stronger σ donor and weaker π acceptor than CO such as PPh₃,[11] pyridine,[12] or CN⁻[13] axial coordination of L is observed. The relative σ-donor and π-acceptor strength of an olefin with respect to CO clearly depends on the type of olefin under investigation. Nevertheless, structural studies on Fe(CO)₄(olefin) type complexes have invariably found the olefinic ligand to occupy an equatorial site with the carbon–carbon double bond approximately in the equatorial plane (for references see Table VIII). This mode

(11) Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159.
(12) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.
(13) Gadfield, S. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 770.

Table IV. Bond Lengths and Bond Angles in Fe(CO)₃(PPh₃)(DEF)

(i) Bond Lengths (Å)

Fe-P	2.274 (1)		
Fe-C(1)	1.766 (5)	C(1)-O(1)	1.141 (6)
Fe-C(2)	1.800 (5)	C(2)-O(2)	1.137 (6)
Fe-C(3)	1.805 (5)	C(3)-O(3)	1.140 (6)
C(4)-C(5)	1.423 (6)		
Fe-C(4)	2.088 (4)	Fe-C(5)	2.069 (5)
C(4)-C(41)	1.467 (6)	C(5)-C(51)	1.462 (7)
C(4)-H(4)	0.90 (4)	C(5)-H(5)	0.92 (4)
C(41)-O(41)	1.201 (5)	C(51)-O(51)	1.202 (5)
C(41)-O(42)	1.345 (6)	C(51)-O(52)	1.343 (5)
O(42)-C(42)	1.462 (6)	O(52)-C(52)	1.452 (6)
C(42)-C(43)	1.486 (9)	C(52)-C(53)	1.504 (8)
P-C(11)	1.841 (2)	P-C(31)	1.838 (3)
P-C(21)	1.838 (2)		

(ii) Bond Angles (Deg)

P-Fe-C(1)	110.0 (2)	C(2)-Fe-C(3)	177.2 (2)
P-Fe-C(2)	87.6 (2)	C(2)-Fe-C(4)	89.4 (2)
P-Fe-C(3)	90.8 (2)	C(2)-Fe-C(5)	94.7 (2)
P-Fe-C(4)	106.2 (1)	C(3)-Fe-C(4)	93.2 (2)
P-Fe-C(5)	146.0 (1)	C(3)-Fe-C(5)	87.8 (2)
C(1)-Fe-C(2)	90.4 (2)	C(4)-Fe-C(5)	40.0 (2)
C(1)-Fe-C(3)	88.0 (2)	Fe-C(1)-O(1)	176.4 (5)
C(1)-Fe-C(4)	143.7 (2)	Fe-C(2)-O(2)	177.0 (5)
C(1)-Fe-C(5)	103.9 (2)	Fe-C(3)-O(3)	174.7 (5)
Fe-C(4)-C(5)	69.3 (2)	Fe-C(5)-C(4)	70.7 (3)
Fe-C(4)-C(41)	116.4 (3)	Fe-C(5)-C(51)	113.8 (3)
Fe-C(4)-H(4)	118 (3)	Fe-C(5)-H(5)	114 (3)
C(5)-C(4)-C(41)	118.7 (4)	C(4)-C(5)-C(51)	120.7 (4)
C(5)-C(4)-H(4)	118 (2)	C(4)-C(5)-H(5)	118 (2)
C(41)-C(4)-H(4)	111 (2)	C(51)-C(5)-H(5)	112 (2)
C(4)-C(41)-O(41)	126.6 (5)	C(5)-C(51)-O(51)	126.9 (4)
C(4)-C(41)-O(42)	111.1 (4)	C(5)-C(51)-O(52)	109.8 (4)
O(41)-C(41)-O(42)	122.4 (5)	O(51)-C(51)-O(52)	123.3 (4)
C(41)-O(42)-C(42)	115.9 (4)	C(51)-O(52)-C(52)	117.7 (4)
O(42)-C(42)-C(43)	106.8 (5)	O(52)-C(52)-C(53)	109.4 (5)
C(11)-P-C(21)	102.1 (1)	Fe-P-C(11)	116.5 (10)
C(11)-P-C(31)	102.2 (1)	Fe-P-C(21)	115.0 (10)
C(21)-P-C(31)	104.6 (1)	Fe-P-C(31)	114.7 (12)

Table V. Bond Lengths and Bond Angles in Fe(CO)₃(PPh₃)(DEM)

(i) Bond Lengths (Å)

Fe-P	2.286 (1)		
Fe-C(1)	1.783 (6)	C(1)-O(1)	1.157 (6)
Fe-C(2)	1.788 (6)	C(2)-C(2)	1.139 (6)
Fe-C(3)	1.796 (6)	C(3)-O(3)	1.134 (6)
C(4)-C(5)	1.415 (8)		
Fe-C(4)	2.077 (5)	Fe-C(5)	2.056 (5)
C(4)-C(41)	1.479 (7)	C(5)-C(51)	1.490 (7)
C(4)-H(4)	0.92 (5)	C(5)-H(5)	0.83 (6)
C(41)-O(41)	1.214 (6)	C(51)-O(51)	1.194 (7)
C(41)-O(42)	1.340 (6)	C(51)-O(52)	1.318 (7)
O(42)-C(42)	1.462 (7)	O(52)-C(52)	1.498 (8)
C(42)-C(43)	1.493 (11)	C(52)-C(53)	1.380 (11)
P-C(11)	1.842 (3)	P-C(31)	1.846 (3)
P-C(21)	1.826 (3)		

(ii) Bond Angles (Deg)

P-Fe-C(1)	87.8 (2)	C(2)-Fe-C(3)	91.7 (3)
P-Fe-C(2)	91.9 (2)	C(2)-Fe-C(4)	135.4 (2)
P-Fe-C(3)	172.2 (2)	C(2)-Fe-C(5)	95.7 (2)
P-Fe-C(4)	88.2 (1)	C(3)-Fe-C(4)	94.1 (2)
P-Fe-C(5)	94.7 (2)	C(3)-Fe-C(5)	91.7 (2)
C(1)-Fe-C(2)	109.6 (3)	C(4)-Fe-C(5)	40.0 (2)
C(1)-Fe-C(3)	84.5 (2)	Fe-C(1)-O(1)	175.3 (5)
C(1)-Fe-C(4)	114.9 (2)	Fe-C(2)-O(2)	177.9 (5)
C(1)-Fe-C(5)	154.5 (2)	Fe-C(3)-O(3)	172.5 (5)
Fe-C(4)-C(5)	69.2 (3)	Fe-C(5)-C(4)	70.8 (3)
Fe-C(4)-C(41)	114.2 (4)	Fe-C(5)-C(51)	119.4 (4)
Fe-C(4)-H(4)	110 (4)	Fe-C(5)-H(5)	119 (4)
C(5)-C(4)-C(41)	123.7 (5)	C(4)-C(5)-C(51)	124.1 (5)
C(5)-C(4)-H(4)	115 (4)	C(4)-C(5)-H(5)	113 (4)
C(41)-C(4)-H(4)	114 (4)	C(51)-C(5)-H(5)	108 (4)
C(4)-C(41)-O(41)	125.2 (5)	C(5)-C(51)-O(51)	128.3 (6)
C(4)-C(41)-O(42)	110.6 (4)	C(5)-C(51)-O(52)	110.0 (6)
O(41)-C(41)-O(42)	124.1 (5)	O(51)-C(51)-O(52)	121.7 (6)
C(41)-O(42)-C(42)	117.4 (5)	C(51)-O(52)-C(52)	118.1 (6)
O(42)-C(42)-C(43)	112.3 (6)	O(52)-C(52)-C(53)	110.5 (8)
C(11)-P-C(21)	103.3 (2)	Fe-P-C(11)	115.9 (11)
C(11)-P-C(31)	103.3 (2)	Fe-P-C(21)	113.9 (15)
C(21)-P-C(31)	103.9 (2)	Fe-P-C(31)	115.1 (11)

of coordination for an olefin is that found for all pentacoordinate d^8 transition-metal complexes and has been predicted also by Hoffmann et al.[1,14] and Veillard et al.[2] for olefins and other "single-faced" π-acceptor ligands. The ostensible reason for such ligand arrangement is that it provides for optimum π-back-bonding interactions. The electronically preferred arrangement of ligands for a complex of the type Fe(CO)₃(phosphine)(olefin) would therefore be axial phosphine and equatorial olefin. This disposition of ligands has been found for Fe(CO)₃(PPh₃)(MA)[15] (MA = methyl acrylate), and it is that observed for Fe(CO)₃(PPh₃)(DEM). However, the equatorial coordination of the phosphine in the fumarate complex is surprising. The anomaly can be satisfactorily rationalized if the importance of steric effects upon coordination geometry and the arrangement of the ligands are also recognized and taken into consideration. The olefin being a single-faced π-acceptor ligand is coordinated equatorially with its double bond lying roughly in the equatorial plane. If the phosphine ligand were now to be coordinated in either axial site, the trans arrangement of the substituents in the diethyl fumarate moiety would give rise to severe unfavorable steric interactions with the bulky phosphine. To avoid this situation, the phosphine prefers to occupy an equatorial position. Clearly, in this instance, steric effects dominate the electronic site preference in determining the final ligand arrangement in the molecule. It should be noted that in both the acrylate and maleate complexes the olefin substituents are directed toward the other side of the molecule away from the tri-

Table VI. Metal Carbonyl Bond Lengths (Å) for Some Trigonal-Bipyramidal Iron Carbonyl Complexes[a]

compd	Fe-C_{ax}	Fe-C_{eq}	ref
Fe(CO)₅			
X-ray	1.813 (2)	1.806 (3)	16
electron diff	1.806 (3)	1.833 (2)	17
[Fe(CO)₄(CN)]⁻	1.723 (8)	1.768 (8)	13
Fe(CO)₄(py)	1.772 (7)	1.805 (8)	12
Fe(CO)₄(pyr)	1.774 (4)	1.810 (4)	12
Fe(CO)₄(PHPh₂)	1.792 (8)	1.793 (9)	18
Fe(CO)₄(PPh₃)	1.795 (2)	1.795 (4)	11
[Fe(CO)₄]₂(C₈H₁₂)	1.805 (7)	1.782 (8)	19
Fe(CO)₄(C₁₂H₈)	1.812 (3)	1.793 (10)	20
[Fe(CO)₄]₂(DPF)	1.816 (6)	1.783 (6)	21
Fe(CO)₄(C₂F₄)	1.823 (10)	1.846 (10)	22
Fe(CO)₃(PPh₃)(MA)	1.784 (2)	1.781 (2)	15
Fe(CO)₃(PPh₃)(DEM)	1.796 (6)	1.786 (6)	this work
Fe(CO)₃(PPh₃)(DEF)	1.803 (5)	1.766 (5)	this work

[a] Abbreviations: py = pyridine, pyr = pyrazine, C₈H₁₂ = 1,5-cyclooctadiene, C₁₂H₈ = acenaphthylene, DPF = diphenylfulvene.

phenylphosphine ligand as to minimize steric repulsions in the compounds.

Rossi and Hoffmann[1] have evaluated also the relative strength of axial and equatorial bonds in trigonal-bipyramidal complexes. Their conclusions concerning d^8 metal compounds can be summarized as follows: Metal–ligand σ bonding results in stronger axial bonds. π donation will weaken the metal–ligand bonds, but greater weakening of the equatorial bonds is anticipated; on the other hand, π-acceptor ligands strengthen the metal–ligand bonding and do so more when the ligand occupies an equatorial site. As expected, the conclusions parallel the site preference arguments. The metal–carbonyl

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bond lengths for several trigonal-bipyramidal iron carbonyl complexes are given in Table VI. On the basis of electron diffraction studies, it appears that, in $Fe(CO)_5$, the axial metal–carbonyl bond is shorter than the equatorial one, although this is not borne out by the most recent X-ray analysis at low temperature.[16] Replacement of an axial CO with a better σ-donor and weaker π-acceptor ligand in general results in a shortening of both axial and equatorial bonds, as expected from the greater amount of back-bonding to the carbonyl ligands in these complexes. As the substitution is axial, the correlation between the electronic nature of the substituent and the M–CO distance is better for the axial carbonyl ligand (Fe–C distance decreases in the order 1.81, 1.793, 1.773, and 1.723 Å for L = CO, phosphine, amine, and cyanide) than for the equatorial carbonyl groups. In $Fe(CO)_4$(olefin) complexes the metal carbonyl distances reflect the relative π acidity of the olefinic ligands. Since the olefin occupies an equatorial position, it is the equatorial metal–carbonyl distances that are most affected by olefin substitution. In general, olefinic ligands are weaker π acids than carbon monoxide, and it is the equatorial carbonyls that are more tightly bonded to iron (cf. structures of $Fe(CO)_4$(1,5-cyclooctadiene),[19] -(acenaphthylene),[20] and -(diphenylfulvene)[21]). Only with the very strong π acceptor tetrafluoroethylene does the converse appear to be true.

In a discussion of the metal–carbonyl bond distances in $Fe(CO)_4(PPh_3)$(olefin) complexes, the distribution of ligands must also be considered. Ligand arrangement in the acrylate and maleate complexes is consistent with the electronic site preference arguments, and as a result, the molecules can be considered to be derivatives of $Fe(CO)_4PPh_3$. Therefore, in comparison of $Fe(CO)_4PPh_3$ with $Fe(CO)_3(PPh_3)$(olefin) (olefin = DEM, MA) little change would be expected in the axial metal–carbonyl bond lengths and the equatorial bonds would be expected to change, dependent on the relative π acidity of the olefin compared to that of CO. The expectations are borne out by the observed distances and indicate that diethyl maleate is comparable in π acidity to CO. The marginal increase in the metal–carbonyl distance from the acrylate to the maleate derivative confirms the view that the latter olefin is a better π acid than the former. In consideration of the fumarate complex our point of reference is an $Fe(CO)_4$(olefin) complex in which the equatorial bonds are almost always shorter than axial bonds. Substitution of an equatorial carbonyl in a $Fe(CO)_4$(olefin) complex by PPh_3, a weaker π acceptor than CO, should strengthen the π interaction between the metal and the sole remaining equatorial carbonyl and thus further shorten this bond length with respect to the axial metal–carbonyl distance. This is indeed what is observed. Finally, we note that the Fe–P distances in these complexes are similar to those found in $Fe(CO)_4PPh_3$[11] (2.244 (11) Å) and $Fe(CO)_3(PPh_3)(MA)$[15] (2.275 (1) Å). Surprisingly the equatorially substituted phosphine in the fumarate derivative has a marginally shorter Fe–P bond (2.274 (1) Å) than the phosphine ligand in the maleate complex, which occupies an axial site (2.286 (1) Å).

The geometrical changes of olefinic ligands upon coordination to a transition metal are well-known and can be satisfactorily explained, at least in a qualitative fashion, by the

Table VII. Angles (Deg) Describing the Geometry of the Coordinated Olefin[a]

		maleate	fumarate
δ	C(41)	105.9 (5)	109.6 (4)
	C(51)	113.0 (6)	106.8 (8)
	H(4)	103 (4)	111 (3)
	H(5)	113 (4)	108 (3)
γ	C(4)	151 (4)	139 (3)
	C(5)	133 (4)	145 (3)
β	C(4)	66 (3)	57 (2)
	C(5)	54 (3)	62 (2)
α		60 (4)	61 (3)

[a] δ and γ are torsion angles about the C(4)–C(5) bond. δ for the substituent atom C(41) is the torsion angle between the Fe–C(4) bond and the C(4)–C(41) bond. The idealized value of δ for no bending back of the olefin is therefore 90°. γ for C(4) is the torsion angle between the C(4)–C(41) and C(4)–H(4) bonds about the C(4)–C(5) bond. The idealized value of γ for no bending back is 180°. α is the angle between the normals to the planes defined by the substituent groups; β's are the angles between the olefin bond and the plane normals.
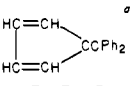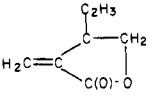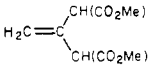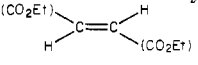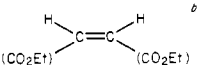
Dewar–Chatt–Duncanson bonding model.[23,24] The synergic σ donation from the filled π orbital of the olefin to the metal and π back-bonding from filled metal d orbitals into empty π* orbitals of the olefin result in a lengthening of the C–C distance and a bending back of the olefinic substituents out of the plane of the olefin away from the metal atom. Consistent trends between the geometry of the metal–olefin fragment and some property of the olefinic substituents are difficult to discern because of the many factors, often conflicting, that affect the bonding and hence the geometry. However, since it has been shown that in electron-rich Fe-(0)–olefin complexes the π component is the most important bonding factor,[25,26] the nonplanarity of the olefin and the metal–carbon and carbon–carbon distances are expected to reflect the π acidity of the olefin.

Although due to the paucity of precise structural data on Fe(0)–olefin complexes, a meaningful test for the degree of deformation of the coordinated olefin is not available; reference to the tabulation of Ittel and Ibers[27] shows that in electron-rich metal–olefin complexes, as predicted, the bending is least for hydrogen atoms, increases for ester and cyano groups, and is the greatest for halogen substituents. The values of α, β, γ, and δ[27] angles for $Fe(CO)_3(PPh_3)(DEF)$ and $Fe(CO)_3$-$(PPh_3)(DEM)$ are listed in Table VII. In the fumarate complex the δ angles are not too dissimilar for the two carboethoxy substituents, 108.6 (4) and 106.8 (4)° for C(41) and C(51), respectively. Both substituent groups are oriented in the same manner with respect to the olefin, and the slightly larger angle at C(41) may be due to steric interactions with the adjacent triphenylphosphine ligand. The value of γ for the fumarate complex is 142 (3)°, slightly smaller than the average value of 150 (4)° found in $Fe(CO)_4$(fumaric acid),[28] and taken together with the other angles of Table VII indicates that the degree of bending back of the olefin is about the same as that observed in the complexes $Ni(t-BuNC)_2(TCNE)$[29] and Pt-$(PPh_3)_2(TCNE)$[30] but not as great as that found for the olefin in $Pt(PPh_3)_2(Cl_2CCCl_2)$[31] or $Fe(CO)_4(F_2CCF_2)$.[22] The ma-

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Table VIII. Fe–C(olefin) and C–C Double-Bond Lengths (Å) in Fe(CO)₄(olefin)[a] and Fe(CO)₃(PPh₃)(olefin)[b] Complexes[c]

olefin	Fe–C(5)	Fe–C(4)	C(5)–C(4)	ref
C₁₂H₈[a]	2.146 (3)	2.156 (4)	1.421 (5)	20
HC=CH / CCPh₂ / HC=CH [a]	2.147 (3)	2.160 (4)	1.404 (4)	21
F₂C=CF₂[a]	1.989 (10)	1.989 (10)	1.530 (16)	22
H₂C=C(C₂H₃)(CH₂)(C(O)–O) [a]	2.098 (5)	2.127 (4)	1.408 (7)	32
H₂C=C(CH(CO₂Me))(CH(CO₂Me)) [a]	2.092 (7)	2.024 (5)	1.401 (9)	33
H₂C=CHCO₂Me[b]	2.092 (2)	2.106 (2)	1.413 (3)	14
(CO₂Et)(H)C=C(H)(CO₂Et) [b]	2.069 (5)	2.088 (4)	1.423 (6)	this work
(H)(CO₂Et)C=C(H)(CO₂Et) [b]	2.056 (5)	2.077 (5)	1.415 (8)	this work

[a] Fe(CO)₄(olefin) complexes. [b] Fe(CO)₃(PPh₃)(olefin) complexes. [c] In the complexed olefin the first olefinic carbon atom as written is labeled C(5) and the second C(4).

leate derivative has δ angles of 105.9 (5) and 113.0 (6)° for C(41) and C(51), respectively. This difference between the two is clearly due to the distinctly different orientations of the two ester substituents. The orientations of the olefin substituents observed in the maleate and fumarate complexes are the result of both steric and electronic influences. Steric interactions between the carboethoxy groups and the axial carbonyl ligands in the fumarate complex are minimized in the conformation observed where the planes formed by atoms O(41)–C(41)–O(42)–C(4) and O(51)–C(51)–O(52)–C(5) are close to being coplanar with the olefin planes C(41)–C(4)–C(5) and C(51)–C(5)–C(4), respectively. This conformation is also found for the ester group in the acrylate complex Fe(CO)₃(PPh₃)(MA).[15] In the maleate complex both substituents cannot adopt such a conformation because the cis olefin makes such an arrangement sterically very unfavorable. The maleate complex therefore has one carboethoxy group oriented as those in the fumarate complex while the other is approximately perpendicular to this. The observed orientations minimize both intraligand (olefin) and interligand steric interactions.

Some relevant bond distances in several Fe(CO)₄(olefin) and Fe(CO)₃(PPh₃)(olefin) complexes are listed in Table VIII. The general trend in the Fe–C bond distances reflects the π acidity of the olefinic ligands; the shortest distances are found with the strongly π-accepting olefin tetrafluoroethylene. The trend corroborates the contention that in these molecules π back bonding is the more important component of the metal–olefin interaction. In the Fe(CO)₃(PPh₃)(olefin) complexes

it can be seen that the greater π acidity of the disubstituted olefins results in shorter metal–carbon bond lengths. However, this greater π acidity is not reflected in significantly different carbon–carbon double-bond lengths. This lack of sensitivity of the bond length of the coordinated olefin to the nature of its substituents has been noted previously[27] and is also evident from Table VIII where only the F₂C=CF₂ distance is significantly different from the other values. Examination of the data listed in the table reveals that the complexes containing unsymmetrically substituted olefins possess unequal metal–olefin carbon bond lengths. With the exception of Feist's acid (H₂CC(CHCO₂Me)₂), the metal–carbon bond length to the carbon carrying the π-withdrawing substituent is longer than the other distance. This bonding asymmetry can be successfully explained by considering the effect of the π-acceptor substituents on the olefin π and π* orbitals.[34] As shown by Libit and Hoffmann, the π and π* orbitals are polarized in opposite senses. However, since in these Fe(0)–olefin complexes the π back bonding is more important than the forward σ donation, it follows from the amplitudes of the carbon p orbitals of the olefin LUMO that a shortening of the metal–carbon bond opposite to the site of the π-acceptor substituent should result.[35] The difference between the two bond lengths in the acrylate complex is significant but small, and this is a little surprising in view of the large asymmetry of the olefin. In the fumarate complex the olefin is symmetrically substituted and the ester functionalities are oriented in the same fashion; the two ends of the olefin are rendered inequivalent by the phosphine ligand occupying an equatorial site of the trigonal bipyramid. The difference in the bond lengths is small and at the limit of being significant. Nevertheless, it is the metal–carbon bond adjacent to the phosphine ligand that is longer. Steric repulsion from the bulky triphenylphosphine is expected to lengthen this bond. Further, since triphenylphosphine is a weaker π acceptor than carbon monoxide, more effective back-bonding to the carbon atom trans to it is expected. Both these effects act to shorten the Fe–C(5) bond relative to the Fe–C(4). In the maleate derivative the situation of having one ester group in a conformation in which it can act as a π-withdrawing group and the other effectively orthogonal to this orientation yields a truly asymmetric olefinic ligand. The difference in metal–carbon distances is again small, but the shorter Fe–C(5) bond is, as predicted, across from the π-accepting ester substituent. The fact that differences in substituent orientation, and the resultant subtle electronic changes, can produce detectable changes in iron–olefin carbon bond lengths, which follow the predictions of Hoffmann's polarization model, bespeaks the usefulness of the theory.

Supplementary Material Available: Tables of structure factor amplitudes, anisotropic thermal parameters, nonrefined hydrogen atom parameters, and rigid phenyl group parameters (25 pages). Ordering information is given on any current masthead page.

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