complexes $[Fe^{II}(TLA)(BF)](ClO_4)$ (**1**) and $[Fe^{II}(TPA)(BF)](ClO_4)$ (**2**), respectively.[14] The X-ray structure of **1**[15] shows that the complex is a distorted octahedron featuring a tetradentate TLA and a bidentate BF ligand (Figure 1). The BF ligand is coordinated to the iron center via the carboxylate oxygen (O1) at 2.001 (4) Å and the carbonyl oxygen (O2) at 2.212 (4) Å; the 0.21-Å bond length difference is probably due to the greater basicity of the carboxylate, and the phenyl group is nearly coplanar with the α-keto acid moiety. Steric interactions between the C27 α-methyl group and the corresponding C17 and C37 groups on the TLA ligand result in Fe–N11 and Fe–N31 distances which are ca. 0.1 Å longer than the Fe–N1 and Fe–N21 distances. Furthermore, the BF ligand is pushed away from the pyridine in the same plane, giving rise to an O1–Fe–N21 angle of 118.7 (2)°.

The UV-visible spectrum of **1** exhibits features at 370 (ε 2400 M^{-1} cm^{-1}), 544 (ε 690 M^{-1} cm^{-1}), and 590 nm (sh, ε 600 M^{-1} cm^{-1}) in CH_3CN, which gives **1** its unusual purple-blue color. Its ^1H NMR spectrum (Figure 2A) shows large isotropic shifts for the BF protons due to delocalization of unpaired spin density through the coordinated carbonyl. In contrast, the analogous TPA complex **2** is yellow in color (λ_{max} = 385 nm, ε 2400 M^{-1} cm^{-1}), and the BF protons are in the diamagnetic region (8–9 ppm, Figure 2B). The loss of color and the small BF paramagnetic shifts suggest that the BF carbonyl oxygen in **2** is not coordinated to the iron center.

Both **1** and **2** react with O_2 in CH_3CN under ambient conditions according to

$$[Fe^{II}L(C_6H_5COCOO)]^+ + O_2 \rightarrow [Fe^{II}L(C_6H_5COO)]^+ + CO_2 + [O]$$

affording benzoic acid in nearly quantitative yield (98% for **1** and 96% for **2** by GC).[16] The reaction of O_2 with **1** proceeds over a 1-week period; ^1H NMR analysis of the reaction solution indicates the nearly quantitative formation of $[Fe^{II}(TLA)(OBz)]^+$ (**3**), whose properties are corroborated by independent synthesis.[17] When the reaction is carried out in the presence of 10 equiv of 2,4-di-*tert*-butylphenol, 0.75 mol of the corresponding biphenol is formed per mole of ferrous complex (by NMR) without altering the yield of the product complex. We can thus trap most of the oxidizing equivalents implied by [O] in the reaction scheme above. The reaction of O_2 with **2**, on the other hand, requires 2 days and affords near-stoichiometric amounts of $[Fe^{III}_2O(OBz)_2(TPA)_2]^{2+}$ (**4**),[18] which results from the further oxidation of the resultant $[Fe^{II}(TPA)(OBz)]^+$ complex.[19]

$^{18}O_2$ labeling studies of the reaction of **1** and **2** with O_2 show the incorporation of one atom of ^{18}O into the benzoate product, as has been observed for corresponding enzymatic reactions,[6b,20] but only one-half of the product molecules are labeled. This incomplete labeling result is likely due to the loss of label from solvent exchange, as a parallel $^{16}O_2$ reaction with **2** carried out in the presence of trace amounts of $H_2{}^{18}O$ shows the incorporation of as many as five atoms of ^{18}O into complex **4**. Further mechanistic investigations are in progress.

In summary, **1** and **2** represent the first complexes to model putative Fe(II)–cofactor interactions for α-keto acid-dependent enzymes. Both complexes undergo nearly quantitative oxidative decarboxylation upon exposure to dioxygen and thus serve as a useful starting point for understanding the bioinorganic chemistry of these fascinating enzymes.

Acknowledgment. We are grateful to Professor J. D. Britton for his expertise in the X-ray diffraction experiments and Dr. Yanhong Dong for the synthesis of TLA. This work has been supported by the National Institutes of Health (GM-33162).

Supplementary Material Available: Tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles for $[Fe^{II}(TLA)(BF)](ClO_4)$ (14 pages). Ordering information is given on any current masthead page.

(14) Complexes **1** and **2** were obtained by combining equimolar amounts (0.5 mmol) of TLA or TPA, benzoylformic acid, Et_3N, and $Fe(ClO_4)_2{\cdot}6H_2O$ in 10 mL of CH_3OH under argon. The solid products obtained by cooling and subsequent filtration corresponded to yields of 78% and 85%, respectively. Elemental analysis for $[Fe^{II}(TLA)(BF)](ClO_4)$ (**1**). Anal. Calcd for $C_{29}H_{29}ClFeN_4O_7$: C, 54.69; H, 4.59; N, 8.80; Cl, 5.57. Found: C, 54.44; H, 4.76; N, 8.65; Cl, 5.39. Elemental analysis for $[Fe^{II}(TPA)(BF)](ClO_4)$ (**2**). Anal. Calcd for $C_{26}H_{23}ClFeN_4O_7$: C, 52.50; H, 3.90; N, 9.42. Found: C, 52.54; H, 4.17; N, 9.18. **Caution**: Perchlorate salts are potentially explosive and should be handled with care.

(15) Diffraction quality crystals of $[Fe(TLA)(BF)](ClO_4)$ were obtained from acetone/diethyl ether. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with a = 8.931 (6) Å, b = 13.366 (7) Å, c = 15.160 (7) Å, α = 75.92 (4)°, β = 81.06 (5)°, γ = 70.78 (5)°, V = 1652 (4) Å^3, and Z = 2. With the use of 6481 unique observed reflections, for which $I_{(obsd)} > 3.0\sigma(I)$, collected at 172 K with Mo Kα (λ = 0.71069 Å) radiation out to $2\theta_{max}$ = 51.9° on an Enraf-Nonius CAD-4 X-ray diffractometer, the structure was solved by direct methods and refined to R = 0.071 and R_w = 0.082.

(16) Oxygenation reactions were run on a 0.1-mmol scale in 20 mL of CH_3CN under ambient conditions. The amount of benzoic acid was quantified by GC following the addition of 3 N HCl to the reaction solution and ether extraction.

(17) FAB-MS: m/z 509.3, corresponding to $[Fe^{II}(TLA)(OBz)]^+$. **3** exhibits NMR features at 43 (OBz *o*-H), 23 (OBz *m*-H), 14 (OBz *p*-H), 51 (TLA β-H), 12 (TLA γ-H), and −50 ppm (TLA α-CH_3), as found for the authentic complex $[Fe^{II}(TLA)(OBz)](ClO_4)$ (Zang, Y., unpublished data). The conversion of **1** to **3** was monitored by NMR by integration of the α-methyl protons of TLA of the two complexes.

(18) FAB-MS: m/z 1049, corresponding to $[4{\cdot}(ClO_4)]^+$. **4** exhibits NMR features at 33 (broad, TPA α-H and/or CH_2), 16 (TPA β-H), 8 (TPA γ-H), and 8–9 ppm (OBz protons), which are similar to the features found for $[Fe^{III}_2O(TPA)_2(OAc)_2]^{2+}$.[19]

(19) We have shown that the corresponding $[Fe^{II}(TPA)(OAc)]_2^{2+}$ complex readily autoxidizes to yield $[Fe^{III}_2O(TPA)_2(OAc)_2]^{2+}$. Menage, S.; Zang, Y.; Hendrich, M. P.; Que, L., Jr. *J. Am. Chem. Soc.*, in press.

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Catalytic Asymmetric Dihydroxylation of Cis-Disubstituted Olefins

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Since the inception of the osmium-catalyzed asymmetric dihydroxylation (AD) in 1988,[1] substantial progress has been attained in the development of ligands that generate ever higher levels of enantioselectivity.[2] With the advent of the dihydroquinidine (DHQD) and dihydroquinine (DHQ) phthalazine ligands, $(DHQD)_2$-PHAL and $(DHQ)_2$-PHAL, enantiomeric excesses (ee's) of greater than 90% are realized with four of the six possible olefin substitution patterns, namely, the mono-, geminal-di-, trans-di-, and trisubstituted olefins (Chart I).[3]

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[‡] The Scripps Research Institute.

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0002-7863/92/1514-7568$03.00/0

Chart I

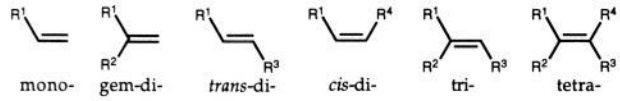
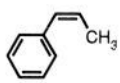
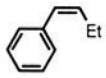
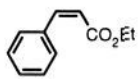
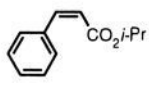
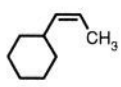


Table I. Enantiomeric Excesses (ee, %) of the Diols Resulting from Catalytic Asymmetric Dihydroxylation of Cis-Disubstituted Olefins with DHQD-IND[d]

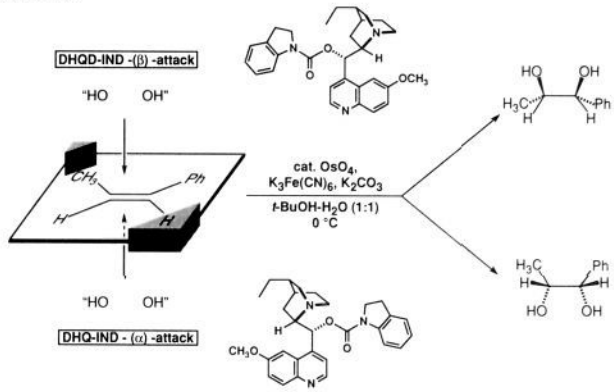
entry	olefin	ee at 0 °C	configuration
1		72	1*R*, 2*S* [a]
2		72	1*R*, 2*S* [a]
3 [c]		78	2*S*,3*R* [b]
4 [c]		80	2*S*,3*R* [b]
5		56	1*R*, 2*S* [a]
6 [c]		16	(1*R*, 2*S*)

[a] The absolute configuration of the diol was determined by comparison of optical rotations with literature values. [b] The absolute configuration of the diol was determined by comparison of optical rotations with that of an authentic sample (entries 3, 4).[8] [c] Methanesulfonamide (1 equiv) is necessary for satisfactory turnover rates. [d] Enantiomeric excesses were determined by GLC or ^{1}H NMR analysis of the derived bis-MTPA esters (see supplementary material for details of analyses).[6] All reactions were performed as described in ref 7. Diols were isolated in 66–90% yield.

However, even with the recent ligand improvements, the AD of cis-disubstituted olefins (with *cis*-β-methylstyrene as test substrate) has not exceeded 35% ee.[4] One limitation involves the "meso problem". When $R_1 = R_4$, AD of this symmetrical cis-disubstituted olefin leads to formation of the meso diol. As R_1 approaches R_4 in size, the vanishing prochiral asymmetry of the olefin renders enantiofacial selection increasingly more difficult. Enantioselectivity in the AD when $R_1 \neq R_4$ can be rationalized as size recognition of the olefinic substituents.

Investigations in the carbamate ligand family have now led to good ee results with the cis-disubstituted class of olefins. In contrast to the ester, ether, or phthalazine ligands,[4] the carbamate ligand (9-*O*-indolinylcarbamoyl)dihydroquinidine (DHQD-IND) (Scheme I) gives up to 80% ee in the AD of cis-disubstituted olefins (Table I). This 40–50% improvement in enantiomeric excess brings asymmetric induction to levels comparable to those initially reported for the catalytic AD of trans-disubstituted olefins.[1] Additionally, the predominant enantiomer obtained is of an absolute configuration consistent with the mnemonic device developed for predicting stereoselectivity in the AD (Scheme I).[2a,3]

Scheme I



Both aliphatic and aromatic olefins were screened, and from the table it is seen that higher ee's are obtained for olefins bearing aromatic groups (entries 1–4) than for those with solely aliphatic functionalities (entry 5). Dihydronaphthalene, (entry 6) a fused styrene-like olefin, is constrained to lie in a planar conformation. The low ee obtained for this substrate suggests that it may be important to have the olefinic bond out of the plane and out of conjugation with the aromatic ring.[5]

Further studies on the AD of cis-disubstituted olefins are necessary before firm conclusions can be drawn regarding enantioselectivity trends. With the discovery of DHQD-IND, the enhanced asymmetric induction observed for cis-disubstituted olefins expands the scope of the AD to include five of the six olefin classes (Chart I).[9]

Acknowledgment. Financial support was provided by a grant (GM28384-12) from the National Institutes of Health. We thank Professor Eric N. Jacobsen for providing synthetic procedures and samples of *cis*-ethyl cinnamate.

Note Added in Proof. The AD with the dihydroquinine ligand DHQ-IND has been shown to deliver lower ee's: entry 1, 59% ee; 4, 72% ee; 5, 44% ee. The lower ee's obtained with DHQ-IND arise from the diastereomeric relationship of DHQD and DHQ; enantiomeric ligands would deliver identical ee's for diols of opposite absolute configurations. The ee decreases for changing the ligand from DHQD to DHQ are the largest we have observed to date.

For a recent report on the stoichiometric asymmetric dihydroxylation of cis-disubstituted olefins, see: Fuji, K.; Tanaka,

(4) (a) Wang, L.; Sharpless, K. B. Presented at the 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 1992, ORGN 88. (b) For other AD results for cis-disubstituted olefins, see: Jeong, K.-S.; Sjö, P.; Sharpless, K. B. *Tetrahedron Lett.* **1992**, *33*(*27*), 3833–3836.

(5) For styrene conformation studies, see: Tsuzuki, S.; Tanabe, K.; Nagawa, Y.; Nakanishi, H. *J. Mol. Struct.* **1989**, *212*, 45–52. Zaitsev, B. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, *9*, 1968–1972. Talati, A. M.; Shah, B. V. *Indian J. Chem.* **1973**, *11* (12), 1328–9.

(6) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(7) Procedure for catalytic AD with DHQD-IND: Example with *cis*-β-methylstyrene. To a well-stirred solution of DHQD-IND (10 mg, 0.02 mmol), 1 g of $K_3Fe(CN)_6$ (3 mmol), and 420 mg of K_2CO_3 (3 mmol) in 10 mL of *t*-BuOH/H_2O (1:1 v/v) is added 4 μL of OsO_4 (0.47 M in toluene, 0.002 mmol) at room temperature. [At this point, methanesulfonamide (95 mg, 1 mmol) is added for cinnamate substrates (entries 3, 4) to ensure reasonable turnover rates at 0 °C. Guidelines for sulfonamide use are provided in ref 3.] The clear yellow solution is cooled to 0 °C to give a viscous orange mixture. At 0 °C, *cis*-β-methylstyrene (117 mg, 1 mmol) is added, and the reaction progress is monitored by TLC. Upon reaction completion (17–22 h), the phases are separated, and the aqueous phase is extracted with methylene chloride (3 × 15 mL). (When methanesulfonamide is used, the combined organic layers are washed with 2 N KOH.) Sodium metabisulfite (1.5 g, 7.9 mmol) is added to the combined organic phases and stirred with $MgSO_4$ for 1 h. The organic phase is filtered and concentrated in vacuo to afford crude diol. Purification by column chromatography (silica, 3:1 CH_2Cl_2/Et_2O) yields a clear colorless oil, which solidifies to a white crystalline solid (132.7 mg, 88%). Determination of enantiomeric excess is performed on bis-MTPA derivatives of the purified diol.[6]

(8) Entries 3 and 4: Authentic L-(−)-*erythro*-1-*C*-phenylglycerol resulted from $LiAlH_4$ reduction of the *cis*-alkylcinnamate diol. (See supplementary material for procedures and physical data.)

(9) The tetrasubstituted class is now beginning to show promise in the AD of enol ethers. Morikawa, K.; Hashiyama, T.; Sharpless, K. B., unpublished results.

K.; Miyamoto, H. *Tetrahedron Lett.* **1992**, *33*(*28*), 4021-4024.

Supplementary Material Available: Experimental procedures and characterization data for new ligands, details for determination of enantiomeric excesses, and absolute configurations of the diols (5 pages). Ordering information is given on any current masthead page.

Selective Asymmetric Dihydroxylation of Dienes

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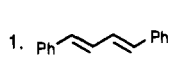
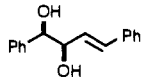
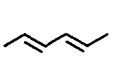
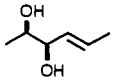
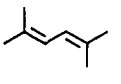
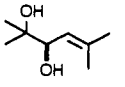
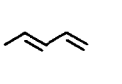
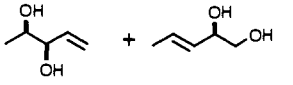
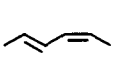
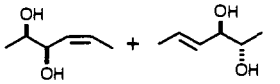
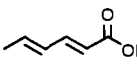
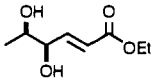
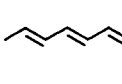
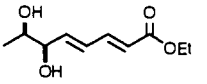
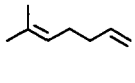
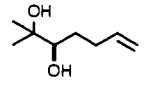
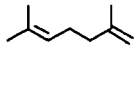
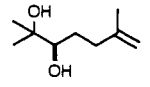
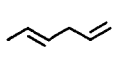
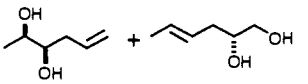
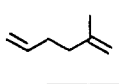
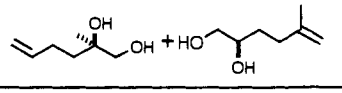
With recent advances, the catalytic asymmetric dihydroxylation (AD) of olefins has reached unprecedented levels of enantioselectivity and simplicity.[1] As part of our continuing effort to broaden the scope of the AD reaction for synthetic applications, the selective mono-dihydroxylation of dienes is a desirable goal. Success in this area would deliver valuable synthetic intermediates, ene diols, with high enantiomeric purity and also address the largely unexplored issues of the regioselectivity of the AD.[2,3]

We selected a symmetrical conjugated diene, 1,4-diphenylbutadiene, as the test substrate, anticipating that the mono-dihydroxylation product ene diol would be sufficiently deactivated by the electron-withdrawing adjacent hydroxyl groups. Using the usual 3 molar equiv of $K_3Fe(CN)_6$ (the normal amount used in AD-mix[1]) as the stoichiometric oxidant and $(DHQD)_2$-PHAL [1,4-bis(9-*O*-dihydroquinidinyl)phthalazine][4] as the ligand, the corresponding ene diol was obtained in 84% yield and very good ee (99%), in excellent agreement with our proposal. Encouraged by this initial result, the AD of a number of conjugated and nonconjugated dienes with different substitution patterns was examined. The results are summarized in Table I.

All of the conjugated dienes gave uniformly high yields of the expected ene diols except *trans*-piperylene (entry 4), which afforded the corresponding diols in moderate yields due to the volatility and water solubility of the products. The tetrol products, if formed, represented only trace amounts in these reaction mixtures. For unsymmetrical conjugated dienes, osmylation occurred preferentially at the more electron-rich double bond. For example, AD of piperylene (entry 4) gave a 3:1 mixture of the ene diols with the diol from the 1,2-disubstituted olefin found in excess. The preference for a trans over a cis olefin is significant and is exemplified by the AD of *trans,cis*-hexadiene, which gives predominately the ene diol corresponding to the dihydroxylation of the trans double bond (entry 5).[5] Similarly, AD of ethyl sorbate (entry 6) gave the 4,5-diol ester as the only isolated product; it is interesting to note that the same product was obtained only in poor yield using the NMO system.[6] Entry 7 nicely illustrates that mono-dihydroxylation of a conjugated trienoic ester can also be achieved with a regioselectivity similar to that for the related dienoic ester.

Table I[a]

olefin	product(s)[b]	% yield, (% ee)[c]
1. 		84(≥99)[d]
2. 		78(93)
3. 		94(93)[d]
4. 		48(90,72) 3:1
5. 		88 (98) 15:1
6. 		78 (92)
7. 		93 (95)
8. 		73(98)
9. 		70(98)
10. 		56(94) 13:1
11. 		42(74) 5:1

[a] The AD was run as described in ref 1 with 0.2-1.0 mol % of OsO_4. See the supplementary material for experimental details. [b] All of the absolute configurations, except that of 2-methyl-5-hexene-1,2-diol (entry 11), are tentatively assigned by using the mnemonic device described in ref 1. [c] The % ee's were determined by GLC analysis of the MTPA esters or by direct injection of the diol on a CDX-B β-cyclodextrin GLC column or a Chiralcel OD HPLC column. The indicated % ee is for the major product, except for entry 4 where both were determined. See the supplementary material for experimental details. [d] This reaction was run at room temperature.

The selectivity observed with nonconjugated dienes is substantial. Entries 8 and 9 reveal the strong preference for trisubstituted over terminal olefins in the AD. No products resulting from oxidation of the terminal olefins were observed in these reactions. The selectivity dropped when less substituted olefins were placed in competition with a terminal olefin: (*E*)-1,4-hexadiene gave a 13:1 preference for the 1,2-disubstituted diol (entry 10), and 2-methyl-1,5-hexadiene, which contains a 1,1-disubstituted olefin, gave only a 5:1 ratio in competition with a monosubstituted olefin (entry 11).[7] This drop in selectivity is always accompanied by a drop in the yield of the ene diol due to tetrol formation (cf. entries 8,9 and 10,11).

The selective ene diol formation from conjugated dienes observed in this study is in sharp contrast to the earlier results reported from our laboratories which showed that dihydroxylation of conjugated dienes employing catalytic amounts of OsO_4 and 1 equiv of NMO gave mainly tetrols and unreacted starting

(1) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768.
(2) Crispino, G. A.; Sharpless, K. B. *Tetrahedron Lett.* **1992**, *33*, 4273.
(3) Some earlier kinetic studies of the stoichiometric osmylation of olefins: (a) Sharpless, K. B.; Williams, D. R. *Tetrahedron Lett.* **1975**, 3045. (b) Toyoshima, K.; Okuyama, T.; Fueno, T. *J. Org. Chem.* **1980**, *45*, 1600.
(4) The structures of our latest ligands, $(DHQD)_2$-PHAL and $(DHQ)_2$-PHAL, are found in ref 1. These ligands are available from Aldrich Chemical Company, Inc.
(5) However, in a competition reaction between *trans*- and *cis*-5-decene, a 2.2:1 ratio of threo to erythro diol was obtained at 5% completion. See also ref 3.
(6) Hirama, M.; Shigemoto, T.; Ito, S. *Tetrahedron Lett.* **1985**, *26*, 4137.
(7) The use of chiral ligand has been shown to have little effect on the regioselectivity in this study.

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