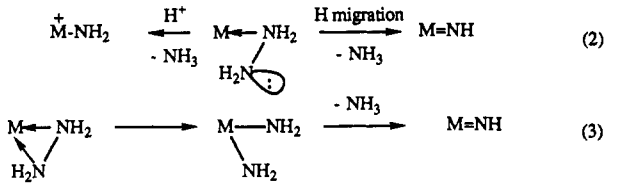

(2)

(3)

is rare,[14] although there are many examples of formation of dinitrogen and ammonia complexes from hydrazine, including $[Ru(NH_3)_5(N_2)]^{2+}$, the first dinitrogen complex.[15] The first four steps that are most plausible on the basis of the observed chemistry are shown in eq 4 (M = MCp^*Me_3). (In brackets are compounds that have not been observed and are believed to be unstable.) Steps that complete the cycle shown in eq 5 are based on the demon-

$$M(N_2H_4)^+ \xrightarrow{e} [M(N_2H_4)] \xrightarrow{-NH_3} M{=}NH \xrightarrow{H^+} [M(NH_2)^+] \xrightarrow{e} M(NH_2) \quad (4)$$

$$M(NH_2) \xrightarrow[-NH_3]{N_2H_4} [M(NHNH_2)] \xrightarrow{H^+} M(N_2H_4)^+ \quad (5)$$

strated reaction between $WCp^*Me_3(NH_2)$ and hydrazine to give $WCp^*Me_3(NNH_2)$ and $WCp^*Me_3(NH)$ as well as ammonia via disproportionation of $WCp^*Me_3(NHNH_2)$ in the absence of protons.[16] (The nature of the disproportionation in the absence of protons is still under investigation.) Support for the last step in eq 5 is protonation of $WCp^*Me_4(NHNH_2)$ to give $[WCp^*Me_4(NH_2NH_2)]^+$.[7] Note that the N-N bond in $WCp^*Me_3(NHNH_2)$ (d^1) in the absence of protons most likely is cleaved in a *disproportionation* reaction, while in $WCp^*Me_3(NH_2NH_2)$ (d^2) it most likely is cleaved *intramolecularly*. Note also that $WCp^*Me_4(NHNH_2)$, $[WCp^*Me_3(NHNH_2)]^+$, and $[WCp^*Me_4(NH_2NH_2)]^+$, all formally d^0 complexes, are relatively stable toward N-N cleavage.

We believe that these findings are relevant to the reduction of dinitrogen. So far we known that $WCp^*Me_3(NNH_2)$, a likely intermediate in a dinitrogen reduction system based on complexes having the MCp^*Me_3 core,[17] can be reduced to give ammonia (Table I) and is a catalyst for reducing hydrazine (Table II). However, reduction of $MCp^*Me_3(OTf)$ complexes under dinitrogen gives little ammonia (Table I). Side reactions (most likely protonations) probably destroy the metal site before dinitrogen can bind and $WCp^*Me_3(NNH_2)$ can form.

We believe that the chemistry of dinitrogen and N_2H_x and NH_y ligands bound to a single Mo or W in a high oxidation state is extensive and will offer further insight into the mechanism of dinitrogen reduction, especially if the metal site can be stabilized toward protons. Efforts in this direction are under way.

Acknowledgment. R.R.S. thanks the National Institutes of Health for support through Grant GM 31978, and M.G.V. and T.E.G. thank the National Science Foundation for predoctoral fellowships.

Supplementary Material Available: Synthetic procedures, NMR and EPR data, and elemental analyses for **1a**, **1b**, and $WCp^*Me_3(NH)$, reduction procedures (stoichiometric and catalytic), and conductivity measurements (4 pages). Ordering information is given on any current masthead page.

(14) (a) Hozumi, Y.; Imasaka, Y.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1983**, 897. (b) Schrauzer, G. N.; Robinson, P. R.; Moorehead, E. L.; Vickrey, T. M. *J. Am. Chem. Soc.* **1976**, *98*, 2815.

(15) Allen, A. D.; Senoff, C. V. *J. Chem. Soc., Chem. Commun.* **1965**, 621.

(16) (a) Similar results are observed in the reaction between $WCp^*Me_3(OTf)$ and LiN_2H_3, the reduction of $WCp^*Me_3(NHNH_2)^+$ with Na/Hg, and the deprotonation of $WCp^*Me_3(NH_2NH_2)^+$. The role of disproportionation reactions in Chatt-type compounds and derivatives has been addressed recently.[16b] (b) Kaul, B. B.; Hayes, R. K.; George, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 2002.

(17) $WCp^*Me_3(OTf)$ is reduced under dinitrogen (no added H^+) to give $Cp^*Me_3W{=}NN{=}WCp^*Me_3$ in >90% yield.[5] The key proposed reaction is electrophilic attack on intermediate $WCp^*Me_3(\eta^1\text{-}N_2)$ by $WCp^*Me_3(OTf)$.

(18) Note added in proof: The proposed structure of **16** (eq 1) has now been proven in an X-ray study.

Bis(oxazolines) as Chiral Ligands in Metal-Catalyzed Asymmetric Reactions. Catalytic, Asymmetric Cyclopropanation of Olefins

David A. Evans,* Keith A. Woerpel, Mira M. Hinman, and Margaret M. Faul

Department of Chemistry, Harvard University Cambridge, Massachusetts 02138

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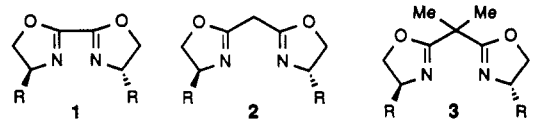
The design of catalytic, asymmetric reactions that proceed with high enantioselectivity is an important goal in chemical synthesis.[1] As a consequence of our continuing interest in asymmetric synthesis, we have been evaluating the potential utility of chiral 4,4′-disubstituted bis(oxazolines) such as **1**-**3** as bidentate ligands for several transition-metal-catalyzed reactions. In order to examine the stereodifferentiating ability of these ligands, and because of the importance of cyclopropanes of defined absolute stereochemistry,[2] we have studied the catalyzed asymmetric cyclopropanation of olefins.[3]



a, R = $CHMe_2$; **b**, R = CMe_3

Recently, chiral oxazoline ligands have been employed in metal-catalyzed asymmetric reactions.[4] Such ligands are attractive as a consequence of their topography and ease of synthesis from readily available chiral amino alcohols. We have constructed a number of such ligands, including the illustrated examples, **1**-**3**. One of these, the neutral ligand **3**, resembles the charged semicorrin ligand recently reported by Pfaltz, who has demonstrated that derived copper(I) complexes deliver high levels of enantioselection in the cyclopropanation of monosubstituted olefins by menthyl diazoacetate esters.[5] The purpose of this communication is to report a Cu(I) complex derived from ligand **3b** and copper(I) triflate which is an attractive catalyst for the cyclopropanation of mono- and 1,1-disubstituted olefins with achiral diazo esters at ambient temperatures. Asymmetric induction in excess of 99% and 1000-fold catalyst turnover are appealing attributes of these processes.

Initially, a search was made for a copper complex to catalyze the cyclopropanation of styrene with ethyl diazoacetate (eq 1). Complexes of chiral bis(oxazolines)[6,7] **1**-**3** with copper(I) triflate[8] were found to be highly effective catalysts for the reaction, which proceeds rapidly at 25 °C. The products were isolated as trans/cis mixtures of the cyclopropyl esters **5** and **6** whose absolute stereochemistry is as shown.[9] Copper(II) triflate complexes do not

(1) Recent reviews: (a) Brunner, H. *Synthesis* **1988**, 645-654. (b) Blystone, S. L. *Chem. Rev.* **1989**, *89*, 1663-1679 and references cited therein.

(2) Recent reviews: (a) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165-198. (b) Salaün, J. *Chem. Rev.* **1989**, *89*, 1247-1270.

(3) Pfaltz, A. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer: Berlin, 1989; Vol. 5, pp 199-248.

(4) For previous uses of oxazoline-derived ligands, see: (a) Brunner, H.; Obermann, U. *Chem. Ber.* **1989**, *122*, 499-507. (b) Brunner, H.; Obermann, U.; Wimmer, P. *Organometallics* **1989**, *8*, 821-826. (c) Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846-848. (d) Balavoine, G.; Clinet, J.; Lellouche, I. *Tetrahedron Lett.* **1989**, *30*, 5141-5144.

(5) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553-1565. With chiral diazoacetate esters, Pfaltz has obtained an 82:18 trans/cis mixture in up to 97% ee for trans, 95% ee for cis.

(6) For a review of C_2-symmetric ligands, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581-1590.

(7) The syntheses of ligands **1**-**3** are contained in the supplementary material.

(8) Solomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300-3310.

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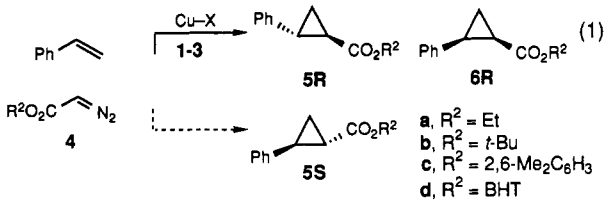
Table I. Asymmetric Cyclopropanation of Styrene



(1)

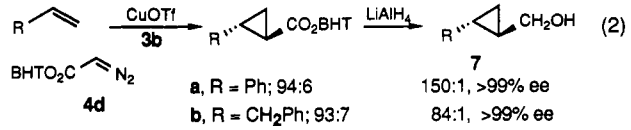
ligand[a]	diazo ester 4: R^2	ratio[b] 5:6	% ee[c] 5R	% ee 6R	% yield[d] 5 + 6
1a	Et	66:34	3	8	
2a[e]	Et	64:36	64	48	
2b[f]	Et	77:23	98	93	
3a[g]	Et	69:31	49	45	
3b[f]	Et	73:27	99	97	77
3b	*t*-Bu	81:19	96	93	75
3b	2,6-$Me_2C_6H_3$	86:14	97	96	68
3b	BHT	94:6	99		85

[a] One mole percent ligand employed; unless otherwise noted, all reactions were carried out at 25 °C in chloroform. [b] Ratios determined by capillary GLC. [c] Determined by conversion to the 1-phenylethylamide. [d] Isolated yields of purified products; these experiments were performed by using 5 equiv of styrene. [e] Reaction performed in dichloromethane. [f] The enantiomeric ligand was used; the enantiomeric products **5S** and **6S** predominated. [g] Reaction was performed at 0 °C.

catalyze the reaction unless they are either heated to 65 °C in the presence of ethyl diazoacetate or pretreated with phenylhydrazine. Other Cu(I) and Cu(II) salts (for example, halide, cyanide, acetate, and perchlorate) show little or no catalytic activity, and the observed enantioselectivity is markedly inferior to that obtained for the triflate–ligand complexes.

The effect of ligand structure on reaction enantioselectivity was evaluated with the ligand–CuOTf complexes formed in situ.[10] As can be seen from the data in Table I, the valine-derived ligands **2a** and **3a** are superior to ligand **1a**, suggesting that six- rather than five-membered chelates are preferred for effective catalyst performance. Replacement of the isopropyl group in ligand **2** with a *tert*-butyl group further improves the enantioselectivity to 98% for the trans cyclopropanation process and 93% ee for the cis diastereomer. These data compare favorably to the optimal results reported to date for this reaction (85% ee in trans manifold; 68% ee in cis manifold).[5] The neutral ligand **3b** [mp 87.8–88.6 °C; $[\alpha]_{365}$ −394° (*c* 0.97, CH_2Cl_2); for *ent*-**3b**, $[\alpha]_{365}$ +384° (*c* 1.22, CH_2Cl_2)], equipped with *tert*-butyl substituents and geminal methyl groups to prevent enolization, has proved to be the optimal ligand for this reaction. In fact, ethyl diazoacetate cyclopropanation of styrene at lower temperatures (0 °C) with 1 mol % of **3b** affords the trans and cis cyclopropyl esters (**5**:**6** = 74:26) in >99% ee for both isomers.

The last four entries in Table I document the influence of diazo ester structure on cis–trans diastereoselectivity. Not unexpectedly, sterically demanding diazoacetates, such as *tert*-butyl and 2,6-dimethylphenyl, display increased diastereoselectivity without greatly affecting the enantioselection, which held at 96–97% ee. Finally, in the case of the diazoacetic acid ester derived from BHT (2,6-di-*tert*-butyl-4-methylphenol),[11] a 94:6 trans/cis mixture was obtained. Although hydrolysis of this ester was precluded,[11] reductive removal of the hindered phenol with $LiAlH_4$ provided the carbinol **7a**, $[\alpha]_D$ −92° (*c* 1.23, C_2H_5OH),[12] in 76% yield (>99% ee) with a significantly enhanced diastereomer ratio (trans:cis = 150:1), presumably due to slower reduction of the cis ester contaminant.[11] This highly selective transformation was also observed for allylbenzene (trans:cis = 84.1, >99% ee) a substrate that also shows no tendency for competing allylic insertion (eq 2).

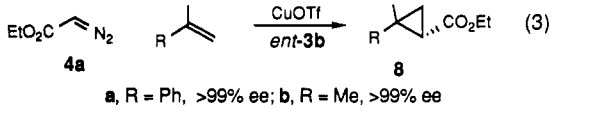


(2)

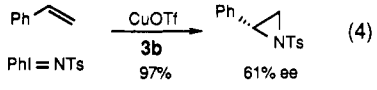
These high levels of asymmetric induction are not limited to monosubstituted olefins. The cyclopropanation of 1,1-diphenylethylene with *ent*-**3b**/CuOTf (eq 3) affords the *S* enantiomer **8a** in >99% ee [70% yield, $[\alpha]_D$ +212° (*c* 0.285, $CHCl_3$) for the derived acid].[13] The catalyst can also be used in lower concentrations and on a large scale, as demonstrated by the cyclopropanation of isobutylene ($CHCl_3$, 0 °C) using 0.1 mol % catalyst, which affords the *S* enantiomer **8b** (>99% ee), in 91% isolated yield on a 35-g scale [the derived acid has a rotation of $[\alpha]_D$ +148° (*c* 1.05, $CHCl_3$), confirming the assignment of absolute stereochemistry].[14,15]

Although the details of these reactions have still not been revealed,[16] we are working under the assumption that metallacyclobutane intermediates are involved. Given this postulate, a square-pyramidal copper center retaining the triflate ligand correlates with the observed sense of asymmetric induction while a tetrahedral copper center (without the triflate ligand) leads to the opposite sense of induction.

We are currently pursuing the use of these ligands in other catalytic processes. In a related experiment, we have performed the first catalytic, asymmetric aziridination of styrene in good yield and enantioselectivity using this catalyst (eq 4). Extension of the cyclopropanation to other olefins will be reported in due course.



(3)



(4)

Note Added in Proof. Since submission of this manuscript a related study has appeared.[17] In the Masamune study, the

(9) The ethyl esters produced with the Cu(I) catalyst derived from *ent*-**3b** were found to have the following optical rotations: **5aS**, $[\alpha]_D$ +296° (*c* 0.88, $CHCl_3$); **6aS**, $[\alpha]_D$ +18.6° (*c* 1.01, $CHCl_3$). The derived carboxylic acids obtained by hydrolysis were found to have the following optical rotations: trans (1*S*,2*S*), $[\alpha]_D$ +336° (*c* 0.78, $CHCl_3$); cis (1*S*,2*R*), $[\alpha]_D$ +27.9° (*c* 1.17, $CHCl_3$). The assignment of absolute stereochemistry was made by comparison with literature values: (a) Inoue, Y.; Sugita, T.; Walborsky, H. M. *Tetrahedron* **1964**, *20*, 1695–1699. (b) Aratani, T.; Nakanishi, Y.; Nozaki, H. *Tetrahedron* **1970**, *26*, 1675–1684. The details of the assignment of absolute configuration are contained in the supplementary material.

(10) The optical purity of the cyclopropanecarboxylate derivatives was determined by conversion to the derived amides of (*R*)-1-phenylethylamine and analysis by capillary GLC.

(11) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K.-L. *J. Am. Chem. Soc.* **1990**, *112*, 1906–1912.

(12) Sugita, T.; Inouye, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1075–1076. The rotation for a sample of **7a** of 51% ee was reported to be $[\alpha]_D$ −46.6° (*c* 2.64, C_2H_5OH).

(13) (a) Brunner, H.; Miehling, W. *Monatsh. Chem.* **1984**, *115*, 1237–1254. (b) Walborsky, H. M.; Pitt, C. G. *J. Am. Chem. Soc.* **1962**, *84*, 4831–4838. The assignment of absolute stereochemistry in this article was a correction of a previous paper (Walborsky, H. M.; Barash, L.; Young, A. E.; Impastato, F. J. *J. Am. Chem. Soc.* **1961**, *83*, 2517–2525). The absolute stereochemistry was also misassigned by Brunner and Miehling.

(14) Aratani, T. *Pure Appl. Chem.* **1985**, *57*, 1839–1844. When the Aratani catalyst was used, the product was isolated in 92% ee.

(15) Asymmetric cyclopropanation of isobutylene: To a suspension of CuOTf (56.1 mg, 0.223 mmol, 0.117 mol %) in 25 mL of anhydrous $CHCl_3$ was added a solution of *ent*-**3b** (67.0 mg, 0.228 mmol, 0.120 mol %) in 9 mL of $CHCl_3$. After 1 h, the resulting blue-green solution was filtered through glass wool under nitrogen into a cooled (0 °C) 500-mL three-necked round-bottom flask previously charged with isobutylene (approximately 110 g, 2.0 mol) and 20 mL of $CHCl_3$. A solution of ethyl diazoacetate (28.8 mL, 273 mmol) in 100 mL of $CHCl_3$ was added to the cooled (0 °C) solution of copper complex and isobutylene by dropping funnel over 5 h. The reaction mixture was allowed to warm to room temperature over 14 h, and isobutylene and $CHCl_3$ were removed by distillation (30 Torr). The product was distilled (30 Torr, bp 45–70 °C) as a clear oil, 35.3 g (91%).

(16) For reviews discussing proposed mechanisms of metal-catalyzed cyclopropanations, see: (a) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919–939. (b) Brookhart, M.; Studebaker, W. B. *Chem. Rev.* **1987**, *87*, 411–432.

conjugate base of **2b** ligated to Cu(I) was investigated as a catalyst in the cyclopropanation of diazoacetate esters with styrene in direct analogy with our parallel studies on the undeprotonated ligand **2b** summarized in Table I. In their study using ethyl diazoacetate, the authors have misassigned the absolute stereochemistry of their major *trans*-cyclopropane product. We have repeated the Masamune experiments using **2b** in both neutral and charged variants and have concluded that their major trans diastereomer **5** should be (1*R*,2*R*) rather than (1*S*,2*S*) as reported. Furthermore, we have shown that base-catalyzed epimerization of the minor cis diastereomer **6R** affords **6S**, the enantiomer of the major product diastereomer. This observation is also inconsistent with the Masamune stereochemical assignment.

Acknowledgment. Dr. Tarek Sammakia is gratefully acknowledged for helpful discussions. Support for this research was provided by the National Science Foundation and the National Institutes of Health. The NIH BRS Shared Instrumentation Grant Program 1 S10 RR01748-01A1 is acknowledged for providing NMR facilities.

Supplementary Material Available: Full details for the synthesis of catalyst **3b** and *ent*-**3b**, spectral and analytical data for ligands **1a**, **2a**,**b**, and **3a**, representative experimental procedures, and characterization of reaction products (8 pages). Ordering information is given on any current masthead page.

(17) Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, *31*, 6005-6008.

Designed Catalyst for Enantioselective Diels-Alder Addition from a C_2-Symmetric Chiral Bis(oxazoline)-Fe(III) Complex

E. J. Corey,* Nobuyuki Imai, and Hong-Yue Zhang

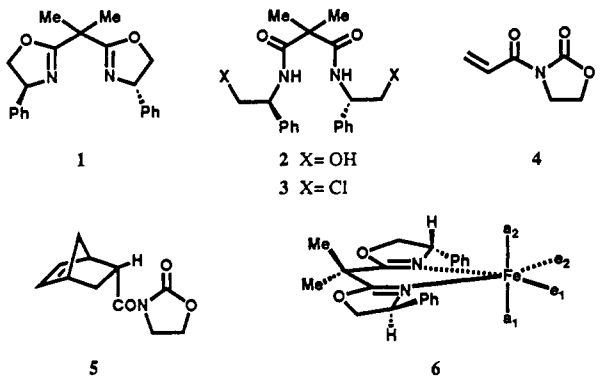
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received October 22, 1990

The Diels-Alder reaction is arguably the most powerful construction process in organic synthesis, and for this reason there has been much research on the development of enantioselective versions,[1] including most recently the use of chiral catalysts.[2] Recent experience with the use of a chiral 1,2-diamino-1,2-diphenylethane as a controller ligand for enantioselective catalytic reactions such as the Diels-Alder and olefin dioxyosmylation cycloadditions[2c,3] suggested the investigation of the rigid ligand 2,2-bis[2-[4(*S*)-phenyl-1,3-oxazolinyl]] propane (**1**) as a component of new catalytic systems.[4] The results of such a study for the Diels-Alder reaction are outlined herein.[5,6]

The chiral ligand **1** was readily prepared as follows. (*S*)-(+)-Phenylglycinol[7] (2 equiv) and Et_3N (2 equiv) in CH_2Cl_2 at 0 °C were treated with 1 equiv of dimethylmalonyl chloride[8] and allowed to react at 23 °C for 16 h to give **2** as a colorless solid (97%), further converted by reaction with excess $SOCl_2$ at reflux for 4 h to **3** [mp 164-166 °C, $[\alpha]^{23}_D$ +86.7° (*c* = 1.1, $CHCl_3$)]. Reaction of **3** with 5.5 equiv of 0.5 M NaOH in 1:1 methanol-water at reflux for 1 h followed by extractive isolation, filtration through silica gel, and distillation (193 °C at 0.03 Torr) afforded **1** as a viscous oil (78% overall from **2**): $[\alpha]^{23}_D$ -171.3° (*c* = 1.0, EtOH); MS, *m/e* 335.1761 (calcd 335.1759); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.64 (s, 6 H), 4.12 (t, 2 H, *J* = 8.4, 7.7 Hz), 4.63 (dd, 2 H, *J* = 10.1, 8.4 Hz), 5.19 (dd, 2 H, *J* = 10.1, 7.7 Hz), 7.18-7.24 (m, 6 H), 7.27-7.30 (m, 4 H).

For catalytic studies of the Diels-Alder reaction using **1** as a chiral controller ligand, Fe(III) halides were selected as the Lewis



acidic metal component, 3-acryloyl-1,3-oxazolidin-2-one (**4**)[9] as a bidentate dienophile, and cyclopentadiene as the prototypical diene component. It was envisaged that a structure in which both **1** and **4** are chelated to FeX_2^+ (X = halogen) with octahedral geometry about iron could be highly activated toward reaction with a 1,3-diene at low temperature. This expectation was confirmed experimentally. An equimolar mixture of anhydrous $FeCl_2$ and ligand **1** was stirred at 40 °C in dry CH_3CN for 1 h, cooled to 23 °C, and treated with 0.5 equiv of I_2. Removal of solvent in vacuo and addition of dry CH_2Cl_2 gave a dark brown solution of the catalytic complex, presumed to be **1**·$FeCl_2I$. The reaction of dienophile **4** and cyclopentadiene (3 equiv) in CH_2Cl_2 at -50 °C for 15 h using 10 mol % of catalyst proceeded with 90:10 enantioselectivity to give the endo adduct **5** (endo:exo ratio 97:3) in 85% isolated yield. The major product was shown to be the 2*R* enantiomer by measurement of rotation, $[\alpha]^{23}_D$ +126.7° (*c* = 1, $CHCl_3$), and comparison with an authentic sample.[2c,9] The 2*R*:2*S* ratio for the endo product was determined either directly or after conversion via the acid to iodo lactone by HPLC analysis of the enantiomeric mixture with a Daicel OD column using 5% *i*-PrOH in hexane, which cleanly separates the enantiomers.[10] The reaction of **4** with cyclopentadiene with the same catalyst, **1**·$FeCl_2I$, in 3:1 CH_2Cl_2-2-nitropropane at -50 °C also afforded **5** as major product with 93:7 enantioselectivity and 99:1 endo/exo selectivity. Similar results were obtained by using as catalyst **1**·$FeBr_3$ or **1**·FeI_3.[11] It was also found that the formation of adduct **5** from cyclopentadiene, **4**, and catalyst **1**·FeI_3 was accelerated by the inclusion of 1 equiv of I_2 in the reaction mixture; only 2 h sufficed for complete reaction at -50 °C to form **5** with 91:9 enantioselectivity and 96:4 endo/exo selectivity. Catalysis of the Diels-

(1) See: (a) *Nachr. Chem., Tech. Lab.* **1987**, *35*, 836-840. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876-889. (c) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer Verlag: Berlin, 1986; Vol. 4, pp 261-306.

(2) (a) Iwasawa, N.; Sugimori, J.; Kawase, Y.; Narasaka, K. *Chem. Lett.* **1989**, 1947-1950 and references cited. (b) Corey, E. J. *Pure Appl. Chem.* **1990**, *62*, 1209-1216. (c) Corey, E. J.; Imwinkelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493-5494. (d) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481-1483.

(3) Corey, E. J.; Jardine, P. D.-S.; Virgil, S.; Yuen, P.-W.; Connell, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 9243-9244.

(4) A series of 2,6-bis[2-[4(*S*)-alkyl-1,3-oxazolinyl]]pyridines has been described recently along with application to the catalytic enantioselective reduction of ketones. See: Nishiyama, H.; Sakaguchi, S.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846-848.

(5) Our colleague Prof. David Evans has kindly informed us of independent studies in his group on the application of Cu(I) complexes of *gem*-bis(oxazolines) to the catalytic enantioselective cyclopropanation of olefins; see: Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(6) Unfortunately, **1** was found neither to complex with OsO_4 nor to accelerate its reaction with olefins in solution.

(7) Prepared in 87% yield by reduction of (*S*)-phenylglycine (Aldrich Co.) with $LiAlH_4$ by the method of Dickman et al.: Dickman, D. A.; Meyers, A. I.; Smith, G. A.; Gawley, R. E. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, pp 530-533.

(8) Pierce, C. C.; Eliel, E. L.; Convery, R. J. *J. Org. Chem.* **1957**, *22*, 347-348.

(9) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109-1112.

(10) The Daicel OD column was obtained from Daicel, Inc., Fort Lee, NJ 07024.

(11) Catalyst **1**·FeI_3 was prepared from **1**, the appropriate amount of I_2, and either Fe or FeI_2 in CH_3CN or CH_2Cl_2.

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