Preparation and Chiroptical Properties of Optically Active Vinyl Ether–Iron and Olefin–Iron Complexes. A CD Quadrant Rule Correlating Absolute Configurations

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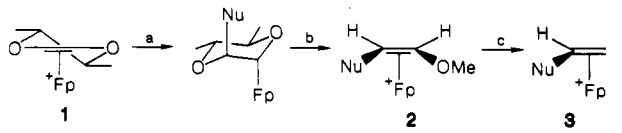
Abstract: Exchange etherification of dicarbonylcyclopentadienyl(η^2-ethyl vinyl ether)iron tetrafluoroborate (**4**) with optically active primary and secondary alcohols yields a mixture of diastereomeric cations. These isomers are in rapid equilibrium at room temperature. The most favorable equilibrium ratio of such diastereomers (4:1) is achieved with (+)- or (−)-menthol, and the absolute configuration of the predominant diastereomer, formed with (−)-menthol, has been determined. Optically active dicarbonylcyclopentadienyl (η^2-olefin)iron tetrafluoroborate may also be prepared from optically active epoxides. A study of the circular dichroism of these optically active complexes, together with those prepared earlier from the dioxene–iron complex (**1**), has been carried out and a mechanism by which asymmetry is induced at the achiral metal center is proposed. These observations provide the basis for a quadrant rule relating the sign of the Cotton effect near 450 nm and the absolute configuration of the olefin–iron complex.

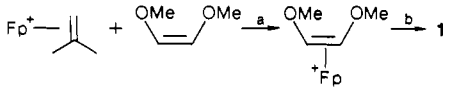
Optically active metal–alkene and –alkenyl complexes, in which the coordinated ligand is the center of asymmetry, constitute reagents with significant potential in asymmetric synthesis, since nucleophilic addition to such ligands provides a means for creating one or more asymmetric saturated carbon centers, with high enantioselectivity. A number of synthetic applications employing such optically active olefin complexes have recently been reported.[1]

We have previously shown that optically active Fp(vinyl ether) **2** and Fp(olefin) **3** cations [Fp = $CpFe(CO)_2$] of known absolute configuration can be prepared from optically active Fp(dioxene) cations **1**.[2] The latter are in turn readily available from 1,2-



(a) Nu^-, THF, 0 °C; (b) TMSOTf or $HBF_4 \cdot Et_2O$, −78 °C; MeOH, 0 °C; (c) $NaBH_4$, NaOMe, THF, −78 °C; $HBF_4 \cdot Et_2O$, −78 °C

dimethoxyethylene by exchange complexation with Fp(isobutylene)BF_4, followed by exchange etherification with an optically active 1,2-glycol.



(a) CH_2Cl_2, 40 °C; (b) (*R,R*)-butane-2,3-diol, CH_2Cl_2, 0 °C

Since Fp(alkyl vinyl ether) cations are particularly good substrates for nucleophilic addition and the racemic complexes are readily obtained from haloacetals or ketals,[3] we have sought alternative methods of preparing these cations in optically active form. The present paper describes a general procedure by which such optically active complexes may be generated from the racemic complex and sets forth a circular dichroism quadrant rule on the basis of which the absolute configuration of Fp(olefin) and Fp(vinyl ether) cations may be assigned.

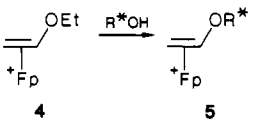
Table I. Diastereomer Ratios for Fp(η^2-vinyl ether)BF_4 Salts (**5**)

alcohol	diastereomer ratio[a]
(−)-menthol	4.0:1
(+)-menthol	3.6:1
(−)-borneol	1.9:1
(−)-isoborneol	2.1:1
(−)-myrtanol	1.2:1
(+)-*sec*-butyl alcohol	1.3:1
(+)-methyl β-hydroxyisobutyrate	1.4:1
(−)-2-(benzyloxy)-1-propanol[b]	1.3:1

[a] Estimated accuracy ±10%. [b] Prepared from (*S*)-ethyl *o*-benzyllactate.[5]

Results and Discussion

Dynamic Resolution of Vinyl Ether–Iron Complexes. Optically active vinyl ether–iron complexes **5** can be readily generated from the racemic ethyl vinyl ether complex **4** by taking advantage of



both the facile exchange of the ethoxy group for OR in the presence of an excess of primary or secondary alcohol, and of the relatively low rotational barrier about the complexed olefin center in these vinyl ether complexes. Thus, when alkoxy exchange is carried out employing an optically active alcohol, the resulting mixture of diastereomeric vinyl alcohol–iron complexes are in rapid equilibrium and partial resolution of the complexed olefin center results.[4] Such *dynamic resolution* has been examined for a number of optically active alcohols. The equilibrium diastereomeric ratios of the resulting vinyl ether complexes, determined by examination of the ^{13}C NMR spectra, are recorded in Table I.

As can be seen from the data, the energy differences for these diastereomeric pairs of complexes are generally small, except for the diastereomer pair derived from optically active menthol. The structural factors which may contribute to these energy differences

(1) Bandara, B. M. R.; Birch, A. J.; Kelly, L. F. *J. Org. Chem.* **1984**, *49*, 2496. Birch, A. J.; Kelly, L. F. *J. Org. Chem.* **1985**, *50*, 712. Birch, A. J.; Raverty, W. D.; Stephenson, G. R. *J. Org. Chem.* **1981**, *46*, 5166. Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893. Faller, J. W.; Chao, K.-H. *Organometallics* **1984**, *3*, 927. Bosnich, B.; Mackenzie, P. B. *Pure Appl. Chem.* **1982**, *54*, 189. Trost, B. M..; Dietsche, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 8200. Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649.

(2) Turnbull, M. M.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1988**, *7*, 200.

(3) Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* **1980**, *102*, 5930. Chang, T. C. T.; Rosenblum, M.; Simms, N. *Org. Synth.* **1987**, *66*, 95. Abram, T. S.; Baker, R. *Synth. React. Inorg. Meet-Org. Chem.* **1979**, *9*, 471.

(4) Such dynamic resolution is not applicable to alkenyl ethers, since the mechanism for rotation about the complexed double bond precludes epimerization of the substituted vinyl carbon center (ref 6).

(5) Schlessinger, R. H.; Graves, D. D. *Tetrahedron Lett.* **1987**, *38*, 4381. Cue, B. W.; Moore, B. S. U.S. Patent 4412958, 1983. Dale, J. A.; Mosher, H. S. *J. Org. Chem.* **1970**, *35*, 4002.

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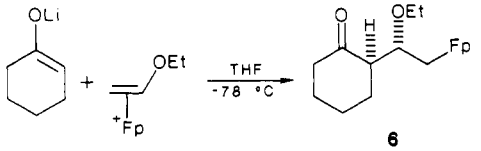
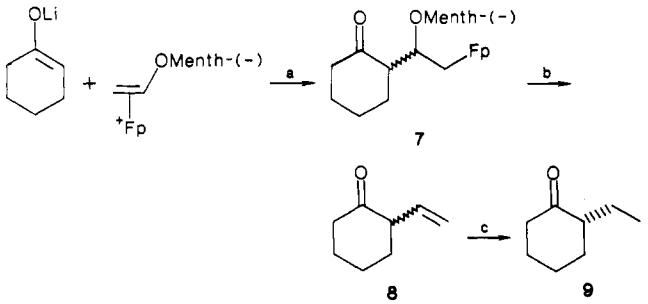
remain to be examined, but a preliminary study of the effect of methyl substitution of the vinyl ligand on the diastereomer ratio of menthol ether shows that this structural change leads to a decrease in the energy difference. Thus, the equilibrium ratio of menthyl ether diastereomers formed in the exchange etherification of Fp(η^2-ethyl isopropenyl ether)BF_4 with (−)-menthol is found to be 2.1:1.

At this point, we were interested in determining the absolute configuration of the major diastereomer formed from (−)-menthol. This has been carried out as follows. We had earlier shown that the condensation of lithium cyclohexanone enolate with Fp(ethyl vinyl ether)BF_4 gave the keto ether **6**[6] as a single diastereomer, in high yield.



6

Similarly, condensation of cyclohexanone lithium enolate with Fp(η^2-(−)-menthyl vinyl ether)BF_4 at −78 °C gave the keto ether **7** (95%) as a 4.5:1 mixture of two diastereomers. These were

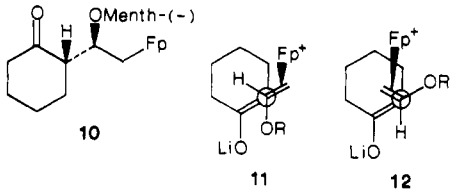


(a) THF, −78 °C; (b) $HBF_4 \cdot Et_2O$, −78 °C; CH_3CN, Δ; (c) H_2/ $RhCl(PPh_3)_3$

readily separated by column chromatography on alumina, and the optical purity of the major product (71%) was assayed by examining its ^{13}C NMR spectrum in the presence of Eu(hfbc)$_3$. No doubling of any of the resonances was observed, whereas a spectrum of **6** showed shifts of 1–4 ppm for the two methyne centers and for the CH_2O and CH_2Fp carbon centers, under the same conditions.[7]

Treatment of the major isomer with tetrafluoroboric acid etherate at −78 °C gave the olefin complex, which was demetalated by heating briefly in acetonitrile solution to give α-vinylcyclohexanone (**8**). Hydrogenation of the olefin in the presence of Wilkinson's catalyst yielded (*R*)-α-ethylcyclohexanone (**9**), $[\theta] = -2280$.[8]

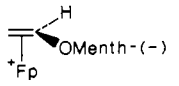
The absolute configuration of the major diastereomeric keto ether **7** may therefore be written as **10**, while that of the activated



10 **11** **12**

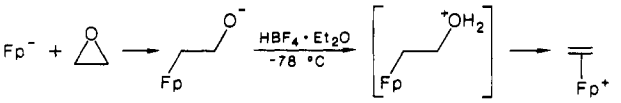
complex for the reaction may be formulated in terms of either the antiperiplanar or the synclinal structures **11** or **12**. We have recently shown that similar structures for the activated complex are consistent with diastereoselectivities observed in the condensation of **4** with 3- and with 6-methylcyclohexanone lithium enolates.[6]

An antiperiplanar relationship of donor and acceptor and acceptor components in acyclic transition states, such as that depicted by **11**, has been invoked for condensations of allylsilanes[9] and of tris(dialkylamino)sulfonium enolates[10] with aldehydes. However, persuasive evidence for a preferred synclinal transition-state geometry, as in **12**, for intramolecular reactions of allylstannanes and allylsilanes with aldehydes has recently been given.[11] The synclinal orientation of reacting components also appears to give a better account of diastereoselectivity in the reactions of the closely related Fp(η^2-1,2-dialkoxyethylene)BF_4 salts with cyclohexanone lithium enolates.[12] The evidence at present does not allow a clear choice between **11** and **12** as representations for the activated complex. However, the absolute configuration of the major condensation product **10** is unrelated to the conformation of the activated complex. Hence, the absolute configuration of the major diastereomer present at equilibrium in the mixture of Fp(η^2-(−)-menthyl vinyl ether)BF_4 salts may be written as shown in structure **13**.



13

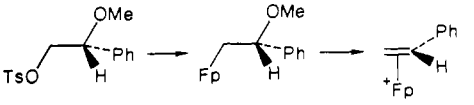
Synthesis from Optically Active Epoxides and Dioxene–Iron Complexes. Two alternative methods have been used for the preparation of the optically active olefin–iron complexes. A number of these compounds are readily available from optically active epoxides,[13] by the sequence shown below or a variant of it, which has been shown to proceed stereospecifically, with retention of configuration.[14]



Alternatively, the optically active dioxene complex **1**, may be employed in the synthesis of either alkenyl alkyl ether–iron complexes or of monosubstituted olefin–iron complexes, as outlined for **2** and **3**. Table II lists the optically active complexes prepared by these methods and summarizes their circular dichroism spectra.

Propene salt **14** was prepared in both enantiomeric forms. Of these, the *S* enantiomer, obtained via the dioxene route, showed a CD maximum at 450 nm which was 83% of that of its enantiomer, prepared by the more direct route from (*S*)-propylene oxide, which suggests some racemization in the longer sequence.

The optically active styrene complex (*S*)-**15** was prepared from (*R*)-2-methoxy-2-phenylethanol, which was converted to the tosylate, metalated with NaFp, and then protonated with $HBF_4 \cdot Et_2O$.



15

The *trans*-1-phenylpropene complex **16** was prepared from (1*R*,2*R*)-1-phenylpropene oxide by treatment with LiFp at 0 °C followed by protonation with 48% HBF_4. The complex is relatively unstable in solution due to its trans geometry, and we were not

(6) Chang, T. C. T.; Coolbaugh, T. S.; Foxman, B. M.; Rosenblum, M.; Simms, N.; Stockman, C. *Organometallics* **1987**, *6*, 2394.

(7) It was necessary to carry out these experiments in order to exclude the possibility that the condensation of lithium cyclohexanone enolate with the Fp(menthyl vinyl ether) complex was less diastereoselective than was the condensation of the Fp(ethyl vinyl ether) complex. Were that true, then the minor and major products (**7**) would be related as diastereomers at C_2 and C_7 and the major product might be a mixture of diastereomers, enantiomeric at these centers.

(8) Meyers, A. I.; Williams, D. R.; Druelinger, M. *J. Am. Chem. Soc.* **1976**, *98*, 3032.

(9) Hayashi, T.; Konishi, T.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963.

(10) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598.

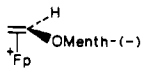
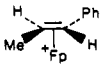
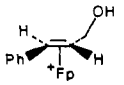
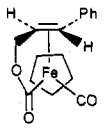
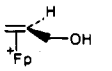
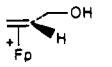
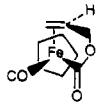
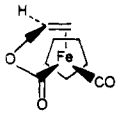
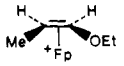
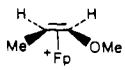
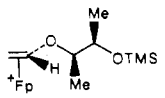
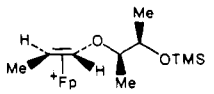
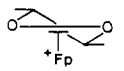
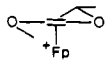
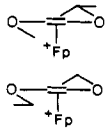
(11) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655.

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

(13) Purchased from Aldrich Chemical Co., 940 West St. Paul Avenue, Milwaukee, WI 53233.

(14) Giering, W. P.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1972**, *94*, 7170.

Table II. CD Spectral Bands for Optically Active Fp(η^2-olefin)BF_4 Complexes[a]

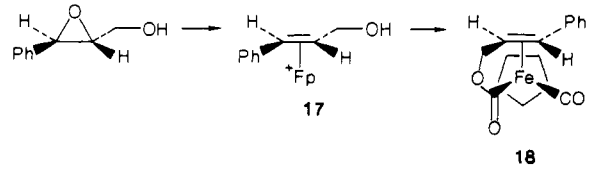
complex		Δε		
structure	no.	400–500 nm	300–400 nm	ref
	(*S*):(*R*)-**13** (4:1)	+1.1 (480)	−2.2 (380)	this work
	(*R*)-**14**	+0.41 (450)	−0.99 (360)	this work
	(*S*)-**14**	−0.34 (445)[b]	*c*	2
	(*S*)-**15**	−0.33 (480)	+2.84 (385)	this work
	(*S*,*S*)-**16**[b]	*c*	*c*	this work
	(*S*,*S*)-**17**	*c*	*c*	this work
	(*S*,*S*)-**18**	−1.68 (465)	+5.26 (395)	this work
	(*R*)-**21**	+0.11 (440) +0.13 (440)	−0.59 (340)[d] −0.75 (340)[e]	this work
	(*S*)-**21**	−0.29 (440)	*c*	this work
	(*R*)-**20**	+1.57 (430) +1.86 (430)	−4.47 (335)[d] −5.57 (335)[e]	this work
	(*S*)-**20**	−2.39 (425)	+6.11 (330)	2
	(1*S*,2*S*)-**25a**	+0.49 (465)	−1.23 (325)	2
	(1*S*,2*S*)-**25b**	+1.54 (460)	−2.97 (340)[g]	2
	(*S*)-**26**	+1.35 (475)	*c*	2
	(*S*,*S*)-**27**	+1.41 (470)	*c*	2
	(2*S*,3*R*,5*R*,6*R*)-**1**	+0.11	*c*	2
	(2*S*,3*R*,5*S*)-**28a**	−0.13 (465)	+4.27 (335)	this work
	(2*R*,3*S*,5*S*)-**28a**:**28b** (2:1)	−0.11 (465)	+2.59 (345)	this work

[a] Determined in acetonitrile solution unless otherwise noted. [b] Determined in methylene chloride solution. [c] Not determined. [d] From (*R*)-glycidyl *p*-nitrobenzoate. [e] From (*R*)-glycidyl tosylate. [f] From (*R*)-3-(tosyloxy)propane-1,2-diol acetonide **22**. [g] Triflate gegenion.

able to observe bands in the CD spectrum in the region of 300–500 nm. However, the complex shows an optical rotation $[\alpha]^{25}_D$ = −34.07° (*c* 0.18, CH_3NO_2).

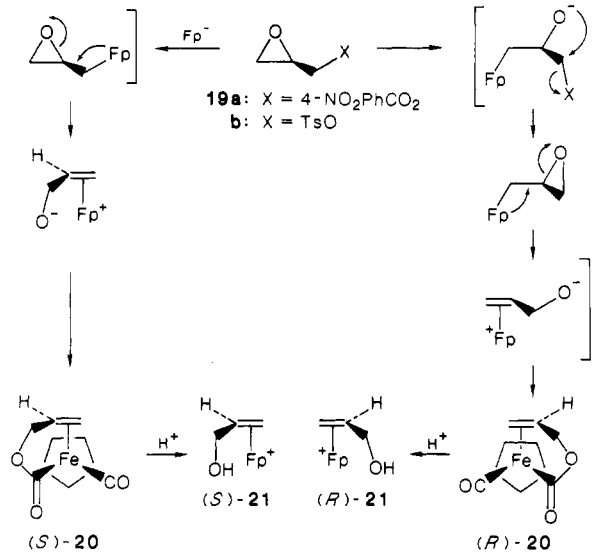
The (*S*,*S*)-*trans*-cinnamyl alcohol complex **17**, prepared from optically active (*R*,*R*)-3-phenylglycidol, was also found to be unstable above 0 °C, even as the solid. The salt, isolated as a

bright yellow solid at −78 °C, was trapped by converting it to the (*S*,*S*)-lactone **18**, by treatment with triethylamine.



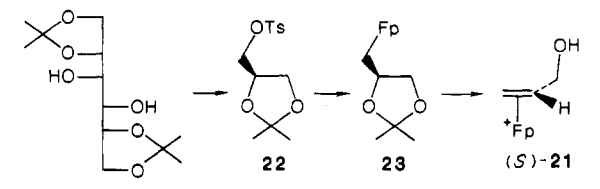
(a) NaFp, THF, 0 °C; HBF_4, −78 °C; (b) Et_3N, acetone, −78 °C

Attempts to convert (*R*)-glycidyl butyrate, (*R*)-glycidyl-4-nitrobenzoate **19a**, or (*R*)-glycidyl tosylate **19b** to the corresponding optically active allyl alcohol ester salt failed. However, when the product mixture, derived from the reaction of either of the latter two epoxides with LiFp, was quenched with water rather than acid, the optically active lactone **20** was obtained in low yield, together with Fp_2 and unreacted epoxide. Both of these products exhibit a positive CD band at 430 nm and a negative band at 335 nm and each is converted, on treatment with HBF_4 to the optically active allyl alcohol complex **21**. The formation of lactone directly from the glycidyl esters may be depicted in terms of initial nucleophilic attack by the Fp anion at either the epoxide or ester, as outlined below, to give either enantiomer.



It has earlier been shown that nucleophilic attack by phenoxide in glycidyl derivatives may occur at either the epoxide or the ester carbon centers depending on the reaction conditions and the leaving group.[15] Hence the absolute configuration of the iron complexes obtained in these reactions cannot be deduced with certainty.

We therefore sought an alternative and less ambiguous route for the preparation of optically active **20** and **21**. This was accomplished with (*R*)-3-(tosyloxy)propane-1,2-diol acetonide **22**, prepared from D-mannitol bisacetonide[16] as shown below.



Metalation of the tosylate with LiFp gave **23**, which on treatment with acid was smoothly converted to (*S*)-Fp(η^2-allyl alcohol)BF_4 ((*S*)-**21**). This was converted, by treatment with triethylamine at 0 °C, to the optically active lactone (*S*)-**20**. A comparison of

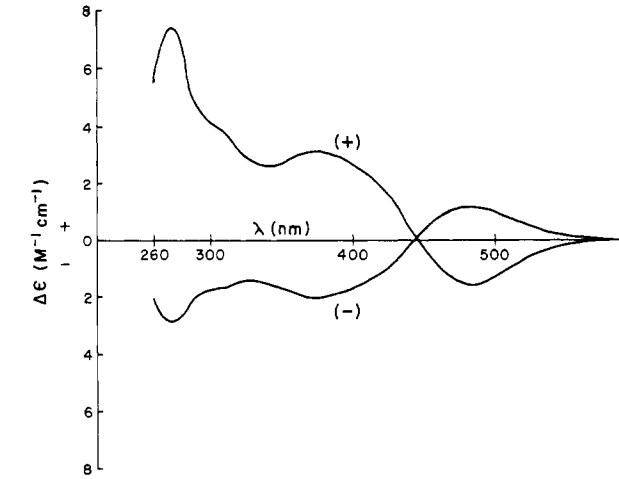


Figure 1. CD spectra of Fp[η^2-(+)-menthylvinyl ether]BF_4 and Fp-[η^2-(−)-menthylvinyl ether]BF_4 taken in methylene chloride solution, on a Jobin-Yvon autodichrograph Mark 5.[32]

the CD spectrum of this product with the allyl and lactone complexes obtained from the glycidyl esters shows that the latter compounds are partially racemized and derive mainly from nucleophilic attack by the Fp anion at the epoxide ring of these esters.

Finally, reaction of LiFp with (*R*)-glycidol, followed by quenching at low temperature by HBF_4, gave the Fp(η^2-allyl alcohol) salt which was largely racemized. The product showed no CD spectrum and a low rotation $[\alpha]^{25}_D = -19.7°$, equivalent to 95% racemization, based on data for this product obtained from the glycidyl esters and from **22**. It is possible that hydrogen bonding of the alcohol group in glucidol with the anionic iron center promotes epoxide ring opening at the internal carbon center of the epoxide ring, leading to an achiral diol intermediate in these reactions.

Chiroptical Studies. The preparation of optically active vinyl ether–iron and olefin–iron complexes prompted us to study the circular dichroism spectra of these compounds in order to examine a possible relationship between their chiroptical properties and absolute configurations. Although a large number of optically active organometallic complexes are known and their chiroptical properties have been studied, these generally owe their optical activity to the presence of an asymmetric metal center.[17] The iron complexes treated here belong to a smaller class of optically active organometallic complexes whose members owe their optical activity alone or in part to planar chirality.[18,1]

The CD spectra of Fp[η^2-(+)-menthyl vinyl ether]BF_4 and of Fp[η^2-(−)-menthyl vinyl ether]BF_4 salts serve to illustrate those features, which appear to be characteristic not only of optically active vinyl ether–iron complexes but of optically active Fp(η^2-olefin) cations in general. These spectra, shown in Figure 1, exhibit four Cotton effect bands in the spectral region between 250 and 500 nm, which correlate with maxima in the UV–vis absorption spectra of these salts near 305, 380, and 440 nm.[19]

A striking feature of the CD spectra of these salts derived from (+)- and (−)-menthol is the near mirror image relationship of the Cotton effect minima and maxima, especially for the two bands above 340 nm. These two bands appear in the CD spectra of all of the optically active Fp(η^2-olefin) cations examined. Since each of the menthol vinyl ether complexes represents an equilibrium mixture of diastereomeric salts, the symmetry relationship of their CD curves suggests that the structural feature which determines the Cotton effect bands is the absolute configuration at the

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(16) Baldwin, J. J.; Raab, A. W.; Mensler, K.; Arison, B. H.; McClure, D. E. *J. Org. Chem.* **1978**, *43*, 4876.

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(19) Due to intense absorption between 200 and 300 nm and the low sensitivity of our instrument, it was not possible to obtain data in this region for all of the optically active compounds prepared.

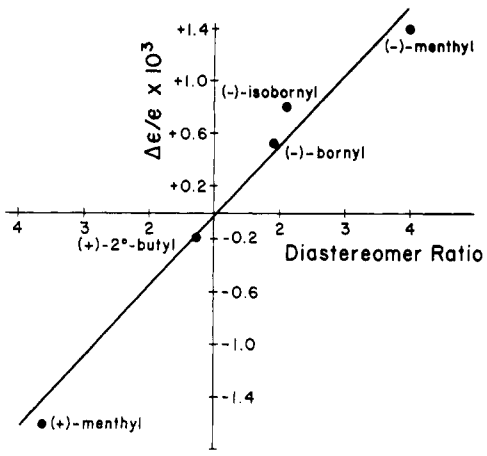
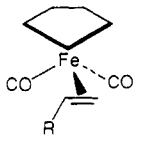


Figure 2. Correlation of normalized differential absorption $\Delta\epsilon/\epsilon$ for a series of Fp(η^2-vinyl ether)BF_4 complexes, derived from optically active alcohols, with the equilibrium ratio of diastereomers determined from ^{13}C spectra. Both measurements are taken at 20 °C.

complexed olefin center, with little if any contribution from the optically active alcohol.[20] Indeed, the presence of these same two bands in optically active Fp(η^2-olefin) cations, which lack any other optical center, clearly establishes this point. We may further anticipate that the intensity of these bands should provide a measure of optical purity at the complexed olefin center for the mixtures of vinyl ether salts, which are in equilibrium. Figure 2 shows that there is indeed a correlation between the diastereomer ratio for a number of Fp(η^2-vinyl ether) cations derived from optically active alcohols, as determined by their ^{13}C spectra, and the normalized differential absorption ($\Delta\epsilon/\epsilon$) of the Cotton effect band near 480 nm for these substances.

Finally we note that the CD bands in these vinyl ether and olefin complexes correspond to electronic transitions which are typical of electronic d–d and charge-transfer transitions,[21] although the metal does not formally constitute an asymmetric center in these complexes.[22]

Such induced asymmetry at an adjacent achiral center is not unlike that observed some years ago by Scott and Wrixon in square planar Pt(II) complexes of optically active olefins, which also show CD spectra characteristic of d–d transitions at the metal center.[23] In the present circumstance, we believe that the induced chirality can be given a more precise description in terms of specific interactions of substituents on the complexed olefin with adjacent metal carbonyl ligands. There is by now ample evidence that the most stable conformation of these cations is best represented by structure **24**, in which the substituent in monosubstituted olefins



24

is anti to the cyclopentadienyl ring and hence proximate to the

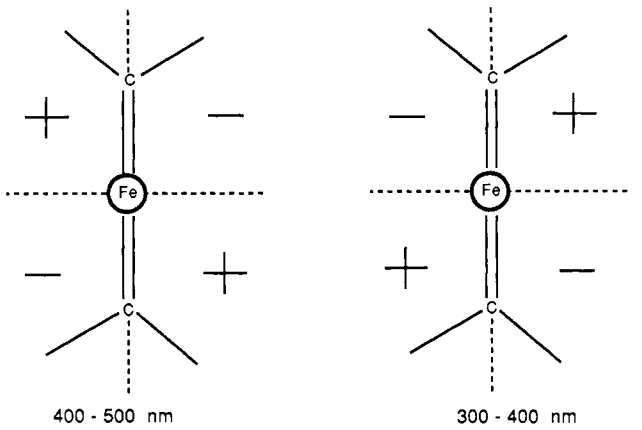


Figure 3. Quadrant rule for optically active Fp(η^2-vinyl ether)BF_4 complexes for Cotton effect bands in the regions of 400–500 and 300–400 nm.

carbonyl centers.[24] The crystal structures of Fp(η^2-methyl vinyl ether)BF_4,[25] Fp(η^2-vinyldimethylamine)BF_4,[23] and Fp(η^2-1,4-dioxene)BF_4[26] illustrate this point. The diastereotopic nature of the carbonyl ligands in these complexes is clearly evident in the ^{13}C chemical shift differences observed in these complexes and in complexes derived from prochiral olefins in general.[23] We propose that a through-space interaction of the olefin substituent with a carbonyl ligand is principally responsible for the differential shielding of carbonyl ligands and hence for the induction of asymmetry at the metal center.

A comparison of the data at hand shows that those olefin–iron complexes which have the absolute configuration A at one or both

of the olefin centers show a negative CD band between 400 and 500 nm and a positive CD band between 300 and 400 nm, while for those with the opposite absolute configuration B show bands of the opposite sign. The results can be put in terms of a local quadrant rule, which is summarized in Figure 3.

The quadrant rule holds for the complex salts **13–15** and **21** and for the neutral lactone complexes **18** and **20** as well. In the disubstituted complex **16**, the absolute configurations at the two complexed carbon centers augment one another with respect to their contribution to the CD bands, while for **25a** and **25b** the two centers provide opposing contributions. The spectra of these latter compounds suggest that the contribution of the alkoxy substituted carbon center provides the dominating influence on the CD spectrum. Complex **16**, for which no CD spectrum could be obtained, nevertheless shows a negative sodium D-line optical rotation, consistent with the anticipated negative long-wavelength Cotton effect band. Complexes **26** and **27** provide the only clear exceptions to the spectral rule. However, models of these show a clear conformational preference for interaction of the more basic ether function with the distal carbonyl ligand rather than the proximate ligand. Such an interaction would be expected to lead to a reversal of the CD Cotton effects for these compounds.

The CD spectra of dioxene complexes **1**, **28a**, and **28b** are particularly instructive. The latter two diastereomeric complexes are formed in the exchange etherification of Fp(η^2-1,2-dimethoxyethylene) with (*S*)-propane-1,2-diol, and **28a** may be separated from its diastereoisomer **28b** by fractional crystallization.[27]

(20) A similar observation has been made for optically active complexes in which the metal is the asymmetric center, in that the CD spectrum is determined principally by the metal chromophore, with the chirality of the ancillary ligands making little contribution (ref 17, p 192). It does not, of course, follow that the assignment of absolute configurations to such asymmetric metal complexes, substituted even by closely related ligands, can be made with confidence on the basis of CD spectral morphologies. See, for example: Brunner, H.; Hammer, B.; Bernal, I.; Draux, M. *Organometallics* **1983**, *2*, 1595.

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(22) The CD spectra of a number of closely related optically active organoiron complexes with an asymmetric metal center have been reported by Chou et al.: Chou, C.-K.; Miles, D. L.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7271.

(23) Scott, A. I.; Wrixon, A. D. *Tetrahedron* **1971**, *27*, 2339.

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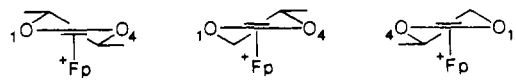

1 **28a** **28b**

The quadrant rule itself provides no guide to the prediction of the CD spectrum of complex **1**, but an examination of its structure suggests that the lone-pair electrons on O_1 are better positioned than those of O_4 to interact with ligand carbonyls. Structurally, the complex is therefore related to those with the absolute configuration B, and it should consequently exhibit a positive long-wavelength Cotton effect near 450 nm, as indeed it does.

For complex **28a** a negative Cotton effect near 480 nm and a positive band near 350 nm may be inferred from the quadrant rule, as is in fact observed. However its diastereomer **28b** would then be expected to show an opposite behavior in these regions if the placement of the methyl group within the quadrant were the determining structural feature. Complex **28b** could not be separated from its diastereomer, but examination of the CD spectrum of a 2:1 mixture of **28a**:**28b** again shows a negative band at 475 nm and a positive band at 335 nm. The differential absorption $\Delta\epsilon$ at 465 nm for this mixture is virtually identical to that observed for **28a** itself. This is what would be predicted from the structures of the most stable conformer for each of these diastereomers, which shows the lone pair electrons for O_4 in **28a** and of O_1 in **28b** are better positioned to interact with a carbonyl ligand. Consequently, both of these complexes are structurally related to those with absolution configuration A and would be expected to behave as observed, notwithstanding the formal enantiofacial relationship of Fp complexation in the two diastereomers.

Further work is in progress which should allow us to subject these chiroptical generalizations to additional scrutiny.

Experimental Section

All reactions were performed in an argon atmosphere, by using standard Schlenk techniques. Transfer of liquids was done by cannula, under a positive pressure of argon. Moisture-sensitive materials were weighed and transferred in a glovebag under nitrogen. Chromatography, material transfer, and recrystallizations were done under a positive pressure of argon.

Anhydrous diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone under nitrogen before use. Methylene chloride and acetonitrile were distilled under nitrogen from calcium hydride. All circular dichroism measurements were performed with solvents of HPLC grade and were recorded on a JASCO J-20 recording spectrophotometer. Alumina refers to basic alumina, activity IV, unless otherwise noted. IR spectra were recorded on a Perkin Elmer 683 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-390 or a Varian XL-300 spectrometer. ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. Chiral epoxides were bought from Aldrich Chemical Co., except for (*R*)-(−)-glycidyl butyrate, which was donated by Genzyme Corp. Elemental analysis were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

General Preparation of Optically Active Fp(olefin) Cations 5 by Exchange Reaction. The following procedure, given for the preparation of Fp(η^2-(−)-menthyl vinyl ether)BF_4, is representative of the general procedure employed. Fp(η^2-ethyl vinyl ether)BF_4 (3 g, 8.9 mmol) and 10 g (64.0 mmol) of (−)-menthol were taken up in 50 mL of methylene chloride, and the solution was stirred at room temperature for 4 h. The solution was then cooled to 0 °C and transferred by cannula to 100 mL of ether cooled to 0 °C. The crystalline product, which separated from solution, was collected and washed with ether thoroughly to remove unreacted menthol, leaving 2.9 g (74%) of yellow crystalline product.

For some exchange reactions it may be advantageous to drive the equilibrium by removal of ethanol. The following procedure, given to the preparation of Fp(η^2-(+)-*sec*-butyl vinyl ether)BF_4 has been applied. Fp(η^2-ethyl vinyl ether)BF_4 (0.5 g, 1.5 mmol) and, 0.65 mL (0.5 g, 6.8 mmol) of (+)-*sec*-butyl alcohol were taken up in 15 mL of 1,2-chloroethane in a round-bottom flask, fitted with a stir bar. The flask was connected to a bulb to bulb distillation apparatus, the system was flushed with argon, and the solution was cooled to −78 °C. The system was evacuated; the cooling bath was removed and transferred to the second bulb. Distillation was allowed to proceed until all of the solvent had been transferred. The product was triturated with ether, filtered, and then washed with ether. Two recrystallizations from ether/methylene chloride gave 0.41 g (74%) of yellow crystalline product.

Spectroscopic Data for Cations 5. R* = (−)-isoborneol: ^{1}H NMR (CD_3NO_2) δ 0.9–2.2 (m, 16 H, CH_3, CH_2), 2.6–2.8 (dd, 1 H, CHO), 2.9–3.2 (dd, 1 H, CH_2=), 4.4 (m, 1 H, CH_2=), 5.5 (s, 5 H, Cp), 7.9 (dd, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 211.0, 208.84, 155.7, 96.4, 86.8, 50.4, 44.7, 37.5, 32.7, 26.6, 22.2, 19.9, 11.4; CD (CH_2Cl_2, c = 1.0 mg/mL) $\Delta\epsilon$ = +0.61 (480), −1.1 (380). Anal. Calcd for $C_{19}H_{25}O_2FeBF_4$: C, 51.39; H, 5.67. Found: C, 51.07; H, 5.76.

R* = (−)-borneol: ^{1}H NMR (CD_3NO_2) δ 0.8–2.0 (m, 16 H, CH_3, CH_2), 2.2–2.8 (m, 1 H, CHO) 2.9–3.2 (m, 1 H, CH_2=), 4.7 (dd, 1 H, CH_2=), 5.4 (s, 5 H, Cp), 7.9 (dd, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 211.0, 208.7, 155.0, 94.6, 86.8, 50.1, 48.2, 44.6, 35.1, 27.8, 26.5, 22.8, 19.6, 18.7, 13.1; CD (CH_2Cl_2, c = 1.0 mg/mL) $\Delta\epsilon$ = +0.35 (480), −0.61 (380). Anal. Calcd for $C_{19}H_{25}O_2FeBF_4$: C, 51.39; H, 5.67. Found: C, 50.36; H, 5.69.

R* = (+)-*sec*-butyl alcohol: ^{1}H NMR (CD_3NO_2) δ 0.97 (t, 3 H, CH_3), 1.45 (d, 3 H, CH_3), 1.6–2.0 (m, 2 H, CH_2), 2.5–2.7 (m, 1 H, CHO), 2.8–3.1 (m, 1 H, CH_2=), 4.58 (dd, 1 H, CH_2=), 5.45 (s, 5 H, Cp), 8.0 (dd, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 155.2, 86.7, 85.8, 29.1, 22.8, 18.8, 8.8, 35.1; CD (CH_2Cl_2, c = 1.0 mg/mL) $\Delta\epsilon$ = −0.12 (480), +0.21 (380). Anal. Calcd for $C_{13}H_{17}O_2FeBF_4$: C, 42.91; H, 4.71. Found: C, 41.44; H, 4.76.

R* = (−)-menthol: ^{1}H NMR (CD_3NO_2) δ 0.7–2.2 (m, 18 H, CH, CH_2, CH_3), 2.4–2.7 (m, 1 H, CHO), 2.8–3.1 (m, 1 H, CH_2=), 4.2–4.5 (m, 1 H, CH_2=), 5.45 (s, 5 H, Cp), 8.0 (m, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 211.6, 208.6, 160.1, 90.4, 86.6, 47.7, 40.3, 33.8, 31.1, 25.8, 23.0, 22.2, 21.3, 20.8, 16.0; CD (CH_2Cl_2, c = 1.2 mg/mL) $\Delta\epsilon$ = +1.1 (480), −2.2 (380). Anal. Calcd for $C_{19}H_{27}O_2FeBF_4$: C, 51.16; H, 6.10. Found: C, 50.96; H, 6.17.

R* = (+)-menthol: ^{13}C NMR ($CDCl_3$) δ 211.4, 208.5, 159.2, 90.2, 86.5, 47.6, 40.2, 33.6, 30.9, 25.7, 22.9, 22.1, 21.3, 20.7, 15.8; CD (CH_2Cl_2, c = 1.0 mg/mL) $\Delta\epsilon$ = −1.2 (480), +2.3 (380).

R* = (−)-myrtanol: ^{13}C NMR ($CDCl_3$) δ 211.2, 207.9, 148.4, 87.1, 79.8, 41.9, 40.6, 39.1, 34.8, 26.6, 25.1, 23.8, 23.2, 20.1, 17.5. Anal. Calcd for $C_{19}H_{23}O_2FeBF_4$: C, 51.16; H, 6.10. Found: C, 49.76; H, 5.96.

R* = (+)-methyl β-hydroxyisobutyrate: ^{1}H NMR (CD_3NO_2) δ 1.3 (d, 3 H, CH_3), 2.7–3.2 (m, 3 H, CH_2, CH), 3.7 (s, 3 H, CH_3), 5.6 (s, 5 H, Cp), 7.8 (dd, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 211.5, 143.8, 88.6, 77.6, 52.9, 40.4, 27.9, 13.9.

Fp(η^2-isopropenyl-(−)-menthyl ether)BF_4: ^{13}C NMR ($CDCl_3$) δ 211.5, 209.6, 85.6, 85.0, 84.2, 48.9, 40.4, 33.19, 31.6, 25.1, 22.6, 21.9, 20.5, 15.6 (the exchange was not carried to completion, and the product contained about 50% starting compound).

Preparation of Keto Ether (7). To a mixture of 0.6 g of the (trimethylsilyl)cyclohexanone enolate (3.5 mmol) in 15 mL of THF in a Schlenk flask fitted with a nitrogen inlet and magnetic stirring bar was added *n*-BuLi (3.5 mmol) in hexane. The mixture was stirred at room temperature for 1 h, after which it was cooled to −78 °C and 1.57 g (3.5 mmol) of (−)-menthyl vinyl ether complex **5** was added. After stirring for an additional 2 h at −78 °C, the mixture was warmed to room temperature and filtered through a plug of activity IV neutral alumina. Removal of the solvent gave **7** as a red-yellow oil in 95% yield. The ratio of diastereomers (4.5:1) was determined by HPLC (column, u-bondapak C18, 3.9 mm × 30 cm; mobile phase, MeOH; flow rate, 1 mL/min; detection, UV at 254 nm). The two diastereomers were easily separated by chromatography on activity IV neutral alumina with 5% ether/hexane as eluent to give a 69% yield of the major isomer and a 10% yield of the minor isomer. Major isomer: IR (CH_2Cl_2) 2009, 1953 (MCO), 1705 (CO) cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 217.6 and 217.5 (MCO), 213.8 (CO), 85.3 (Cp), 76.5 and 73.5 (CHO), 53.5, 48.1, 42.5, 39.9, 34.6, 31.5, 26.8, 25.03, 24.96, 24.85, 23.0, 22.6, 21.4, 15.8 and 4.4 ($FpCH_2$). Anal. Calcd for $C_{25}H_{36}FeO_4$: C, 65.79; H, 7.95. Found: C, 65.80; H, 8.17. Minor isomer: IR (CH_2Cl_2) 2008, 1952 (MCO), 1707 (CO) cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 217.5 and 217.4 (MCO), 213.2 (CO), 85.6 (Cp), 83.5 and 75.3 (CHO), 54.2, 49.0, 42.7, 34.5, 31.9, 27.9, 26.7, 24.9, 24.3, 23.2, 22.5, 21.4, 16.3, 2.1 ($FpCH_2$).

Protonation and Demetalation of 7. Preparation of (*S*)-2-Vinylcyclohexanone (8). Tetrafluoroboric acid etherate (0.32 mL, 2 mmol) was added dropwise to a solution of compound **6** (0.9 g, 2 mmol) in 20 mL of methylene chloride at −78 °C. After stirring of the mixture for 0.5 h, ether was added and the yellow crystals which precipitated from the solution were transferred by cannula to a Schlenk tube at −78 °C and dried under a stream of nitrogen. The yellow solid was allowed to warm to −20 °C and dissolved in 12 mL of acetonitrile. After refluxing for 2 h, the solution was cooled to room temperature. The solvent was removed, the residue was extracted with ether, and the ether phase was washed with 3 × 10 mL of water and finally dried over anhydrous $MgSO_4$. Filtration, followed by removal of the solvent, gave the product

(27) Unpublished work with X.-Y. Zhu and K.-H. Chu.

8 as a yellow oil in 80% yield. IR (CH_2Cl_2) 1715, 1647, 912 cm^{-1}. The product was identified by comparison of its ^1H NMR spectral data with that reported by Marvell and Rusay:[28] ^1H NMR ($CDCl_3$) δ 6.1–5.9 (m, 1 H, CH=), 5.2–5.0 (m, 2 H, CH_2=), 3.0 (m, 1 H, CH), 2.5–1.5 (m, 8 H, CH_2). CD (MeOH) $[\theta]_{290} = -2400$, $\Delta\epsilon = -0.80$ (290).

Hydrogenation of 8. Preparation of (*R*)-2-Ethylcyclohexanone. To a 25-mL round-bottom flask was added 25 mg of Wilkinson's catalyst, $RhCl(PPh_3)_3$. The flask was flushed with dry hydrogen and then 5 mL of benzene which had been passed through activity I neutral alumina and then degassed in vacuo was added by syringe. Then 100 mg of **8** was added by syringe and the solution was stirred under 1 atm of hydrogen for 20 h. The solution was then filtered through an activity IV neutral alumina pad. Removal of the solvent gave the product (100%) in 92% purity by GC (column, OV-101; oven temperature, 70–300 °C; rate, 20 °C/min; injection temperature, 225 °C; detector, FID; flow rate, 14.2 mL/min). Distillation gave 60 mg (60%) of (*R*)-2-ethylcyclohexanone as a pale yellow oil: IR (CH_2Cl_2) 1712 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.4 Hz, CH_3), 1.1–2.5 (m, 11 H); lit.[29] ^1H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7.0 Hz, CH_3), 1.1–2.5 (11 H); CD (MeOH) $\Delta\epsilon = -0.69$ (290); $[\theta]_{290} = -2280$; lit.[30] CD (MeOH) $[\theta]_{289} = -2110$.

Preparation of (*R*)-(−)-2-Methoxy-2-phenylethyl Tosylate. This was prepared in 72% yield, following the procedure used to prepare the *S* isomer by Valentine et al.:[31] ^1H NMR ($CDCl_3$) δ 7.0–7.9 (m, 9 H, C_6H_5, C_6H_4), 4.4 (t, 1 H, J = 6 Hz, OCH), 4.09 (d, 2 H, J = 6 Hz, CH_2O), 3.25 (s, 3 H, OCH_3), 2.44 (s, 3 H, $CH_3C_6H_4$). $[\alpha]^{28}_D = -98.1°$ (*c* 1.79, C_6H_6), lit.[30] (for enantiomer) $[\alpha] = +92.6°$. Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.73; H, 5.92; S, 10.46. Found: C, 62.94; H, 5.91; S, 10.20.

Preparation of (*S*)-Dicarbonyl(η^5-cyclopentadienyl)(η^2-styrene)iron Tetrafluoroborate (15). The above tosylate (0.30 g, 0.99 mmol) was added dropwise at 0 °C to a solution of FpLi (0.99 mmol) in 5 mL of THF. The resulting mixture was warmed to room temperature and stirred for 3 h. The solution was filtered through a short plug of Celite which was washed with 3 × 5 mL of ether. Removal of the solvent in vacuo left the product as a red oil (0.33 g, 1.06 mmol). This was taken up in 5 mL of methylene chloride, the solution was cooled to −78 °C, and $HBF_4 \cdot Et_2O$ (0.14 mL, 1.06 mmol) was added dropwise via a syringe. A yellow precipitate formed. Precipitation was completed by the addition of 30 mL of ether. The solid was collected, washed with ether, and then dried in vacuo at room temperature to give 0.19 g of product (51% based on tosylate). The crude product was recrystallized from acetonitrile/ether at 0 °C to give the salt as yellow flakes, 0.11 g (30%): IR (CH_3CN) 2083, 2046 (FeCO) cm^{-1}; ^1H NMR (CD_3NO_2) δ 7.48 (s, 5 H, C_6H_5), 6.22 (dd, 1 H, J = 9 Hz, J' = 15 Hz, Ph*CH*=), 5.68 (s, 5 H, Cp), 4.23 (dd, 1 H, J = 15 Hz, J' = 1 Hz, =CH_2 trans), 4.13 (dd, 1 H, J = 9 Hz, J' = 1 Hz, =CH_2 cis); ^{13}C NMR (CD_3NO_2) δ 211.28, 209.14 (FeCO), 136.68 (i-Ph), 132.30 (m-Ph), 131.10 (p-Ph), 129.24 (o-Ph), 90.87 (Cp), 87.05 (=*CH*Ph), 49.24 (=CH_2).

Preparation of (*S*,*S*)-Dicarbonyl(η^5-cyclopentadienyl)(η^2-*trans*-1-phenylpropene)iron Tetrafluoroborate (16). (1*R*,2*R*)-1-Phenylpropylene oxide (0.21 g, 1.56 mmol) in 4 mL of THF was added dropwise, at 0 °C, to a solution of FpLi (1.56 mmol) in 7 mL of THF. The resulting mixture was stirred at 0 °C for 1 h when the solution turned dark green. Then 48% HBF_4 (0.57 mL, 3.2 mmol) was added at −78 °C. The Fp salt was precipitated by slow addition of ether, filtered in a jacketed Schlenk tube at −78 °C, and washed with 5 × 10 mL of precooled ether. The product was then recrystallized from 1:1 CH_2Cl_2–acetone/ether at −78 °C, dried under a nitrogen atmosphere for 1 h at −78 °C, and finally dried in vacuo at room temperature to give a yellow solid, 0.39 g (66%): IR (KBr) 2048, 1998 (FeCO) cm^{-1}; ^1H NMR (acetone-d_6) δ 7.41 (m, 6 H, C_6H_5), 6.27 (d, 1 H, J = 15 Hz, *CH*C_6H_5), 5.78 (s, 5 H, Cp), 5.48 (m, 1 H, *CH*CH_3), 1.89 (d, 3 H, J = 6 Hz, CH_3); ^{13}C NMR (acetone-d_6) δ 207.0 (FeCO), 138.0 (i-Ph), 130.2 (m-Ph), 129.8 (p-Ph), 127.9 (o-Ph), 90.5 (Cp), 83.1 (*C*HC_6H_5), 75.5 (*C*HCH_3), 22.3 (CH_3). $[\alpha]^{25}_D = -34.07°$ (*c* 0.18, CH_3NO_2).

This compound decomposes rapidly in solution (CH_2Cl_2, CH_3CN, CH_3NO_2, CH_3COCH_3) near room temperature. All the spectral data were obtained at −50 °C. Anal. Calcd for $C_{16}H_{15}O_2FeBF_4$: C, 50.32; H, 3.96. Found: C, 48.98; H, 4.08.

Preparation of (*S*,*S*)-Dicarbonyl(η^5-cyclopentadienyl)(η^2-*trans*-cinnamyl alcohol)iron Tetrafluoroborate (17). (2*R*,3*R*)-3-Phenylglycidol (0.36 g, 2.40 mmol) dissolved in 4 mL of THF was slowly added dropwise at 0 °C to a solution of FpLi (2.14 mmol) in 8 mL of THF. After 2 h at 0 °C, the reaction mixture became dark green. The mixture was cooled to −78 °C and 48% HBF_4 (0.88 mL, 4.79 mmol) was added dropwise. The mixture was then added slowly, via a cannula, to 100 mL of ether cooled to −78 °C. The precipitate was collected in a jacketed Schlenk tube at −78 °C, washed with 5 × 10 mL of precooled ether, and finally dried under argon at −78 °C for 1 h. The yellow solid was highly unstable at room temperature. In subsequent transformations, this compound was prepared at −78 °C and used directly.

Preparation of (*S*,*S*)-Lactone 18. The salt **17** was prepared as above on a 1.24-mmol scale and the product was dissolved in 15 mL of acetone at 78 °C. Triethylamine (0.17 mL, 1.24 mmol) was added. After 0.5 h at −78 °C, the mixture was brought to room temperature and solvent was removed to give an orange oil. Chromatography on alumina with ether/methylene chloride gave a thick, orange yellow oil, 92.2 mg (24%): IR (CH_2Cl_2) 1988 (FeCO), 1664 (FeCO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (s, 5 H, Ph), 5.76 (ddd, 1 H, J = 12 Hz, J' = 9 Hz, J'' = 6 Hz, =*CH*CH_2), 4.65 (d, 1 H, J = 12 Hz, *CH*Ph), 4.54 (dd, 1 H, J = 10 Hz, J' = 6 Hz, O*CH*$_2$), 4.47 (s, 5 H, Cp), 2.66 (dd, 1 H, J = 10 Hz, J' = 9 Hz, OCH_2); ^{13}C NMR ($CDCl_3$) δ 218.2 (FeCO), 209.4 (FeCO), 141.4 (i-Ph), 128.9 (m-Ph), 127.3 (p-Ph), 126.3 (o-Ph), 89.9 (Cp), 70.8 (=*C*HCH_2O), 68.0 (=*CH*Ph), 67.2 (OCH_2). Anal. Calcd for $C_{16}H_{14}O_3Fe$: C, 61.97; H, 4.55. Found: C, 62.07; H, 4.51.

Formation of (*R*)-Lactone 20 from (*R*)-Glycidyl 4-Nitrobenzoate. (*R*)-Glycidyl 4-nitrobenzoate (0.20 g, 0.90 mmol) in 5 mL of THF was added dropwise at 0 °C to FpLi (0.90 mmol) in 10 mL of THF. The resulting mixture, which changed from orange yellow to reddish brown while the epoxide was added, was stirred for 4 h. Workup of an aliquot by addition of 1 equiv of 48% HBF_4 at −78 °C followed by addition of ether failed to produce a precipitate. The reaction mixture was allowed to warm to room temperature and was evaporated to dryness. Then 30 mL of water was added and the mixture was extracted with methylene chloride until the extracts were colorless. The combined organic extract was dried on $MgSO_4$ and filtered, and the solvent was removed in vacuo to give a dark brownish red oil. Preparative thin-layer chromatography on alumina gave three fractions, Fp dimer (76.7 mg, 48%), starting epoxide (61.4 mg, 31%), and the lactone **20** as a yellow solid, 16.3 mg (8%): IR (CH_2Cl_2) 1988 (FeCO), 1664 (OCO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.14 (m, 1 H, =CH), 4.87 (s, 5 H, Cp), 4.37 (dd, 1 H, J = 6, J' = 10 Hz, CH_2O), 3.29 (d, 1 H, J = 7.5 Hz, =CH_2, cis), 2.80 (d, 1 H, J = 12 Hz, =CH_2, trans), 2.3 (t, 1 H, J = 10 Hz, OCH_2); ^{13}C NMR ($CDCl_3$) δ 216.80 (FeCO), 209.20 (CO), 87.73 (Cp), 72.37 (=CH), 67.80 (OCH_2), 46.72 (=CH_2).

Similar reaction of glycidyl tosylate gave the (*R*)-lactone (**20**) in 4% yield.

Preparation of (*R*)-Dicarbonyl(η^5-cyclopentadienyl)(η^2-allyl alcohol)iron Tetrafluoroborate from the (*R*)-Lactone 20. The lactone obtained above (20.5 mg, 0.09 mmol) was dissolved in 3 mL of CH_2Cl_2, filtered, and cooled to 0 °C and $HBF_4 \cdot Et_2O$ (14.2 mg, 0.02 mL, 0.09 mmol) was added dropwise. Ether (20 mL) was added to complete the precipitation of the salt. The salt was washed with ether and dried in vacuo at room temperature to give the product as a yellow solid, 28.4 mg (100%): IR (CH_3CN) 2085, 2046 (FeCO) cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.68 (s, 5 H, Cp), 5.00–5.5 (m, 1 H, =CH), 4.3 (m, 2 H, CH_2O), 3.9 (d, 1 H, J = 8 Hz, =CH_2, cis), 3.63 (d, 1 H, J = 15 Hz, =CH_2, trans); ^{13}C NMR (CD_3NO_2) δ 210.87, 209.74 (FeCO), 90.33 (Cp), 87.86 (=CH), 60.30 (OCH_2), 50.88 (=CH_2).

Preparation of [(*R*)-3-(Propanediol acetonido)]dicarbonylcyclopentadienyliron. (*R*)-3-(Tosyloxy)propanediol acetonide[15] (0.86 g, 2.99 mmol) in 4 mL of THF was added dropwise to LiFp (2.99 mmol) in 12 mL of THF at 0 °C. The resulting mixture was stirred at room temperature for 3 h. The mixture was concentrated in vacuo, ether was added, and the mixture was filtered through a short plug of Celite. Removal of solvent left a brownish yellow solid, 0.88 g, which was chromatographed on basic alumina (III) with a 1:1 mixture of CH_2Cl_2/petroleum ether to give the product as a yellow solid, 0.55 g (63%): CD (CH_3CN) $\Delta\epsilon_{298} = -0.62$ M^{-1} cm^{-1}; IR (CH_2Cl_2) 2013, 1960 (FeCO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.84 (s, 5 H, Cp), 4.07 (m, 2 H, OCH_2), 3.37 (m, 1 H, OCH), 1.66 (dd, 1 H, J = 6 Hz, J' = 10 Hz, $FpCH_2$), 1.34 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.2 (m, 1 H, $FpCH_2$); ^{13}C NMR ($CDCl_3$) δ 216.0, 216.8 (FeCO), 108.26 (OCO), 85.27 (Cp), 82.99 (OCH), 71.96 (OCH_2), 27.20, 26.29 (2 CH_3), 1.96 ($FpCH_2$); $[\alpha]^{25}_D = +33.6$ (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{13}H_{16}O_4Fe$: C, 53.45; H, 5.52. Found: C, 53.47; H, 5.34.

Preparation of (*S*)-Dicarbonyl(η^5-cyclopentadienyl)(η^2-allyl alcohol)iron Tetrafluoroborate. The acetonide prepared above (0.10 g, 0.35

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(32) The significant differences in the intensities of the Cotton effect bands for the two diastereomers, especially near 270 and 300 nm, may not be real since the compounds are readily hydrolyzed in the presence of trace amounts of moisture, and differential hydrolysis of the samples may have taken place progressively in the course of the CD determination.

mmol) was dissolved in 2 mL of CH_2Cl_2, cooled to −78 °C, and $HBF_4{\cdot}Et_2O$ (0.05 mL, 0.06 g, 0.37 mmol) was added slowly with stirring. Ether was added to complete the precipitation of the product. The yellow solid was filtered, washed with ether, and recrystallized from acetone/ether at 0 °C to give (*S*)-**21**, 90.0 mg (81%).

Preparation of (*S*)-Lactone 20. The salt above was taken up in 4 mL of nitromethane, cooled to 0 °C, and treated with 10% molar excess of NEt_3. The solvent was removed in vacuo, leaving an orange yellow oil, which was chromatographed on basic alumina (III) with ether/CH_2Cl_2 to give the (*S*)-lactone **20** (70.0 mg 75%): $[\alpha]^{25}_D$ = −292° (*c* 0.1, CH_3CN).

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Molecular Metals with Widely Tunable Band Filling. Structure/Stoichiometry/Counterion Relationships in the Electrochemistry of a Cofacially Joined Polymeric Phthalocyanine Metal

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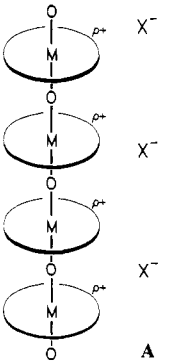
Abstract: The oxidative electrochemistry of the cofacially joined phthalocyanine polymer $[Si(Pc)O]_n$ to yield molecular metals/conductive polymers of the type $\{[Si(Pc)O]X_y\}_n$ is studied by a combination of X-ray diffractometric and spectroscopic techniques. Electrochemical methodology includes controlled-potential coulometry and electrochemical potential spectroscopy (ECPS) applied to rapidly stirred slurries or to microcompactions of the solid polymer. For $X^- = BF_4^-$ in acetonitrile, oxidation ("doping") of as-polymerized orthorhombic $[Si(Pc)O]_n$ to yield tetragonal $\{[Si(Pc)O](BF_4)_y\}_n$ ($y \approx 0.50$) is accompanied by a significant overpotential, minimal tunability in y, and involves a first-order structural phase transformation. Electrochemical undoping occurs smoothly and over a broader potential range (0.90 V) to afford tetragonal $[Si(Pc)O]_n$, which is also accessible by thermally undoping $\{[Si(Pc)O]I_{1.1}\}_n$. Once in the more open tetragonal structure, both the electrochemical and diffraction data argue that y (hence, conduction band filling) can be homogeneously/continuously tuned between 0.0 and 0.50. This result verifies the crystal structural basis of the polymer electrochemical "break-in" phenomenon. It also represents the first case in which the band filling of a molecular metal is broadly tunable. In tetrahydrofuran, tetragonal $[Si(Pc)O]_n$ can also be reversibly *n*-doped to yield $\{[N(n\text{-butyl})_4]_{0.09}[Si(Pc)O]\}_n$. Oxidative ECPS studies with a number of anions in acetonitrile (PF_6^-, SbF_6^-, tosylate, $CF_3(CF_2)_nSO_3^-$, n = 0, 3, 7) demonstrate that maximum doping stoichiometries achievable (y, hence band filling) are largely a function of anion size, i.e., packing constraints within the tetragonal $\{[Si(Pc)O]X_y\}_n$ crystal structure. In contrast to these results, ECPS studies of solid Ni(Pc) (monoclinic slipped-stack β phase) reveal a first-order structural transformation to yield tetragonal $Ni(Pc)(BF_4)_y$ ($y \approx 0.48$) upon oxidative doping, and a subsequent first-order transformation to another slipped-stack Ni(Pc) structure (monoclinic slipped-stack γ phase) upon undoping. Doping/undoping occurs over a relatively narrow potential range; consequently there is far less tunability in y than in the $\{[Si(Pc)O]X_y\}_n$ materials, and large overpotentials are observed. ECPS studies of $[Ge(Pc)O]_n$ reveal irreversible oxidative processes, and polymer decomposition via Ge–O bond cleavage is implicated.

The electrical, optical, and magnetic properties of "molecular metals"[1] are a delicate function of complex architectural and electronic structural interactions that, traditionally, have been both difficult to control and to disentangle. For example, attempts to introduce potentially informative electronic structural perturbations have typically been frustrated by concurrent and unavoidable changes in crystal structure. Over the past several years, we have demonstrated that robust, highly crystalline, and structurally well-defined macromolecules of the type $[M(Pc)O]_n$ (A: M = Si, Ge, Sn; Pc = phthalocyaninato, B)[2] offer an unprecedented opportunity to sequentially vary many of the essential charac-



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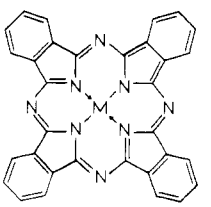

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