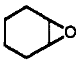
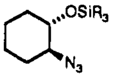
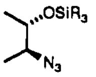
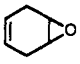
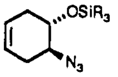
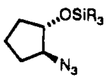
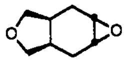
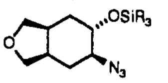
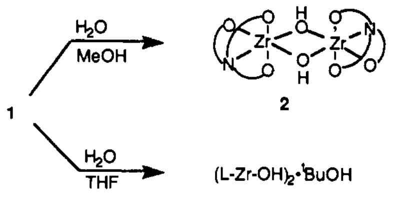
Table II. Enantioselective Cleavage of Meso Epoxides with Azidosilanes Catalyzed by 3[a]

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).



(4a)

(4b)

3

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.

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(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)$_2$]·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 $P2_12_12$.