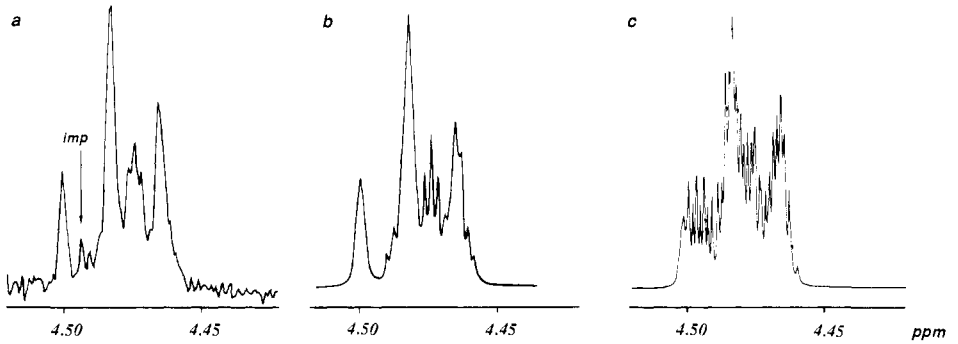
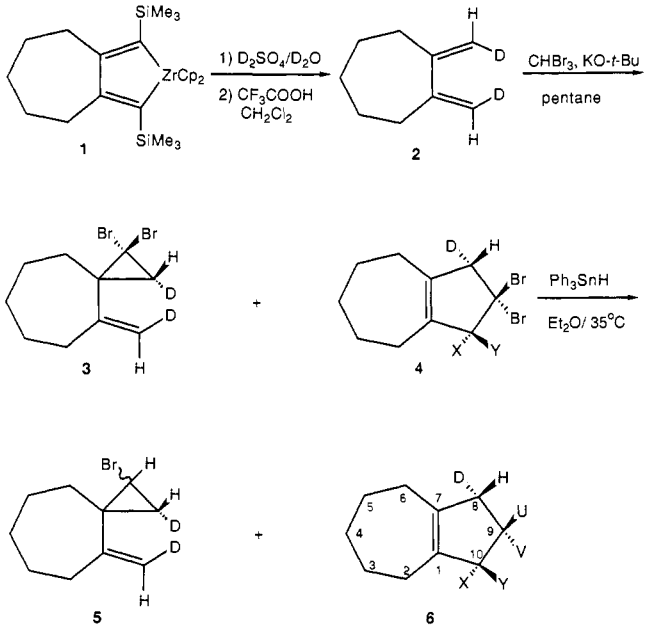


Figure 1. 400 MHz ^{1}H NMR spectrum of **6** in the region of H(9): (a) experimental spectrum, (b) simulated spectrum of a 1:1 mixture of **6b,c**, (c) simulated spectrum of a statistical (2:1:1) mixture of **6a,b,c**.

Scheme I[a]



[a] **a**: X = H, Y = D, U = H, V = Br; **b**: X = D, Y = H, U = Br, V = H; **c**: X = D, Y = H, U = H, V = Br.

a 1:1 mixture of **6b**[5] and **6c** (derived from the disrotatory adduct **4b**); the respective signals of H(9) were simulated with the PANIC program[7] with ^2J(H,H) = 15.0 Hz, Z ^3J(H,H) = 7.0 Hz, and E ^3J(H,H) = 4.0 Hz (taken from the spectrum of the unlabeled **6H**[5]) and the relation J(H,H) $\approx$ 6.51 J(H,D).[8] As shown in Figure 1b, the simulated spectrum of a 1:1 mixture of **6b** and **6c** reproduces the experimental one[9] quite well; for comparison, the calculated spectrum of a random, statistical mixture (**6a**:**6b**:**6c** = 2:1:1) is presented in Figure 1c. Because of the relatively low D_2-incorporation (90.6%), the difference spectrum from Figure 1 (parts b and a) was irregular and did not permit a conclusion on the possible presence of minor quantities of **6a**. However, the addition of increasing percentages of the simulated spectrum of **6a** to that in Figure 1b showed that approximately 15% **6a** would have been detectable. This implies a disrotatory stereospecificity of the 1,4-addition for 70% or more. Thus, a necessary requirement for concertedness of the 1,4-addition of a carbene has been established. At the same time, we have shown that the process, if concerted, is (predominantly) of the linear type.[3]

Acknowledgment. We thank Dr. F. J. J. de Kanter for help with the NMR measurements and simulations, Dr. B. L. M. van Baar for recording the HRMS spectra, and the Netherlands Foundation for Chemical Research (SON) for support with financial aid (P.A.K.) from the Netherlands Organization for the Advancement of Science (NWO).

Registry No. **1**, 122924-25-8; **2**, 122901-97-7; **3**, 122901-98-8; **4a**, 122901-99-9; **4b**, 122902-00-5; **5**, 122902-01-6; **6a**, 122902-02-7; **6b**, 122902-03-8; **6c**, 122902-04-9; **6H**, 122902-05-0; dibromocarbene, 4371-77-1; 1,2-dimethylenecycloheptane, 58738-52-6.

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Diastereoselective Nucleophilic Addition to Coordinated Cyclohexadienyl Rings in Chiral Manganese Complexes

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Received June 1, 1989

The transition-metal-mediated synthesis of difunctionalized cyclohexadienes by nucleophilic addition to coordinated arenes has been investigated with a number of systems:[1-4] $(arene)_2Fe^{2+}$, $CpCo(arene)^{2+}$, and $(arene)Mn(CO)_2L^+$ (L = CO, PR_3). The manganese reactions generally involve single nucleophilic addition to give $(cyclohexadienyl)Mn(CO)_2L$ complexes which are reactivated toward a second nucleophilic attack by conversion to $(cyclohexadienyl)Mn(CO)(NO)L^+$ cations.[4] It has been shown[5]

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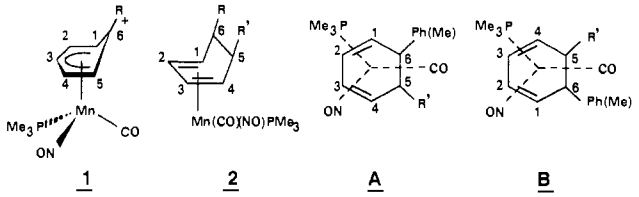
0002-7863/89/1511-8535$01.50/0

Table I. Proton Nuclear Magnetic Resonance Data for (Cyclohexadiene)Mn(CO)(NO)(PMe_3) Complexes **2**

R	R′	isomer	^{1}H NMR: δ
Ph[a]	mal[b]	A	2.21 (m, J = 11, 8, 3, H_1), 5.3 (m, $H_{2,3}$), 3.11 (dd, J = 5.0, 3.3, H_4), 3.56 (dd, J = 11, 10.5, H_5), 3.26 (ddd, J = 10.8, 3, 1.5, H_6), 3.73, 3.15 (s, s, CO_2Me), 2.92 (d, J = 11.7, CH), 1.37 (d, J = 9.0, PMe_3), 7.2 (m, Ph)
Ph[a]	mal[b]	B	3.35 (ddd, J = 6.7, 2.7, 1.5, H_1), 5.2 (m, $H_{2,3}$), 2.00 (m, J = 9.3, 5, 4, H_4), 3.00 (dd, J = 11.4, 9.1, H_5), 3.81 (dd, J = 10.4, 2.4, H_6), 3.62, 3.12 (s, s, CO_2Me), 2.83 (d, J = 11.5, CH), 1.40 (d, J = 8.9, PMe_3), 7.2 (m, Ph)
Ph[a]	H	B	3.45 (dd, J = 6.6, 3.3, H_1), 5.21 (dd, J = 6.7, 4.1, H_2), 5.25 (m, H_3), 2.32 (m, J = 7, 7, 3, H_4), 2.08 (dd, J = 15, 10.5, $H_{5'endo}$), 1.64 (d, J = 15.4, $H_{5'exo}$), 3.59 (d, J = 11, H_6), 1.39 (d, J = 8.8, PMe_3), 7.2 (m, Ph)
Ph[a]	H	A	2.27 (m, J = 9, 8, H_1), 5.19 (m, H_2), 5.30 (m, H_3), 3.49 (m, H_4), 2.60 (dd, J = 15, 10, $H_{5'endo}$), 1.93 (d, J = 15.4, $H_{5'exo}$), 2.97 (d, J = 10.4, H_6), 1.37 (d, J = 8.9, PMe_3), 7.2 (m, Ph)
Me[c]	mal[b]	A	1.90 (m, J = 9, 7, 4, H_1), 4.69 (t, J = 6.5, H_2), 5.05 (m, J = 6.3, 4.0, 1.8, H_3), 3.36 (dd, J = 6.5, 2.7, H_4), 3.77 (tt, J = 10.8, 2.2, H_5), 2.34 (m, H_6), 3.51 (d, J = 11.2, CH), 3.28, 3.27 (s, s, CO_2Me), 0.85 (d, J = 8.8, Me), 0.75 (d, J = 8.8, PMe_3)
Me[c]	mal[b]	B	3.2 (m, H_1), 4.86 (m, $H_{2,3}$), 2.03 (m, J = 11, 2.5, H_4), 3.08 (t, J = 10.4, H_5), 2.76 (m, J = 11, H_6), 3.36 (d, J = 10.3, CH), 3.30, 3.23 (s, s, CO_2Me), 0.87 (d, J = 6.9, Me), 0.76 (d, J = 6.8, PMe_3)
Me[c]	H	B	3.43 (ddd, J = 6.9, 3.3, 1.6, H_1), 4.94 (m, H_2), 4.88 (m, H_3), 1.9 (m, H_4), 1.9 (m, $H_{5'endo}$), 1.23 (d, $H_{5'exo}$), 2.59 (m, J = 10.5, H_6), 1.02 (d, J = 6.8, Me), 0.81 (d, J = 8.8, PMe_3)
Me[c]	H	A	2.0 (m, H_1), 4.75 (m, H_2), 5.05 (dd, J = 6.7, 4.0, H_3), 3.37 (m, J = 7.2, 2.6, H_4), 2.42 (dd, J = 13.2, 13, $H_{5'endo}$), 1.49 (d, $H_{5'exo}$), 2.0 (m, H_6), 0.86 (d, J = 6.6, Me), 0.80 (d, J = 8.8, PMe_3)

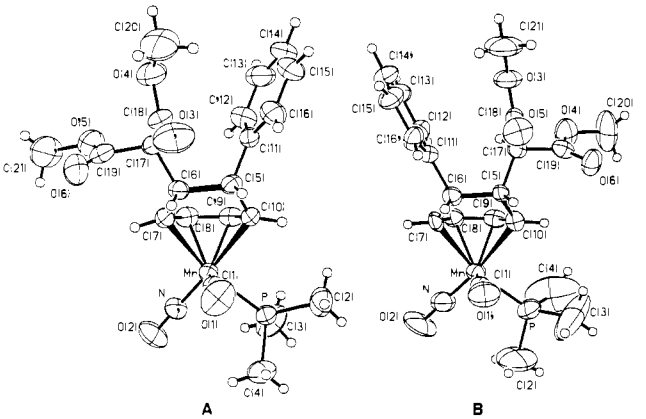
[a] In $CDCl_3$ at room temperature. [b] Mal is $CH(CO_2Me)_2$. [c] In C_6D_6.

that addition to the ring in (cyclohexadienyl)$Fe(CO)_2L^+$ cations is diastereoselective when the nucleophile and the cyclohexadienyl ring are chiral. Likewise, CN^- adds diastereoselectively to $(C_6H_7)Fe(CO)_2L^+$ when L is a chiral phosphine. Herein we report that the addition of R′ (H^-, $CH(CO_2Me)_2^-$) to **1** (R = Ph, Me), in which the metal is the center of chirality, proceeds with significant asymmetric induction; the diastereomers of **2** so formed have been separated and characterized via X-ray diffraction.



1 **2** **A** **B**

It is known[6] from X-ray studies that the CO ligand in **1** lies under the saturated C-6 carbon. A nucleophile can attack at C-5 or C-1, i.e., cis to NO or PMe_3. The addition of $NaCH(CO_2Me)_2$ to **1** (R = Ph) (THF, −78 °C, N_2, 2.5 h) produced an 80% isolated yield of **2** as diastereomers in a 2:1 ratio as judged by ^{1}H NMR (Table I). Separation of the diastereomers was effected on neutral alumina by using 2:1 hexane/ether. Figure 1 gives the structures of the isomers.[7] The major isomer is A, which arises from attack of malonate at C-5, cis to the NO ligand in **1**. This site preference agrees with observations by others with $CpMo(CO)(NO)(allyl)^+$ complexes.[8] Addition of $CH(CO_2Me)_2^-$ to **1** (R = Me) also occurred cleanly with an A:B ratio of ca. 2:1. A correlation of the ^{1}H NMR and structural results shows that $\delta(H_1)$ is much lower



A **B**

Figure 1. ORTEP drawings of diastereomers A and B (**2**; R = Ph, R′ = $CH(CO_2Me)_2$) with the thermal ellipsoids at the 50% probability level.

than $\delta(H_4)$ in A and that the opposite is true in B. Furthermore, coupling to ^{31}P (ca. 10 Hz) is seen only with the hydrogen cis to PMe_3 (H_1 in A and H_4 in B).

The addition of $NaBH_4$ to **1** (R = Ph, Me) (THF, 0 °C, 2.5 h) produced **2** (R′ = H) in an isolated yield of 85%. The diastereomers were separated for the R = Ph product by chromatography on neutral alumina (5% ether in hexane eluant). In contrast to the results with malonate, the ca. 2:1 diastereoselectivity observed with the hydride donor occurred in favor of the B isomer, as judged from the chemical shifts and coupling constants of H_1 and H_4 (Table I). This difference is probably due to the (unusual) preference for hydride to add stereospecifically endo to complexes like **1**; malonate and most other nucleophiles add in the (usual) exo manner (as shown in **2**).[4]

The diene ring in **2** (R = Ph, R′ = H) was liberated in 90% isolated yield from the metal by treatment with excess $FeCl_3$ (THF, 25 °C, 1 h), followed by solvent removal, addition of 2 M HCl, and extraction with CH_2Cl_2. Comparison of the ^{1}H NMR with literature data[9] verified that the product was C_6H_7Ph. We are currently attempting to resolve the cation **1**, since the procedures described above can then be used to synthesize enantiomerically pure mono- and difunctionalized cyclohexadienes. In a related series of experiments, the lithium enolate of (−)-bornyl acetate was added to $(C_6H_6)Mn(CO)_2PMe_3^+$ to give (C_6H_6R)-$Mn(CO)_2PMe_3$ (72% yield). Interestingly, reactivation with $NOPF_6$ produced a *single* diastereomer of **1** (73% yield) as judged from ^{1}H, ^{13}C, and ^{31}P NMR. This suggests that nucleophilic addition to this **1** complex will produce two enantiomerically pure diastereomers, possibly with greater than the ca. 2:1 selectivity found in the cases discussed above since the nucleophile attacks in close proximity to one of the chiral centers.

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(7) Crystal data for isomer A: space group *Cc* with a = 6.688 (1) Å, b = 29.218 (8) Å, c = 11.965 (2) Å, β = 96.99 (1)°, V = 2320.7 Å^3, Z = 4, D_{calc} = 1.35 g cm^{-3}; data collected at 22 °C with Mo Kα radiation, μ = 6.47 cm^{-1}, 2θ limits 5.0–45°, 280 variables refined with 1602 unique reflections $I > 1.0\sigma(I)$ to R = 0.034 (R_w = 0.034). Crystal data for isomer B: space group *Cc* with a = 9.906 (3) Å, b = 27.812 (6) Å, c = 8.704 (2) Å, β = 101.32 (2)°, V = 2351.5 Å^3, Z = 4, D_{calcd} 1.34 g cm^{-3}; data collected at 22 °C, μ = 6.38 cm^{-1}, 2θ limits 5.0–45°, 272 variables refined with 1516 unique reflections $I > 1.0\sigma(I)$ to R = 0.052 (R_w = 0.043). Both structures were solved by direct methods by using the SHELXTL 5.1 program. Absolute structures (Jones, P. G. *Acta Crystallogr.* **1984**, *A40*, 660) were tested by η refinement (Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734) with the following results: A, η = 0.91 (0.09); B, η = 0.91 (0.13). In each case this result verifies the consistency of the sense of the *a* and *c* axes with the structure and, hence, indicates the quality of the data.

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Acknowledgment. This work was supported by a grant from the National Science Foundation (No. CHE-8821588).

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for the diastereomers of **2** (R = Ph, R' = $CH(CO_2Me)_2$) (9 pages); observed and calculated structure factors for the diastereomers of **2** (R = Ph, R' = $CH(CO_2Me)_2$) (20 pages). Ordering information is given on any current masthead page.

Asymmetric Hydroxylation by a Chiral Iron Porphyrin

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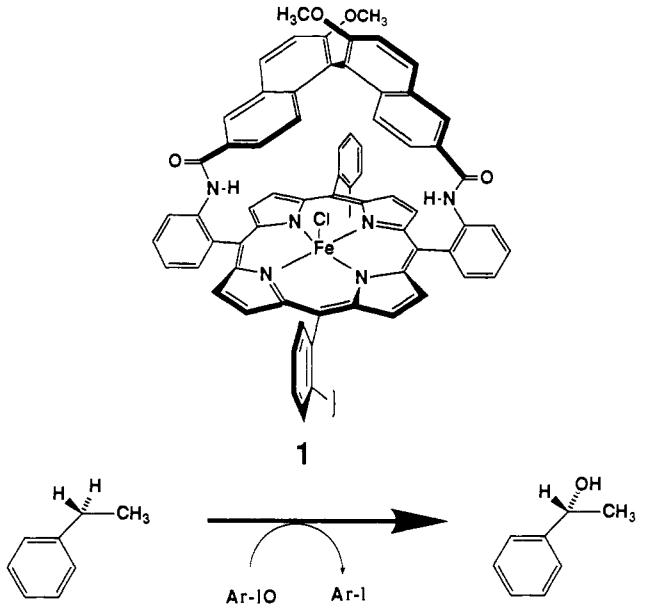
One of the most interesting features of the cytochrome P-450 family of enzymes is the ability to convert alkanes to alcohols, often with high regioselectivity and stereospecificity.[1-3] There is now abundant evidence that the hydroxylation process is stepwise and that C–H bond scission is an event stereochemically discrete from the subsequent formation of the new C–O bond of the product alcohol. Thus, the hydroxylation of norbornane by cytochrome $P\text{-}450_{LM2}$ was demonstrated in our laboratory to afford both the *exo*- and *endo*-norborneols and that either product could derive from initial removal of either the exo or endo hydrogen.[4a] Likewise, it has been shown that the selective exo-C-5 hydroxylation of camphor by $P\text{-}450_{CAM}$ occurs with a considerable degree of stereochemical indiscrimination for hydrogen removal,[5] that the allylic hydroxylation of olefins occurs with significant allylic scrambling,[4b] and that the benzylic hydroxylation of ethylbenzene is nonstereospecific.[6,7] By contrast, predominant retention[4] of configuration has been reported for the hydroxylation of isotopically chiral methyl groups.[8] The central question becomes whether hydroxylation with retention of configuration at carbon is a mechanistically enforced outcome or whether the enzyme can adequately control the stereochemical outcome of a stepwise, free-radical process.

Many of the essential features of oxygen transfer by cytochrome P-450 have been modeled with synthetic metalloporphyrin catalysts by using iodosylbenzene[9] or other oxygen donors[10-17] as oxidants.

Scheme I



In this paper we describe the stereochemical course of the hydroxylation of ethylbenzene with a chiral iron porphyrin catalyst. The results indicate that the degree of stereospecificity is related to the fit of the substrate into the catalyst and provide insight into how a stepwise free-radical reaction may proceed with apparent retention of configuration at carbon.

In a typical reaction, the hydroxylation of ethylbenzene was carried out under anaerobic conditions in dichloromethane at 0 °C by using the chiral binaphthyl iron porphyrin **1** (Scheme I) we have described elsewhere[18] as the catalyst. Reactions were initiated by the addition of iodosylbenzene (100 equiv based on **1**) to a dichloromethane solution of **1** (1.5 mg in 2 mL) and ethylbenzene (1000 equiv). The product alcohols were isolated by chromatography on silica and esterified with (*R*)-(−)-2-phenylpropionyl chloride. Yields, enantiomeric excesses, and alcohol:ketone ratios were determined by GC, and the deuterium content of each diastereomeric ester was measured by GC–MS (Table I).

Ethylbenzene afforded a 40% yield of 1-phenylethanol with a 71:29 ratio of the *R* and *S* enantiomers, respectively (41% ee). Some acetophenone was also detected but was shown not to be due to further oxidation of the alcohol product. Samples of optically pure (*R*)- and (*S*)-(1-deuterioethyl)benzene were prepared by the method of Mosher.[19] (*R*)-(1-deuterioethyl)benzene provided the *S* alcohol in excess (16% ee) while (*S*)-(1-deuterioethyl)benzene afforded the *R* alcohol but with a much higher, isotopically enhanced stereoselectivity (77% ee). Multiple determinations of at least three oxidations indicated that the enantiomeric excesses were reproducible and accurate to ±2%.

The deuterium content of the enantiomeric alcohols derived from (*R*)- and (*S*)-(1-deuterioethyl)benzene was determined from the mass spectra of the diastereomeric 1-phenylpropionyl esters. The base-line separation of the GC peaks and the uncomplicated parent region for these compounds (no m-1 peak) allowed an unambiguous determination. Tabulations of the mass spectra of the diastereomeric esters and the deuterium content of each diastereomer derived from the data are shown in Table I. The primary data provide a measure of the stereoselectivity of these hydroxylations and the proton/deuterium inventory for each stereoisomeric product. Two things are immediately apparent: (1) the major hydroxylation product was determined by the stereochemistry of the deuteration and (2) *the extent of deuteration of the major product was indistinguishable from 100% whereas the minor product in each case contained nearly equal*

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