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Absolute Configuration of Organometallic Compounds. 4.[1] X-Ray Determination of the Structure and Absolute Configuration of $(-)_{579}$-$(\eta^5$-$C_5H_5)Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$

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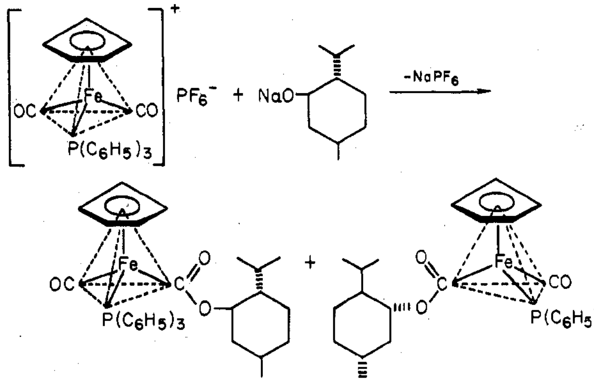
The structure and the absolute configuration of $(-)_{579}$-$(\eta^5$-$C_5H_5)Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$ ($C_{10}H_{19}$ = menthyl) have been determined by single-crystal x-ray diffraction methods using data acquired by a computer-controlled diffractometer and Bijvoet's technique. The substance crystallizes in the orthorhombic system, space group $P2_12_12_1$, with cell constants of a = 11.221 (4), b = 14.817 (7), and c = 18.958 (3) Å. The observed and calculated densities are 1.25 (2) and 1.25 g/cm^3 (for Z = 4 molecules/unit cell). The Fe–$(\eta^5$-$C_5H_5)$ fragment has normal distances and angles and the Cp ring is planar, as expected. The Fe–$P(C_6H_5)_3$ group has stereochemical parameters which are well within the values found in the literature (i.e., Fe–P = 2.214 (2) Å, P–C = 1.830 (6), 1.838 (4), and 1.853 (6) Å), and the dihedral angles of the three phenyl rings are canted at arbitrary values dictated by packing. The most important features of the stereochemistry of the molecule are the following: (1) the Fe—C(C≡O) and C≡O distances are, respectively, 1.670 (7) and 1.206 (9) Å. The former is the shortest iron to carbonyl carbon distance observed thus far. (2) The Fe–ester fragment shows a large angular distortion at the C atom such that Fe—C═O = 132.1 (5), Fe—C—$OC_{10}H_{19}$ = 117.7 (4), and O═C—O = 108.8 (5)°. Concomitant with this distortion is a shortening of the Fe-C(ester) bond to 1.825 (6) Å. Both of these observations point to an enhanced π-bonding interaction between the iron atom and the carbons of the carbonyl and ester group. When the current rules for ranking groups are applied, the configuration at the iron atom is specified to be *S*.

Introduction

In 1969, the first optically active organometallic compounds, $(+)_{579}$- and $(-)_{579}$-$C_5H_5Mn(NO)[P(C_6H_5)_3]COOC_{10}H_{19}$, in which a transition metal was the chiral center, were prepared.[3a] Since then, work on the syntheses, properties, and uses of these optically active complexes for stereochemical studies has progressed rapidly[3b,4,5] and has been extended to other transition-metal derivatives, especially to iron compounds.[6-21] However, most of the stereochemical conclusions have had to be based on relative comparisons as the determination of absolute configurations has lagged behind, up to now being mainly confined to square-pyramidal Mo complexes.[21-24] In this study, we report the structure and the absolute configuration of $(-)_{579}$-$(\eta^5$-$C_5H_5)Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$, Ia, with $C_{10}H_{19}$ = menthyl, preliminary results of which have been published in a short communication.[21]

In the reaction of $[C_5H_5Fe(CO)_2P(C_6H_5)_3]PF_6$ with $NaOC_{10}H_{19}$, the menthoxide anion adds to either one of the two enantiotopic carbonyl groups in the prochiral cation $[C_5H_5Fe(CO)_2P(C_6H_5)_3]^+$ giving rise to a pair of diastereoisomers $(-)_{579}$- and $(+)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$, Ia and Ib, which differ only in the configuration at the iron atom (eq 1).[6,10]



Ia

Ib

(1)

The less soluble $(-)_{579}$-diastereoisomer Ia used in the present x-ray study was the starting material for the preparation of other optically active complexes: reaction with $LiCH_3$ gave the acetyl derivative $(+)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$,[8,14] which could be reduced to $(+)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH_3$[14] and decarbonylated to $(-)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$.[12] With the determination of the absolute configuration for $(-)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$, Ia, and the stereochemistry of the reactions involved known, all of the absolute configurations of this series of interrelated iron compounds could be determined.

Experimental Section

The synthesis and isolation of $(-)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$ have been given before.[6,10] A fragment of more or less equal dimensions was selected from a yellow mass of crystalline material and measured under the microscope using a U.S. Bureau of Standards certified scale. The dimensions ranged from 0.3 to 0.4 mm, approximately. It was mounted on a goniometer head and placed on an Enraf–Nonius CAD-4 computer-controlled diffractometer. The instrument centered the crystal automatically and gave an orientation matrix, cell constants, and a Niggle matrix[25] which indicated that the system was orthorhombic. The routines used were SEARCH, INDEX, and DETCELL.[26] Using the routine MODE = −1,[26] the instrument was asked to scan reflections which would test for axial absences and for a series of reflections which are common to the orthorhombic space

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Table I. Crystal Data

Mol formula	$C_{35}H_{39}O_3PFe$
Mol wt	594.52
Crystal shape	Irregular fragment
Crystal size	Max dimension 0.4 mm
Space group	$P2_12_12_1$
Unit cell data	$a = 11.221$ (4) Å $b = 14.817$ (7) Å $c = 18.958$ (3) Å $V = 3152$ (3) Å^3
Density measd	1.25 (2) g/cm^3
Density calcd ($Z = 4$)	1.25 g/cm^3
Radiation used for data collection	λ(Mo Kα) 0.710 69 Å
Linear absorption coeff	5.88 cm^{-1}
No. of parameters refined in the final least squares	576
No. of reflections used in last least squares	3426

groups having glide planes. The only systematic absences found during this test were those associated with 2_1 screw axes. The instrument was then programmed to collect reflections in the range of $30 \leq 2\theta \leq 43°$ using a fast prescan check of about 5° min^{-1} to estimate whether the reflection would have 400 counts above background. If not, the reflection was considered absent. Reflections of the type *hkl* and $hk\bar{l}$ were scanned, and the 45 strongest ones were used for the determination of cell constants. The instrument was programmed to center these, and the set was used in conjuction with program PARAM of the X-Ray '72 System[27] to obtain the cell constants listed in Table I, which also lists all the important crystallographic parameters used in this study. A density of 1.25 g/cm^3 measured by flotation in aqueous $ZnBr_2$ is identical with the value of 1.25 g/cm^3 calculated for four formula units in the cell (erroneously reported elsewhere[21] as 1.12 and 1.10 g/cm^3, respectively).

A detailed search of the absent reflections confirmed the space group to be $P2_12_12_1$, which was consistent with a chiral compound. All of the subsequent checks on the complete data set and the least-squares refinement showed this assumption to be correct. The intensity set of data was collected with Mo Kα radiation (λ 0.710 69 Å) which had been monochromatized by a dense graphite crystal set at a takeoff angle of 5.85°. The radiation was selected to minimize absorption problems which could get in the way of accurate measurements of Friedel pairs. In that regard, a check of the intensity of three reflections about the scattering vector (every 5° over a range of 180°) showed that the differences between maximum and minimum values were much less than the square root of the mean value of the measured intensities.

The diffracted intensities were collected using the θ–2θ scan technique. The scan speed was decided by a prescan of 5° min^{-1} in which, if the reflection had more than 75 net counts above background, the reflection was deemed observed and rescanned at a rate such that a minimum of 2000 counts above background was achieved. The maximum time allowed was 450 s. Backgrounds were measured for 25% of the total scan time on either side of the peak, and for any measured reflection the width of the scan was calculated by

$$\text{scan range} = A + B \tan \theta \tag{2}$$

with $A = 1.00°$ and $B = 0.40°$ for the low-angle data (see below) and $A = 1.00°$ and $B = 0.50°$ for the high-angle data. For both sets, the width of the horizontally variable aperture was calculated using eq 2 also, and the values of A and B were set to 5.20 and 2.11 mm, respectively. The crystal-to-source and the crystal-to-detector distances were respectively 216 and 173 mm. The reliability of the electronics and the stability of the sample crystal were monitored using only one reflection $(2,5,\overline{13})$ for the low-angle data and three reflections $(5\bar{3}5$, $\bar{5}35$, $535)$ for the high-angle data. In both cases the standards were measured after every group of 30 reflections. No significant variations in the standards were detected. The low-angle data ($4 \leq 2\theta \leq 34°$) collection was stopped due to a failure in the operation of the attenuators, details of which have already been given elsewhere.[28] Since this was the best crystal we had, it was removed while the diffractometer was being tested and repaired. The crystal was remounted and reoriented, and the data were collected in the range $34 \leq 2\theta \leq 60°$.

The two data sets were processed separately with their respective orientation matrices and refined using separate scale factors. A total of 4422 independent data points were collected in the range $4 \leq 2\theta \leq 60°$ of which 3426 were used in the final least-squares cycles. These were corrected for Lorentz and polarization effects which included the partial polarization of the incident beam due to the use of a monochromator. No correction for absorption was made due to the nature of the crystal and to the fact that the corrections were known (see above) to be small, if not negligible. All subsequent calculations were carried out with the total data set and by using the programs of the X-Ray '72 System.[27]

Solution and Refinement of Structure

A three-dimensional Patterson map was computed and the position of the Fe atom was determined. All of the remaining nonhydrogen atoms were easily found by successive difference Fourier maps. Full-matrix least-squares refinement with isotropic models for all nonhydrogen atoms gave an R factor of 0.091. Anisotropic refinement reduced this index to 0.076. At this stage we found 10 reflections (004, 013, 012, 032, 031, 040, 110, 111, 102, 211) which were strong and were clearly out of line with the rest of the data. The crystal was remounted on the diffractometer and the 10 reflections were found to have been badly measured due to the attenuator problem mentioned previously and detailed elsewhere.[28] Since we had sufficient data to justify dropping these badly measured reflections and since incorporating them into the main body of data with a separate scale factor seemed unwarranted, we omitted them by using the "ignore reflection" option of the X-Ray '72 System.[27] After these reflections were omitted, hydrogen atoms were added at the theoretically calculated positions (C–H = 0.95 Å). Further anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogens yielded the following unweighted and weighted agreement factors:

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.066$$

$$R_w = [\Sigma w(|F_o| - |F_o|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.071$$

The function minimized during all least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ where w is the weighting factor. The weighting scheme used is that described in the X-Ray '72 manual.[27] The standard deviations of the intensities, $\sigma(I)$, were calculated from simple Poisson statistics. Since some C–H distances were found to be too large, new theoretical positions for the hydrogen atoms were calculated (Table IV).

The final results are summarized in Tables II–IV which list the atomic coordinates and the thermal parameters of the nonhydrogen atoms. Bond lengths and angles are listed in Tables V and VI. The equations of the least-squares planes are given in Table VII. The stereodrawings (Figures 1–3) were obtained by using Johnson's ORTEP2.[29]

A table of observed and calculated structure factors is available as supplementary material.

Determination of the Absolute Configuration

When the refinement of all of the atoms had been carried to completion using for the heavy atoms the scattering curves of Cromer and Mann[30] and for hydrogen the curve of Stewart et al.,[31] the anomalous scattering corrections[32] for Fe and P were added in order to test the enantiomorph. Twenty-six reflections (see Table VIII) showed marked differences between $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$. These reflections were measured, each four times, using the diffractometer routine MODE = −1[26] in the order *hkl*, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}\bar{l}$, *hkl*, *hkl*, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}\bar{l}$, *hkl*, and the four independently measured values were then averaged. The results are given in Table VIII, where it is shown that the coordinates initially chosen, fortuitously, correspond to those of the correct enantiomer. The absolute configuration of the molecule is shown correctly in Figures 1 and 2, as well as in the packing diagram, Figure 3. It should be emphasized that no effort was made to use the known absolute configuration of the three chiral centers[32–34] of menthol; rather, our determination, based strictly on the anomalous scattering of Fe and P, provides a separate and independent test of the absolute configuration of this chiral species. The absolute configuration shown in Figures 1–3 agrees with the chemical work

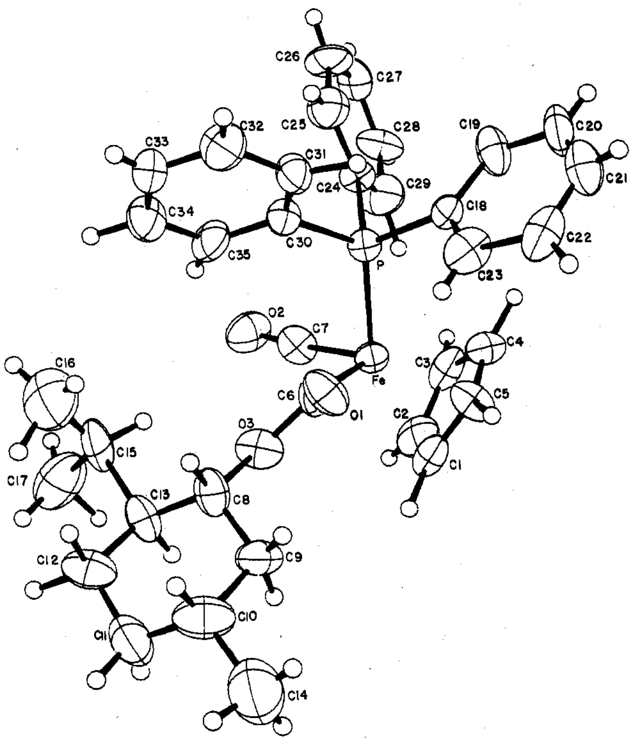

Figure 1. General view of Ia showing the labeling scheme used in the crystallographic study. The ellipsoids of thermal motion are 50% envelopes. The molecule is shown in its correct absolute configuration.

Table II. Final Positional Parameters of the Nonhydrogen Atoms

Atom	*x*	*y*	*z*
Fe	0.13340 (7)[a]	0.00064 (5)	−0.14945 (4)
P	0.13431 (15)	0.14358 (9)	−0.18356 (7)
C1	0.2022 (7)	−0.1313 (5)	−0.1441 (5)
C2	0.2181 (6)	−0.0918 (5)	−0.0815 (3)
C3	0.2909 (7)	−0.0185 (4)	−0.0923 (4)
C4	0.3220 (7)	−0.0104 (5)	−0.1625 (3)
C5	0.2598 (7)	−0.0827 (5)	−0.2015 (4)
C6	0.0432 (6)	0.0311 (4)	−0.0729 (3)
C7	0.0109 (7)	−0.0209 (4)	−0.1966 (3)
C8	−0.1271 (5)	−0.0185 (4)	0.0103 (3)
C9	−0.0589 (7)	−0.0574 (4)	0.0688 (3)
C10	−0.1408 (8)	−0.0548 (5)	0.1399 (3)
C11	−0.2568 (7)	−0.1027 (7)	0.1268 (4)
C12	−0.3198 (8)	−0.0648 (4)	0.0632 (4)
C13	−0.2425 (6)	−0.0715 (5)	−0.0042 (4)
C14	−0.0687 (9)	−0.0968 (9)	0.2005 (6)
C15	−0.3146 (6)	−0.0320 (6)	−0.0762 (4)
C16	−0.3726 (10)	0.0553 (6)	−0.0681 (6)
C17	−0.3928 (9)	−0.1095 (7)	−0.0955 (5)
C18	0.2660 (5)	0.2089 (4)	−0.1584 (3)
C19	0.3474 (6)	0.2459 (5)	−0.2106 (4)
C20	0.4454 (7)	0.2920 (5)	−0.1848 (4)
C21	0.4688 (6)	0.3015 (5)	−0.1123 (4)
C22	0.3982 (6)	0.2608 (5)	−0.0612 (4)
C23	0.2889 (7)	0.2182 (4)	−0.0879 (3)
C24	0.1300 (6)	0.1601 (4)	−0.2796 (2)
C25	0.0906 (7)	0.2398 (5)	−0.3101 (4)
C26	0.0967 (7)	0.2500 (4)	−0.3829 (3)
C27	0.1379 (6)	0.1838 (5)	−0.4272 (3)
C28	0.1733 (8)	0.1022 (5)	−0.3982 (4)
C29	0.1682 (8)	0.0900 (5)	−0.3227 (4)
C30	0.0124 (5)	0.2199 (4)	−0.1555 (3)
C31	0.0357 (5)	0.3061 (4)	−0.1280 (3)
C32	−0.0627 (7)	0.3641 (5)	−0.1115 (4)
C33	−0.1763 (6)	0.3294 (5)	−0.1205 (3)
C34	−0.1957 (6)	0.2447 (5)	−0.1409 (4)
C35	−0.1052 (6)	0.1886 (4)	−0.1594 (4)
O1	0.0604 (4)	0.0882 (3)	−0.0220 (2)
O2	−0.0730 (5)	−0.0345 (3)	−0.2349 (2)
O3	−0.0546 (4)	−0.0291 (2)	−0.0535 (2)

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits in this and succeeding tables.

of Prelog[32] and with the two crystallographic determinations carried out for totally different derivatives of menthol.[33,34]

Description of the Structure and Discussion

As shown in Figures 1–3, the molecule consists of an iron atom surrounded by the P of $P(C_6H_5)_3$, the carbons of a carbonyl and an ester group, and the C_5H_5 ring. It is generally assumed that this is a distorted-tetrahedral geometry derived from an octahedral arrangement by the collapse of three facial points. As such, the three angles associated with P, C6, and C7 are close to 90° (see Table VI), and this is a commonly observed phenomenon for compounds of the general type $C_5H_5ML_1L_2L_3$, as found in $(\eta^5$-$C_5H_5)Fe(CO)_3{}^+$[45] (XII; Table IX), where all three C–Fe–C angles are a little greater than 90°. In Ia the deviations from 90° are smaller than in $[(\eta^5$-$C_5H_5)Fe(CO)_3]PF_6$, the largest being P–Fe–C7 (91.7°).

Table IX gives a useful comparison of the bonding parameters in Ia with those of a number of molecules having ligands in common. One notes immediately that the Fe–(ring centroid) distances in the compounds listed in Table IX fall into two groups. Ferrocence derivatives (X and XI) are known to have Fe–(ring centroid) distances of about 1.65 Å[43,44] while those of C_5H_5Fe–$L_1L_2L_3$ have longer distances reflecting the ability of L_1, L_2, and L_3 to compete for the Fe electrons. A good example is XII in which the distance is now 1.703 Å. It is interesting to note that all of the other derivatives listed (Ia, VII, VIII, IX) have longer Fe–(ring centroid) distances but that their internal differences are quite small (the mean and deviation from the mean (in parentheses) being 1.747 (5) Å). The $(C_5H_5)Fe(CO)_3{}^+$ cation, as noted by Gress and

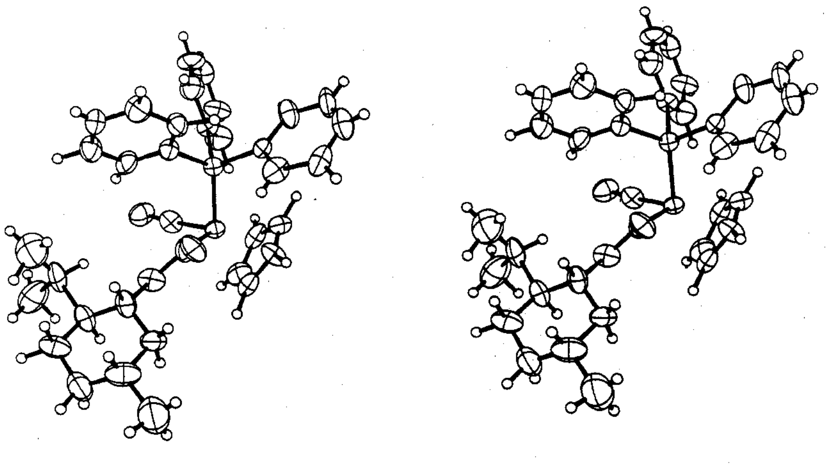

Figure 2. Stereopair of the molecular conformation and correct absolute configuration of Ia. The envelopes are 50% probability ellipsoids.

Table III. Final Thermal Parameters of the Nonhydrogen Atoms ($\times 10^3$)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	43.8 (6)	34.8 (4)	37.9 (5)	0.5 (5)	−1.1 (4)	0.5 (4)
P	41.0 (11)	37.0 (8)	32.7 (8)	0.5 (8)	0.4 (8)	−2.6 (7)
C1	69 (6)	41 (4)	110 (6)	19 (4)	−1 (5)	8 (4)
C2	48 (4)	64 (4)	52 (4)	19 (4)	−10 (4)	−2 (3)
C3	67 (5)	23 (3)	69 (4)	−3 (3)	−1 (4)	−17 (3)
C4	59 (5)	54 (4)	55 (4)	4 (4)	0 (4)	16 (4)
C5	53 (5)	78 (5)	55 (4)	27 (4)	−11 (4)	−6 (4)
C6	44 (5)	55 (4)	67 (4)	−5 (3)	−15 (3)	−8 (3)
C7	58 (5)	53 (4)	26 (3)	−4 (4)	5 (4)	−17 (3)
C8	44 (4)	67 (4)	51 (4)	3 (4)	12 (3)	−17 (3)
C9	67 (5)	48 (4)	49 (5)	−10 (4)	−7 (4)	12 (3)
C10	114 (7)	75 (5)	44 (4)	−4 (5)	−2 (5)	5 (3)
C11	54 (6)	118 (7)	78 (6)	−17 (6)	8 (5)	15 (5)
C12	95 (7)	31 (3)	63 (5)	−15 (4)	8 (5)	−3 (3)
C13	42 (5)	76 (5)	63 (5)	−2 (4)	21 (4)	−5 (4)
C14	84 (8)	204 (10)	100 (7)	−16 (8)	−2 (6)	21 (7)
C15	32 (5)	103 (6)	67 (5)	−17 (4)	3 (4)	−12 (4)
C16	106 (10)	76 (6)	156 (9)	15 (6)	20 (9)	−17 (6)
C17	104 (8)	124 (8)	79 (5)	3 (7)	−29 (5)	−11 (5)
C18	34 (4)	37 (3)	53 (4)	5 (3)	−1 (3)	5 (3)
C19	38 (5)	58 (4)	76 (5)	−3 (4)	11 (4)	−23 (4)
C20	28 (5)	69 (5)	102 (7)	−9 (4)	−4 (4)	−7 (6)
C21	42 (5)	66 (5)	76 (5)	−8 (4)	3 (4)	−26 (4)
C22	56 (6)	76 (5)	79 (5)	17 (4)	−22 (4)	−8 (4)
C23	71 (5)	46 (4)	53 (4)	−1 (4)	−19 (4)	−16 (3)
C24	49 (4)	58 (3)	5 (2)	−6 (3)	−8 (3)	2 (2)
C25	64 (6)	68 (6)	72 (5)	12 (4)	11 (4)	7 (4)
C26	86 (7)	71 (5)	35 (4)	16 (5)	19 (4)	27 (3)
C27	50 (5)	77 (4)	36 (3)	−10 (4)	9 (3)	−7 (3)
C28	89 (7)	60 (4)	60 (4)	−13 (5)	9 (4)	17 (3)
C29	86 (6)	59 (4)	79 (5)	20 (4)	27 (5)	−2 (4)
C30	37 (4)	40 (3)	44 (3)	1 (3)	−1 (3)	−3 (3)
C31	39 (4)	38 (3)	71 (4)	2 (3)	8 (3)	−2 (3)
C32	64 (6)	52 (4)	70 (5)	13 (4)	9 (4)	−10 (4)
C33	37 (5)	61 (5)	67 (5)	8 (4)	4 (3)	5 (4)
C34	46 (5)	49 (5)	75 (5)	−7 (4)	−7 (4)	−9 (4)
C35	48 (6)	38 (3)	91 (5)	12 (4)	−4 (4)	2 (3)
O(1)	59 (3)	68 (3)	47 (3)	−16 (2)	18 (2)	−11 (2)
O(2)	78 (4)	67 (3)	59 (3)	−3 (3)	−25 (3)	0 (2)
O(3)	77 (3)	37 (2)	46 (2)	2 (2)	11 (2)	−18 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and $U_{ij} = \beta_{ij}/2\pi^2(a_i^*a_j^*)$ Å^2.

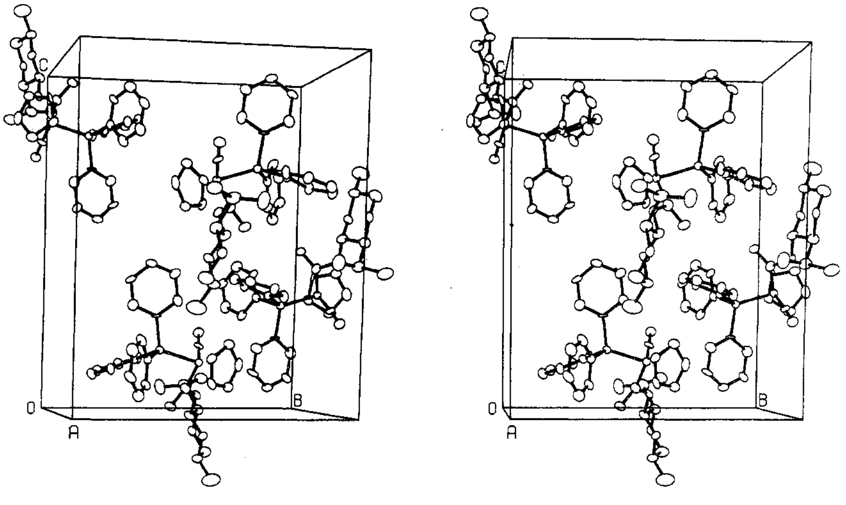

Figure 3. Packing diagram of the molecules of Ia which are depicted in their correct absolute configuration.

Jacobson,[45] probably has a shorter Fe–(ring centroid) distance by virtue of its positive charge, which also has an effect on the Fe—C(CO) and C≡O bond lengths. For compounds Ia and VII–IX, the Fe–C(Cp) distances are equal to within one or two standard deviations, and these variations, as well as variations in the C–C distances of the C_5H_5 ring, are known to be due to librational motion of the Cp rings.[54–60] The value of the deviation from the mean for XI, which seems to be anomalously large given the Fe–(ring centroid) distance, reflects the strain on the rings due to the short SO_2–NH bridge holding the two C_5H_4 ligands canted at an angle of 23°, while the iron is asymmetrically bound to them;[44] thus the individual Fe–C(Cp) distances range from 1.983 (8) to 2.096 (8) Å.

The Fe–P distances do not vary much and the mean value and the deviation thereof is 2.229 (27) Å for the examples listed in Table IX. In general, these variations are the result of changes in the substituents at the phosphorus ligands, as was elegantly demonstrated by Sim and co-workers[37] in their

Table IV. Theoretical Positions of the Hydrogen Atoms[a]

Atom	x	y	z
H1	0.1581	−0.1854	−0.1504
H2	0.1852	−0.1108	−0.0378
H3	0.3166	0.0214	−0.0561
H4	0.3738	0.0336	−0.1821
H5	0.2579	−0.0944	−0.2508
H6	−0.3066	−0.0959	0.1669
H7	−0.0384	−0.1180	0.0580
H8	−0.1472	0.0421	0.0216
H9	0.0116	−0.0232	0.0761
H10	−0.1563	0.0062	0.1524
H11	−0.2414	−0.1650	0.1191
H12	−0.3916	−0.0975	0.0560
H13	−0.2243	−0.1329	−0.0140
H14	−0.1164	−0.0953	0.2419
H15	−0.0490	−0.1580	0.1893
H16	0.0023	−0.0632	0.2078
H17	−0.2582	−0.0232	−0.1133
H18	−0.3133	0.0982	−0.0555
H19	0.3340	0.2389	−0.2598
H20	0.4993	0.3183	−0.2175
H21	0.5762	0.3359	−0.0985
H22	0.4191	0.2606	−0.0127
H23	0.2320	0.1963	−0.0549
H24	−0.3379	−0.0032	0.0718
H25	0.0597	0.2870	−0.2815
H26	0.0710	0.3055	−0.4030
H27	0.1421	0.1936	−0.4767
H28	0.2007	0.0548	−0.4227
H29	0.1910	0.0339	−0.3025
H30	−0.4131	0.0775	−0.1085
H31	0.1153	0.3256	−0.1203
H32	−0.0504	0.4240	−0.0951
H33	−0.2429	0.3675	−0.1118
H34	−0.2753	0.2229	−0.1426
H35	−0.1222	0.1288	−0.1748
H36	−0.4291	0.0503	−0.0310
H37	−0.4471	−0.1233	−0.0585
H38	−0.4333	−0.0873	−0.1359
H39	−0.3472	−0.1617	−0.1065

[a] Calculated after the structure refined to $R = 0.066$.

Table V. Interatomic Distances (Å)[a]

		Phenyl Rings	
Fe–P	2.214 (2)		
–C6	1.825 (6)	C18–C19	1.455 (9)
–C7	1.670 (6)	–C23	1.367 (9)
–C1	2.105 (7)	C19–C20	1.383 (10)
–C2	2.107 (7)	C20–C21	1.405 (11)
–C3	2.092 (7)	C21–C22	1.388 (10)
–C4	2.136 (7)	C22–C23	1.470 (10)
–C5	2.125 (8)	Mean	1.411 (38)[b]
P–C18	1.830 (6)	C24–C25	1.389 (9)
–C24	1.838 (4)	–C29	1.388 (9)
–C30	1.853 (6)	C25–C26	1.443 (10)
C6–O1	1.297 (7)	C26–C27	1.386 (10)
–O3	1.463 (7)	C27–C28	1.372 (9)
C7–O2	1.206 (9)	C28–C29	1.390 (10)
O3–C8	1.465 (7)	Mean	1.395 (22)[b]
C1–C2	1.334 (10)	C30–C31	1.404 (8)
C2–C3	1.374 (10)	–C35	1.401 (9)
C3–C4	1.380 (9)	C31–C32	1.434 (10)
C4–C5	1.478 (10)	C32–C33	1.386 (10)
C5–C1	1.457 (11)	C33–C34	1.331 (10)
C8–C9	1.466 (9)	C34–C35	1.359 (10)
–C13	1.539 (9)	Mean	1.386 (33)[b]
C9–C10	1.632 (10)		
C10–C11	1.504 (12)		
C10–C14	1.537 (14)		
C11–C12	1.505 (11)		
C12–C13	1.547 (11)		
C13–C15	1.692 (10)		
C15–C16	1.457 (13)		
–C17	1.492 (13)		

[a] Estimated standard deviations in parentheses. [b] Values in parentheses are deviations from the mean.

Table VI. Angles (deg) and Their Estimated Standard Deviations

		Phenyl Rings	
P–Fe–C6	89.9 (2)		
P–Fe–C7	91.7 (2)	C19–C18–C23	120.6 (6)
C6–Fe–C7	90.9 (3)	C18–C19–C20	116.4 (6)
Fe–C6–O1	132.1 (5)	C18–C23–C22	112.4 (6)
Fe–C6–O3	117.7 (4)	C19–C20–C21	122.9 (7)
Fe–C7–O2	175.3 (6)	C20–C21–C22	122.1 (7)
O1–C6–O3	108.8 (5)	C21–C22–C23	115.0 (6)
C6–O3–C8	123.9 (4)	Mean	120 (3)
O3–C8–C9	107.0 (5)		
–C13	105.4 (5)	C25–C24–C29	119.3 (5)
C9–C8–C13	111.9 (5)	C24–C25–C26	119.4 (6)
C8–C13–C15	111.6 (5)	C24–C29–C28	120.1 (6)
–C12	107.0 (6)	C25–C26–C27	123.1 (6)
C12–C13–C15	112.1 (5)	C26–C27–C28	118.5 (6)
C13–C15–C16	115.9 (7)	C27–C28–C29	119.5 (6)
–C17	102.2 (7)	Mean	120 (1)
C8–C9–C10	108.8 (6)	C31–C30–C34	119.8 (5)
C9–C10–C11	109.9 (6)	C30–C31–C32	118.9 (6)
–C14	108.2 (7)	C30–C35–C34	119.2 (6)
C11–C10–C14	112.8 (7)	C31–C32–C33	117.3 (6)
C10–C11–C12	119.2 (7)	C32–C33–C34	122.4 (7)
C11–C12–C13	111.9 (7)	C33–C34–C35	122.0 (6)
C16–C15–C17	116.6 (8)	Mean	120 (2)
Fe–P–C18	115.7 (2)		
–C24	114.6 (2)	Cp Ring	
–C30	119.8 (2)	C2–C1–C5	112.9 (6)
C18–P–C24	102.1 (3)	C1–C2–C3	107.1 (6)
–C30	101.4 (3)	C2–C3–C4	111.2 (6)
C24–P–C30	100.6 (3)	C3–C4–C5	107.5 (6)
P–C18–C19	121.9 (5)	C4–C5–C1	101.1 (6)
–C18–C23	117.4 (5)	Mean	108 (4)
–C24–C25	122.3 (5)		
–C24–C29	118.4 (4)		
–C30–C31	121.6 (4)		
–C30–C35	118.5 (4)		

Table VII. Least-Squares Planes[a] through Selected Groups of Atoms and Deviations of Atoms from These Planes (Å)

A. Plane through C1· · ·C5 (Cp Ring)

$$0.80450x - 0.57774y + 0.13738z = 2.55147$$

C1	−0.022	C4	0.020
C2	−0.100	C5	−0.024
C3	−0.008	Fe	−1.743

B. Plane through C18· · ·C23

$$-0.51594x + 0.85614y + 0.02886z = 1.01774$$

Fe	−1.864	C20	0.006
P	−0.074	C21	0.031
C18	0.005	C22	−0.048
C19	−0.024	C23	0.030

C. Plane through C24· · ·C29

$$0.93126x + 0.35610y + 0.07718z = 1.77239$$

Fe	−0.594	C26	−0.003
P	0.120	C27	0.013
C24	0.022	C28	−0.005
C25	−0.014	C29	−0.012

D. Plane through C30· · ·C35

$$0.03214x - 0.33764y + 0.94073z = -3.83253$$

Fe	1.212	C32	−0.001
P	−0.111	C33	−0.028
C30	−0.036	C34	0.024
C31	0.032	C35	0.009

E. Plane through Fe, C6, O1, and O3

$$0.58561x - 0.61278y + 0.53063z = -0.65579$$

Fe	0.023	O1	0.030
C6	−0.076	O3	0.022

[a] Planes are expressed as $px + qy + rz = s$ in orthogonal (Å) space.

study of III and IV in which the $(CF_3)_2P$ ligand was oxidized to $(CF_3)_2PO$ with an attendant change in Fe–P distance of 0.074 Å (significant to the extent of 17.5σ). However, the extent of the change in Fe–P distance is surprisingly small when one considers the drastic rearrangement in the electronic environment at the phosphorus atom. If we limit ourselves

Table VIII. Determination of the Absolute Configuration of $(-)_{579}$-η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$

Reflecn no.	Indices	$F_c(hkl)$	$F_c(\bar{h}\bar{k}\bar{l})$	Calcd F ratio[a]	Measd F ratio[b]
1	1,12,6	17.99	16.16	1.11	1.11
2	1,12,2	20.54	18.00	1.14	1.15
3	1,11,3	18.15	20.56	0.88	0.87
4	193	34.98	33.15	1.05	1.04
5	196	28.86	26.96	1.07	1.06
6	1,9,10	42.77	44.60	0.96	0.94
7	176	59.85	57.80	1.04	1.03
8	1,7,13	13.79	15.73	0.88	0.87
9	1,6,12	7.68	10.62	0.72	0.77
10	165	23.99	26.01	0.92	0.94
11	156	42.12	39.64	1.06	1.05
12	1,4,15	25.34	27.18	0.93	0.91
13	148	45.00	41.66	1.08	1.09
14	144	13.82	11.84	1.17	1.15
15	142	74.98	72.30	1.04	1.04
16	141	51.42	53.48	0.96	0.96
17	133	50.24	46.71	1.08	1.09
18	137	16.82	13.88	1.21	1.20
19	1,3,13	42.66	40.77	1.05	1.02
20	1,2,12	39.57	41.53	0.95	0.97
21	125	39.91	37.71	1.06	1.02
22	121	54.42	56.97	0.96	0.95
23	116	82.05	79.46	1.03	1.03
24	117	46.56	44.31	1.05	1.08
25	219	17.46	14.61	1.19	1.05
26	1,2,13	16.71	17.43	0.96	0.96

[a] $F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})$. [b] Ratio of experimentally measured $F(hkl)/F(\bar{h}\bar{k}\bar{l})$.

to phosphine complexes, the examples listed in Table IX have, in the extremes, a difference in Fe–P bonds of 0.051 Å (significant to the extent of 14.1σ) and this is brought about by a drastic change in phosphorus ligands (i.e., from $P(C_6H_5)_3$ in Ia vs. $(CF_3)_2P$ in III). The Fe—C(C≡O) distance in Ia is shorter than in any of the examples listed in Table IX, and, as it then should be, the C≡O distance is longer, implying that the carbonyl ligand forms a higher order Fe–C bond than in the other examples listed. Interestingly, this also holds for the bonding parameters within the metal ester group (see Table X) for which the Fe–C distance is only 1.825 (6) Å. The Fe–$C(O)OC_{10}H_{19}$ fragment falls in the category of compounds recently discussed by Churchill and Chen[46] for which they proposed that the (rather electronegative) second oxygen might be expected to enhance the drift of π electrons from the metal onto the α carbon. When this is added to the known fact that with respect to carbonyl groups phosphines are electron donors to metals and that, therefore, the iron atom in Ia has a high electron density available for increased π bonding to both the carbonyl and the ester carbon atoms, we can understand the reasons for the values of the Fe–C bonds found here. Note that the C═O distance for the carbonyl oxygen of the ester group is also distinctly longer than those in the other examples listed in Table X. The changes in bond lengths for Fe—C(═O)—R/Fe—C(═O)—OR (R = alkyl) are similar to the corresponding changes which occur in dialkylamino–carbene complexes $(CO)_5Cr$–C(–NR_2)–R′/$(CO)_5Cr$–C(–NR_2)–OR′/(R, R′ = CH_3, C_2H_5).[61,62] In $(CO)_5Cr$–C[–$N(C_2H_5)_2$]–CH_3 the Cr–C bond [2.16 (1) Å] is slightly longer and the C–N bond [1.31 (1) Å] is somewhat shorter than in $(CO)_5Cr$–C[–$N(CH_3)_2$]–OC_2H_5 with Cr–C = 2.133 (4) Å and C–N = 1.328 (5) Å.

The arrangement of the ester group Fe—C(═O)—OR with respect to the Fe–P bond as a reference is defined by the torsional angles about the Fe–C6 bond P–Fe/C6–O1 = −56.89° and P–Fe/C6–O3 = +138.35°. Concerning the geometry of the Fe–ester fragment, a large Fe—C═O angle is observed (132.1 (5)°) and a concomitantly small O–C–

Table IX. Comparison of Molecular Bond Lengths (Å) and Angles (deg) with Literature Values

No.	Compd	Fe–P	Fe–C(≡O)	C≡O	Fe–C≡O	⟨Fe–C(Cp)⟩[a]	Fe–RC[e]	Ref
Ia	$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COOC_{10}H_{19})$[f]	2.214 (2)	1.670 (7)	1.206 (9)	175.3 (6)	2.113 (16)	1.743 (7)	This study
II	$(ON)_2(OC)Fe(PPh_3)$[c]	2.260 (3)	1.709 (17)[b]	1.148 (11)[b]	177.9 (7)			36
III	$(\eta^5\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$	2.265 (3)	1.768 (7)	1.138 (8)	*d*	2.097 (7)	*d*	37
IV	$(\eta^5\text{-}C_5H_5)Fe(CO)_2P(O)(CF_3)_2$	2.191 (3)	1.780 (7)	1.134 (7)	*d*	2.090 (7)	*d*	37
V	$Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$	2.213 (2) 2.224 (2)	*d*	*d*	*d*			38
VI	$Fe_2(CO)_6[P(p\text{-}C_6H_4CH_3)_2](OH)$	2.238 (3)[b]	1.795 (29)[b]	1.137 (8)[b]	176.3 (3.1)[b]			39
VII	$(CH_3C_5H_4)(OC)Fe(CO)_2Co(CO)$-$[C_4H_4(CH_3)_2]$		1.748 (7)	1.150 (8)	178.6 (6)	2.119 (33)	1.747 (7)	40
VIII	$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$-*trans*		1.748 (6)	1.157 (7)	178.4 (8)	2.106 (15)	1.754 (6)	41
IX	$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$-*cis*		1.730 (7) 1.760 (8)	1.159 (9) 1.147 (10)	176.5 (8) 176.7 (7)	2.114 (26) 2.104 (6)	1.742 (5) 1.749 (5)	42
X	$\mu\text{-}S_3(\eta^5\text{-}C_5H_4)_2Fe$					2.044 (10)	1.653 (10)[b]	43
XI	$\mu\text{-}SO_2NH(\eta^5\text{-}C_5H_4)_2Fe$					2.030 (45)	1.64 (–)[b]	44
XII	$[(\eta^5\text{-}C_5H_5)Fe(CO)_3]PF_6$					2.070 (14)	1.703	45

[a] Mean and standard deviation from mean (in parentheses). [b] Mean of several independent values and deviations from mean. [c] NO and CO disorder. [d] Not given; also cannot be calculated since fractional coordinates are not listed. [e] RC = ring centroid. [f] $C_{10}H_{19}$ = menthyl.

Table X. Comparison of Distances (Å) and Angles (deg) at the Fe–C(=O)–R Fragment with Literature Values

No.	Compd	Fe–C=O	O=C–R	Fe–C–R	Fe–C	C=O	Ref
Ia	$(\eta^5\text{-}C_5H_5)(OC)(PPh_3)Fe\text{–}C(=O)\text{–}OC_{10}H_{19}$[b]	132.1 (5)	108.8 (5)	117.7 (4)	1.825 (6)	1.297 (7)	This study
XIII	$Me_2C_2H_4OCOFe(CO)_3$	127.23 (20)	116.08 (21)	116.69 (17)	1.9848 (24)	1.2112 (29)	46
XIV	$(\eta^5\text{-}C_5H_5)Fe\text{–}C(=O)\text{–}CF_2(\eta^4\text{-}C_5H_5)$	133.3 (8)[a]	116.8 (8)[a]	109.9 (7)[a]	1.990 (10)	1.213 (12)	47
XV	$C_{11}H_{10}OFe_2(CO)_6$				1.991 (10)		48
XVI	$[\eta^5\text{-}C_5H_4\text{–}C_6H_4CO]Fe_2(CO)_5$	126.94 (23)	117.37 (26)	115.68 (20)	1.9596 (30)	1.206 (4)	49
XVII	$[HB(pyr)_3]Fe(CO)_2(COCH_3)$	124.3 (4)	116.7 (5)	119.0 (4)	1.968 (5)	1.193 (6)	50
XVIII	$(OC)_3Fe\text{–}C(=O)\text{–}C_2H_2(\eta^5\text{-}C_6H_6)$	127.4 (5)	112.6 (5)	120.0 (5)	1.979 (5)	1.208 (7)	51
XIX	$(OC)_2Fe\text{–}C(=O)\text{–}O(\eta^3\text{-}C_5H_5)$		113 (2)		2.03 (2)		52
XX	$(OC)_4Fe[O_2C_4(CH_3)(C_3H_3)]$	124.4 (5) 125.7 (5)	122.2 (7) 120.7 (5)	113.4 (4) 113.6 (4)	2.035 (7) 2.012 (5)	1.206 (7) 1.201 (7)	53

[a] These numbers are not available in ref 47 and were kindly provided by Professor F. G. A. Stone and Dr. A. J. Welch, whom we thank. [b] $C_{10}H_{19}$ = menthyl.

$OC_{10}H_{19}$ angle of 108.8 (5)°. The Fe–CO_2 fragment is planar and the Fe–C–$OC_{10}H_{19}$ angle remains largely undisturbed and quite similar to those in the other examples. The origin of the distortion of the Fe—C=O angle from 120° is probably electronic in origin and due to the effect just described, as shown by comparison with the results of Churchill and Chen[46] for compound XIII in which both of those angles are distorted in the same direction, albeit somewhat less.

Another potential contributing factor to the angular distortion observed may come from the contacts between O1 and H8, H9, and H23 which are 2.56, 2.55, and 2.58 Å, respectively. These contacts are slightly less than the sum of the van der Waals radii for O and H (2.60 Å). The question is whether part of the distortion is an effort to avoid making these contacts worse. In connection with the question of stereochemistry and absolute configurations of molecules of this class, mentioned in the Introduction, we are currently investigating this aspect of the geometry of metal acyls and metal esters.

For the specification of the configuration at the iron atom the extension of the *R*,*S* system[63] for *polyhapto* ligands in organometallic compounds[64] was used. In the Cahn, Ingold, and Prelog treatment of multiple bonds with duplicate representations and phantom atoms,[63] priority has to be given to $C(=O)OC_{10}H_{19}$ over $C\equiv O$. Thus, the priority sequence of the ligands in $(-)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$, Ia, is $C_5H_5 > P(C_6H_5)_3 > COOC_{10}H_{19} > CO$. Applying the sequence rule[63] the configuration at the iron atom in Ia is *S*.

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Registry No. $(-)_{579}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$, 32005-37-1.

Supplementary Material Available: Structure factor tables (19 pages). Ordering information is given on any current masthead page.

References and Notes

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