ibid., **98,** 8271 (1976); (c) B. E. Firth and L. L. Miller, *ibid.,* **98,** 8273 (1976); (d) M. R. Van De Mark and L. L. Miller, *ibid.,* **100,** 3223 (1978).

(10) (a) N. R. Armstrong, A. W. C. Lin, M. Fujihira, and T. Kuwana, *Anal. Chem.,* **48,** 741 (1976); (b) J. F. Evans, T. Kuwana, M. T. Henne, and G. P. Royer, *J. Electroanal. Chem.,* **80,** 409 (1977).

(11) (a) A. Diaz, *J. Am. Chem. Soc.,* **99,** 5838 (1977); (b) A. F. Diaz, U. Hetzler, and E. Kay, *ibid.,* **99,** 6780 (1977).

(12) (a) M. Fujihira, T. Matsue, and T. Osa, *Chem. Lett.,* 875 (1976); (b) T. Osa and M. Fujihira, *Nature (London),* **264,** 349 (1976); (c) M. Fujihira, A. Tamura, and T. Osa, *Chem. Lett.,* 361 (1977); (d) M. Fujihira, N. Ohishi, and T. Osa, *Nature (London),* **268,** 226 (1977).

(13) (a) J. R. Lenhard and R. W. Murray, *J. Electroanal. Chem.,* **78,** 195 (1977); (b) P. R. Moses and R. W. Murray, *J. Am. Chem. Soc.,* **98,** 7435 (1976); *J. Electroanal. Chem.,* **77,** 393 (1977); (c) C. M. Elliott and R. W. Murray, *Anal. Chem.,* **48,** 1247 (1976); (d) D. G. David and R. W. Murray, *ibid.,* **49,** 194 (1977); (e) J. C. Lennox and R. W. Murray, *J. Electroanal. Chem.,* **78,** 395 (1977).

(14) (a) A. P. Brown and F. C. Anson, *Anal. Chem.,* **49,** 1589 (1977); *J. Electroanal. Chem.,* **83,** 203 (1977); (b) C. A. Koval and F. C. Anson, *Anal. Chem.,* **50,** 223 (1978).

(15) (a) K. S. V. Santhanam, J. Jespersen, and A. J. Bard, *J. Am. Chem. Soc.,* **99,** 274 (1977); (b) A. Merz and A. J. Bard, *ibid.,* **100,** 3222 (1978), and

private communication.

(16) J. M. Bolts and M. S. Wrighton, *J. Am. Chem. Soc.,* **100,** 5257 (1978).

(17) J. M. Bolts, A. B. Bocarsly, M. C. Palazzotto, E. G. Walton, N. S. Lewis, and M. S. Wrighton, submitted for publication.

(18) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.,* **93,** 3603 (1971).

(19) (a) A. G. Osbourne and R. H. Whitely, *J. Organomet. Chem.,* **101,** C27 (1975); (b) H. Stoeckli-Evans, A. G. Osbourne, and R. H. Whitely, *Helv. Chim. Acta,* **59,** 2402 (1976).

(20) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook", Vol. II, Academic Press, New York, N.Y., 1973, and references cited therein.

(21) E. Laviron, *J. Electroanal. Chem.,* **39,** 1 (1972).

(22) R. S. Nicholson and I. Shain, *Anal. Chem.,* **36,** 706 (1976), and references cited therein.

(23) W. H. Morrison, Jr., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.,* **12,** 1998 (1973).

(24) T. Dickinson, A. F. Povey, and P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 1,* **71,** 299 (1975).

(25) D. Seyferth, H. P. Hoffman, R. Burton, and J. F. Helling, *Inorg. Chem.,* **1,** 227 (1962).

(26) J. C. Smart, Ph.D. Thesis, Massachusetts Institute of Technology, 1974.

Crystallographic Determination of the Absolute Configuration at Iron of a Series of Chiral Iron Alkyls. Empirical Circular Dichroism Spectroscopic Correlations

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Abstract: The absolute configurations of two optically active iron complexes, $(+)_{578}$-$CpFe(CO)(PPh_3)(CH_2O$-menthyl) (**1**) and $(+)_{578}$-$CpFe(CO)(PPh_3)(CH_2COO$-menthyl) (**2**), have been determined by single-crystal X-ray diffraction methods and have been correlated with their circular dichroism spectra. The configuration of **1** is *S* and that of **2** is *R* (based on the sequencing rules proposed recently by Stanley and Baird). Anomalous dispersion effects were used to elucidate the absolute configuration of **1**, while that of **2** was determined using the $(-)$-menthyl group as a reference. From these results, the absolute configurations of a large number of complexes of the type $CpFe(CO)(PPh_3)(X)$ can be deduced and compared to their CD spectra [X = Br, I, Me, Et, *n*-Pr, *i*-Bu, CH_2-c-C_3H_5, CH_2Cl, CH_2Br, CH_2I, CH_2Ph, $C(O)Me$, $S(O)_2R$, $CH_2S(O)_2O$(menthyl), $(\eta^2$-$C_2H_4)^+BF_4^-$]. It is concluded that the maxima found at the 300–350- and 350–450-nm regions of the CD spectra can serve as a reliable indicator of the absolute configuration at iron, provided that the X groups are not too dissimilar. Crystal details: **1**-*S* crystallizes in space group $P2_1$ (monoclinic) with $a = 10.882$ (3) Å, $b = 11.054$ (4) Å, $c = 13.664$ (4) Å, $\beta = 102.66$ (2)°, $V = 1603.7$ Å^3, $Z = 2$; **2**-*R* crystallizes in space group $P1$ (triclinic) with $a = 7.660$ (1) Å, $b = 13.806$ (1) Å, $c = 15.948$ (1) Å, $\alpha = 108.23$ (1)°, $\beta = 88.62$ (1)°, $\gamma = 95.06$ (1)°, $V = 1595.5$ Å^3, $Z = 2$. Final agreement factors are for **1**-*S*, $R = 6.2\%$ (3655 reflections); for **2**-*R*, $R = 8.4\%$ (3665 reflections).

Introduction

Detailed understanding of the chemistry of any element which may exist in a chiral bonding environment requires development of methods of synthesis and resolution of this chiral center, and thorough investigation of the stereochemical consequences of its various characteristic reaction types. It is necessary to establish the absolute configuration of a number of molecules, to accumulate a basic set of reactions of known stereochemical outcome, and to correlate chiroptical properties with absolute configuration.

A sizable body of data is now available for molecules containing chiral silicon, phosphorus, and sulfur, and for chiral coordination complexes of the transition elements. In the rapidly maturing area of organotransition metal chemistry, however, only relatively recently has attention turned toward investigations based on resolution of chiral metal centers.[2-8]

Because $CpFe(CO)_2X$ systems (Cp ≡ η^5-C_5H_5; X is a wide variety of functional groups) are synthetically so accessible and are so well behaved experimentally, they have been the object
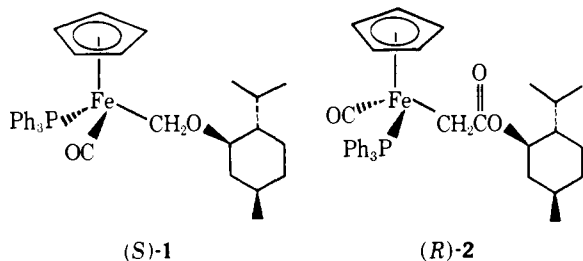
of considerable synthetic and mechanistic investigation. The metal alkyls $CpFe(CO)_2R$ have been valuable as model compounds in the examination of the chemistry of the metal–carbon σ bond.[9] In the same way, $CpFe(CO)(PR_3)X$ compounds have significant potential for use in this area because of their chirality. Such molecules are generally nonlabile to dissociation under ambient conditions, and therefore tend to be optically stable. A number of these chiral iron molecules have already been resolved, and have yielded useful mechanistic information.[3-6]

Because of the potential interest of these chiral iron systems, we have established the absolute configuration of two iron alkyls, (*S*)-**1** and (*R*)-**2**, by X-ray crystallographic structure determinations.[10] This paper describes these structures, and also describes the circular dichroism spectra of these and a number of other derivatives $CpFe(CO)(PPh_3)X$ which we have prepared. In this way, the absolute configuration at iron of at least 12 such compounds has been established. In addition to our work, the absolute configurations of (*S*)-$[CpFe(CO)$-$(PPh_3)\{C((S)=N^+HCHMePh)Me\}]BF_4^-$ (**3**)[11] and (*S*)-

Table I. Crystal Data for **1** and **2**

molecular formula	1	2
molecular formula	CpFe(CO)(PPh₃)-(CH₂OMen)	CpFe(CO)(PPh₃)-(CH₂COOMen)
stereochemical designation[a]	S	R
crystal type	monoclinic	triclinic
space group	P2₁ (no. 4)	P1̄ (no. 1)
cell constants:		
a	10.882 (3) Å	7.660 (1) Å
b	11.054 (4) Å	13.806 (1) Å
c	13.664 (4) Å	15.948 (1) Å
α	90.00°	108.23 (1)°
β	102.66 (2)°	88.62 (1)°
γ	90.00°	95.06 (1)°
cell volume	1603.7 Å³	1595.5 Å³
number of molecules in the unit cell	2	2
molecular weight	580.5	608.5
calculated density	1.20 g cm⁻³	1.22 g cm⁻³
observed density[b]	1.18 g cm⁻³	1.20 g cm⁻³
radiation used	Mo Kα	Mo Kα
absorption coefficient	5.69 cm⁻¹	5.81 cm⁻¹
data collection limit	2θ = 45°	2θ = 45°
number of reflections used in structure analysis	3655	3665
final agreement factor	R = 6.2%	R = 8.4%

[a] See footnote 10. [b] Obtained by flotation in an aqueous zinc iodide solution.

Table II. Ratios[a] of the largest Bijvoet Differences for CpFe(CO)-(PPh₃)CH₂O[(−)-menthyl] (**1**)

				$F_{hkl}/F_{h\bar{k}l}$ (calcd)	
h	k	l	$F_{hkl}/F_{h\bar{k}l}$(obsd)	S	R
3̄	2	0	0.96	0.95	1.04
3̄	3	2	0.90	0.86	1.14
5	2	3	0.98	0.97	1.03
6̄	5	3	0.91	0.89	1.12
5̄	1	4	0.93	0.87	1.12
2	1	4	0.91	0.90	1.10
8	1	5	0.83	0.78	1.25
2	4	7	0.94	0.91	1.09
1̄	1	9	0.85	0.74	1.30
5̄	5	10	0.77	0.57	1.29
2̄	2	11	0.94	0.89	1.11
4	4	12	0.59	0.83	0.80
10	5	0	1.07	1.10	0.91
6̄	2	1	1.59	1.28	0.79
8̄	3	1	1.02	1.11	0.91
2	4	2	1.05	1.05	0.96
4	7	2	1.07	1.20	0.85
3	7	3	1.29	1.17	0.87
4	1	4	1.10	1.08	0.93
0̄	1	5	1.25	1.16	0.88
1̄	4	6	1.15	1.12	0.90
6	7	6	1.04	1.21	0.83
3̄	3	7	1.05	1.11	0.91
4	2	9	1.08	1.09	0.93
2	1	10	1.02	1.12	0.90

[a] For example see ref 18.

(S)-**1**   (R)-**2**

CpFe(CO)(PPh₃)C(O)O[(−)-menthyl] (**4**)[12] have been determined by X-ray crystallography.

Experimental Section

Materials. Preparation of **1**, **2**, and CpFe(CO)(PPh₃)X [where X = Me, Et, *n*-Pr, *i*-Bu, Bz, CH₂-c-C₃H₅, CH₂CN, CH₂Br, CH₂Cl, CH₂S(O)₂OMe, CH₂S(O)₂O(menthyl), S(O)₂Me, S(O)₂Et, S(O)₂-*n*-Pr, S(O)₂-*i*-Bu, S(O)₂CH₂CH₂CH=CH₂, S(O)₂Bz] have been reported,[6] as have those where X = I and O₂CCF₃.[13] Optically active [CpFe(CO)(PPh₃)(η²-CH₂=CH₂)]⁺BF₄⁻ has been characterized but its preparation will be reported with its chemistry.[14]

Circular Dichroism Spectra. CD spectra were run on a Cary 61 spectrophotometer using the least polar solvent consistent with a compound's solubility, at concentrations generally of ca. 0.2 mg/mL. Chlorocarbons were avoided (particularly for iron alkyls) because of their tendency to promote photoracemization. Spectra were recorded in the region of 300–550 nm, the short wavelength limit being determined by the strong absorption of the compounds.

Structure Analysis of (+)₅₇₈-**CpFe(CO)(PPh₃)CH₂O[(−)-menthyl]** (**1**). Suitable crystals of **1** were obtained via recrystallization from an ether/pentane solution under an inert atmosphere. A specimen of approximate dimensions 0.32 × 0.40 × 0.56 mm was selected for diffraction work. The crystal was mounted along what was later shown to be the 10̄1 axis in a thin-walled glass capillary tube. Precession photographs indicated a monoclinic unit cell, with systematic extinctions (0k0 = 2n + 1 absent) consistent with space group P2₁ (no. 4). The unit cell parameters, obtained by carefully measuring the setting angles of 36 reflections on a Nonius CAD-3 automated X-ray diffractometer, are given together with other relevant crystal data in Table I.

A total of 4161 reflections (including 70 check reflections), representing a half-sphere of data, were collected with Zr-filtered Mo Kα radiation in the θ/2θ scan mode. General details of data collection and reduction are reported in the following paper. At the end of data reduction, 3655 reflections with I < 3 σ, representing two quadrants of data, were retained for the subsequent structure analysis.

Scattering factors for Fe, P, O, and C were taken from the "International Tables for X-ray Crystallography"[15] and the effects of anomalous dispersion (Δf′ and Δf′′) for Fe were included in the calculations.

A three-dimensional Patterson map was used to obtain the coordinates of Fe and P atoms. With these coordinates a structure factor calculation and difference Fourier map revealed the positions of cyclopentadienyl, carbonyl, triphenylphosphine, and menthyl groups very clearly. All of the measured coordinates were then refined by a least-squares process to an R factor of 8.5%.[16] In this refinement, anisotropic temperature factors were assigned to Fe and P and isotropic ones to the rest of the atoms.

At this point the absolute configuration of the complex was investigated. The structure analysis had so far proceeded with the absolute configuration actually corresponding to the one shown in **1**. Changing the signs of the *y* coordinates of all the atoms has the effect of inverting the molecule through a mirror plane, in other words, converting **1** to its mirror image. A repeat of the least-squares refinement with this inverted molecule resulted in an R factor of 9.4%, very significantly inferior to the 8.5% obtained earlier. This difference, according to Hamilton's R factor significance test,[17] indicates that the probability of **1** being the correct configuration is well over 99.5%.

Examination of the ratios[18] of observed and calculated values of F_{hkl} and $F_{h\bar{k}l}$ (Table II) further substantiates the S form as the correct stereochemical designation.

Resumption of the least-squares refinement with the original configuration (**1**), now using anisotropic temperature factors for all atoms, resulted in the final agreement factors R = 6.2% and R_w = 7.8% for all 3655 reflections.[16]

It was comforting to note that the absolute configuration of the (−)-menthyl group derived from this work is identical with that obtained from another X-ray anomalous dispersion study, that of (−)-menthyl-*p*-bromophenylglyoxylate.[19]

Structure Analysis of (+)₅₇₈-**CpFe(CO)(PPh₃)CH₂CO₂[(−)-menthyl]** (**2**). Crystals of **2** were grown by slow recrystallization from dichloromethane under an inert atmosphere. A Schlenk flask con-

Table III. Selected Distances and Angles in (+)₅₇₈-CpFe(CO)-(PPh₃)CH₂O(menthyl) (1)[a]

bond distances, Å		bond angles, deg	
Fe–P	2.181 (2)	Fe–C(1)–O(1)	177.4 (8)
Fe–C(1)	1.744 (8)	Fe–C(2)–O(2)	109.6 (5)
Fe–C(2)	2.001 (8)	Fe–P–C(19)	119.5 (3)
Fe–C(14)	2.093 (9)	Fe–P–C(25)	114.9 (3)
Fe–C(15)	2.115 (10)	Fe–P–C(31)	114.7 (3)
Fe–C(16)	2.109 (9)	P–Fe–C(1)	91.7 (3)
Fe–C(17)	2.105 (9)	P–Fe–C(2)	92.0 (2)
Fe–C(18)	2.115 (9)	O(2)–C(4)–C(5)	111.1 (6)
C(1)–O(1)	1.127 (10)	O(2)–C(4)–C(9)	107.3 (6)
C(2)–O(2)	1.474 (9)	C(1)–Fe–C(2)	89.2 (4)
C(4)–O(2)	1.391 (8)	C(2)–O(2)–C(4)	114.4 (6)

[a] Numbering system shown in Figure 1.

Figure 1. The absolute configuration of (+)₅₇₈-CpFe(CO)(PPh₃)-CH₂O(menthyl) [(S)-1], as determined by X-ray anomalous dispersion methods.

Figure 2. An alternative view of the molecular geometry of **1.** The absolute configuration of the menthyl group, which is shown very clearly in this plot, confirms that derived from an earlier X-ray study (ref 19). Note the all-equatorial disposition of the substituents around the cyclohexane ring.

taining a small volume of a concentrated solution of **2** was placed in a refrigerator. The volume of solvent was slowly decreased by periodically flushing the flask with dry nitrogen. Most of these efforts, however, produced twinned crystals. It was found that crystal quality could be improved by extending the time interval between flushes to 1 or 2 weeks. After innumerable attempts spanning a period of several months, suitable crystals were finally obtained. A check of optical rotation of these crystals showed that the optical purity of the material had not deteriorated during this time.

A specimen of approximate dimensions 0.40 × 0.56 × 0.65 mm was selected for structural analysis. The crystal was mounted in a thin-walled glass capillary. Precession photographs indicated a triclinic system. Because of the optical activity of the compound, the only possible space group is P1 (no. 1). The unit cell parameters together with other relevant crystal data are presented in Table I.

A half-sphere of data was collected by the θ/2θ scan technique using zirconium-filtered Mo radiation up to a 2θ limit of 45°. Altogether 4266 reflections (including 74 check reflections) were collected in the same manner as described earlier. At the end of data reduction, 3665 nonzero reflections were left.
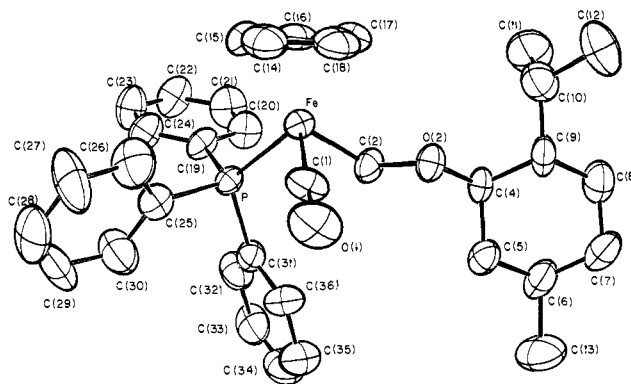
Space group P1 with Z = 2 requires two independent molecules in the unit cell. A three-dimensional Patterson map was used to obtain the coordinates of the Fe and P atoms. This was followed by a series of structure factor calculations and difference Fourier maps, which revealed the positions of the cyclopentadienyl and triphenylphosphine groups of both molecules. The carbonyl and menthyl groups, however, remained ill defined. The reason for this was readily apparent: the two separate (C₅H₅)Fe(PPh₃) fragments located up to that point were related by a pseudo-center of symmetry, and hence every difference Fourier phased by those atoms also had this false inversion center. It was clear that the pseudosymmetry element had to be removed before the structure could be solved. Accordingly, a single carbonyl group on one of the molecules was added to the list of known atoms: this disturbed the pseudosymmetry sufficiently to reveal the position of a few additional atoms. Repeated cycling through this procedure (structure factor calculation + difference Fourier map), each time adding two or three more atoms, resulted in a gradual improvement of the atomic list and a steady deterioration of the false symmetry element. Eventually, after 11 such steps, the entire molecular structure became known.

The absolute configuration of **2** was determined by using the menthyl group, whose absolute configuration was confirmed in the earlier structure determination of **1,** as a reference. A molecular plot of the trial structure at this stage showed the absolute configuration of the menthyl group to be incorrect (i.e., opposite to that found in **1**), thereby indicating that the coordinates used were in fact reversed. Changing the signs of all coordinates now gave the correct configuration.
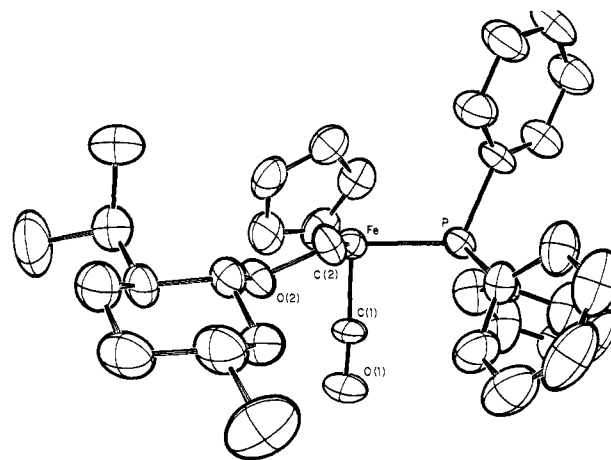
The structure analysis was concluded with several cycles of least-squares refinement, in which the phenyl atoms were refined isotropically and the other atoms anisotropically. Final R factors are R = 8.4% and R_w = 10.2%.[16]

Results and Discussion

Structure and Optical Configuration of (+)₅₇₈-CpFe(CO)-(PPh₃)CH₂O[(−)-menthyl] (1). Selected bond distances and

angles are shown in Table III with their estimated standard deviations. Final atomic parameters and listings of the observed and calculated structure factors are available.[20] The overall geometry and absolute configuration of (+)₅₇₈-**1** are shown in Figures 1 and 2. The absolute configuration at iron was determined to be S[10] by the technique of anomalous dispersion[21] and confirmed by comparing Bijvoet differences as described in the Experimental Section. The assignment of configuration could be further confirmed by the presence of (−)-menthol in the molecule. Our result, in fact, constitutes an independent confirmation of the absolute configuration of the (−)-menthyl group, which was earlier determined by spectroscopic[22] and crystallographic[19] methods.

Considering the extensive chemical investigations carried out on iron alkyls CpFe(CO)LR (L = CO, phosphine, or phosphite), there are surprisingly few X-ray crystallographic structure determinations of these species. Of those structures which have been determined, the only one of a molecule containing an Fe–C(sp³) bond which has been determined with good precision appears to be **5.**[23] Some of the more interesting


5
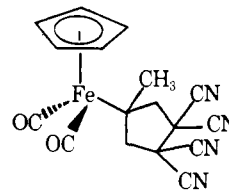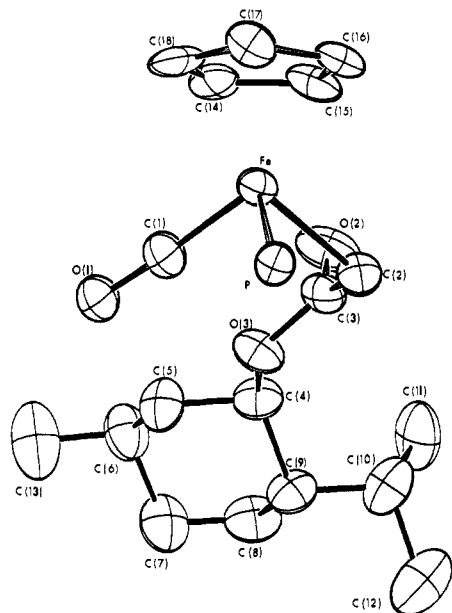
Figure 3. The absolute configuration of (+)$_{578}$-CpFe(CO)(PPh$_3$)-CH$_2$C(O)O(menthyl) [(R)-2], showing an opposite chirality at iron from 1. This plot illustrates one of the two independent molecules in the unit cell, with phenyl groups omitted for clarity. The absolute configuration was determined by using the menthyl group as reference. Note also the manner in which the carbonyl group of the ester is tilted toward Fe.

bond lengths and angles of 1, 2, and 5 are listed in Table IV for comparison. In view of the extensive discussion of molecular dimensions available for 5,[23] it need only be said that replacement of one CO ligand by PPh$_3$ does not cause any significant changes in geometry. The Fe-P distance of 1 is very close to that of three other CpFe(CO)(PPh$_3$)X molecules which have been determined.[24]

The Fe-C-O-C partial structure bears particular scrutiny because of the special lability of the ether linkage in substitution reactions.[4,6] This reactivity is believed to arise from the electron-donating ability of the iron atom whose effect may be represented by the polar resonance contribution 6b. To the extent that contribution of 6b might cause changes in the ground state geometry, the Fe-C$_\alpha$ bond should be shortened and the C$_\alpha$-O bond should be lengthened. From Table IV it may be seen that the Fe-C$_\alpha$ bond of 1 is 0.104 Å shorter than that of ester 2 ($\sim$7σ where σ = [σ(1)^2 + σ(2)^2]$^{1/2}$), and it is 0.097 Å ($\sim$12σ) shorter than the same bond in 5. In addition, the C$_\alpha$-O ether bond of 1 is longer than in a typical ether (1.426 (5) Å)[25] by 0.048 Å ($\sim$5σ) and O-C$_\gamma$ is shorter by 0.035 Å ($\sim$4σ). These observations, especially the shortening of the Fe-C$_\alpha$ bond, are consistent with a strong "α effect" of the metal atom on the ether linkage as in 6b.

$$FeCH_2OR \leftrightarrow Fe^+{=}CH_2 \ OR$$

| 6a | 6b |
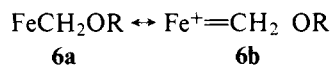
Structure and Optical Configuration (+)$_{578}$-CpFe(CO)-(PPh$_3$)CH$_2$CO$_2$[(−)-menthyl] (2). Some distances and angles in the molecule are given in Table V. Final atomic positions, thermal parameters, and calculated and observed structure factors are available.[20] The overall geometry and absolute configuration of (+)$_{578}$-2 is shown for one of the two crystallographically independent molecules in Figure 3. The absolute configuration of the iron center was assigned by comparison with the known[19,22] configuration of the (−)-menthyl moiety of the molecule and was found to be R.[10]

Of particular interest for this molecule is the arrangement of the atoms shown in partial structure 7. The interaction of

Table IV. Comparison of Representative Bond Lengths and Angles in Compounds 1, 2, and 5

	ether 1	ester 2[a]	5[a,b]
	Bond Lengths, Å		
C≡O	1.127 (10)	1.161 (16)	1.149 (3)
Fe-CO	1.744 (8)	1.703 (13)	1.751 (2)
Fe-C$_\alpha$	2.001 (8)	2.105 (13)[c]	2.098 (2)
Fe···C$_\beta$	2.856 (8)[d]	2.931 (12)	3.009 (2)[e]
Fe-P	2.181 (2)	2.195 (4)	
	Bond Angles, deg		
Fe-C$_\alpha$-C$_\beta$	109.6 (5)[f]	108.4 (9)	111.2 (2)
OC-Fe-P	91.7 (3)	92.8 (4)	95.5 (1)[g]
C$_\alpha$-Fe-CO	89.2 (4)	98.0 (6)	88.9 (1)
C$_\alpha$-Fe-P	92.0 (2)	91.3 (4)	91.5 (1)[h]

[a] Data are the average for the two crystallographically independent molecules. [b] Data taken from ref 23. Some values are rounded off. [c] Length for the two molecules differed by 0.002 Å. [d] Distance from Fe to the ether oxygen. [e] The average of six distances. These follow: molecule 1, 3.063, 2.980, 2.986; molecule 2, 2.977, 3.053, and 2.992 Å. [f] Fe-CH$_2$-O angle. [g] OC-Fe-CO angle. [h] C$_\alpha$-Fe-CO angle.

Table V. Selected Distances and Angles in (+)$_{578}$-CpFe(CO)-(PPh$_3$)CH$_2$C(O)O(menthyl) (2)[a]

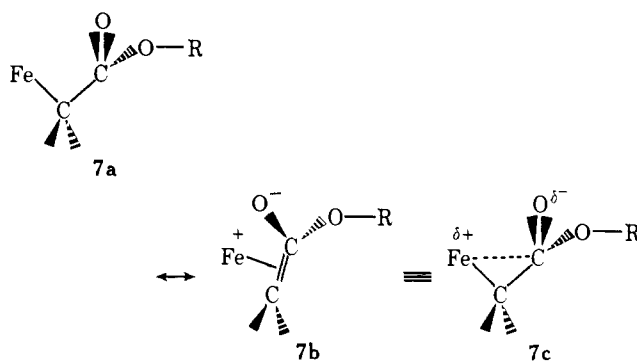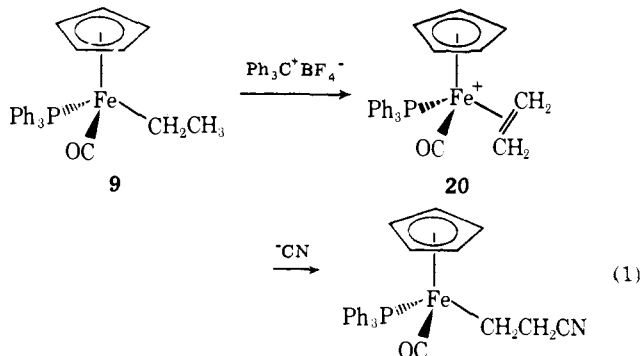|	molecule 1	molecule 2
	A. Bond Distances, Å	
Fe-P	2.198 (3)	2.193 (4)
Fe-C(1)	1.672 (11)	1.733 (13)
Fe-C(2)	2.106 (13)	2.104 (12)
Fe-C(14)	2.087 (14)	2.081 (13)
Fe-C(15)	2.106 (16)	2.098 (13)
Fe-C(16)	2.100 (13)	2.123 (13)
Fe-C(17)	2.115 (13)	2.119 (15)
Fe-C(18)	2.144 (14)	2.161 (14)
C(1)-O(1)	1.194 (15)	1.128 (16)
C(3)-O(2)	1.218 (18)	1.217 (15)
C(3)-O(3)	1.364 (16)	1.340 (15)
O(3)-C(4)	1.471 (19)	1.443 (17)
C(2)-C(3)	1.466 (20)	1.502 (19)
	B. Bond Angles, deg	
P-Fe-C(1)	92.8 (4)	92.8 (4)
P-Fe-C(2)	91.0 (4)	91.6 (3)
C(1)-Fe-C(2)	95.9 (5)	100.0 (6)
Fe-P-C(19)	116.8 (4)	112.4 (4)
Fe-P-C(25)	117.5 (4)	118.6 (4)
Fe-P-C(31)	115.4 (4)	117.8 (4)
Fe-C(1)-O(1)	176.8 (11)	172.4 (11)
Fe-C(2)-C(3)	107.1 (9)	109.5 (8)
C(3)-O(3)-C(4)	116.5 (11)	119.2 (10)
O(2)-C(3)-C(2)	128.2 (13)	124.8 (12)
O(3)-C(3)-C(2)	110.1 (11)	113.7 (10)
O(2)-C(3)-O(3)	121.5 (14)	121.5 (12)

[a] Numbering system shown in Figure 3.

Table VI. CpFe(CO)(PPh₃)X Molecules Having the Configuration Shown for (S)-1

compd, X =		ORD (sign)₅₇₈	R or Sᵃ
1	-CH₂O(menthyl)	(+)	S
2	-CH₂C(O)O(menthyl)	(−)	S
3	-[CMe(NHCHMePh)]⁺BF₄⁻ ᵇ	(+)	S
4	-C(O)O(menthyl)ᶜ	(+)	R
8	-Me; 9 -Et; 10 -n-Pr	(+)	S
11	-i-Bu; 12 -CH₂-c-C₃H₅	(+)	S
13	-CH₂Cl; 14 -CH₂Br; 15 -CH₂I	(+)	R
16	-CH₂Ph	(−)	S
17	-S(O)₂Rᵈ	(−)	S
18	-CH₂S(O)₂O(menthyl)	(−)	R
19	-C(O)Me	(+)	S
20	-(η²-C₂H₄)⁺BF₄⁻	[CD, (+)₄₀₀]	R
21	-I; 22 -Br	[CD, (+)₃₅₀]	R
23	-CH₃ᵉ	(−)	S
24	-I,ᵉ 25-Br,ᵉ 26-Clᵉ	(+)₃₆₅	R

ᵃ For a description of the conventions used for *R*-*S* designations, see ref 10. See the Discussion for the basis of these configurational assignments. ᵇ Reference 11. ᶜ Reference 12. ᵈ R = Me, Et, *n*-Pr, *i*-Bu, Bz, 3-butenyl, and -CH₂CO₂(menthyl). The configuration of these is known from X-ray structure determination of the *i*-Bu compound: ref 30. ᵉ The phosphine ligand in this molecule was (S)-PPh₂(NMeCHMePh) rather than PPh₃: ref 3.
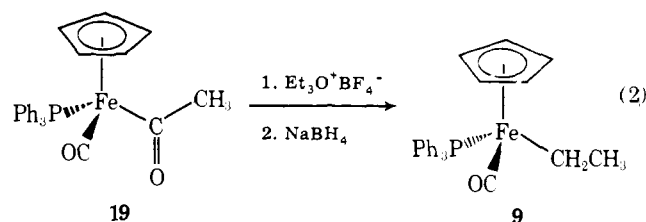
transition metals with the β functional group of metal alkyls is a well-established phenomenon,[26] and in ester **2**, the β effect is evident from the fact that infrared stretching frequency of the acyl group is lowered by ca. 85 cm⁻¹ to 1650 cm⁻¹. This presumably results from contribution of the dipolar resonance structure **7b** to the ground state, and consistent with this, in both molecules of **2** in the unit cell, the acyl π system is directed toward the metal (**7c** and Figure 3) as would be required for a β interaction. Whether this is due to steric and crystal packing forces or to electronic factors is difficult to say, but there are no notable geometric distortions of the ester group as would be predicted for a sizable contribution of **7b** (Table V). The same orientation has been found in CpFe(CO)₂-CH₂CO₂H.[27]

Configurations of Other Iron Molecules. The absolute configuration of a large number of organoiron molecules of the type CpFe(CO)(PPh₃)X is established by these determinations (Table VI). The configurations of all those where X is CH₂Y, in addition to **1** and **2**, are known because they have been prepared from **1** without alteration of the Fe-C bond.[4,6] The configuration of **20** is reasonably certain because the configuration of **9** from which it is prepared is known, and a double inversion process for the sequence shown in eq 1 seems chemically unreasonable.[14] The configuration of **3** has been established, as mentioned above, from an X-ray crystallographic structure determination.[11] Compound (+)₅₇₈-**19** is known to be *S* because it may be reduced to (S)-**9** without loss of ste-

reochemistry at iron (eq 2).[28] Inversion in this reduction seems highly unlikely.

$$Ph_3P\text{-}Fe\text{-}C(O)CH_3 \xrightarrow[\text{2. NaBH}_4]{\text{1. Et}_3O^+BF_4^-} Ph_3P\text{-}Fe\text{-}CH_2CH_3 \quad (2)$$

19 → **9**

Circumstantial evidence points to the likely configuration of **21** as shown in eq 3, wherein the iodide is formed in these
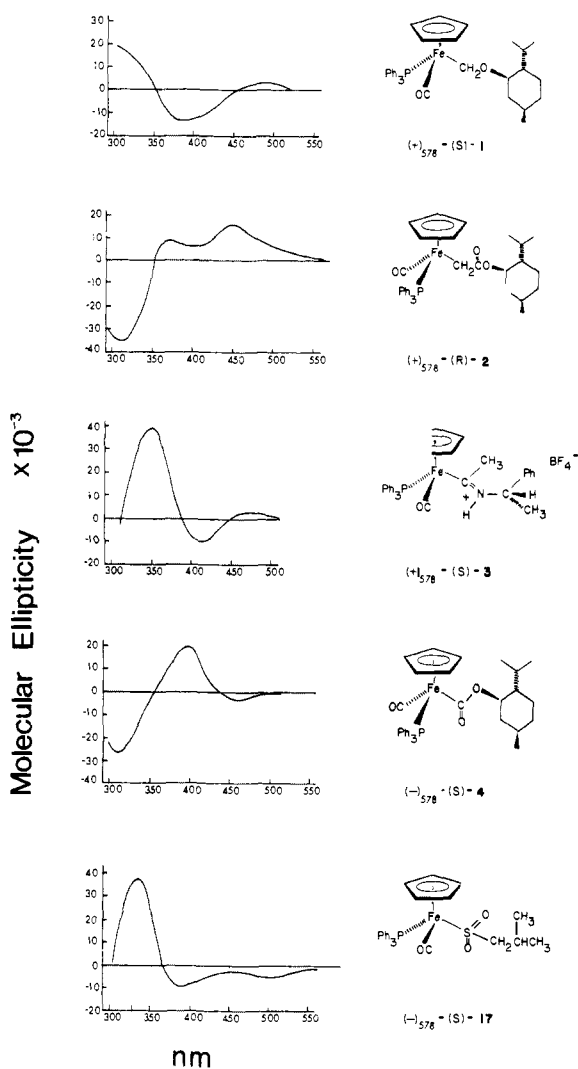
$$\quad (3)$$

21
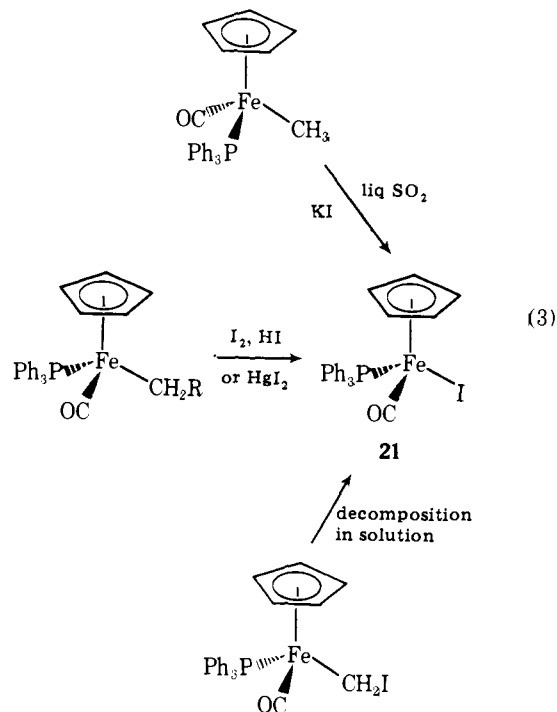
reactions in varying yields and varying enantiomeric excess, but with the same configuration.[13] Further substantiation of this argument comes from the work of Brunner and Wallner,[3] wherein the cleavage of the Fe-CH₃ bond in CpFe(CO)-[PPh₂(NMeCHMePh)]CH₃ (**23**) by I₂ was shown by a cyclic series of reactions to very likely proceed to form CpFe(CO)-[PPh₂(NMeCHMePh)]I (**24**) with retention of configuration of iron. Similarly, the configuration at iron of the ester (−)₅₇₈-**4** could be predicted to be as shown in eq 4 (*S*) because data relevant to the mechanism of the reaction in eq 4 indicate that

$$\xrightarrow{CH_3Li} \quad (4)$$

4 → **19**
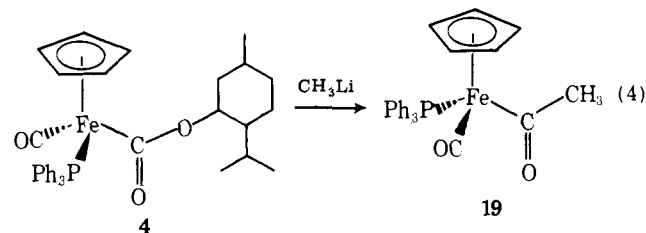
CH₃Li attacks at -C≡O and not at -CO₂R, resulting in inversion of configuration at iron.[29] Arguments based on CD spectra are consistent with this notion (vide infra). Recently, the publication of the X-ray structure determination of **4** has confirmed these predictions.[12]

Circular Dichroism Spectra. The CD spectra of the five compounds whose absolute configurations have been determined by X-ray methods, (S)-**1**, (R)-**2**, (S)-**3**,[11] (S)-**4**,[12] and (S)-(−)₅₇₈-CpFe(CO)(PPh₃)S(O)₂-*i*-Bu,[30] are given in Figure 4. Those of other molecules listed in Table VI are shown in Figures 5-10. Figure 5 shows the CD and UV spectra of
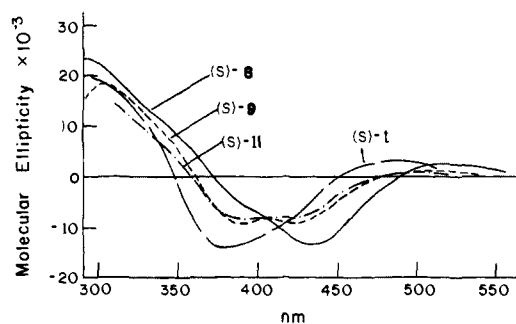
$$Ph_3C^+BF_4^- \quad (1)$$

9 → **20**

$$\xrightarrow{-CN}$$

Figure 5. UV spectrum (———) and CD spectrum (- - -) of (R)-**21**. Figures 5–9 all refer to CpFe(CO)(PPh₃)X molecules having the same absolute configuration as (S)-**1**. For (R)-**21**, X = 1.

Figure 4. The circular dichroism spectra of five molecules whose absolute configurations have been established by X-ray methods: (+)₅₇₈-(S)-**1** (this work), (+)₅₇₈-(R)-**2** (this work), (+)₅₇₈-(S)-**3** (ref 11), (−)₅₇₈-(S)-**4** (ref 12), and (−)₅₇₈-(S)-**17** (ref 30). The CD spectra of **1**, **3**, and **17**, which have the same absolute configuration at iron, are similar except for a low-energy shift of the CD bands of **3** and **17**. On the other hand, the 300–400-nm regions of the spectra of **1**, **3**, and **17** are approximately reversed from those of **2** and **4**, reflecting the opposite chiralities of these last two compounds at iron.

Figure 6. CD spectra of (S)-**1** [X = CH₂O(menthyl)] (— —); (S)-**8** [X = Me] (———); (S)-**9** [X = Et] (- - -); and (S)-**11** [X = *i*-Bu] (· - · - ·). See ref 38.
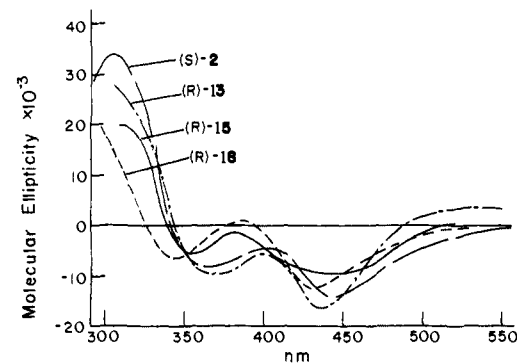
Figure 7. CD spectra of (S)-**2** [X = CH₂C(O)O(menthyl)] (— —); (R)-**13** [X = CH₂Cl] (· - · - ·), [θ] × 10; (R)-**15** [X = CH₂I] (———) from ref 37; and (R)-**18** [X = CH₂S(O)₂O(menthyl)], (- - -), [θ] × 2. See ref 38.

compound **21**, from which it is evident that there is no simple correspondence between the CD and UV maxima. This is true of all these molecules as a rule. At first sight the CD spectra of many of these compounds appear to be rather simple, consisting of three Cotton effects in the 300–550-nm region, as in the case of **2** (Figure 7), **3**, and **17** (Figure 8). Examination of methyliron **8** (Figure 6), on the other hand, reveals at least five transitions, and many other spectra show at least four.

Electronic transitions are present in the 300–500-nm spectral region of simple carbonyls (M(CO)ₙ),[31] sandwich compounds (MCp₂),[32] and mixed complexes ((arene)M(CO)ₙ).[33] The prevalent current assignment of these bands in these first two classes of molecules is to d–d transitions,[31,32] but more specific assignment than this has not been a simple matter, even for ferrocene.[32] Assignments of bands in spectra of complexes (arene)M(CO)ₙ appear to be even less clear, but these transitions are thought to be a mixture of the d–d and metal to ligand charge transfer types.[33] The ability to make correlations of CD bands with UV bands and assignment of UV bands to specific d–d transitions in numerous classical octahedral

complexes has resulted in the ability to make fairly accurate predictions of the absolute configuration of new molecules using empirical correlations based on such data from known complexes.[34] Because of the total asymmetry of the pseudo-tetrahedral molecules at hand, and because of the complexity of and lack of correspondence between UV and CD spectra, it does not presently seem feasible to correlate the chiroptical properties of these molecules with their absolute configuration in any reliable way.

Nevertheless, in the face of this difficulty, some observations may be made. The morphology of many of these CD curves is substantially similar: an intense maximum between 300 and 350 nm, a maximum (or double maximum) of opposite sign between 350 and 450 nm, and a maximum of either sign at 450–500 nm. Potentially the most reliable indicator of configuration appears to be the 300–350- and 350–450-nm max-
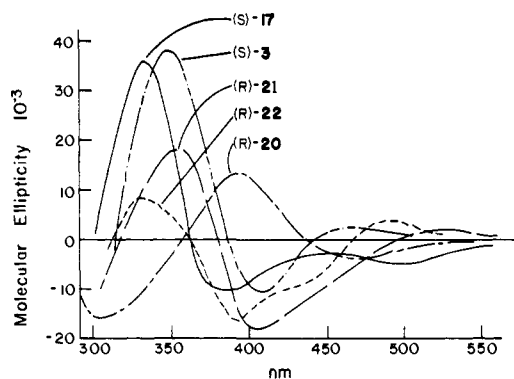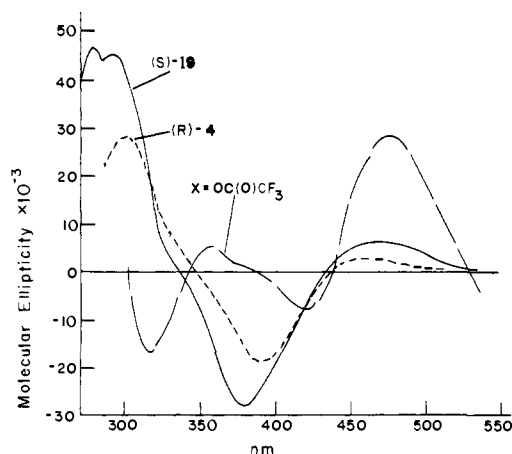
Figure 8. CD spectra of (S)-3 [X = {CMe(NHCHMePh)}+BF4−] (- · − − − · -), from ref 11; (S)-17 [X = S(O)2R] (———); (R)-20 [X = (η2-C2H4)+BF4−] (· - · - ·), [θ] × 1.5; (R)-21 [X = I] (— —); and (R)-22 [X = Br] (- - -), [θ] × 20. See ref 38.

Figure 9. CD spectra of CpFe(CO)(PPh3)OC(O)CF3 (configuration unknown) (— —), [θ] × 5; (S)-19 [X = C(O)Me] (———), from ref 29; and (R)-4 [X = C(O)O(menthyl)] (- - -), from ref 29. See ref 38.

Figure 10. CD spectra of (R)-8 [X = Me] (- - -); (S)-21 [X = I] (— —); (−)365-23 [X = CH3] (———), [θ] × 10, from ref 3; (−)365-24 [X = I] (· - - · ·), [θ] × 10, from ref 3. For 23 and 24 the phosphine ligand in the molecule is (S)-PPh2(NMeCHMePh) rather than PPh3. See ref 38.

ima. The argument has been made several times in the literature that molecules CpFe(CO)(PPh3)X, differing only in the group X, which exhibit CD spectra of the same sign and very similar morphology may reasonably be predicted to have the same absolute configuration.[2a,4,35,36] From the present X-ray crystal data (Figure 4) and the chemical arguments summarized above, the absolute configuration of a significant number of these molecules is known, and examination of the CD spectra in Figures 6–10 reveals that to a large extent this empirical CD argument does actually work. There are, however, significant problems.
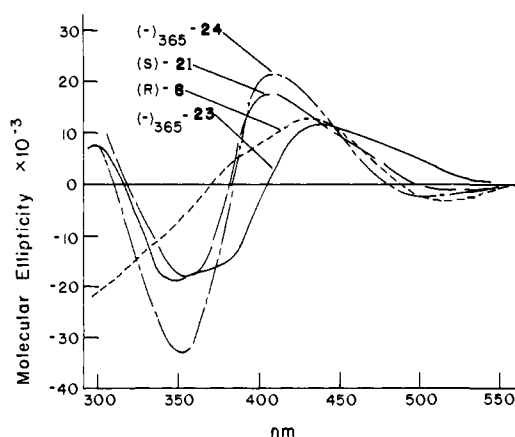
Consider the position of the shortest wavelength CD transition. All of the iron alkyls having the configuration shown for (S)-1, such as 8, 9, and 11 (Figure 6), and even those alkyls having strongly σ-electron withdrawing groups such as 1, 2, 13, and 18 (Figure 7), exhibit positive maxima near 300 nm. On the other hand, groups X in CpFe(CO)(PPh3)X which are good π-accepting ligands or are regarded in organic systems as leaving groups seem to impart a bathochromic shift to this band so that it appears near 350 nm in carbene cation complex 3, sulfinate 17, and halides 21 and 22 (Figure 8). The spectrum of the cationic ethylene complex 20 appears at first sight to be nearly the mirror image of that of iodide 21, for example (Figure 8). It may be that because of the much higher effective charge on iron in 20 than in 3, 17, or 21, the maximum of interest has shifted to 393 nm, but this is clearly a post facto argument. Similarly, if it is the effective charge on iron or the π-accepting ability of the ligand which determines the position of the 300–350-nm CD band, it is not clear why acyl complex 19 and carboalkoxyiron 4 should have maxima at ca. 290 rather than 350 nm (Figure 9). Lastly, the CD spectra of some of the molecules are very different from the others, as in the case of CpFe(CO)(PPh3)OC(O)CF3 (Figure 9), thus precluding any chance of using chiroptical properties for configurational assignments.

The conclusion appears to be, then, that when two groups X in the molecules CpFe(CO)(L)X are very similar in nature, and when the morphology of the corresponding CD curves is very similar, then one may draw tentative conclusions about absolute configurations. For example, the reaction of eq 4 interconverts two molecules with very similar X groups, and the CD curves are nearly mirror images. This strongly implies inversion of configuration at iron.

Previously,[35] we have made the argument that sulfur dioxide insertion into the Fe–C bond of 2 proceeds with retention of configuration at iron based on the facts that (1) such an outcome is chemically reasonable,[6] and (2) the CD spectra of 2 and the corresponding sulfinate 17 are very similar and of the same sign. In view of the above discussion and the accumulation of CD spectra shown here, the second argument was cer-

tainly tenuous. We have since shown that the conclusion is correct by carrying out the X-ray structure determination of a sulfinate derivative (17, R = *i*-Bu).[30]

One prediction can be made, and has been included in Table VI. As stated above, Brunner and Wallner[3] have resolved the species CpFe(CO)(PPh2[NMeCHPhMe])X where X = CH3 (23) and X = I (24). From Figure 10 it can be seen that the CD spectra of 8 and 23 are not extremely similar. However, the CD spectra of 21 and 24 are essentially identical. We therefore predict that (−)365-24, and hence by Brunner and Wallner's arguments, also (−)365-23, will be shown to be of S and R configuration, respectively.

Supplementary Material Available: Listings of the observed and calculated structure factors and final atomic parameters for 1 and 2 (29 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Fellows of the Alfred P. Sloan Foundation: (a) 1974–1976; (b) 1977–1979.

(2) Henri Brunner carried out the first extensive investigations in this area: (a) H. Brunner, *Angew. Chem.*, **83**, 274 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 249 (1971); (b) *Ann. N.Y. Acad. Sci.*, **239**, 213 (1974); (c) *Top. Curr. Chem.*, **56**, 67 (1975).

(3) A more recent leading reference: H. Brunner and G. Wallner, *Chem. Ber.*, **109**, 1053 (1976).

(4) A. Davison and M. Martinez, *J. Organomet. Chem.*, **74**, C17 (1974).

(5) T. G. Attig and A. Wojcicki, *J. Organomet. Chem.*, **82**, 397 (1974).

(6) T. C. Flood, F. J. DiSanti, and D. L. Miles, *Inorg. Chem.*, **15**, 1910 (1976).

(7) G. Jaouen, A. Meyer, and G. Simonneaux, *Tetrahedron*, **31**, 1889 (1975).

(8) C. Moise, J. C. Leblanc, and J. Tirouflet, *J. Am. Chem. Soc.*, **97**, 6272 (1975).

(9) For example: (a) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974); (b) J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 1 (1964); (c) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974); (d) A. Wojcicki, *Adv. Organomet. Chem.*, **12**, 31 (1974).

(10) The sequencing rules used here for the assignment of *R* and *S* stereochemical designations are those of K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, **97**, 6598 (1975). Note that these are different than and supplant the conventions used in ref 4 and 6.

(11) V. W. Day and A. Davison, unpublished work.

(12) M. G. Reisner, I. Bernal, H. Brunner, and M. Muschiol, *Angew. Chem., Int. Ed. Engl.*, **15**, 776 (1976).

(13) T. C. Flood and D. L. Miles, *J. Organomet. Chem.*, **127**, 33 (1977).

(14) T. C. Flood and D. L. Miles, unpublished results.

(15) "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968.

(16) $R = \Sigma||F_o| - |F_c||/\Sigma F_o; R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

(17) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(18) G. Kartha, F. R. Ahmed, and W. H. Barnes, *Acta Crystallogr.*, **15**, 326 (1962).

(19) R. Parthasarathy, J. Ohrt, A. Horeau, J. P. Vigneron, and H. B. Kagan, *Tetrahedron*, **26**, 4705 (1970).

(20) See paragraph at end of paper regarding supplementary material.

(21) J. M. Bijvoet, A. F. Peerdeman, and A. J. vanBommel, *Nature (London)*, **168**, 271 (1951).

(22) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

(23) M. R. Churchill and S. W. Y. Chang, *J. Am. Chem. Soc.*, **95**, 5931 (1973).

(24) Structures of several related molecules CpFe(CO)(PPh₃)R have been determined: R = C₆H₅, V. A. Semion and Yu. T. Struchkov, *J. Struct. Chem.*, **10**, 80 (1969); R = C(O)C₆H₅, *ibid.*, **10**, 563 (1969); R = α-thiophenyl, Y. G. Andrianov, G. N. Sergeeva, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and A. S. Beschastnov, *ibid.*, **11**, 163 (1970).

(25) "Tables of Interatomic Distances and Configuration in Molecules and Ions: Supplement 1956–1959", *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

(26) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, p 211 ff.

(27) J. K. P. Ariyaratne, A. M. Bierrum, M. L. H. Green, M. Ishaq, C. K. Prout, and M. G. Swanwich, *J. Chem. Soc. A*, 1309 (1969).

(28) A. Davison and D. L. Reger, *J. Am. Chem. Soc.*, **94**, 9237 (1972).

(29) H. Brunner and E. Schmidt, *J. Organomet. Chem.*, **36**, C18 (1972); **50**, 219 (1973).

(30) The configuration of (−)₅₇₈-CpFe(CO)(PPh₃)S(O)₂-*i*-Bu has been shown to be *S* by X-ray crystallographic determination: S. L. Miles, D. L. Miles, R. Bau, and T. C. Flood, *J. Am. Chem. Soc.*, following paper in this issue.

(31) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).

(32) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).

(33) D. G. Carroll and S. P. McGlynn, *Inorg. Chem.*, **7**, 1285 (1968).

(34) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley, New York, N.Y., 1971.

(35) T. C. Flood and D. L. Miles, *J. Am. Chem. Soc.*, **95**, 6460 (1973).

(36) H. Brunner and E. Schmidt, *J. Organomet. Chem.*, **36**, C18 (1972).

(37) A. Davison, W. C. Krusell, and R. C. Michaelson, *J. Organomet. Chem.*, **72**, C7 (1974).

(38) CD spectra of compounds **1–4, 8, 9, 11, 17–19, 23**, and **24** are of compounds of >90% ee. Spectra of **20, 21**, and CpFe(CO)(PPh₃)OCOCF₃ correspond to materials of ~80, >80, and ~56% ee, respectively. Optical purities of **13, 15**, and **22** are unknown.

Stereochemistry at Iron of the Sulfur Dioxide Insertion Reaction of Iron Alkyls. Crystallographic Determination of the Absolute Configuration at Iron of a Chiral Iron Sulfinate

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Abstract: The absolute configuration of (−)₅₇₈-CpFe(CO)(PPh₃)S(O)₂CH₂CH(CH₃)₂ has been shown by X-ray anomalous dispersion techniques to be *S* (nomenclature based on the sequencing rules recently formulated by Stanley and Baird). The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 13.800$ (4), $b = 13.523$ (5), $c = 13.649$ (5) Å. Refinement of the structure with two Friedel-related sets of data (3059 reflections) yielded $R = 6.4\%$ for the *S* configuration, as opposed to $R = 7.0\%$ for the *R* configuration. The structure of this compound, which was prepared from the isoconfigurational alkyl complex (+)₅₇₈-(*S*)-CpFe(CO)(PPh₃)CH₂CH(CH₃)₂, confirms prevailing beliefs that the stereochemistry of the SO₂-insertion reaction involves retention of configuration at iron.

Introduction

Since its discovery in 1964 by Bibler and Wojcicki,[2] the reaction of sulfur dioxide with metal–carbon σ bonds has been the object of intense scrutiny.[3,4] This is presumably not because the reaction itself is of especial synthetic importance, but rather it seemed to be another well-defined member of the class of reactions often called "insertions",[5] of which carbon monoxide insertion is probably the best known example. It was assumed at first by many that all of these reactions proceed by essentially the same mechanism, so that thorough investigation of the SO₂ insertion should yield more insight into this class of reactions which is important generally in metal-catalyzed transformations of organic molecules.

The reactions of metal alkyls with SO₂ and CO are now known to be very different.[3–5] The most striking dissimilarity is that insertion of SO₂ into the Fe–C bond of *threo*- or *erythro*-CpFe(CO)₂CHDCHDC(CH₃)₃ (Cp = η⁵-C₅H₅) proceeds with inversion of configuration at carbon, while insertion of CO proceeds with retention.[6] Only half of the stereochemical information necessary for a detailed mechanistic understanding resides at carbon, so we[7] and others[8,9] have undertaken to examine the stereochemical outcome at iron of these insertions in molecules of types **1**[7,8b,9] (where R is a variety of alkyl groups) and **2**.[8]

1   2