to a transition state conformation that places the benzylic methine (rather than the CH_2OMOM group) in the imide plane so that the ylide approaches the *pro-R* imide carbonyl from the exo face.[14] Hydrogenation of **11** (1400 psi of H_2/Raney Ni (W2), EtOH, 65-70 °C) occurred from the exo face to afford nearly equal amounts of **12** and the overreduced byproduct **13** in 64% combined yield. Saponification of **12** (LiOH, THF-H_2O) produced the carboxylic acid **14** in quantitative yield. Alternatively, the sultam auxiliary could be removed from **11** (LiOH) and the resulting acid esterified (CH_2N_2, 63% overall) to provide **15**, which underwent clean hydrogenation to **16** in 67% yield. Select NOE experiments on both **15** and **16** served to confirm our structure assignments at this stage.

Following the protocol that Evans used in his cyanocycline A synthesis,[15] the hindered lactam of **14** could be partially reduced with Li/NH_3 and the resulting hemiaminal converted directly to the stable amino nitrile **17** (NaCN, H_2O, 60% overall). The racemic version of **17** was an intermediate in Fukuyama's synthesis of (±)-quinocarcin. Deprotection of **17** (NaI, TMSCl, MeCN, 72%) afforded a compound corresponding to **3**, which was then converted to (-)-quinocarcin (**1**) ($AgNO_3$, MeOH, H_2O, 89%). The ^1H and ^{13}C NMR data obtained for synthetic **1** matched those reported in the literature[1a] as well as those of an authentic sample. Comparison of the optical rotation of synthetic **1** ($[\alpha]^{25}_D$ -30° (*c* 0.2, H_2O)) with that of natural quinocarcin (lit.[1a] $[\alpha]^{25}_D$ -32° (*c* 0.50, H_2O)) confirms that the absolute configuration of the natural product is as shown.

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Supplementary Material Available: HPLC, ^1H NMR, ^{13}C NMR, and HRMS data for synthetic (-)-quinocarcin (**1**) (4 pages). Ordering information is given on any current masthead page.

(14) For a similar argument governing a highly stereoselective *intramolecular* cycloaddition, see: Garner, P.; Sunitha, K.; Ho, W. B.; Youngs, W. J.; Kennedy, V. O.; Djebli, A. *J. Org. Chem.* **1989**, *54*, 2041.

(15) (a) Evans, D. A.; Illig, C. R.; Saddler, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2478. (b) Illig, C. R. The Total Synthesis of (±)-Cyanocycline A and (+)-Cyanocycline A. Ph.D. Dissertation, Harvard University, 1987.

Chiral Lewis Acid Catalysis. Enantioselective Addition of Azide to Meso Epoxides

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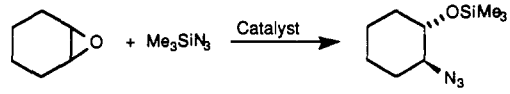
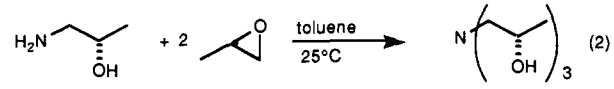
Chiral Lewis acid catalysis is emerging as a powerful tool for enantioselective synthesis.[1] One potentially useful class of reactions has heretofore proven elusive. The asymmetric cleavage of meso epoxides exemplified by eq 1 simultaneously establishes two contiguous stereogenic centers.[2] We now report a successful approach to this problem utilizing a novel type of chiral Lewis acid.



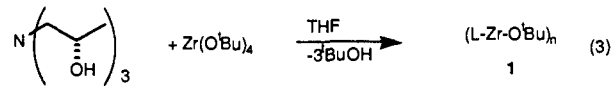
(1)

It has been reported[3,4] that eq 1 proceeds in modest enantiomeric excess in the presence of a stoichiometric amount of titanium isopropoxide/dimethyl tartrate. However, use of a catalytic amount of the titanium alkoxide resulted in essentially racemic product.[3] This suggested to us that the chiral ligand was being lost in the presence of excess azidotrimethylsilane and that this might be overcome by use of a tightly binding multidentate ligand. Trialkanolamines seemed an especially advantageous choice as ligand; they are easy to prepare, and the parent triethanolamine is known to form stable alkoxides with many early transition metals.[5] To test this notion, (+)-(*S*,*S*,*S*)-triisopropanolamine[6,7] (88% de) was prepared quantitatively by the reaction of commercially available (*S*)-(+)-1-amino-2-propanol (Aldrich, 91% ee) and (*S*)-(-)-propylene oxide (Aldrich, 98.6% ee) according to eq 2.[8]



(2)

Treatment of zirconium *tert*-butoxide in THF with this trialkanolamine (LH_3 in eq 3) followed by distillation of the solvent affords **1** as a white powder. As expected,[9] the spectroscopic



(3)

(1) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481-1483. Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 789. Review: Narasaka, K. *Synthesis* **1991**, 1-11.

Table I. Effect of Catalyst and Promoter on Enantioselectivity of Eq 1[a]

catalyst/ promoter	enantiomeric excess (%) and sign of rotation			
	none	HOAc[b]	HO_2CCF_3[c]	$Me_3SiO_2CCF_3$[d]
1	6 (+)	19 (-)	13 (+)	3 (+)
2	3 (+)	2 (+)	19 (-)	11 (-)
3	19 (-)	70 (-)	87 (-)	86 (-)

[a] All runs contain cyclohexene oxide (1.2 mmol), Me_3SiN_3 (1.2 mmol), and catalyst (0.1 mmol of Zr) in 1,2-dichlorobutane (3.0 mL), 18 h, 25 °C. [b] Additionally contains 1.0 μL of 50% aqueous acetic acid. [c] Additionally contains 1.0 μL of 50% aqueous trifluoroacetic acid. [d] Additionally contains 3.0 μL of trimethylsilyl trifluoroacetate.

(2) For other examples of "the meso trick", see: Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1320-1367.

(3) Emziane, M.; Sutowardoyo, K. I.; Sinou, D. *J. Organomet. Chem.* **1988**, *346*, C7-C10. See also: Hayashi, M.; Kohmura, K.; Oguni, N. *Synlett* **1991**, 774-776.

(4) Yamashita, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1213.

(5) (a) Bostwick, C. O. U.S. Patent 2,824,114, 1958; *Chem. Abstr.* **1958**, *52*, 7734. (b) Taube, R.; Knoth, P. *Z. Anorg. Allg. Chem.* **1990**, *581*, 89. (c) Astakhov, A. I.; Kas'yanenko, A. I. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1972**, *15*, 1620; *Chem. Abstr.* **1973**, *78*, 66407. (d) Mehrota, R. C.; Kapoor, P. N. *J. Indian Chem. Soc.* **1967**, *44*, 467. (e) Mehrota, R. C.; Kapoor, R. N. *Indian J. Chem.* **1967**, *5*, 5051. (f) Menge, W. M. B. P.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 4628-4631.

(6) (*S*,*S*,*S*)-Triisopropanolamine has been used previously as a chiral auxiliary for the asymmetric reduction of ketones with metal hydrides: Morrison, J. D.; Grandbois, E. R.; Weisman, G. R. In *Asymmetric Reactions and Processes in Chemistry*; Eliel, E. L., Otsuka, S., Eds.; ACS Symposium Series 185; American Chemical Society: Washington, DC, 1982.

(7) For diastereoisomeric mixtures of transition metal alkoxides prepared from racemic triisopropanolamine: Tandura, S. N.; Voronkov, M. G.; Kisin, A. V.; Shestakov, E. E.; Ovchinnikova, Z. A.; Baryshok, V. P. *Zh. Obshch. Khim.* **1984**, *54*, 2010. Voronkov, M. G.; Faitel'son, F. D. *Khim. Geterotsikl. Soedin.* **1967**, 39; *Chem. Abstr.* **1967**, *67*, 64321.

(8) Alternatively, this trialkanolamine could be made directly (in 94% de) from (-)-(*S*)-propylene oxide and ammonia: Grassi, M.; Di Silvestro, G.; Farina, M. *Tetrahedron* **1985**, *41*, 177-181.

(9) Bradley, D. C.; Mehrota, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.

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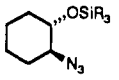
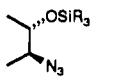
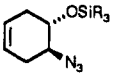
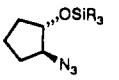
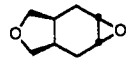
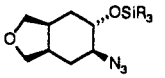
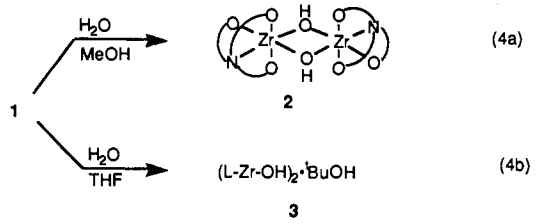
Table II. Enantioselective Cleavage of Meso Epoxides with Azidosilanes Catalyzed by **3**[a]

epoxide	azide	temp (°C)	product	yield (%)[b]	ee (%)[c]	$[\alpha]^{25}_D$ (deg)[d]
	$iPrMe_2SiN_3$	0		86	93	−18.0
	$iPrMe_2SiN_3$	0		59	87	+15.8
	$iPrMe_2SiN_3$	25		79	89	−15.0
	$iPrMe_2SiN_3$	25		64	83	+32.6
	Me_3SiN_3	25		78	88	−12.0

[a] All runs contain epoxide (2.4 mmol), azidosilane (2.5 mmol), **3** (0.2 mmol of Zr), and trimethylsilyl trifluoroacetate (0.05 mmol), 48 h. [b] Isolated yield after flash chromatography. [c] GC analysis. [d] $c = 5$ ($CHCl_3$).

properties of **1** are complex, reflecting aggregate formation in solution. Modification of **1** via partial hydrolysis was also undertaken.[10] Treatment with excess wet methanol in THF affords the discrete hexane-insoluble hydroxo-bridged dimer **2**. In contrast, simply treating a THF solution of **1** with water (H_2O/Zr = 1:1) gave a hexane-soluble white solid, **3**, which reproducibly analyzes as retaining $^1/_2$ equiv of *tert*-butyl alcohol per zirconium (eqs 4a,b).



Zirconium alkoxides **1–3** were investigated as catalysts for eq 1 both alone and in the presence of additives intended to enhance their Lewis acidity (Table I). Under the conditions of our screen, the combination of catalyst **3** and trimethylsilyl trifluoroacetate gave (−)-(1*S*,2*S*)-1-azido-2-[(trimethylsilyl)oxy]cyclohexane in 86% enantiomeric excess.[11] The enantioselectivity could be increased to 93% by lowering the reaction temperature to 0 °C and utilizing the bulkier azide reagent $iPrMe_2SiN_3$. High enantioselectivities were likewise observed with several other meso epoxides[12] as summarized in Table II. The products derived from 1,2-epoxycyclopentane and *cis*-2,3-epoxybutane were again found to possess *S,S* absolute configuration,[11] and on this basis the other products are also tentatively assigned as the *S,S*-enantiomers.

It should be possible to prepare a variety of other chiral trialkanolamines since a range of enantiomerically pure epoxides are either commercially available or easily synthesized. Thus, we expect that the enantioselectivity of this reaction may be further increased. More generally, we anticipate that trialkanolamines, and also their dialkanolamine counterparts,[13] should prove broadly useful as ligands for asymmetric catalysis.

Supplementary Material Available: Preparation of catalyst **3**, detailed procedure for its use, and characterization of products from Table II (3 pages). Ordering information is given on any current masthead page.

(10) Several cases where partially hydrolyzed group 4 alkoxides exhibit enhanced catalytic activity when compared with the simple $M(OR)_4$ derivatives have been reported: Pitchen, P.; Dunach, E.; Deshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 8188. Suda, S.; Mukaiyama, T. *Chem. Lett.* **1991**, 431–434 and references therein. Burkhardt, T. J.; Funk, F. W.; Langer, A. W. *Abstracts of Papers*, 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; American Chemical Society: Washington, DC, 1990; INOR 600. See also: Chabardes, P. *Tetrahedron Lett.* **1988**, *29*, 6253.

(11) All enantiomeric excesses were determined by capillary GC chromatography of crude reaction mixtures with a commercially available Cyclodex-B column (J&W Scientific, Folsom, CA 95630, 30 m × 0.25 mm i.d., 0.25-μm film. Absolute configurations are based on correlation of the signs of the optical rotation with those established in ref 4.

(12) Highly hindered epoxides including those of norbornene, cyclooctene, and bicyclo[2.2.2]oct-2-ene reacted very slowly.

(13) For example, we have found that the bis-μ-oxo bridged titanium dimer supported by *N*-benzylbis-(*S,S*)-isopropanolamine ligands catalyzes the addition of diethylzinc to benzaldehyde to form (+)-1-phenyl-1-propanol in 96% enantiomeric excess (97% yield, 10% catalyst, toluene, 25 °C, 3 h).

Additions and Corrections

Transition-Metal Complexes with Sulfur Ligands. 57. Stabilization of High-Valent Fe(IV) Centers and Vacant Coordination Sites by Sulfur π-Donation: Syntheses, X-ray Structures, and Properties of $[Fe("S_2")_2(PMe_3)_n]$ (n = 1, 2) and $(NMe_4)[Fe("S_2")_2(PMe_3)_2]\cdot CH_3OH$ ("S_2"$^{2-}$ = 1,2-Benzenedithiolate(2−)) [*J. Am. Chem. Soc.* **1991**, *113*, 3819–3828]. DIETER SELLMANN,* MICHAEL GECK, FALK KNOCH, GERHARD RITTER, and JOACHIM DENGLER

Abstract and Table I: The space group $P2_12_12_1$ for **1** should read $P2_12_12$.