

Optically Active Organoiron Complexes. Preparation and Chemistry

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The achiral and optically active Fp(dioxene)BF₄ complexes **2a** and **2b** (Fp = dicarbonylcyclopentadienyliron) are readily prepared from Fp(1,2-dimethoxyethylene)BF₄ by glycol exchange reactions. The barrier to ring inversion in these compounds is estimated to be 7.6 kcal/mol from low-temperature ¹³C NMR spectral measurements. A crystal structure determination of **2a** shows significant distortions due to transannular steric interactions between the Fp carbonyl groups and an axial ring proton. Lateral displacement of the Fp group along the C-C double-bond axis is also suggested by the X-ray data and is supported by ¹³C and ¹H NMR spectral analyses. Both **2a** and **2b** add a number of carbon nucleophiles. These reactions with **2b** are highly regioselective and yield a single enantiomeric product, **4**, in which the nucleophile and Fp substituents are diaxial on the dioxane ring. An X-ray structure determination of a cyano adduct, **4c**, has been carried out. The methyl adduct **4b** has been converted to optically active Fp(*cis*-propenyl methyl ether)BF₄ and to Fp(propene)BF₄. Ring opening of the phenyl adduct **4d** may take place through phenyl rather than Fp assistance and, under those circumstances, leads to loss of optical activity in the product olefin complex. Fp-assisted ring opening of the dioxene complex **4a** is shown to be highly dependent on the conformation of the Fp substituent.

Introduction

Metal olefin complexes provide unique substrates in carbon-carbon bond-forming reactions, since complexation renders an olefin center, which would otherwise be unreactive to nucleophile addition, susceptible to such attack. Such activation has been observed for a number of transition metal-olefin complexes,² including those of Mo,³ W,² Fe,⁴ Ru,⁵ Rh,⁶ Pd,⁷ and Pt,⁸ and forms an essential step

in the industrial oxidation of ethylene by Pd(II) to acetaldehyde.⁹ A theoretical analysis of factors responsible for olefin activation by metal complexation has recently been given by Eisenstein and Hoffmann.¹⁰

For olefins that lack a C₂ axis of symmetry in the plane of the double bond, metal complexation provides a potential means of asymmetric bond formation through enantioface selective addition of a nucleophile to an optically active complex in which the complex olefin is the sole center of asymmetry.¹¹ If the optically active complex is not available, asymmetric induction can, in principle, be achieved through diastereoface selective addition to an olefin complex in which a chiral auxiliary is incorporated within either the olefin ligand or another ligand complexed to the metal or is present at the metal center itself. However, in these cases some mechanism must exist for the exchange of diastereomers which results in either preferential complexation of one enantioface of the olefin or a rapid exchange of the enantiofaces.¹² Finally, even complexes derived from 1,2-disubstituted olefins that have a C₂ axis of symmetry may serve as platforms for asymmetric bond formation, provided another chiral center is present in the molecule. For these interesting cases, the diastereoselectivity of nucleophile addition is reduced to a problem of regioselectivity.¹³

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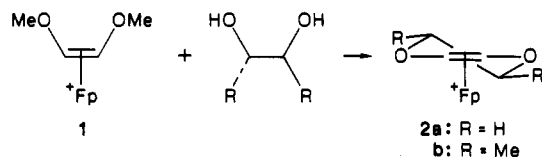
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We recently reported briefly on the preparation and reactions of the optically active iron complex **2b** [$\text{Fp} = (\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$], a member of this latter class of complex.¹⁴ The present report provides a full account of the chemistry of this substance and its congeners and of the use of **2b** in the synthesis of a number of optically active olefin complexes in which the metal-complexed olefin center is the sole site of asymmetry.

Results and Discussion

The preparation of $\text{Fp}(\eta\text{-cis-1,2-dimethoxyethylene})\text{BF}_4$ (**1**) by exchange complexation has earlier been reported.¹⁵ Brief treatment of **1** with ethylene glycol in methylene chloride solution at 0 °C gave the dihydrodioxin complex **2a** in 92% yield. The facility of this transesterification reaction is illustrative of the high reactivity of $\text{Fp}(\eta\text{-vinyl ether})$ cations to a variety of nucleophiles. Similarly, treatment of **1** with (*R,R*)-2,3-butanediol gave the optically active salt **2b**.



The proton NMR spectrum of **2b** shows that the methyl groups on the dihydrodioxin ring in this complex are diequatorial ($J_{2,3} = 8$ Hz). A lower limit of 0.4 kcal/mol may be estimated as the conformational preference for this conformer, taking a value of 0.65 kcal/mol as the conformational energy of a methyl group on a dioxene ring¹⁶ and 0.9 kcal/mol for a gauche butane interaction on this ring. The energy associated with the interaction of an axial methyl group with the complexed Fp group must be added to this, and while this steric interaction is difficult to estimate, it is likely to be substantial (vide infra). The vinyl protons in **2b** are observed as a pair of doublets at δ 7.70 and 7.25 ($J = 1.5$ Hz), while those in the parent complex **2a** appear as a broad singlet at δ 7.45. Similarly, a proton-decoupled carbon-13 spectrum of the parent complex shows the vinyl carbon centers as a broad singlet at δ 102.7. This signal broadens progressively as the temperature is lowered and almost disappears into the base line at -100 °C, the lowest temperature for which spectra could be recorded in acetone-*d*₆. By contrast, the optically active complex **2b** shows two resonances at δ 108.6 and 95.5 for the vinyl carbon centers, symmetrically displaced upfield and downfield from the single peak observed for the parent compound. If the ¹³C spectrum, observed at -100 °C for **2a**, represents a reasonable approximation of the coalescence point associated with the process of ring inversion, and the shift difference between the vinyl carbons of **2b** is taken as equal to that for **2a** in the slow-exchange limit, a value of 7.3 kcal/mol is derived for the barrier to ring inversion in the parent complex. This compares closely with the value of 7.6 kcal/mol for the ring inversion barrier in 1,4-dioxene, determined from its temperature-dependent proton spectrum.¹⁷ Since asymmetric induction in **2b** is

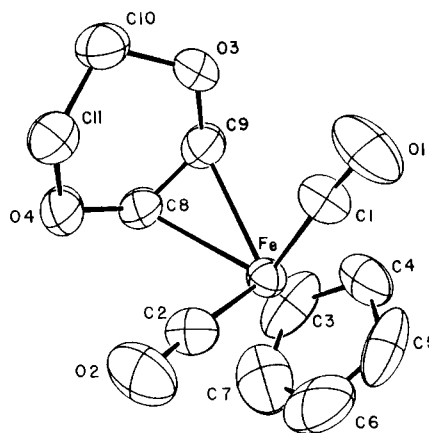


Figure 1. Molecular structure of **2a**, showing labeling scheme and 50% probability ellipsoids for atoms refined by using anisotropic temperature factors.

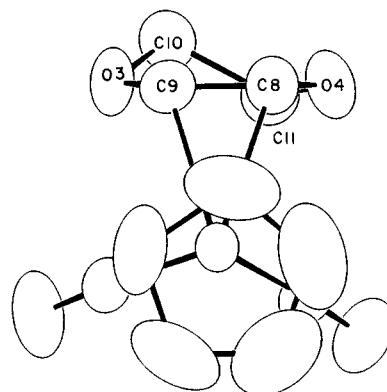


Figure 2. Molecular structure of **2a**, showing positions of C(11) [$+0.182$ (9) Å] and C(10) [-0.493 (9) Å] relative to the C(8)-C(9)-O(3)-O(4) plane.

dependent upon the regioselective addition of nucleophiles to this cation, we were pleased to observe the large difference (13 ppm) in chemical shielding for the vinyl carbon centers in this compound. Such differential shielding had earlier been associated with unsymmetrical bonding of the metal to olefin in $\text{Fp}(\eta^2\text{-vinyl ether})$ complexes¹⁸ and with the characteristic high regioselectivity of nucleophile addition to these complexes.¹⁹

In order to shed some light on the character of metal-olefin bonding in the dioxene complexes, we attempted to carry out a crystal structure determination on **2b**. However, satisfactory crystals suitable for X-ray analysis could not be obtained, and we therefore turned to an examination of the parent complex **2a**. This substance gave satisfactory crystals for an X-ray analysis. Details of the experimental procedure, in outline form, are given in Table I, while atomic coordinates appear in Table II. A view of the molecular cation and labeling scheme are shown in Figure 1. The steric interactions between the Fp group and the ligand are significant and are principally reflected in the movement of C(11) nearly into the plane defined by the olefinic carbon atoms O(3) and O(4) (see Figure 2). This deformation may be associated with a corresponding bending of the Fp group away and out from under the dioxene ligand, as reflected by the Fe-C(9)-C(8)-O(4) and

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Table I. Data for the X-ray Diffraction Study of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_5\text{O}_2)]\text{BF}_4$ (2a**)**

(A) Crystal Data at 21 (1) °C	
crystal system: monoclinic	$Z = 4$
space group: $P2_1/c [C_{2h}^6]$; No. 14	cryst size: $0.40 \times 0.40 \times 0.15$ mm
$a = 7.459$ (2) Å	fw: 349.86
$b = 6.999$ (2) Å	$\rho_{\text{obsd}} = 1.725^a$ g cm ⁻³
$c = 25.887$ (5) Å	$\rho_{\text{calcd}} = 1.73$ g cm ⁻³
$\beta = 96.80$ (1)°	$\mu = 11.8$ cm ⁻¹ (Mo K α)
$V = 1342.0$ Å ³	

Cell constant determination: 12 pairs of $\pm(hkl)$ and refined 2θ , ω , χ values in the range $18 \leq |2\theta| \leq 24^\circ$ ($\lambda(\text{Mo K}\alpha) = 0.71073$ Å)

(B) Measurement of Intensity Data

radiation: Mo K α , graphite monochromator
 reflctns measd: $\pm h, k, l$ (to $2\theta = 50^\circ$)
 scan type, speed: θ - 2θ vble, 2, 66–5.33°/min
 scan range: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]^\circ$
 no. of reflctns measd: 2653; 2378 in unique set
 std reflctns: 006, 200, 020; period 60
 absorpnt correctn: empirical, normalized transmission factors 0.817–1.000
 data reductn: as before;^b linear decomposition correction applied^c
 statistical informatn: $R_{\text{av}} = 0.012$ ($0kl$ reflections)

(C) Refinement

refinement,^d with 1677 data for which $I > 1.96\sigma(I)$
 weighting of reflctns: as before,^d $p = 0.04$
 solution: Patterson, difference Fourier
 refinement:^e full-matrix least squares, with anisotropic temperature factors for Fe, C, B, E, and O atoms; isotropic temperature factors for H atoms; $R = 0.072$; $R_w = 0.086$; $\text{SDU} = 2.57$; R (structure factor calcn with all 2378 reflections) = 0.111
 final difference map: 10 peaks, 0.949–0.500 e/Å³ near BF₄; other peaks random and ≤ 0.46 e/Å³

^a Measured by neutral buoyancy in C₂H₄Br₂-CCl₄. ^b Foxman, B. M.; Goldberg, P. L.; Mazurek, H. *Inorg. Chem.* **1981**, *20*, 4381. All computations in the present work were carried out by using the Enraf-Nonius structure determination package. ^c A linear decomposition correction was applied to all data; the total decay correction reached a maximum of 18%. The correction factors on I ranged from 1.029 to 1.105 with an average value of 1.064. ^d Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197. ^e $R_{\text{av}} = \sum |I - I_{\text{av}}| / \sum I$; $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = \{ \sum w [|F_o| - |F_c|]^2 / \sum w |F_o|^2 \}^{1/2}$; $\text{SDU} = \{ \sum w [|F_o| - |F_c|]^2 / (m - n) \}^{1/2}$ where m (= 1677) is the number of observations and n (= 190) is the number of parameters.

Fe–C(8)–C(9)–O(3) torsion angles (111.0 (7) and 114.7 (7)°, respectively). The principal contributor to these deformations may be assigned to steric interactions between the Fp carbonyl ligands and the axial hydrogen atom at C(11). These interactions may also be responsible for the small displacement of the Fe center laterally along the olefin bond. The internuclear distances Fe–C(8) and Fe–C(9) (Table III) differ by 0.038 (11) Å, with the iron atom displaced in the direction expected. However, the distortion is small in absolute terms and may not be highly significant. The distortion of Fe–olefin bonding no doubt contributes to the relative kinetic instability of both **2a** and **2b** toward displacement by coordinating solvents.²⁰ Such instability is reminiscent of that earlier observed for Fp(η -cyclohexene)⁺, which on the basis of models had been attributed to transannular interaction of an axial hydrogen atom with the Fp group.²¹ The free dioxene and (*R*,

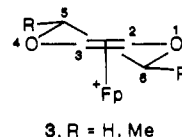
Table II. Atomic Coordinates for $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_5\text{O}_2)]\text{BF}_4$

atom	x	y	z	B, Å ²
Fe	0.3135 (1)	0.0831 (2)	0.12116 (4)	2.83 (2)
F(1)	0.758 (2)	0.471 (2)	0.0382 (3)	18.6 (4)
F(2)	0.786 (2)	0.364 (2)	0.1119 (4)	18.8 (4)
F(3)	0.953 (1)	0.565 (2)	0.0955 (6)	22.6 (5)
F(4)	0.693 (2)	0.630 (2)	0.0955 (6)	34.5 (5)
O(1)	0.324 (1)	0.4727 (8)	0.1598 (3)	6.9 (2)
O(2)	0.6402 (8)	-0.025 (1)	0.1870 (3)	6.2 (2)
O(3)	0.0766 (8)	0.1853 (8)	0.2104 (2)	4.6 (1)
O(4)	0.2624 (8)	-0.1654 (8)	0.2209 (2)	4.7 (1)
C(1)	0.315 (1)	0.322 (1)	0.1459 (3)	3.7 (2)
C(2)	0.509 (1)	0.016 (1)	0.1624 (3)	3.9 (2)
C(3)	0.159 (1)	-0.049 (2)	0.0575 (3)	6.6 (3)
C(4)	0.174 (1)	0.151 (1)	0.0487 (3)	5.9 (2)
C(5)	0.365 (2)	0.186 (2)	0.0487 (4)	6.9 (3)
C(6)	0.450 (2)	0.025 (2)	0.0583 (4)	8.6 (4)
C(7)	0.335 (2)	-0.117 (2)	0.0630 (4)	8.3 (3)
C(8)	0.166 (1)	-0.107 (1)	0.1757 (3)	3.7 (2)
C(9)	0.081 (1)	0.063 (1)	0.1702 (3)	3.8 (2)
C(10)	0.113 (1)	0.099 (1)	0.2601 (3)	4.4 (2)
C(11)	0.279 (1)	-0.021 (1)	0.2619 (3)	4.4 (2)
B	0.798 (1)	0.516 (2)	0.0841 (4)	4.4 (2)

^a Atoms refined by using anisotropic temperature factors are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab \cos \gamma B_{12} + ac \cos \beta B_{13} + bc \cos \alpha B_{23}]$. ^b Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

R)-2,3-dimethyldioxene ligands were cleanly displaced when acetone solutions of **2a** or **2b** were allowed to stand overnight at room temperature.

The direction of lateral distortion of the Fe–olefin bond in the crystal structure of **2a** is supported as well for **2b** by the NMR spectrum of this compound. Displacement of an Fp group along the axis of the coordinated double bond in **2b** should lead to increased deshielding at the saturated carbon center, across the ring, bonded to the distal oxygen atom, as positive charge builds up at this center. Hence the carbon resonances in **2b** at δ 75.4 and 76.4 may be assigned to proximate and distal carbon centers, respectively (C-5 and C-6, respectively, in structure 3). The proton spectrum of **2b** shows the two methine



proton resonances at these centers at δ 3.60 and 3.45. We had earlier shown that protons lying along the Cp–Fe axis in Fp(olefin) cations are shielded,²² and models as well as the crystal structure of **2a** show that H-6 lies significantly closer to the Cp–Fe axis than does H-5. It remained now to associate each of these protons with the two carbon centers. This was done by single-frequency proton-coupled ¹³C NMR spectra that identify the carbon bearing the more highly shielded proton as the more deshielded. Thus the spectral data for **2b** is in accord with the crystal structure of **2a** in suggesting a displacement of the Fp group laterally along the olefin axis away from the axial proton at C-6.

Both complexes **2a** and **2b**, like their acyclic analogue **1**, were found to undergo nucleophilic addition with a number of carbon and heteroatomic nucleophiles (Table IV). Nucleophilic addition to **2b** gave a single diastereomeric adduct as determined by ¹³C NMR, and hence

(20) In acetone-*d*₆ at 37 °C, the half-life of the parent complex is about 15 min. A ¹H NMR spectrum of the decomposition mixture indicates that Fp-acetone(1+), free dioxene, and the oxygen-coordinated cationic Fp complex are present. The latter complex is transitory and is converted completely to free dioxene and Fp-acetone(1+) within a few hours.

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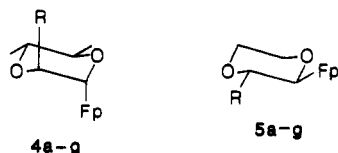
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Table III. Bond Lengths (Å) and Angles (deg) for $[(\eta^5\text{-C}_6\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_6\text{O}_2)]\text{BF}_4$

atom 1	atom 2	dist	atom 1	atom 2	dist
Fe	C(1)	1.787 (8)	O(1)	C(1)	1.117 (10)
Fe	C(2)	1.764 (8)	O(2)	C(2)	1.141 (10)
Fe	C(3)	2.110 (9)	O(3)	C(9)	1.351 (10)
Fe	C(4)	2.090 (9)	O(3)	C(10)	1.417 (10)
Fe	C(5)	2.088 (10)	O(4)	C(8)	1.361 (9)
Fe	C(6)	2.063 (11)	O(4)	C(11)	1.458 (10)
Fe	C(7)	2.075 (11)	C(3)	C(4)	1.43 (2)
Fe	C(8)	2.308 (8)	C(3)	C(7)	1.39 (2)
Fe	C(9)	2.270 (8)	C(4)	C(5)	1.44 (2)
F(1)	B	1.23 (1)	C(5)	C(6)	1.31 (2)
F(2)	B	1.29 (2)	C(6)	C(7)	1.33 (2)
F(3)	B	1.21 (2)	C(8)	C(9)	1.35 (1)
F(4)	B	1.18 (2)	C(10)	C(11)	1.50 (1)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(1)	Fe	C(2)	93.6 (4)	O(4)	C(8)	C(9)	123.5 (7)
C(1)	Fe	C(8)	107.6 (3)	Fe	C(9)	O(3)	118.9 (5)
C(1)	Fe	C(9)	80.3 (3)	Fe	C(9)	C(8)	74.4 (5)
C(2)	Fe	C(8)	84.0 (3)	O(3)	C(9)	C(8)	122.0 (7)
C(2)	Fe	C(9)	106.0 (3)	O(3)	C(10)	C(11)	109.7 (7)
Fe	C(1)	O(1)	176.3 (8)	O(4)	C(11)	C(10)	111.6 (6)
Fe	C(2)	O(2)	176.4 (8)	C(9)	O(3)	C(10)	114.3 (6)
C(4)	C(3)	C(7)	105.2 (9)	C(8)	O(4)	C(11)	114.1 (6)
C(3)	C(4)	C(5)	105.3 (9)	F(1)	B	F(2)	107 (1)
C(4)	C(5)	C(6)	108 (1)	F(1)	B	F(3)	115 (1)
C(5)	C(6)	C(7)	111 (1)	F(1)	B	F(4)	109 (1)
C(3)	C(7)	C(6)	111 (1)	F(2)	B	F(3)	103 (1)
Fe	C(8)	O(4)	117.4 (6)	F(2)	B	F(4)	109 (1)
Fe	C(8)	C(9)	71.3 (5)	F(3)	B	F(4)	113 (1)


a single enantiomer, for all of the reactions examined, but the reaction product was not that anticipated on the basis of olefin bond polarization. However, bond polarization in **2b** is relatively small compared with that observed in the Fp(methyl vinyl ether) cation, which exhibits a high degree of nucleophile stereoselectivity.¹⁸ Instead, stereoelectronic factors associated with a preference for a chair conformation transition state for nucleophile addition to **2b** appear to control the regioselectivity of these reactions, leading in all of the cases examined to the adducts **4**. The axial conformation of nucleophile and Fp substituents in these adducts is supported by their proton spectra, which show coupling constants $J_{2,3}$ of less than 1 Hz, in accord with literature values for eq-eq coupling in 1,4-dioxanes.²³ By contrast **2a**, which also reacted well with the same nucleophiles, gave adducts **5**, all of which showed coupling constants $J_{2,3}$ of 6–9 Hz, as expected for a diequatorial conformation of substituents.



a, R = H; b, R = Me; c, R = CN; d, R = Ph; e, R = CH₂=CH;
f, R = PhCH₂S; g, R = 2-oxocyclohexyl

Further support for the structures of the adducts **4** is provided by a single-crystal X-ray diffraction study of the cyano addition product **4c**. Pertinent data relating to the crystal, data collection, and refinement are given in Table V, while atomic coordinates are listed in Table VI and bond lengths and angles appear in Table VII. Bond lengths and angles in the compound lie within normal ranges. The absolute configuration of this compound was established by the known stereochemistry of the backbone carbon atoms as well as by a Hamilton R-factor test.

Table IV. Nucleophilic Reagents and Product Yields from the Reaction of **2a,b**

reagent	yield, %	
	4	5
a. NaBH ₃ CN, NaOMe	49	67
b. LiMeCuCN	55	72
c. Et ₄ NCN	94	93
d. PhMgBr	80	58
e. CH ₂ =CHMgBr	57	
f. PhCH ₂ SNa		81
g. 	95 ^a	96 ^a

^a Reference 24.

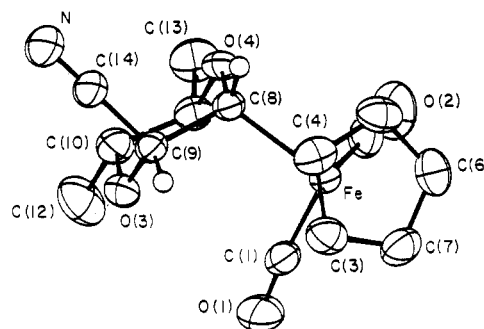


Figure 3. Molecular structure of **4c**, showing labeling scheme and 50% probability ellipsoids for atoms refined by using anisotropic temperature factors. Atoms H(8) and H(9) (attached to C(8) and C(9), respectively) are drawn at an arbitrary size to show their near-orthogonality.

As can be seen from the molecular structure (Figure 3), the Fp and cyano groups occupy diaxial positions on the dioxane ring, but with a dihedral angle of 154° rather than 180°. This has the effect of rotating the C(8)–C(9) bond so that the protons on C(8) and C(9) are nearly orthogonal (dihedral angle 86°), which accounts for the lack of observed coupling between these protons. A similar distortion is likely to be responsible for the absence of coupling in the proton NMR spectra of the remaining adducts **4**.

(23) Chen, C. Y.; LeFevre, R. J. W. *J. Chem. Soc. B* 1966, 544. Gatti, G.; Segre, A. L.; Morandi, C. *Tetrahedron* 1967, 23, 4385. Fuchs, B.; Ellenowier, A. *Nouv. J. Chem.* 1979, 3, 145.

Table V. Data for the X-ray Diffraction Study of $(\eta^5\text{-C}_6\text{H}_5)_2\text{Fe}(\text{CO})_2(\text{C}_7\text{H}_{10}\text{O}_2\text{N})$ (4c)

(A) Crystal Data at 21 (1) °C	
cryst system: monoclinic	$Z = 2$
space group: $P2_1 [(C_2^2); \text{No. } 4]$	cryst size: ^a 0.40×0.80 $\times 0.05$ mm
$a = 7.859$ (2) Å	fw: 317.12
$b = 7.625$ (2) Å	$\rho_{\text{obsd}} = 1.45$ (1) ^b g cm ⁻³
$c = 12.212$ (3) Å	$\rho_{\text{calcd}} = 1.459$ g cm ⁻³
$\beta = 99.54$ (3)°	$\mu = 10.9$ cm ⁻¹ (Mo K α)
$V = 721.72$ Å ³	

Cell constant determination: 12 pairs $\pm(hkl)$ and refined 2θ , ω , χ values in the range $23 \leq |2\theta| \leq 25^\circ$ ($\lambda(\text{Mo K}\alpha) = 0.71073$ Å)

(B) Measurement of Intensity Data
 radiation: Mo K α , graphite monochromator
 reflections measured: $h, k, \pm l$ (to $2\theta = 60^\circ$)
 scan type, speed: θ - 2θ , vble, 3.08–6.51°/min
 scan range: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]^\circ$
 no. of reflctns measd: 2416, 2270 in unique set
 std reflctns: 600, 060, 006; measured after each 60 reflections;
 variation $\leq 3\sigma(I)$ for each
 absorpnt correctn: empirical, normalized transmission factors
 0.868–1.000
 statistical informatn: $R_s = 0.010$; $R_{av} = 0.006$ ($0kl$ reflections)

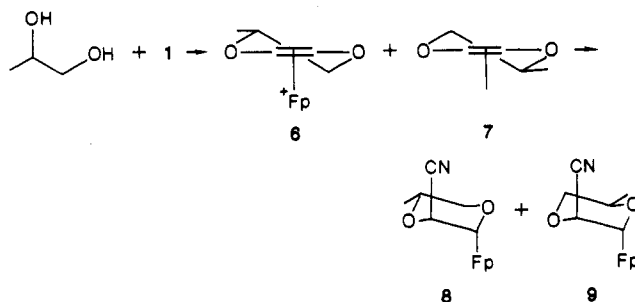
(C) Solution and Refinement with 2104 Data for Which $F > 3.92\sigma(F)$
 weighting of reflections: as before,^c $p = 0.035$
 solution: Patterson, difference Fourier, routine
 refinement:^d full-matrix least squares, with anisotropic temperature factors for Fe, C, N, O atoms; H atoms at fixed positions (0.95 Å); $R = 0.022$;^e $R_w = 0.032$; SDU = 0.809; R (structure factor calcn with all 2270 reflections) = 0.025
 final difference map: 2 peaks, 0.20, 0.23 d/Å³ near Fe; other peaks random and ≤ 0.18 e/Å³
 weighting scheme analysis: no systematic dependence on magnitude of $|F_o|$, $(\sin \theta)/\lambda$, or indices

^aThis size is within the uniform beam area as determined experimentally in this laboratory. The crystal was optically centered with great care. ^bMeasured by neutral buoyancy in CCl₄/hexane. ^cFoxman, B. M.; Mazurek, H. *Inorg. Chem.* 1979, 18, 113 and references therein. ^d $R_s = \sum(\sigma(|F_o|)/\sum|F_o|)$; $R_{av} = \sum I - I_{av}/\sum I$; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$; SDU = $\{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$ where m (= 2104) is the number of observations and n (= 180) is the number of parameters. ^eWithout H atoms included in the calculation, the correct enantiomer had $R = 0.036$ and $R_w = 0.054$; the opposite chirality had $R = 0.039$ and $R_w = 0.057$.

A predominance of an axial Fp conformer for compounds 4b–g may be attributed to a combination of a low axial conformational energy for the Fp group coupled with a significant gauche Fp–R interaction in these compounds. However, the latter factor cannot contribute to the conformational energy balance in 4a, which also appears to exist largely in the axial Fp conformation, as indicated by the presence of a doublet resonance ($J = 3$ Hz) for the FpCH proton. The low conformational energy of the Fp group, notwithstanding its size, is no doubt largely a consequence of the length of the Fe–C bond in Fp–R complexes (2.07 Å in 4c).

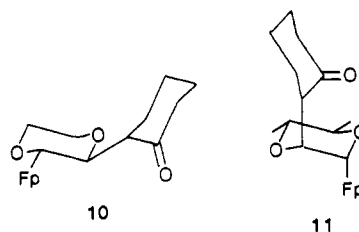
A further illustration of the low conformational energy of the Fp group is provided by the diastereoisomeric monomethyl dioxene complexes 6 and 7, formed as a 1:1 mixture in the reaction of 1 with propylene glycol. This mixture of diastereomers reacts with tetraethylammonium cyanide to give a 1:1 mixture of products 8 and 9, with no evidence in the proton NMR spectrum for the presence of axial methyl conformers of 8 and 9.

The observation that each of the diastereoisomers 6 and 7 gives a single product, resulting from stereoelectronic control in the addition reaction, has another more interesting consequence. Although these products are derived from a mixture of diastereomeric Fp(olefin) cations, the absolute configuration at each of the new chiral centers



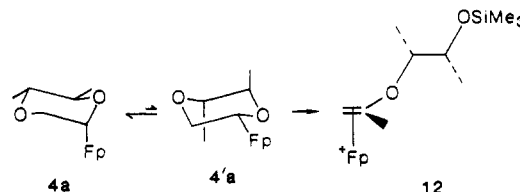
in the products 8 and 9 are identical for any given configuration in the propylene glycol starting material. This greatly increases the number of potentially useful diols from which optically active dioxene complexes should be preparable and eliminates the need for the diol to possess C_2 symmetry. Furthermore, although complexes such as 8 and 9 can be separated chromatographically, they need not be, if in the course of asymmetric synthesis the ethylenedioxy backbone is removed, as is illustrated by some of the transformations described below.

As with the addition of lithium cyclohexanone enolate to Fp(η -ethyl vinyl ether)BF₄, a single diastereomeric product, 10, is obtained from the reaction of this enolate with 2a and a single enantiomeric product 11 from the reaction with 2b. Proof for the structures of these products and their transformation to tricyclic tetrahydrofurans was recently reported by us.²⁴



The optically active complexes 4a–g may serve as starting materials for the synthesis of optically active Fp(vinyl ether) and Fp(olefin) cations of defined absolute configuration, and several such transformations have been examined.

Treatment of 4a with trimethylsilyl triflate at -78°C converts this compound to the optically active salt (*R*)-12. The ¹³C spectrum of this compound, taken at 18 °C, shows it to be a single diastereomer, and the CD spectrum of this compound shows a large positive Cotton effect band centered at 480 nm, with $\Delta\epsilon = 1.34$ mol⁻¹ cm⁻¹. The assignment of absolute stereochemistry to 12 follows from the stereochemistry of 4a and its conversion, either directly or possibly through its high-energy conformer 4'a, in which the Fp and leaving group are antiperiplanar, by a concerted ring-opening process to the olefin complex. Racemization of the asymmetric olefin center in 12 through rotation about the carbon–carbon bond^{15,18} occurs slowly, and an equilibrium value of $\Delta\epsilon = 0.03$ (± 0.0006) in the CD spectrum is reached after 19 h at room temperature.



(24) Rosenblum, M.; Foxman, B. M.; Turnbull, M. M. *Heterocycles* 1987, 25, 419.

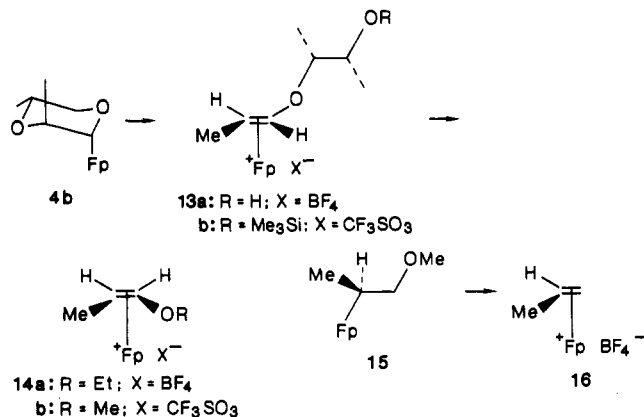
Table VI. Atomic Coordinates for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_7\text{H}_{10}\text{O}_2\text{N})^a$

atom	x	y	z	B, Å ²
Fe	0.01938 (3)	0.250	0.23647 (2)	2.568 (4)
O(1)	0.1497 (3)	0.5980 (3)	0.2978 (2)	5.53 (5)
O(2)	-0.0413 (4)	0.1542 (4)	0.4565 (2)	5.95 (6)
O(3)	-0.2410 (2)	0.6429 (2)	0.1867 (1)	3.24 (3)
O(4)	-0.3361 (2)	0.3351 (2)	0.2825 (1)	2.83 (3)
N	-0.5717 (3)	0.4939 (4)	-0.0010 (3)	5.57 (6)
C(1)	0.0906 (3)	0.4644 (3)	0.2744 (2)	3.49 (4)
C(2)	-0.0194 (3)	0.1926 (3)	0.3696 (2)	3.70 (4)
C(3)	0.1491 (3)	0.2413 (5)	0.0985 (2)	3.97 (4)
C(4)	-0.0040 (3)	0.1434 (4)	0.0750 (2)	3.71 (4)
C(5)	0.0041 (3)	0.0070 (3)	0.1526 (2)	4.01 (5)
C(6)	0.1665 (4)	0.0201 (3)	0.2239 (2)	4.35 (5)
C(7)	0.2556 (3)	0.1648 (4)	0.1906 (3)	4.26 (5)
C(8)	-0.2380 (2)	0.3211 (3)	0.1943 (1)	2.50 (3)
C(9)	-0.2645 (2)	0.4875 (3)	0.1237 (2)	2.83 (3)
C(10)	-0.3473 (3)	0.6500 (3)	0.2724 (2)	3.55 (4)
C(11)	-0.3057 (3)	0.4915 (3)	0.3466 (2)	3.10 (4)
C(12)	-0.3086 (5)	0.8232 (5)	0.3295 (3)	5.76 (8)
C(13)	-0.4137 (4)	0.4767 (5)	0.4391 (2)	4.73 (6)
C(14)	-0.4401 (3)	0.4901 (4)	0.0534 (2)	3.75 (5)

^a Atoms refined by using anisotropic temperature factors are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab \cos \gamma B_{12} + ac \cos \beta B_{13} + bc \cos \alpha B_{23}]$.

Similarly, treatment of **4b** with either BF_3 etherate or trimethylsilyltriflate at -78°C gave the *trans*-propenyl complexes **13a,b**, which were converted to the *cis*-ethoxy and *cis*-methoxy complexes **14a**¹⁵ and **14b**, respectively, by dissolution in ethanol or methanol and reprecipitation of the salt with ether. Reduction of this salt with sodium borohydride in methanol containing sodium methoxide gave **15**, and this was converted by protonation with fluoroboric acid etherate at -78°C to the optically active propene complex **16**. Complex **16** exhibits a CD band at 485 nm ($\Delta\epsilon = -0.34 \text{ mol}^{-1} \text{ cm}^{-1}$) and owes its optical activity entirely to the asymmetry of metal complexation.

An attempt was made to determine the optical purity of **14** through an examination of the ¹³C NMR spectrum of an appropriate diastereomeric salt. To this end, the ¹³C NMR spectrum of racemic Fp-propene with a chiral genion, (*R*)-10-camphorsulfonic acid, was examined.



However, these spectra, determined in CD_3NO_2 , CD_2Cl_2 , or acetone-*d*₆ at varying concentrations showed no evidence for the presence of ion-paired diastereomers.

The synthesis and conversion of the adduct **4d** to the methoxystyrene complex **19** provides an interesting counterpoint to the reactions of the methyl analogue **4b**. Addition of phenylmagnesium bromide to **2b** at -78°C gave a 1:1 mixture of **4d** and a second (alkyl)Fp complex, which was separated from **4d** and identified as the dioxolane complex **18**. A close examination of this reaction showed that, depending on the reaction conditions, either of these compounds could be made the predominant or sole product of the reaction. These results are summarized in Table VIII.

The formation of the dioxolane ring opening of the initial product **4d** through the intermediate cationic vinyl ether complex **17**. Evidence for this is provided by conversion of **4d** to **18** in the presence of a number of Lewis acids such as MgCl_2 , AgBF_4 , or BF_3 etherate. The isomerization of **4d** to **18** in the presence of BF_3 etherate is complete within a half-hour at room temperature but is only 50% complete after 12 h at 55°C in the presence of MgCl_2 . The complex salt MgBrBF_4 , generated in the course of the Grignard addition to **4d** must be more effective than these (runs 1–3), but the presence of an amine base or of a mildly basic solvent is sufficient to prevent the isomerization reaction

Table VII. Bond Lengths (Å) and Angles (deg) for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{C}_7\text{H}_{10}\text{O}_2\text{N})$

atom 1	atom 2	dist	atom 1	atom 2	dist
Fe	C(1)	1.765 (2)	O(4)	C(11)	1.425 (3)
Fe	C(2)	1.759 (2)	N	C(14)	1.133 (3)
Fe	C(3)	2.110 (3)	C(3)	C(4)	1.404 (4)
Fe	C(4)	2.112 (2)	C(3)	C(7)	1.412 (4)
Fe	C(5)	2.111 (2)	C(4)	C(5)	1.401 (4)
Fe	C(6)	2.120 (3)	C(5)	C(6)	1.424 (4)
Fe	C(7)	2.127 (3)	C(6)	C(7)	1.402 (4)
Fe	C(8)	2.075 (2)	C(8)	C(9)	1.529 (3)
O(1)	C(1)	1.137 (3)	C(9)	C(14)	1.500 (3)
O(2)	C(2)	1.141 (3)	C(10)	C(11)	1.513 (3)
O(3)	C(9)	1.408 (3)	C(10)	C(12)	1.501 (4)
O(3)	C(10)	1.445 (3)	C(11)	C(13)	1.526 (4)
O(4)	C(8)	1.430 (2)			

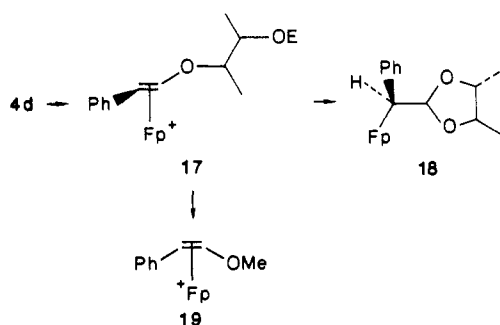
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(1)	Fe	C(2)	94.8 (1)	C(4)	C(3)	C(7)	108.5 (3)
C(1)	Fe	C(8)	94.41 (9)	C(3)	C(4)	C(5)	108.4 (3)
C(2)	Fe	C(8)	89.06 (9)	C(4)	C(5)	C(6)	107.3 (2)
O(3)	C(9)	C(8)	113.4 (1)	C(5)	C(6)	C(7)	108.5 (2)
O(3)	C(9)	C(14)	109.1 (2)	C(3)	C(7)	C(6)	107.3 (2)
C(8)	C(9)	C(14)	111.1 (2)	O(4)	C(8)	C(9)	108.8 (2)
O(3)	C(10)	C(11)	108.1 (2)	C(11)	C(10)	C(12)	114.7 (2)
O(3)	C(10)	C(12)	105.8 (2)	O(4)	C(11)	C(10)	109.9 (2)
C(9)	O(3)	C(10)	112.8 (2)	O(4)	C(11)	C(13)	106.4 (3)
C(8)	O(4)	C(11)	114.5 (2)	C(10)	C(11)	C(13)	114.3 (2)
Fe	C(1)	O(1)	174.3 (2)	N	C(14)	C(9)	178.8 (3)
Fe	C(2)	O(2)	178.7 (2)				

Table VIII. Product Distribution from the Reaction of 2b with PhMgBr

run	solvent	temp, °C	rxn time, h	yield, %	4b:18
1	10% CH ₃ CN/CH ₂ Cl ₂	-78	0.5	71	1:1
2	CH ₂ Cl ₂	-78	0.5	58	3:2
3	CH ₂ Cl ₂	-78 ^a	1.5	85	18 only
4	THF	-78	4.0	35-55	4b only
5	7% py/CH ₂ Cl ₂	-78	1.0	72	4b only
6	THF	-78	8.0	76	1:1 ^b
7	THF	-78	8.0	90	8:1 ^c

^a Reaction solution allowed to warm to room temperature before workup. ^b Product distribution after chromatography. ^c Product distribution by fractional crystallization.

over a short period of time (runs 4 and 5). Finally, it appears that isomerization may also occur during chromatography (runs 6 and 7).

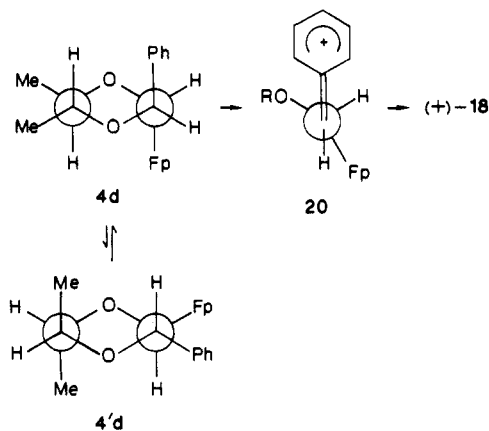


Of further interest with respect to the detailed mechanism of Lewis acid promoted ring opening of 4d is the observation that the dioxolane complex 18, formed by treatment of 4d with either AgBF₄ or BF₃ etherate, is a mixture of diastereomers. Racemization of the chiral tertiary carbon bonded to the Fp group is evident from the ¹H NMR spectrum of the product, which shows the acetal proton as a pair of doublets near δ 5.30 ($J = 5$ Hz). Similarly, the (methoxystyrene)Fp complex, formed by treatment of 4d with trimethylsilyl triflate, followed by exposure of the salt to methanol to effect alkoxy exchange, gave a *cis*-methoxystyrene complex, 19, which exhibited only a weak Cotton effect at 480 nm. By contrast, the dioxolane isolated either directly from the reaction of 4d with phenylmagnesium bromide at low temperature or by treatment of 4d with magnesium chloride at higher temperatures is formed as a single enantiomer.

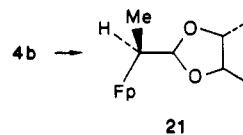
It seems likely that the transformation of optically active 4d to racemic 18 or 19 is due to phenyl participation in the ring-opening process, which promotes ring opening through the phenonium ion 20, in which the stereochemistry at the chiral center is lost. Those reactions, which yield optically active 18, must then proceed through the high-energy conformer 4'd in which an equatorial Fp group is better able, through its antiperiplanar relationship with the leaving group, to assist in the ring-opening process.

The importance of the phenyl group in the ring opening of 4d is seen in the contrasting behavior of the methyl-substituted dioxane complex 4b. On treatment with BF₃ etherate this substance undergoes quantitative conversion to the dioxolane complex 21 with no apparent racemization. Furthermore, the reaction is almost 2 orders of magnitude slower than is the conversion of 4d to 18 in the presence of BF₃ etherate, suggesting that opening of the ring in 4b may take place preferentially through the minor conformer in which the Fp is equatorial.

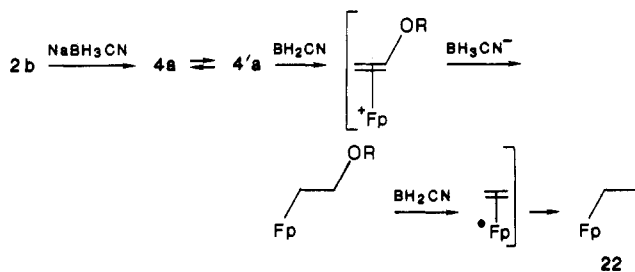
Finally, the importance of the stereochemistry of the Fp group in promoting ring-opening reactions in dioxane complexes may be inferred from the reactions of 2a and



2b with sodium cyanoborohydride. In the presence of this reagent, 2b yields a mixture of 4a and (ethyl)Fp (22). The latter product must derive from 4a through cyanoborane promoted ring opening, followed by further reduction of the Fp(vinyl ether) cation formed in this reaction.



By contrast, 2a reacts with sodium cyanoborohydride under similar conditions to give only the fully reduced complex 22. The dioxane complex 5a is a likely intermediate in this reaction as well, but unlike the methylated analogue 4a, in which the predominant conformer has an axial Fp substituent, the Fp substituent in 5a is equatorial and consequently ring opening is greatly accelerated.



Overreduction of both 2a and 2b can be avoided by carrying out the reaction with sodium borohydride in the presence of sodium methoxide, a procedure first introduced by Brookhart and Tucker to prevent overreduction of metal-stabilized cationic carbenes.²⁵ Under these conditions 4a and 5a are obtained in good yield, free of 22.

Further examination of the chemistry of Fp(dioxene)BF₄ complexes and of their use in asymmetric synthesis is in progress.

Experimental Section

Reactions were carried out by using standard Schlenk technique under an argon atmosphere. THF and Et₂O were distilled under nitrogen from sodium/benzophenone. Methylene chloride was distilled from CaH₂ under N₂. IR spectra were recorded on a PE-683 spectrophotometer in methylene chloride solution and referenced to polystyrene. ¹H NMR spectra were recorded on a Varian EM-390 or Varian XL300 spectrometer and referenced to internal TMS. ¹³C NMR spectra were recorded on a Varian XL300 spectrometer and referenced to solvent. CD spectra were recorded on a JASCO J-20 recording spectrophotometer. Alumina refers to basic alumina, activity four, unless otherwise noted.

Petroleum ether refers to the fraction boiling at 20–40 °C. *L*-Selectride and *n*-butyllithium were purchased from Aldrich Chemical and used without further purification. (*R,R*)-2,3-Butanediol was purchased from Strem Chemical and used without further purification. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Dicarbonyl(η -cyclopentadienyl)(η -*cis*-1,2-dimethoxyethene)iron(II) Tetrafluoroborate (1). Fp(isobutylene) tetrafluoroborate (5.00 g, 16 mmol) and *cis*-dimethoxyethene²⁸ (2.50 mL, 2.32 g, 26 mmol) were dissolved in 20 mL of CH₂Cl₂ and refluxed for 4 h. Workup of an aliquot, as described below, showed the exchange was complete by the absence of isobutylene peaks in the ¹H NMR. The reaction mixture was cooled to 0 °C, and 30 mL of ether was added to precipitate an orange solid. The solid was collected by filtration, washed with ether, and dried under vacuum to give an orange powder: 4.81 g (86%); IR (C-H₂Cl₂) 2080, 2030 (C=O) cm⁻¹; ¹H NMR (CD₃NO₂) δ 6.4 (s, 2 H, =CH), 5.45 (s, 5 H, Cp), 4.0 (s, 6 H, CH₃); ¹³C NMR (CD₃NO₂) δ 210.8 (C=O), 104.9 (=CH), 89.3 (Cp), 62.7 (CH₃).

Dicarbonyl(η -cyclopentadienyl)(η -5,6-dihydrodioxin)iron(II) Tetrafluoroborate (2a). Fp(*cis*-dimethoxyethene) tetrafluoroborate (1) (2.00 g, 5.7 mmol) was slurried in 10 mL of CH₂Cl₂ at 0 °C, and ethylene glycol (1.56 mL, 1.76 g, 28.5 mmol, 5 equiv) was added. After about 5 min the slurry dissolved and then a precipitate formed. The mixture was stirred for an additional 15 min, then 10 mL of ether added, and the solid collected by filtration. The precipitate was washed with 3 \times 5 mL of ether and dried under vacuum to give a bright yellow solid: 1.92 g (97%); IR (CH₃NO₂) 2070, 2030 (C=O) cm⁻¹; ¹H NMR (CD₃NO₂) δ 7.75 (b s, 2 H, CH=CH), 5.50 (s, 5 H, Cp), 4.05 (m, 4 H, CH₂CH₂); ¹³C NMR (CD₃NO₂) δ 210.9 (C=O), 102.7 (CH=), 89.3 (Cp), 67.4 (CH₂). Anal. Calcd for C₁₁H₁₁BF₄FeO₄: C, 37.76; H, 3.17. Found: C, 37.76; H, 3.17.

Dicarbonyl(η -cyclopentadienyl)[η -(5*R*,6*R*)-5,6-dimethyl-5,6-dihydrodioxin]iron(II) Tetrafluoroborate (2b). A slurry of Fp(*cis*-dimethoxyethene) tetrafluoroborate (1) (1.87 g, 5.3 mmol) in 15 mL of CH₂Cl₂ at 0 °C was treated with (*R,R*)-2,3-butanediol (0.97 mL, 0.95 g, 10.6 mmol). After the solution was stirred for 1 h, the solvent was removed in vacuo. CH₂Cl₂ (15 mL) was then added, the mixture stirred an additional 0.5 h, and the solvent again removed. A third 15-mL portion of CH₂Cl₂ was added, the mixture stirred for 0.5 h, and then 30 mL of ether was added. The resulting precipitate was collected by filtration and washed with 10 mL of 30% CH₂Cl₂/ether followed by 10 mL of ether. The solid was dried under vacuum to give an orange powder: 1.78 g (89%); CD (CH₂Cl₂) $\Delta\epsilon_{460} = +0.114$ M⁻¹ cm⁻¹; IR (CH₂Cl₂) 2060, 2025 (C=O) cm⁻¹; ¹H NMR (CD₃NO₂) δ 7.70 (d, 1 H, *J* = 1.5 Hz, CH=), 7.25 (d, 1 H, *J* = 1.5 Hz, =CH), 5.50 (s, 5 H, Cp), 3.60 (m, 1 H, OCH), 3.45 (m, 1 H, OCH), 1.30 (d, 3 H, *J* = 4.5 Hz, CH₃), 1.20 (d, 3 H, *J* = 4.5 Hz, CH₃); ¹³C NMR (CD₃NO₂) δ 211.2, 210.5 (C=O), 108.6, 95.5 (CH=CH), 89.1 (Cp), 76.4, 75.4 (OCHCHO), 16.7 (b, CH₃). Anal. Calcd for C₁₃H₁₅BF₄FeO₄: C, 41.32; H, 4.00. Found: C, 40.40; H, 3.67.

***cis*- and *trans*-Dicarbonyl(η -cyclopentadienyl)(η -5-methyl-5,6-dihydro-1,4-dioxin)iron(II) Tetrafluoroborate (6 and 7).** Fp(dimethoxyethene) tetrafluoroborate (1) (1.00 g, 2.88 mmol) and 1,2-propanediol (1.05 mL, 1.09 g, 14.4 mmol, 5 equiv) were dissolved in 8 mL of CH₂Cl₂ at 0 °C and stirred for 1 h. The addition of 10 mL of ether produced a red gum that became an orange powder on exhaustive trituration with ether. The solid was collected by filtration and dried under vacuum to give an orange powder, 0.92 g (88%). Spectra show the product to be a 1:1 mixture of the two possible diastereomers: IR (CH₂Cl₂) 2073, 2027 (C=O) cm⁻¹; ¹H NMR (CDCl₃) δ 7.70, 7.65 (two d, 1 H each, *J* = 2 Hz, =CH), 7.25 (app t, 2 H, *J* = 2 Hz, =CH), 5.50 (two s, 10 H, Cp's), 4.2–3.2 (m, 6 H, OCH₂CHO's), 1.20 (app t, 6 H, *J* = 6 Hz, CH₃'s); ¹³C NMR (CD₃NO₂) δ 210.7b (C=O), 108.2/107.7 (diast =CH), 96.1/95.9 (diast =CH), 89.1 (Cp), 71.4/70.3 (diast CH₃CH), 69.5/68.5 (diast OCH₂), 16.0/15.8 (diast CH₃). Anal. Calcd for C₁₂H₁₃BF₄FeO₄: C, 39.61; H, 3.60. Found: C, 36.60; H, 3.95.

[(2*R*,5*R*,6*R*)-5,6-Dimethyl-1,4-dioxan-2-yl]dicarbonyl(η -cyclopentadienyl)iron(II) (4a). Fp(dimethyldioxene) tetrafluoroborate (2b) (0.30 g, 0.95 mmol), sodium cyanoborohydride

(0.65 g, 0.794 mmol), and 5 mL of THF were combined at 0 °C and stirred for 2 h, at which time no Fp salt was detectable by IR. Ether (10 mL) was added, the mixture filtered through a short plug of alumina, and the solvent removed in vacuo to give a mixed solid/oil. The residue was extracted with petroleum ether until the extracts were colorless. The organic layers were combined, and the solvent was removed in vacuo to give a yellow oil. Chromatography on alumina with 25% ether/petroleum ether gave two fractions, the first being (ethyl)Fp and the second the desired product as a bright yellow crystalline solid: 0.114 g (49%); IR (CH₂Cl₂) 2004, 1945 (C=O) cm⁻¹; ¹H NMR (CDCl₃) δ 6.15 (d, 1 H, *J* = 3 Hz, FpCH), 4.75 (s, 5 H, Cp), 4.00 (d of d, 1 H, *J* = 12, 3 Hz, FpCHCH_{cis}), 3.55 (d, 1 H, *J* = 12 Hz, FpCHCH_{trans}), 3.35 (m, 2 H, CH₃CH), 1.15 (d, 3 H, *J* = 10 Hz, CH₃), 1.10 (d, 3 H, *J* = 10 Hz, CH₃); ¹³C NMR (CDCl₃) δ 218.0, 217.0 (C=O), 86.4 (Cp) 77.0 (FpCH), 76.8 (FpCHCH₂), 75.5, 71.6 (OCHCHO), 17.8, 17.4 (CH₃'s). Anal. Calcd for C₁₃H₁₆FeO₄: C, 53.45; H, 5.52. Found: C, 53.03; H, 5.33.

(1,4-Dioxan-2-yl)dicarbonyl(η -cyclopentadienyl)iron(II) (5a). Sodium borohydride (0.054 g, 1.43 mmol) and sodium methoxide (0.085 g, 1.57 mmol, 10% excess) were slurried in 10 mL of THF and cooled to -20 °C. Solid Fp(dioxene) tetrafluoroborate (2a) (0.50 g, 1.43 mmol) was added. The reaction was monitored by TLC (alumina, 30% ether/petroleum ether) to detect the formation of product (*R_f* 0.3, yellow) and of the "overreduction" product (*R_f* 0.9, yellow). When the latter appeared (1.5 h), the reaction was quenched by addition of 0.5 mL of H₂O. The reaction mixture was then stirred for 5 min and filtered through alumina and the solvent removed from the filtrate to give a yellow solid. Brief trituration with petroleum ether at -20 °C removed the traces of Fp₂, 1, and (ethyl)Fp and yielded a bright yellow crystalline solid, 0.255 g (67%). If larger amounts of impurities are present, the product may be purified by chromatography on alumina with 50% ether/petroleum ether: IR (C-H₂Cl₂) 2018, 1958 (C=O) cm⁻¹; ¹H NMR (CDCl₃) δ 5.25 (d of d, 1 H, *J* = 9, 3 Hz, FpCH), 4.80 (s, 5 H, Cp), 3.85, 3.60 (two m, 2 H, *J*_{AB} = 12 Hz, FpCHCH₂), 3.70 (b s, 4 H, OCH₂CH₂O); ¹³C NMR (CDCl₃) δ 216.1, 215.7 (C=O), 88.2 (Cp), 78.3 (FpCHCH₂), 77.0 (FpCH), 71.4, 67.4 (OCH₂CH₂O). Anal. Calcd for C₁₁H₁₂FeO₄: C, 50.03; H, 4.58. Found: C, 50.04; H, 4.68.

[(2*R*,3*R*,5*R*,6*R*)-3,5,6-Trimethyl-1,4-dioxan-2-yl]dicarbonyl(η -cyclopentadienyl)iron(II) (4b). Cuprous iodide (0.45 g, 2.38 mmol, 3 equiv) was slurried in 10 mL of THF at 0 °C and methylolithium (2.8 mL, 1.7 M, 4.75 mmol, 6 equiv) added dropwise. The mixture was cooled to -78 °C and added via cannula to a slurry of 2b (0.30 g, 0.794 mmol) in 10 mL of THF at -78 °C. After 1 h, the mixture was allowed to warm to room temperature and filtered through a short plug of alumina and the alumina washed with 2 \times 10 mL of ether. The solvent was removed from the combined filtrate and washings in vacuo to give a reddish/yellow oil which was chromatographed (alumina, 20% ether/petroleum ether). The solvent was removed in vacuo from the mobile yellow fraction to give a bright yellow crystalline solid: 0.135 g (55%); IR (CH₂Cl₂) 2015, 1950 (C=O) cm⁻¹; ¹H NMR (CDCl₃) δ 5.95 (s, 1 H, FpCH), 4.80 (s, 5 H, Cp), 3.75 (q, 1 H, *J* = 6 Hz, FpCHCH), 3.50 (m, 2 H, CH₃CHCH₃), 1.35 (d, 3 H, *J* = 6 Hz, FpCHCHCH₃), 1.20 (d, 3 H, *J* = 6 Hz, CH₃), 1.10 (d, 3 H, *J* = 6 Hz, CH₃); ¹³C NMR (CDCl₃) δ 217.8, 217.0 (C=O), 86.4 (Cp), 79.2, 78.2 (FpCHCH), 71.6, 68.7 (CH₃CHCHCH₃), 19.1 (FpCHCHCH₃), 17.5 (b, CH₃CHCHCH₃). Anal. Calcd for C₁₄H₁₈FeO₄: C, 54.93; H, 5.93. Found: C, 54.83; H, 5.89.

(*trans*-3-Methyl-1,4-dioxan-2-yl)dicarbonyl(η -cyclopentadienyl)iron(II) (5b). Cuprous iodide (0.29 g, 1.54 mmol) was slurried in 10 mL of THF at 0 °C and methylolithium (2.37 mL, 1.3 M, 3.09 mmol) added dropwise. The mixture was then cooled to -78 °C and solid Fp(dioxene) tetrafluoroborate (11) (0.360 g, 1.03 mmol) added in one portion. The reaction mixture was stirred for 1 h and then allowed to warm to room temperature. Ether (10 mL) was added, and the mixture was filtered through a short plug of alumina which was washed with 2 \times 10 mL of ether. The solvent was removed in vacuo from the combined filtrate and washings to give a yellow oil: 0.207 g (72%); IR (CH₂Cl₂) 2020, 1958 (C=O) cm⁻¹; ¹H NMR (CDCl₃) δ 4.85 (s, 5 H, Cp), 4.50 (d, 1 H, *J* = 8 Hz, FpCH), 3.70 (m, 5 H, CH₃CHOCH₂CH₂O), 1.15 (d, 3 H, *J* = 7 Hz, CH₃); ¹³C NMR (CDCl₃) δ 216 (C=O), 85.5 (Cp), 83.3, 82.5 (FpCHCH), 71.4, 67.9 (CH₂CH₂), 20.3 (CH₃). Anal.

Calcd for $C_{12}H_{14}FeO_4$: C, 51.83; H, 5.07. Found: C, 51.44; H, 5.11.

[(2R,3R,5R,6R)-3-Cyano-5,6-dimethyl-1,4-dioxan-2-yl]dicarbonyl(η -cyclopentadienyl)iron(II) (4c). Fp(dimethyl-dioxene) tetrafluoroborate (**2b**) (0.90 g, 2.37 mmol), tetraethylammonium cyanide (0.407 g, 2.61 mmol), and 10 mL of CH_2Cl_2 were combined at 0 °C, and the mixture was stirred for 0.5 h. Addition of 10 mL of ether precipitated a white solid (Et_4NBF_4). The mixture was filtered through a short plug of alumina which was washed with 3×10 mL of ether. The solvent was removed in vacuo from the combined filtrate and washings to give a bright yellow crystalline solid: 0.71 g (94%); IR (CH_2Cl_2) 2340 (CN), 2015, 1958 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.10 (s, 1 H, FpCH), 4.85 (s, 5 H, Cp), 4.30 (s, 1, CHCN), 3.55 (m, 2 H, $CH_3CHCHCH_3$), 1.20 (d, 3 H, $J = 6$ Hz, CH_3), 1.10 (d, 3 H, $J = 6$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 216.7, 215.8 (C=O), 118.2 (CN), 86.6 (Cp), 74.1, 73.8 (FpCHCHCN), 72.6, 71.8 ($CH_3CHCHCH_3$), 17.5, 16.8 (CH_3 's). Anal. Calcd for $C_{14}H_{15}FeNO_4$: C, 53.02; H, 4.77; N, 4.22. Found: C, 52.72; H, 4.54; N, 4.39.

(3-Cyano-1,4-dioxan-2-yl)dicarbonyl(η -cyclopentadienyl)iron(II) (5c). Fp(dioxene) tetrafluoroborate (**2a**) (0.4m g, 1.34 mmol) was dissolved in 10 mL of CH_2Cl_2 and cooled to 0 °C and tetraethylammonium cyanide (0.20 g, 1.48 mmol) added. After 0.5 h the solvent was removed in vacuo and the resulting oily yellow solid was extracted with 5-mL portions of ether until the ether layer was nearly colorless. The solvent was removed in vacuo from the combined ether extracts to give a bright yellow crystalline solid; 0.362 g (93%); IR (CH_2Cl_2) 2260 (CN), 2030, 1970 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 5.15 (d, 1 H, $J = 9$ Hz, FpCH), 4.90 s, 5 H, Cp), 4.55 nd, 1 H, $J = 9$ Hz, CH—CN), 3.75 (m, 4 H, $O-CH_2CH_2-O$); ^{13}C NMR ($CDCl_3$) δ 215.6, 214.3 (C=O), 117.8 (CN), 85.6 (Cp), 76.0, 75.3 (FpCHCH), 69.5, 66.9 (CH_2CH_2). Anal. Calcd for $C_{12}H_{11}FeNO_4$: C, 49.86; H, 3.84; N, 4.85. Found: C, 49.93; H, 3.78; N, 4.82.

[(2R,3R,5R,6R)-3-Phenyl-5,6-dimethyl-1,4-dioxan-2-yl]dicarbonyl(η -cyclopentadienyl)iron(II) (4d). Fp(dimethyl-dioxene) tetrafluoroborate (**2a**) (1.50 g, 3.97 mmol) was slurried in 30 mL of THF at -78 °C and phenylmagnesium bromide (1.40 mL, 3.0 M, 4.17 mmol, 5% xs) added dropwise via syringe, *very slowly*. Too rapid addition of the Grignard causes its precipitation and freezing of the stirring bar. The subsequent warming required to free the bar significantly increases the Fp₂ formation at the expense of product. After 8 h at -78 °C, 10 drops of MeOH was added and the mixture stirred one additional hour. Ether (20 mL) was added, and the mixture was filtered through a short plug of alumina. The solvent was removed from the filtrate in vacuo to give an oily yellow solid. The mixture was triturated with 20 mL of petroleum ether and stored for 10 h at -10 °C, and the supernate was decanted. The remaining bright yellow crystals were dried under vacuum to give 1.17 g of **4d** (80%). The petroleum ether was removed from the supernate in vacuo to give the isomeric Fp(phenyldioxolane) (**18**) as a bright yellow: 0.12 g (8%); IR (**4d**) (CH_2Cl_2) 2005, 1946 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.40 (m, 5 H, Ph), 6.75 (b s, 1 H, FpCH), 4.80 (s, 5 H, Cp), 4.55 (b s, 1 H, PhCH), 3.60 (m, 2 H, $CH_3CHCHCH_3$), 1.15 (d, 3 H, $J = 5$ Hz, CH_3), 1.10 (d, 3 H, $J = 5$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.5, 217.2 (C=O), 142.0 (ipso-Ph), 128.4, 128.1 (*o*-, *m*-Ph), 127.2 (*p*-Ph), 86.4 (Cp), 83.2 (PhCH), 75.2 (FpCH), 72.0, 69.7 ($CH_3CHCHCH_3$), 17.7, 17.3 (CH_3 's). Anal. Calcd for $C_{19}H_{20}FeO_4$: C, 62.15; H, 5.49. Found: C, 62.09; H, 5.42.

(trans-3-Phenyl-1,4-dioxan-2-yl)dicarbonyl(η -cyclopentadienyl)iron(II) (5d). Fp(dioxene) tetrafluoroborate (**2a**) (0.500 g, 1.43 mmol) was slurried in 15 mL of THF at -78 °C and phenylmagnesium bromide (0.47 mL, 3.0 M, 1.43 mmol) added dropwise via syringe. The reaction mixture was stirred for 17 h after which time 15 mL of ether and 4 drops of MeOH were added and the mixture stirred an additional 1.5 h. The mixture was filtered through a short plug of alumina, the alumina washed with 3×10 mL of ether, and the solvent removed from the combined filtrate and washings to give a red oil. Chromatography on alumina (gradient elution, petroleum ether to 10% ether/petroleum ether), after the solvent was removed in vacuo, gave a bright yellow solid: 0.283 g (58%); IR (CH_2Cl_2) 2015, 1950 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.35 (m, 5 H, Ph), 5.15 (d, 1 H, $J = 9.0$ Hz, FpCH), 4.7 (d, 1 H, $J = 9.0$ Hz, PhCH), 4.60 (s, 5 H, Cp), 3.85 (m, 4 H, OCH_2CH_2O); ^{13}C NMR ($CDCl_3$) δ 216.4, 214.8 (C=O), 141.0

(ipso-Ph), 128.3 (*o*-, *p*-Ph), 127.9 (*m*-Ph), 89.8 (FpCH), 85.5 (Cp), 81.2 (PhCH), 71.2, 67.9 (CH_2). Anal. Calcd for $C_{17}H_{16}FeO_4$: C, 60.03; H, 4.74. Found: C, 58.99; H, 4.74.

[(2R,3R,5R,6R)-3-Vinyl-5,6-dimethyl-1,4-dioxan-2-yl]dicarbonyl(η -cyclopentadienyl)iron(II) (4e). Fp(dimethyl-dioxene) tetrafluoroborate (**2b**) (0.55 g, 1.46 mmol) was slurried in 10 mL of THF at -78 °C and vinylmagnesium bromide (1.5 mL, 1.0 M, 1.5 mmol) added dropwise via syringe. After 4 h, 15 mL of ether was added and the mixture filtered through a short plug of alumina which was washed with 2×10 mL of ether. The solvent was removed from the combined filtrate and washings in vacuo to give a red/brown oil. The oil was chromatographed on alumina with 10% ether/petroleum ether to give a bright yellow oil: 0.274 g (57%); IR (CH_2Cl_2) 2005, 1945 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.25 (d of d of d, 1 H, $J = 7, 10, 17$ Hz, =CH) 6.20 (s, 1 H, FpCH), 5.22 (d, 1 H, $J = 17$ Hz, =CH_{2trans}), 5.18 nd, 1 H, $J = 10$ Hz, =CH_{2cis}), 4.80 ns, 5 H, Cp), 3.90 (d, 1 H, $J = 7$ Hz, FpCHCH), 3.60 (m, 1 H, CH_3CH), 3.45 (m, 1 H, CH_3CH), 1.15 (d, 3 H, $J = 5.5$ Hz, CH_3), 1.10 (d, 3 H, $J = 5.5$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.4, 216.8 (C=O), 138.0 (=CH), 116.5 (=CH₂), 86.2 (Cp), 83.5, 77.1 (FpCHCH), 71.6, 69.7 ($CH_3CHCHCH_3$), 17.5, 17.3 (CH_3 's). Anal. Calcd for $C_{15}H_{13}FeO_4$: C, 56.63; H, 5.70. Found: C, 56.30; H, 5.74.

[trans-3-(Thiobenzyl)oxy-1,4-dioxan-2-yl]dicarbonyl(η -cyclopentadienyl)iron(II) (5f). Sodium hydride (0.10 g, 50% dispersion, 2.0 mmol) was washed with 3×3 mL of petroleum ether to remove the mineral oil and then slurried in 20 mL of THF. Benzenethiol (0.19 mL, 0.20 g, 1.60 mmol) was added dropwise via syringe. The resulting white slurry was cooled to -78 °C and solid Fp(dioxene) tetrafluoroborate (**2a**) (0.60 g, 1.71 mmol, 5% excess) added in one portion. The reaction mixture was stirred for 0.5 h at which time the thiolate and Fp salt had completely dissolved. The solvent was removed from the mixture in vacuo and the resulting oily solid extracted with ether until the extracts were nearly colorless. The ether layers were combined and filtered through alumina, and the solvent was removed in vacuo to give a yellow oil. Chromatography on alumina (50% ether/petroleum ether) gave the product as a yellow oil: 0.50 g (81%); IR (CH_2Cl_2) 2013, 1954 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.30 (m, 5 H, Ph), 5.45 nd, 1 H, $J = 5$ Hz, FpCH), 4.65 (s, 5 H, Cp), 4.60 (d, 1 H, $J = 6$ Hz, SCH), 4.30–3.50 (m, 6 H, all CH_2 's); ^{13}C NMR ($CDCl_3$) δ 216.3, 216.1 (C=O), 138.7 (ipso-Ph), 129.0, 128.3 (*o*-, *m*-Ph), 126.8 (*p*-Ph), 89.5 (SCH), 86.0 (Cp), 78.0 (FpCH), 65.9, 63.0 (CH_2CH_2), 34.5 (SCH₂). Anal. Calcd for $C_{18}H_{18}FeO_4S$: C, 55.97; H, 4.70. Found: C, 56.78; H, 4.99.

(trans-3-Cyano-cis-5-methyl-1,4-dioxan-2-yl)dicarbonyl(η -cyclopentadienyl)iron(II) (8) and (trans-3-Cyano-trans-6-methyl-1,4-dioxan-2-yl)dicarbonyl(η -cyclopentadienyl)iron(II) (9). The mixture of Fp(methyl-dioxene) tetrafluoroborates **6** and **7** (0.92 g, 2.53 mmol) was dissolved in 10 mL of CH_2Cl_2 at 0 °C and tetraethylammonium cyanide (0.41 g, 2.65 mmol, 5% excess) added. After 0.5 h, 10 mL of ether was added, the mixture filtered through a short plug of alumina, and the alumina washed with 2×10 mL of ether. The solvent was removed from the combined filtrate and washings in vacuo to give a red oil (0.50 g, 67% crude). The oil was chromatographed on alumina with 50% ether/petroleum ether and the product collected from two adjacent yellow bands, first the trans,trans compound (0.129 g) and then the trans,cis compound (0.124 g). Total yield: 33%. (A small fraction was collected between the bands that contained a nearly 1:1 mixture of the isomers. This mixture was submitted for elemental analysis). **8**: IR (CH_2Cl_2) 2350 b (CN), 2012, 1954 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.05 (b s, 1 H, FpCH), 4.85 (s, 5 H, Cp), 4.35 (b s, 1 H, CHCN), 3.75 (m, 3 H, $OCHCH_2O$), 1.15 (d, 3 H, $J = 6$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 216.4, 215.7 (C=O), 117.8 (CN), 86.5 (Cp), 73.4, 72.2 (FpCHCHCN), 68.5 (CH_2), 66.4 (CH_2CH). **9**: IR (CH_2Cl_2) 2350 b (CN) 2011, 1954 (C=O) cm^{-1} ; 1H NMR ($CDCl_3$) δ 5.90 (d, 1 H, $J = 1$ Hz, FpCH), 4.90 (s, 5 H, Cp), 4.40 (d, 1 H, $J = 1$ Hz, CHCN), 3.55 (m, 3 H, $OCHCH_2O$), 1.20 (d, 3 H, $J = 6$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 216.5, 215.6 (C=O), 118.1 (CN), 86.5 (Cp), 74.2, 72.3 (FpCHCHCN), 68.1 (CH_2CH), 67.6 (CH_2). Anal. Calcd for $C_{13}H_{13}FeNO_4$: C, 51.52; H, 4.32. Found (mixture of **8** and **9**): C, 51.44; H, 4.43.

[η -(R,R,R)-Vinyl 3-(2-trimethylsiloxy)butyl ether]dicarbonyl(η -cyclopentadienyl)iron(II) Trifluoromethane-

sulfonate (12). Fp(dimethyldioxane) (18) (62 mg, 0.21 mmol) was dissolved in 5 mL of ether and cooled to -78°C , and a standard solution of Me_3SiOTf (0.21 mL, 1.04 mmol/mL in CH_2Cl_2) was added dropwise via syringe. An oily yellow precipitate formed immediately. An additional 10 mL of ether were added. The ether layer was decanted and the oil triturated with another 10-mL portion of ether, still at -78°C . The ether layer was again decanted, and the yellow gum was dried under vacuum while the temperature was maintained below 0°C , to give 113 mg of product (102%): CD (CH_2Cl_2 , 0°C) $\Delta\epsilon_{460} = +1.34 \text{ M}^{-1} \text{ cm}^{-1}$; IR (CH_2Cl_2) 2065, 2025 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}$ (CD_3NO_2) δ 8.1 (b, 1 H, $=\text{CH}$), 5.45 (s, 5 H, Cp), 3.75 (m, 2 H, OCHCHO), 2.90 (b, d, 1 H, $J_{\text{app}} = 12 \text{ Hz}$, $=\text{CH}_2$ cis), 2.55 (b, 1 H, $=\text{CH}_2$ trans), 1.35 (d, 3 H, $J = 6 \text{ Hz}$, CH_3), 1.15 (d, 3 H, $J = 6 \text{ Hz}$, CH_3), 0.10 (s, 9 H, OSiMe_3); $^{13}\text{C NMR}$ (CD_3NO_2) δ 210.2, 20.9/213.5, 213.1 ($\text{C}=\text{O}$), 154.5/154.8 ($\text{OCH}=\text{}$), 88.3/88.7 (Cp), 71.6b, 71.1 (OCHCHO), 23.9b ($=\text{CH}_2$), 19.4 b, 16.6 b ($\text{CH}_3\text{-CHCH-CH}_3$), 1.0 b (OTMS).

$[\eta\text{-}(S,S)\text{-cis-1-Ethoxypropene}]$ dicarbonyl($\eta\text{-cyclopentadienyl}$)iron(II) Tetrafluoroborate (14a). Complex 4b (0.11 g, 0.36 mmol) was dissolved in 8 mL of ether and cooled to -78°C and $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.05 mL, 0.058 g, 0.36 mmol) added dropwise via syringe. A yellow precipitate formed that was isolated via cannula filtration. The solid turned to an oil as it reached room temperature. This was intermediate 13a: $^1\text{H NMR}$ (CD_3NO_2) δ 7.90 (d, 1 H, $J = 4 \text{ Hz}$, $\text{OCH}=\text{}$), 5.50 (s, 5 H, Cp), 3.80 (d of q, 1 H, $J_{\text{d}} = 4 \text{ Hz}$, $J_{\text{q}} = 6 \text{ Hz}$, $\text{CH}_3\text{CH}=\text{}$), 3.45 (m, 2 H, OCHCOO), 1.65 nd, 3 H, $J = 6 \text{ Hz}$, $=\text{CHCH}_3$), 1.35 (d, 3 H, $J = 6 \text{ Hz}$, CH_3), 1.15 (d, 3 H, $J = 6 \text{ Hz}$, CH_3). The oil was then dissolved in ethanol at 0°C and reprecipitated with ether to give a bright yellow solid: 0.020 g (16% from 4b); CD (CH_3CN) $\Delta\epsilon_{465} = +0.488 \text{ M}^{-1} \text{ cm}^{-1}$; IR (CH_2Cl_2) 2070, 2025 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}$ (acetone- d_6) δ 8.05 (d, 1 H, $J = 4.5 \text{ Hz}$, $\text{OCH}=\text{}$), 5.70 (ns, 5 H, Cp), 4.50 (q, 2 H, $J = 7 \text{ Hz}$, OCH_2), 3.80 (d of q, 1 H, $J_{\text{d}} = 5 \text{ Hz}$, $J_{\text{q}} = 6 \text{ Hz}$, $\text{CH}_3\text{CH}=\text{}$), 1.60 (d, 3 H, $J = 6 \text{ Hz}$, $=\text{CHCH}_3$), 1.25 (t, 3 H, $J = 6 \text{ Hz}$, CH_2CH_3).

$[\eta\text{-}(S,S)\text{-cis-1-Methoxypropene}]$ dicarbonyl($\eta\text{-cyclopentadienyl}$)iron(II) Trifluoromethanesulfonate (14b). Complex 4b (0.134 g, 0.44 mmol) was dissolved in 10 mL of ether and cooled to -78°C , and a standard solution of Me_3SiOTf (0.80 mL, 0.44 mmol, 0.55 M in CH_2Cl_2) was added dropwise via syringe. After 15 min, IR spectra showed the reaction to be incomplete and an additional portion of Me_3SiOTf was added (0.30 mL, total 0.61 mmol). After an additional 0.5 h, 10 mL of ether was added and most of the solvent was removed via cannula filtration. The yellow precipitate was washed with $2 \times 5 \text{ mL}$ of ether and then dried in vacuo while the temperature was maintained below 0°C . This was intermediate 13b: IR (CH_2Cl_2) 2060, 2020 ($\text{C}=\text{O}$) cm^{-1} ; CD (CH_3CN) $\Delta\epsilon_{460} = +1.41 \text{ M}^{-1} \text{ cm}^{-1}$. (Compound 13b epimerizes rapidly as seen by the decrease in amplitude of the 460-nm band. After 45 min $\Delta\epsilon_{460} = +0.80 \text{ M}^{-1} \text{ cm}^{-1}$.) The oil was then dissolved in 2 mL of methanol, the methanol was removed in vacuo, and the resulting solid was triturated with ether to give bright yellow plates: 0.137 g (78%); CD (CH_3CN) $\Delta\epsilon_{460} = +1.54 \text{ M}^{-1} \text{ cm}^{-1}$; IR (CH_2Cl_2) 2080, 2040 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}$ (acetone- d_6) δ 7.95 (d, 1 H, $J = 5 \text{ Hz}$, $\text{OCH}=\text{}$), 5.75 (s, 5 H, Cp), 4.15 (s, 3 H, OCH_3), 3.80 (d of q, 1 H, $J_{\text{d}} = 5 \text{ Hz}$, $J_{\text{q}} = 6 \text{ Hz}$, $\text{CH}_3\text{CH}=\text{}$), 1.55 (d, 3 H, $J = 6 \text{ Hz}$, CHCH_3); $^{13}\text{C NMR}$ (acetone- d_6) δ 213.1, 208.7 ($\text{C}=\text{O}$), 135.0 ($\text{OCH}=\text{}$), 62.5 (OCH_3), 47.0 ($=\text{CHCH}_3$), 13.7 ($=\text{CHCH}_3$).

$[(S)\text{-2-Methoxy-1-methylethyl}]$ dicarbonyl($\eta\text{-cyclopentadienyl}$)iron(II) (15). Fp(methoxypropene) BF_4 (14b) (0.13 g, 0.326 mmol) was dissolved in 5 mL of MeOH and cooled to -78°C , and sodium methoxide (19.3 mg, 0.358 mmol) and sodium borohydride (12.5 mg, 0.326 mmol) were added sequentially. After 15 min the mixture had become a transparent yellow solution and TLC (alumina, 50% ether/petroleum ether) showed a single mobile yellow spot. Water (0.5 mL) was added and the reaction mixture stirred for 10 min. Then the mixture was filtered quickly through alumina and the alumina washed with ether until the washings were colorless. The solvent was removed from the combined organic layers in vacuo, the residue dissolved in ether, dried over MgSO_4 , and filtered, and the solvent again removed in vacuo to give a yellow oil: 67 mg (82%); $^1\text{H NMR}$ (CDCl_3) δ 4.75 (s, 5 H, Cp), 3.45 (m, 2 H, CH_2), 3.35 (s, 3 H, OCH_3), 2.60 (m, 1 H, CH), 1.35 (d, 3 H, $J = 6 \text{ Hz}$, CHCH_3); $^{13}\text{C NMR}$ (CDCl_3) δ 217.4, 217.3 ($\text{C}=\text{O}$), 85.4 (Cp), 84.5 (CH_2), 57.8 (OCH_3), 26.5 (CH), 17.1 (CHCH_3).

$[\eta\text{-}(S)\text{-Propene}]$ dicarbonyl($\eta\text{-cyclopentadienyl}$)iron(II) Tetrafluoroborate (16). Complex 15 (67 mg, 0.26 mmol) was dissolved in 5 mL of ether and cooled to -78°C and $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.10 mL, 0.12 g, 0.73 mmol) added dropwise via syringe. The resulting bright yellow precipitate was isolated via cannula filtration, washed with ether, and recrystallized from acetone/ether to give a yellow powder: 69 mg (84%); CD (CH_3CN) $\Delta\epsilon_{445} = -0.034 \text{ M}^{-1} \text{ cm}^{-1}$; $^1\text{H NMR}$ (acetone- d_6) δ 4.85 (s, 5 H, Cp), 5.35 (m, 1 H, $\text{CH}=\text{}$), 4.05 (d, 1 H, $J = 8 \text{ Hz}$, $=\text{CH}_2$ trans), 3.65 (d, 1 H, $J = 14 \text{ Hz}$, $=\text{CH}_2$ cis), 1.90 (d, 3 H, $J = 6 \text{ Hz}$, CH_3); $^{13}\text{C NMR}$ (acetone- d_6) δ 90.1 (Cp), 85.8 ($\text{CH}=\text{}$), 56.0 ($=\text{CH}_2$).

$[(R,R)\text{-4,5-Dihydro-4,5-dimethyl-1,3-dioxol-2-yl}]$ phenylmethyl]dicarbonyl($\eta\text{-cyclopentadienyl}$)iron(II) (18). Complex 4d (30 mg, 0.082 mmol) was dissolved in CDCl_3 and a trace of $\text{BF}_3\cdot\text{Et}_2\text{O}$ added. The isomerization was monitored by $^1\text{H NMR}$ and appeared complete after one-half at room temperature. The reaction mixture was filtered through alumina, the alumina washed with ether, and the solvent removed in vacuo from the combined organics to give a yellow oil: 24 mg (80%); IR (CH_2Cl_2) 2010, 1950 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 7.20 (m, 5 H, Ph), 5.35 (app t, 1 H, $J = 4.5 \text{ Hz}$, OCHO), 4.60 (s, 5 H, Cp), 3.80–3.40 (b m, 2 H, OCHCHO), 3.55 (d, 1 H, $J = 4.50 \text{ Hz}$, FpCH), 1.25 (d, 3 H, $J = 6 \text{ Hz}$, CH_3), 1.15 (d, 3 H, $J = 5 \text{ Hz}$, CH_3); $^{13}\text{C NMR}$ (CDCl_3) δ 211.8 ($\text{C}=\text{O}$), 145.6 (CHO_2) 135.7 (ipso-Ph), 128.1, 128.0 (o-, m-pH), 125.6 (p-Ph), 105.9 (FpCHPh), 84.5 (Cp), 70.6 (OCHCHO), 18.3, 16.6 (CH_3 's). This material may also be isolated as a by-product of the synthesis of Fp-phenyl dimethyldioxane 21 either chromatographically or from the petroleum ether wash. When isolated in this manner, a single epimer is present, presumably with the S configuration at C(2). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{FeO}_4$: C, 62.15; H, 5.49. Found: C, 61.79; H, 5.58.

Dicarbonyl($\eta\text{-cyclopentadienyl}$)($\eta\text{-cis-methoxystyrene}$)iron(II) Trifluoromethanesulfonate (19). Complex 4d (0.10 g, 0.272 mmol) was dissolved in CH_2Cl_2 and cooled to -78°C and a standard solution of Me_3SiTf (0.61 mL, 0.346 mmol, 0.54 M in CH_2Cl_2) added dropwise via syringe. After 1 h, 0.5 mL of MeOH was added and the reaction mixture was warmed to room temperature, stirred for 10 min, and then recooled to -78°C . Addition of ether caused the slow formation of a precipitate that was collected via cannula, filtered, and recrystallized from CH_2Cl_2 /ether at -78°C to give the product as a yellow solid: 0.102 g (82%); IR (CH_2Cl_2) 2065, 2030 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}$ (CD_3NO_2) δ 7.4 (b m, Ph), 6.2 nd, $J = 7 \text{ Hz}$, $\text{OCH}=\text{}$), 5.5 (s, Cp), 5.4 (d, $J = 5 \text{ Hz}$, $\text{OCH}=\text{}$), 5.3 (s, Cp), 5.2 (d, $J = 7 \text{ Hz}$, $\text{PhCH}=\text{}$), 4.5 (d, $J = 5 \text{ Hz}$, $\text{PhCH}=\text{O}$), 3.70 (s, OCH_3), 3.60 (s, OCH_3). This compound decomposes rapidly in solution near room temperature, and clean spectra were not obtained. The $^1\text{H NMR}$ data given above represents a mixture of the Fp complex and the free ligand.

$[(S,R,R)\text{-4,5-Dihydro-4,5-dimethyl-1,3-dioxol-2-yl}]$ ethyl]dicarbonyl($\eta\text{-cyclopentadienyl}$)iron(II) (21). The dioxane complex 4b (26 mg, 0.085 mmol) was dissolved in CDCl_3 and a trace of $\text{BF}_3\cdot\text{Et}_2\text{O}$ added. The reaction, followed by $^1\text{H NMR}$, appeared complete after 3 days at room temperature. The reaction mixture was filtered through alumina, the alumina washed with ether, and the solvent removed in vacuo from the combined filtrate and washings to give a yellow oil: 19 mg (73%); IR (CH_2Cl_2) 2005, 1947 ($\text{C}=\text{O}$) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 5.15 (d, 1 H, $J = 3 \text{ Hz}$, OCHO), 4.80 (s, 5 H, Cp), 3.55 (m, 2 H, OCHCHO), 2.35 (q of d, 1 H, $J_{\text{q}} = 8 \text{ Hz}$, $J_{\text{d}} = 3 \text{ Hz}$, FpCH), 1.20 (m, 9 H, CH_3 's); $^{13}\text{C NMR}$ (CDCl_3) δ 217.5, 217.0 ($\text{C}=\text{O}$), 111.6 (OCHO), 85.3 (Cp), 79.9, 78.5 (OCHCHO), 22.3 (FpCH), 19.2 (FpCHCH $_3$), 17.5, 16.7 ($\text{CH}_3\text{CHCHCH}_3$).

2,3-Dihydrodioxin. A portion of compound 2a was dissolved in acetone- d_6 at room temperature and left overnight. ^1H and ^{13}C NMR spectra showed the displacement of the ligand by acetone to be complete. The resonances for Fp(acetone- d_6) tetrafluoroborate did not interfere with those of 62, and the compound was not isolated: $^1\text{H NMR}$ (acetone- d_6) δ 5.85 (s, 1 H, $=\text{CH}$), 4.0 (b s, 2 H, OCH_2); $^{13}\text{C NMR}$ (acetone- d_6) δ 127.3 ($=\text{CH}$), 65.0 (CH_2).

(2R,3R)-trans-2,3-Dimethyl-2,3-dihydrodioxin. A sample of complex 2b was dissolved in acetone- d_6 and left at room temperature for 18 h after which time NMR spectra showed the displacement of the ligand by acetone to be complete. The resonances for Fp-acetone- d_6 tetrafluoroborate did not interfere with those for the product 63, and the compound was not isolated:

^1H NMR (acetone- d_6) δ 5.95 (s, 1 H, =CH), 3.55 (m, 1 H, CH_2CH), 1.15 (d, 3 H, $J = 6$ Hz, CH_3); ^{13}C NMR (acetone- d_6) δ 126.8 (=CH), 75.0 (CH_2CH), 17.1 (CH_3).

Structure Determination of 2a. Single crystals were grown by slow diffusion from methylene chloride/diethyl ether. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of good quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2₁ diffractometer. Operations were performed as described previously.²⁷ The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations.²⁸ All computational work was carried out on a VAX 8600 computer using the Enraf-Nonius SDP software package. Details of the structure analysis, in outline form, are presented in Table I. Atomic coordinates for all non-hydrogen atoms appear in Table II.

Structure Determination of 4c. Single crystals were grown by slow diffusion from petroleum ether/diethyl ether. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of excellent quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2₁ diffractometer. Operations were performed as described previously.²⁷ The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anom-

alous scattering for Fe were included in the calculations.²⁸ All computational work was carried out on a NOVA 1200 computer using the Syntex XTL package. Details of the structure analysis, in outline form, are presented in Table V. Atomic coordinates for all non-hydrogen atoms appear in Table VI.

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Registry No. 1, 78251-23-7; 2a, 110725-92-3; 2b, 110772-33-3; 4a, 101224-97-9; 4b, 101224-98-0; 4c, 101225-00-7; 4d, 110903-56-5; 4e, 101225-01-8; 5a, 101224-92-4; 5b, 101224-93-5; 5c, 101224-95-7; 5d, 110903-57-6; 5f, 110903-58-7; 6, 110903-60-1; 7, 111002-62-1; 8, 110903-62-3; 9, 111002-55-2; 12, 108857-47-2; 13a, 110903-64-5; 13b, 111002-59-6; 14a, 111002-57-4; 14b, 111002-58-5; 15, 110903-65-6; 16, 111002-60-9; 18, 110903-61-2; 19, 110903-67-8; 21, 110903-68-9; NaBH_3CN , 25895-60-7; LiMeCuCN , 41753-78-0; Et_4NCN , 13435-20-6; PhMgBr , 100-58-3; $\text{CH}_2=\text{CHMgBr}$, 1826-67-1; PhCH_2SNa , 3492-64-6; $\text{Fp}(\text{isobutylene})$ tetrafluoroborate, 41707-16-8; *cis*-dimethoxyethene, 7062-96-6; $\text{Fp}(\text{acetone-}d_6)$ tetrafluoroborate, 110903-69-0; ethylene glycol, 107-21-1; (*R,R*)-2,3-butanediol, 24347-58-8; 1,2-propanediol, 57-55-6; 2,3-dihydrodioxin, 543-75-9; (*2R,3R*)-*trans*-2,3-dimethyl-2,3-dihydrodioxin, 110874-64-1.

Supplementary Material Available: Tables SI through SIV, listing thermal parameters and atomic coordinates for hydrogen atoms for each structure (4 pages); tables of observed and calculated structure factors for each structure (15 pages). Ordering information is given on any current masthead page.

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Organogermanium and Organotin Amido Derivatives of Carbon Suboxide. Crystal and Molecular Structure of $(\text{Me}_3\text{M})_2\text{C}(\text{CONMe}_2)_2$ ($\text{M} = \text{Ge}, \text{Sn}$)

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The compounds $(\text{Me}_3\text{Ge})_2\text{C}(\text{CONMe}_2)_2$ (A) and $(\text{Me}_3\text{Sn})_2\text{C}(\text{CONMe}_2)_2$ (B) have been synthesized. They are isomorphous and crystallize in the orthorhombic space group $P2_12_12_1$ with $a = 14.437$ (4) Å, $b = 13.243$ (4) Å, and $c = 9.826$ (3) Å for A and $a = 14.706$ (4) Å, $b = 13.420$ (4) Å, and $c = 9.920$ (3) Å for B, respectively. The coordination geometry about Ge and Sn is almost undistorted tetrahedral. However two short intramolecular contact distances $\text{Ge}\cdots\text{O}$ and $\text{Sn}\cdots\text{O}$ of 2.89, 2.92 Å and 2.95, 2.97 Å, respectively, are found. Structural considerations as well as NMR spectra exclude the possibility that any bond interaction exists between metal and oxygen atoms. The shift of CO stretching bands to unusually low frequencies is explained in terms of electron withdrawal due to the presence of the metals.

Introduction

Recently two of us started a systematic study of molecular structures of compounds of the type R_2MX_2 ($\text{X} = \text{Ge}, \text{Sn}$)^{1,2} in order to elucidate the much discussed problem

of the coordination number attributed to M when X is a halogen.³⁻⁷ The same problem seems to be more in dispute

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