Asymmetric Synthesis and Metalation of C_2-Symmetric Annulated Bicyclooctylcyclopentadienes

Zhuoliang Chen, Klaas Eriks, and Ronald L. Halterman*

Department of Chemistry, Boston University, Boston, Massachusetts 02215

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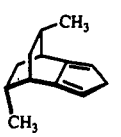
The cyclopentadienes (+)-(1*R*,7*R*,8*R*,10*R*)-8,10-diisopropyltricyclo[5.2.2.0^{2,6}]undeca-2,5-diene (**1a**) and (−)-(1*S*,7*S*,8*R*,10*R*)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]undeca-2,5-diene (**1b**), abbreviated dialkyl-BCO-Cp, are chiral ligands possessing C_2 symmetry. These dienes are efficiently prepared in five steps via (1) Birch reduced of 1,4-dialkylbenzene, (2) asymmetric dihydroboration–oxidation using enantiomerically pure isopinocamphenylborane, (3) bis(methanesulfonate) formation, (4) bisalkylation of cyclopentadiene to form spiro-annulated cyclopentadiene, and (5) sigmatropic rearrangement in toluene at 220 °C to form the fused dienes **1a** and **1b**. The enantiomeric purities of **1a** and **1b** were confirmed with the use of a chiral lanthanide ^{1}H NMR shift reagent. The cyclopentadienes **1** were metalated to form the following complexes: bis(BCO-Cp)dichlorotitanium, bis(BCO-Cp)dichlorozirconium, and bis(BCO-Cp)chloroxoniobium. All complexes were ientified by their spectral and analytical data. The structure of the enantiomerically pure bis(dimethyl-BCO-Cp)dichlorotitanium complex **14** was determined by X-ray crystallography (two independent molecules in the $P2_1$ space group, a = 7.216 Å, b = 18.621 Å, c = 17.557 Å, β = 91.48°, d = 1.31 (calcd, Z = 4) g cm^{-3}). The structure was resolved by direct methods and refined by least squares to R = 4.1% (R_w = 4.6%).

Introduction

Due to their unique advantages, we are engaged in the design, synthesis, and application of C_2-symmetric annulated cyclopentadienyl ligands in asymmetric synthesis using chiral organometallic catalysts.[1,2] The successful use of a bicyclo[2.2.2]octane fragment fused to a cyclopentadiene as a scaffolding to hold sterically different groups over the cyclopentadienyl moiety has been demonstrated with a titanocene complex derived from the diphenyltricycloundecadiene ligand, abbreviated diphenyl-BCO-Cp which is highly selective in asymmetric hydrogenase of nonfunctionalized alkenes.[3] We give here a full report of the efficient and general synthesis of two C_2-symmetrical ligands based on the bicyclo[2.2.2]octane framework, diisopropyl- and dimethyl-BCO-Cp ligands **1a** and **1b**, the formation of their organometallic complexes with titanium, zirconium, and niobium, and the determination of the X-ray crystal structure of a chiral dichlorotitanocene complex.

(1*R*,7*R*,8*R*,10*R*)-(+)-**1a**



(1*S*,7*S*,8*R*,10*R*)-(-)-**1b**

Results and Discussion

Ligand Syntheses. We based our strategy for the synthesis of the chiral, annulated ligands **1a** and **1b** on the established bisalkylation of cyclopentadiene.[3,4] The previous synthesis of an enantiomerically enriched diphenyl-BCO-Cp ligand required the chromatographic separation of diastereomeric camphorsulfonate esters. Wishing to avoid any resolutions in the current synthesis of the diisopropyl-substituted ligand, we viewed the asymmetric preparation of the enantiomerically pure C_2-symmetric 1,4-cyclohexanediol **4**, which has each isopropyl group appropriately placed trans to the adjacent hydroxyl group, as being the key to a practical synthesis of ligand **1a**. It was apparent that the desired trans relationship between the hydroxyl and isopropyl moieties could be introduced by a hydroboration–oxidation sequence. Moreover, an asymmetric dihydroboration of the cyclohexadiene **3** should favor the generation of one enantiomer of the desired C_2-symmetric diol **4** over the competing formation of the unwanted C_i- and enantiomeric C_2-symmetric diol isomers.

The starting material in the asymmetric synthesis of **1a** (Scheme I) was 1,4-diisopropylbenzene (**2**), which was converted into the cyclohexadiene **3** by a modified Birch reduction of **2**.[5] Standard Birch reduction conditions gave a large amount of dialkylcyclohexenes and cyclohexanes. Enantiomerically pure isopinocamphenylborane was prepared by a Brown procedure[6] from either (+)- or (−)-α-pinene, which are commercially available in ca. 90% enantiomeric excess (ee). Exposure of cyclohexadiene **3** to excess enantiomerically pure isopinocamphenylborane (from (+)-α-pinene) followed by oxidation with basic hydrogen peroxide gave an initial mixture of C_2- and C_i-symmetric diols in a ratio of 6:1.[6] After separation by silica gel chromatography, the enantiomeric excess of the C_2-symmetric diol was determined by Mosher ester analysis to be around 83%.[7] The absolute configuration shown is that predicted when using (+)-α-pinene to form the reagent.[8] Fortunately, by performing a simple recrystallization from 20:1 1,2-dichloroethane:ethanol, the enantiomeric purity of this diol could be increased to greater than 95% as determined by ^{1}H NMR spectroscopic analysis of Mosher ester derivatives. In this way, we have obtained multigram quantities of enantiomerically en-

* To whom correspondence should be addressed at the Department of Chemistry, University of Oklahoma, 620 Parrington Oval, Norman, OK 73019-0370.

(1) (a) Colletti, S. L.; Halterman, R. L. *Tetrahedron Lett.* **1989**, *30*, 3513. (b) Chen, Z.; Halterman, R. L. *Synlett* **1990**, *1*, 107.
(2) Colletti, S. L.; Halterman, R. L. *Organometallics*, preceding article in this issue.
(3) BCO-Cp is an abbreviation for the bicyclooctyl-fused cyclopentadienes [e.g., dimethyl-BCO-Cp is (1*S*,7*S*,8*R*,10*R*)-(−)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadiene]. Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105.
(4) Mironov, V. A.; Ivanov, A. P.; Kimelfeld, Ya. M.; Petrovskaya, L. I.; Akhrem, A. A. *Tetrahedron Lett.* **1969**, 3347.
(5) Kwart, H.; Conley, R. A. *J. Org. Chem.* **1973**, *38*, 2011.
(6) (a) Brown, H. C.; Jadhav, A. K.; Mandal, A. K. *J. Org. Chem.* **1982**, *47*, 5074. (b) Brown, H. C.; Schwier, J. R.; Singaram, B. *J. Org. Chem.* **1978**, *43*, 4395.
(7) (a) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. (b) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.
(8) Brown, H. C.; Singaram, B. *J. Am. Chem. Soc.* **1984**, *106*, 1797.

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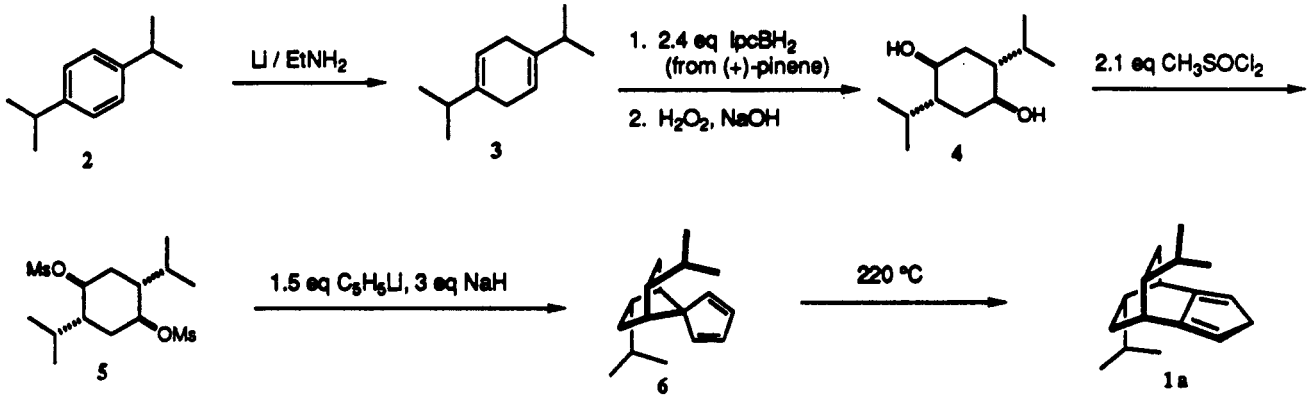
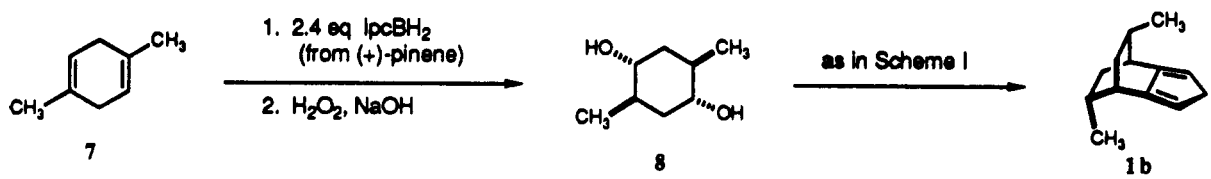
Scheme I



Scheme II



riched diol. Bisalkylation of cyclopentadiene with the bis(methanesulfonate) ester **5** in the presence of sodium hydride provided the spiro-annulated cyclopentadiene **6** in 78% yield.[3,9] We have noted that the yield of this alkylation reaction can be improved to 95% by using 2 equiv of HMPA as a reaction cosolvent. Thermolysis of spirodiene **6** at 220 °C in a resealable tube of toluene effected a [1,5]-sigmatropic alkyl shift followed by successive hydrogen shifts resulting in the formation of the thermodynamically stable fused cyclopentadiene (1*R*,7*R*,8*R*,10*R*)-(+)-**1a** in 95% yield.[9] The thermolysis reaction was carried out under dilute conditions (0.03 M), and the toluene was removed at room temperature under vacuum to minimize dimerization or other side reactions. When the toluene was removed with heating, the yield of the desired cyclopentadiene was much lower. The cyclopentadiene ligand **1a** and the spiro-annulated diene **6** are stable in the freezer under an inert atmosphere and have been stored for weeks without serious decomposition. The enantiomeric integrity of this desired chiral ligand was confired by using a complex chiral shift reagent.[10] Adding aliquots of a solution of $Yb(tfc)_3$ (0.1 M) and Ag(FOD) (0.2 M in $CDCl_3$) to the cyclopentadiene **1a** (0.04 M in $CDCl_3$) and examining the ^1H NMR spectrum showed for *rac*-**1a** in the presence of 0.39 equiv of the Yb reagent two sets of signals for the vinyl and the bridgehead allylic hydrogens. When the spectrum of (−)-**1a** was recorded under the same conditions, the three signals mentioned were observed at 5.76, 2.90, and 2.74 ppm, while the corresponding signals for (+)-**1a** were seen at 5.69, 2.82, and 2.77 ppm.

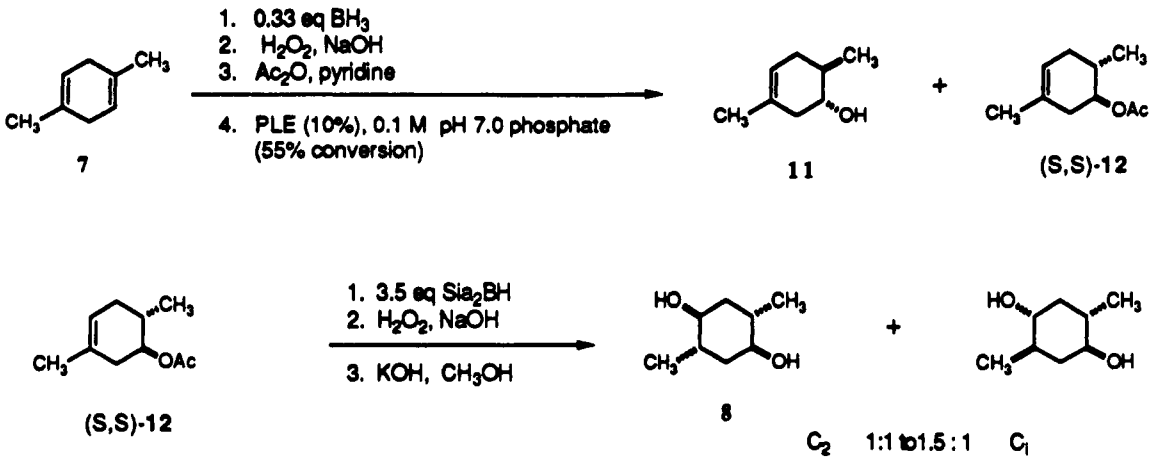
We have been able to prepare the enantiomerically enriched dimethyl-BCO-Cp ligand **1b** asymmetrically according to the above synthesis using 1,4-dimethyl-1,4-cyclohexadiene (**7**) as the starting material. The key asymmetric hydroboration[6] produced a 3.6:1 mixture of C_2- and C_i-symmetric diols. The C_2-symmetric isomer **8** was separated by silica gel chromatography (55% yield) and exhibited an enantiomeric purity of >95% as determined by ^1H NMR spectroscopic analysis of the Mosher ester derivative.[7] The synthesis of the dimethyl-BCO-Cp ligand (1*S*,7*S*,8*R*,10*R*)-(−)-**1b** was carried out by conversion of diol **8** to the bis(methanesulfonate) ester **9** (99% yield), bisalkylation of cyclopentadiene (76% yield using HMPA as cosolvent), and thermolysis in toluene of the spiro-annulated cyclopentadiene **10** (73% yield) as shown in Scheme II. The dimethyl-BCO-Cp ligand **1b** is thermally more sensitive than the corresponding diisopropyl ligand and was obtained in 73% yield.

The racemic dimethyl-BCO-Cp ligand **1b** can be readily obtained according to an analogous reaction sequence using racemic diol **8**. Treating the dimethylcyclohexadiene **7** with borane–THF (THF = tetrahydrofuran) followed by oxidation produced a 1:1 mixture of racemic C_2- and C_i-symmetrical diols. In the large-scale preparation of racemic ligand, we have found it convenient to recrystallize the initial diol mixture from benzene to remove much of the less soluble C_i-symmetrical diol. The 9:1 mixture of diols obtained from the mother liquor was further purified by silica gel chromatography. The remaining conversion of the racemic C_2-symmetrical diol **8** into the racemic dimethyl-BCO-Cp ligand **1b** was analogous to the procedure shown in Scheme II. Likewise, the hydroboration–oxidation of the diisopropylcyclohexadiene **3** gave a mixture of racemic C_2- and C_i-symmetrical diols in a 1.5:1 mixture. The racemic C_2-symmetrical diol **4** could be purified by silica gel chromatography and carried forward as in Scheme I to the racemic diisopropyl-BCO-Cp ligand **1a**.

Enzymatic Kinetic Resolution. In an attempt to improve on the stoichiometric replication of pinene's chirality, an alternative route to the enantiomerically pure C_2-symmetric dimethylcyclohexanediol **8** relying on the catalytic enzymatic kinetic resolution of the racemic dimethylcyclohexenyl acetate **12** using pig liver esterase[11] was examined. The racemic alcohol **11** is available by the monohydroboration–oxidation of **7** (Scheme III). The kinetic resolution of racemic acetate **12** is facile and fairly selective, producing a 44% yield of recovered acetate **12** with an enantiomeric purity of 88% at 55% conversion.

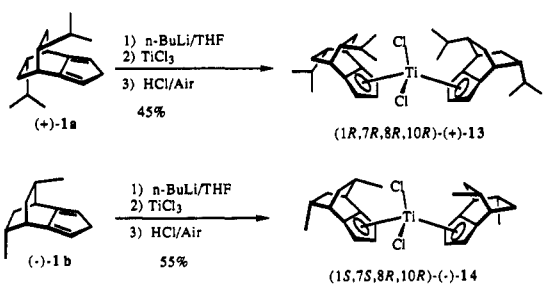
(9) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883.
(10) Wenzel, T. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 382.
(11) (a) Whitesell, J. K.; Chen, H.-H.; Lawrence, R. M. *J. Org. Chem.* **1985**, *50*, 4663. (b) Arita, M.; Adachi, K.; Ito, Y.; Sawai, H.; Ohno, M. *J. Am. Chem. Soc.* **1983**, *105*, 4049. (c) Laumen, K.; Reimerdes, E. H.; Schneider, M. *Tetrahedron Lett.* **1985**, *26*, 407.

Scheme III



The hydroboration of either the acetate **12** or the alcohol **11** with a variety of boranes (borane, dicyclohexylborane, thexylborane, disiamylborane) produced a disappointingly poor ratio (1:1 to 1.5:1) of desired C_2- to C_1-symmetric diols, rendering this route less efficient overall than the asymmetric hydroboration route. Kinetic resolution of the racemic monoacetate **12** followed by asymmetric hydroboration of the recovered acetate gives ca. 29% yield of greater than 96% enantiomerically enriched diol **8**. Although this route gave highly enantiomerically enriched diol, it is longer than the direct asymmetric double hydroboration.[12] The asymmetric dihydroboration described above remains the most efficient route to the BCO-Cp ligands.

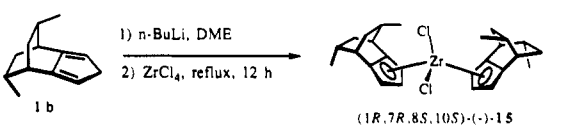
Metalation: Titanocene and Zirconocene Complexes. In order to establish the ability to form metal complexes of these fairly hindered BCO-Cp ligands, we studied the preparation of titanocene and zirconocene dichlorides. Starting from racemic BCO-Cp **1**, both the *dl*- and the *meso*-bis(BCO-Cp)dichlorotitanium complexes can potentially be formed, whereas using enantiomerically pure BCO-Cp **1** allows only the C_2-symmetrical *d* or *l* metal complex to be generated. Thus, treatment[13] of the *n*-butyllithium-generated anion of either diisopropyl-substituted (1*R*,7*R*,8*R*,10*R*)-(+)-**1a** of dimethyl-substituted (1*S*,7*S*,8*R*,10*R*)-(−)-**1b** with trichlorotitanium, followed by oxidation with HCl in air,[14] produced the chiral, enantiomerically pure substituted titanocene dichlorides (1*R*,7*R*,8*R*,10*R*)-(+)-**13** and (1*S*,7*S*,8*R*,10*R*)-(−)-**14**, which



can be precipitated from methylene chloride by the addition of hexane. The spectral and analytical data for these dichlorotitanium complexes support our formulation of the structures. The two substituted cyclopentadienyl ligands are identical in a C_2-symmetrical titanocene dichloride, and their ^{1}H NMR spectrum should show one set of cyclopentadienyl resonances; we observe the three expected signals at 6.47, 6.31, and 5.77 ppm and at 6.51, 6.44, and 5.91 ppm for the titanocene dichloride complexes **13** and **14**, respectively. The C_2 symmetry of the complexes was confirmed by the measurement of optical rotations of 482 and −534° for the two complexes **13** and **14**, a result not consistent with optically inactive meso isomers. The mass spectra indicate the presence of a titanium dichloride. Finally, we were able to obtain a single crystal of the (dimethyl-BCO-Cp)$_2$TiCl$_2$ complex **14** by recrystallization from CH_2Cl_2/hexane. The structure of this complex was determined by X-ray crystallography and is discussed below. The diisopropyl analogue **13**, on the other hand, was too soluble to afford suitable crystals.

Interestingly, the ^{1}H NMR spectrum recorded at 20 °C of the (diisopropyl-BCO-Cp)$_2$TiCl$_2$ complex **13** exhibited two broad methyl signals at 1.08 and 0.77 ppm and two sharp methyl doublets at 0.91 and 0.65 ppm. When the sample was heated to 60 °C, all four methyl signals appeared as sharp doublets. The two broad methyl signals were seen by COSY spectroscopy to be on the same isopropyl group. We interpret the broadening as being due to hindered rotation of the isopropyl group in the sterically more hindered position near the titanium. Thus, the isopropyl moiety near the metal has a downfield shift relative to the isopropyl group on the BCO-Cp ligand distal to the metal. By analogy in the case of the (dimethyl-BCO-Cp)$_2$TiCl$_2$ complex **14**, the lower field doublet (0.93 ppm) is assigned to the methyl group syn to the metal, whereas the higher field signal (0.54 ppm) is assigned to the methyl group near the uncoordinated face of the cyclopentadienyl ring.

The enantiomerically pure C_2-symmetrical (dimethyl-BCO-Cp)$_2$ZrCl$_2$ complex **15** was synthesized from enantiomerically pure dimethyl-BCO-Cp following an established metalation procedure.[15] Addition of $ZrCl_4$ in DME



to a THF solution of the *n*-butyllithium-generated anion

(12) Kinetic resolution of the readily available diacetate of racemic diol **7** using pig liver esterase was extremely sluggish, and the small amount of diol isolated was low in enantiomeric excess.

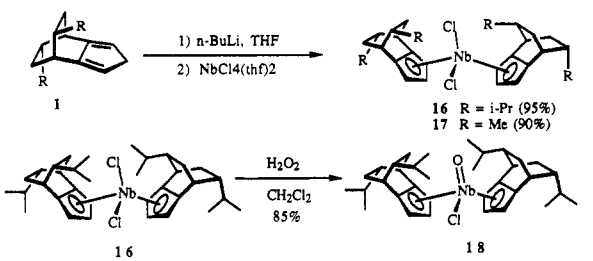
(13) Paquette, L. A.; Moriarty, K. J.; Rogers, R. D. *Organometallics* **1989**, *8*, 1506, 1512 (g) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Ibid.* **1989**, *8*, 1707.

(14) Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159.

(15) Bajgur, C. R.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

of (1*S*,7*S*,8*R*,10*R*)-dimethyl-BCO-Cp at 0 °C followed by stirring at 23 °C overnight and at 50 °C for 2 h produced a light yellow reaction mixture. After solvent removal, the resulting solid was sublimed to give white–yellow crystals of the zirconium complex **15** (65% yield). Since the metalation was performed on a single enantiomer of the dimethyl-BCO-Cp ligand, only a C_2-symmetric isomer could be formed. The spectral characteristics of the product were found to be very similar to the C_2-symmetric titanocene complex **14**. The resonances for the cyclopentadienyl hydrogens appeared at 6.24 and 6.10 ppm in the ^{1}H NMR spectrum. The optical rotation of this complex was 138°, confirming the formation of a C_2-symmetric zirconocene dichloride. The metalation of the diisopropyl-BCO-Cp ligand **1a** with zirconium tetrachloride also gave a new complex whose crude ^{1}H NMR spectrum indicates the formation of the desired zirconocene dichloride. Due to the high solubility of this complex in hydrocarbons and the production of free ligand in attempted sublimations, the desired (diisopropyl-BCO-Cp)$_2$ZrCl$_2$ complex could not be purified and fully characterized.

Metalation: Niobocene Complexes. In order to establish our ability to form complexes with group 5 metals and gain an entry into the study of potential asymmetric reactions of chiral niobocene compounds,[16] we studied the synthesis of bis(cyclopentadienyl)dichloroniobium and bis(cyclopentadienyl)chlorooxoniobium complexes with our chiral BCO-Cp ligands. Treatment of the *n*-butyllithium-generated anion of either the diisopropyl-BCO-Cp **1a** or the dimethyl-BCO-Cp **1b** with NbCl$_4$–thf$_2$[19] in THF produced in good yield the paramagetic dichloride complexes **16** and **17**, which could be purified by extraction. In the



absence of diamagnetic NMR spectra, these niobium species were characterized by inspecting their infrared and mass spectral data. The latter gave for both compounds clear evidence for the expected molecular weight of bis(BCO-Cp)dichloroniobium complexes. Oxidation of the niobium(IV) dichloride **16** with hydrogen peroxide produced the diamagnetic bis(diisopropyl-BCO-Cp)chlorooxoniobium complex **18**. Oxidation of niobocene dichlorides under these conditions has been reported to give peroxo complexes of chloroniobium. The mass spectrum of **18** indicated the presence of only a single oxygen atom. Our assignment of the monooxoniobium structure to **18** was further based on the presence of the niobium–oxo stretching signal ($\nu_{Nb=O}$ 820 cm^{-1}) and the lack of the peroxo oxygen–oxygen stretch (ν_{O-O}) at ca. 870 cm^{-1} and the lack of $\nu_{asym(NbO_2)}$ and $\nu_{sym(NbO_2)}$ at 550 and 525 cm^{-1} in the near infrared spectrum.[18] Due to the incorporation of the additional chiratopic niobium atom in this complex, the C_2 symmetry present in the previous metallocene dichlorides is lost and the ^{1}H NMR spectrum shows different signals for each of the methyl groups.

Table I. Summary of Crystallographic Data for (dimethyl-BCO-Cp)$_2$TiCl$_2$ (14)

empirical formula	$C_{26}H_{34}Cl_2Ti$
fw	465.361
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
cryst size, mm	0.2 × 0.2 × 0.35
cryst color	red
cell dimens	15 rflns, $10 \le 2\theta \le 25°$
a, Å	7.216 (4)
b, Å	18.621 (15)
c, Å	17.557 (8)
β, deg	91.48 (4)
V, Å^3	2358.3 (4.3)
Z	4
d(calc), g/cm^3	1.311
abs coeff, cm^{-1}	5.93
T, K	293
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
scan limit, deg	$5 \le 2\theta \le 40$
scan speed, deg min^{-1}	4–20
data collected	$0 \le h \le 9$, $-22 \le k \le 22$, $-20 \le l \le 20$
no. of rflns collected	4714
no. of unique rflns	4257
no. of obsd reflns ($\ge 3\sigma$)	3089
R_{int}	0.032
structure soln	direct methods (TEXSAN)
no. of variables	522
R	0.041
R_w	0.046
GOF	1.23
max param shift/esd	0.043
max resid e density, e Å^{-3}	0.41 (−0.45)

X-ray Crystallographic Structure of 14. In an effort to gain further understanding of the chirality produced around metals coordinated to the BCO-Cp ligand, we sought to determine the solid-state structure of the (dimethyl-BCO-Cp)$_2$TiCl$_2$ complex **14** by X-ray diffraction of a single crystal. Slow evaporation of a hexane/dichloromethane solution of enantiomerically pure **14** at room termperature for several days produced a number of red cubes as single crystals. The crystal structure of one of these cubes was determined. The unit cell was comprised of two independent conformations of enantiomerically pure **14** ($P2_1$ space group, see Table I for a summary of crystallographic data). The absolute stereochemistry of complex **14** shown is that predicted by the use of (+)-pinene in the synthesis of the chiral cyclopentadiene **1b**. The two independent molecules in the unit cell differ by a small change in the conformation of the two cyclopentadienyl rings relative to one another. The solid-state structure of one independent molecule of enantiomerically pure **14** is shown in Figure 1. Atomic coordinates, bond distances, and bond angles for this molecule are listed in Tables II, III, and IV, respectively; see the supplementary material for a complete listing of both molecules. A stereoview of the unit cell showing both independent molecules is shown in Figure 2.

Summary. In summary, the synthesis of substituted BCO-Cp ligands based on the asymmetric dihydroboration of 1,4-dialkylcyclohexadienes provides the most efficient route to multigram quantities of these annulated chiral C_2-symmetric cyclopentadienes. The preparation of chiral bis(cyclopentadienyl)metal complexes of titanium, zirconium, and niobium using these ligands is successful.

Experimental Section

General Methods. A description of the general methods is in ref 2, the preceding article in this issue. Abbreviations: DME, dimethoxyethane; IPCBH$_2$, isopinocamphenylborane; tfc, tri-

(16) Sala-Pala, J.; Roue, J.; Guerchais, J. E. *J. Mol. Catal.* **1980**, *7*, 141.
(17) Bax, A.; Freeman, R.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 169.
(18) Antinolo, A.; Martinez del Larguya, J.; Otero, A.; Royo, P. *J. Chem. Soc., Dalton Trans.* **1988**, 2685.
(19) (a) Manzer, L. E. *Inorg. Chem.* **1977**, *16*, 525. (b) Hithcock, P. B.; Lappert, M. F.; Milne, C. R. *J. Chem. Soc., Dalton Trans.* **1981**, 180.

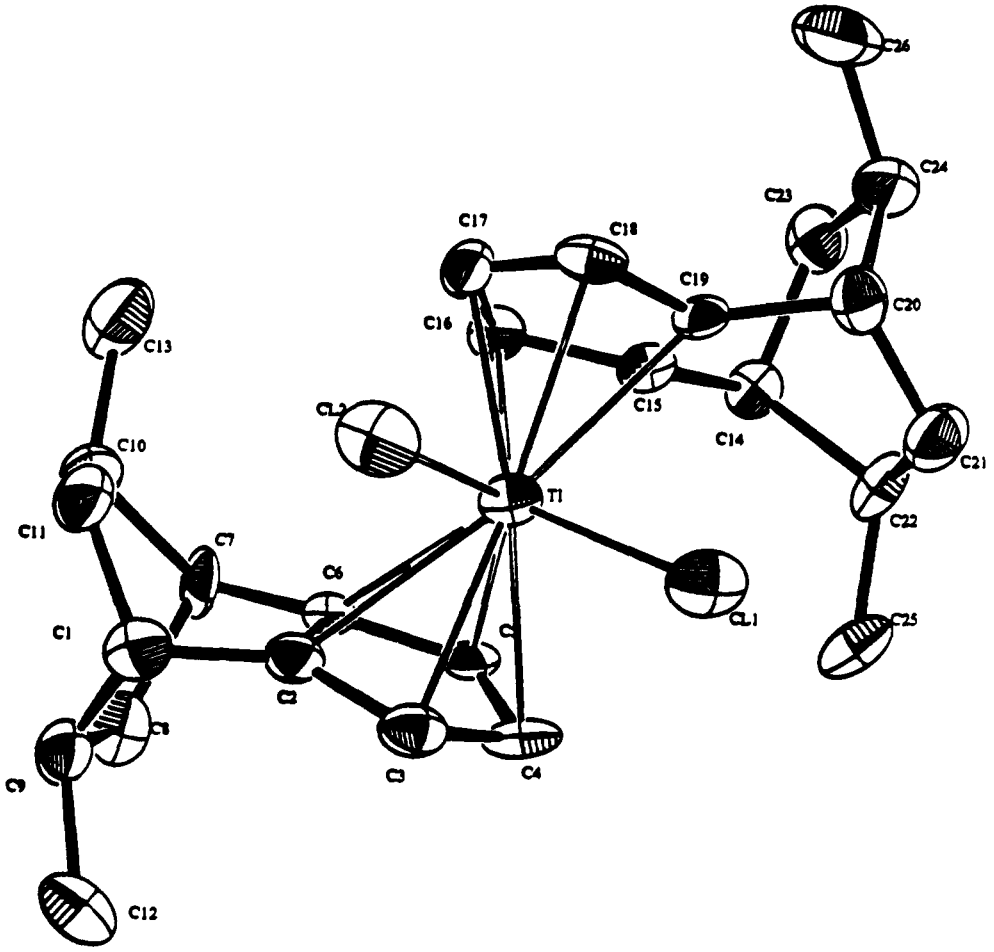


Figure 1. ORTEP plot (30% probability ellipsoids) for (dimethyl-BCO-Cp)$_2$TiCl$_2$ (14) with the labeling scheme.

Table II. Positional Parameters and *B*(eq) Values (Å^2) for (dimethyl-BCO-Cp)$_2$TiCl$_2$ (14)

atom	*x*	*y*	*z*	*B*(eq)
Ti	0.3254 (2)	0.3466	0.2109 (1)	3.52 (8)
Cl(1)	0.1507 (3)	0.3923 (2)	0.1063 (2)	5.8 (2)
Cl(2)	0.0545 (3)	0.3145 (2)	0.2765 (2)	6.4 (2)
C(1)	0.307 (1)	0.4145 (5)	0.4104 (6)	4.7 (6)
C(2)	0.355 (1)	0.4213 (5)	0.3289 (6)	3.7 (6)
C(3)	0.287 (1)	0.4604 (5)	0.2665 (6)	4.4 (6)
C(4)	0.427 (2)	0.4657 (5)	0.2108 (7)	4.4 (6)
C(5)	0.579 (1)	0.4249 (5)	0.2382 (6)	3.5 (5)
C(6)	0.539 (1)	0.3992 (4)	0.3118 (6)	3.3 (5)
C(7)	0.651 (1)	0.3805 (5)	0.3804 (5)	4.2 (6)
C(8)	0.642 (2)	0.4528 (6)	0.4254 (6)	5.4 (6)
C(9)	0.441 (2)	0.4642 (6)	0.4526 (5)	5.2 (6)
C(10)	0.566 (1)	0.3247 (5)	0.4340 (5)	5.1 (6)
C(11)	0.357 (1)	0.3374 (6)	0.4361 (5)	5.5 (6)
C(12)	0.385 (1)	0.5439 (6)	0.4482 (6)	6.5 (7)
C(13)	0.621 (2)	0.2468 (7)	0.4172 (6)	7.0 (8)
C(14)	0.714 (1)	0.2938 (5)	0.0840 (5)	3.4 (5)
C(15)	0.563 (1)	0.2818 (4)	0.1383 (6)	3.0 (5)
C(16)	0.569 (1)	0.2615 (5)	0.2177 (6)	3.5 (5)
C(17)	0.395 (2)	0.2291 (5)	0.2296 (6)	4.2 (6)
C(18)	0.294 (1)	0.2271 (5)	0.1623 (7)	3.8 (6)
C(19)	0.400 (1)	0.2578 (5)	0.1067 (6)	3.6 (6)
C(20)	0.398 (1)	0.2522 (6)	0.0226 (6)	4.9 (6)
C(21)	0.462 (1)	0.3223 (6)	−0.0148 (6)	6.0 (6)
C(22)	0.655 (1)	0.3447 (6)	0.0184 (5)	4.7 (5)
C(23)	0.733 (1)	0.2197 (6)	0.0477 (6)	4.8 (6)
C(24)	0.549 (2)	0.1955 (6)	0.0078 (6)	5.4 (6)
C(25)	0.668 (1)	0.4242 (6)	0.0349 (6)	5.2 (6)
C(26)	0.494 (2)	0.1194 (6)	0.0296 (7)	7.7 (8)

Table III. Selected Bond Distances (Å) for 14

atom	atom	distance	atom	atom	distance
Ti	Cl(1)	2.358 (3)	C(2)	C(3)	1.40 (1)
Ti	Cl(2)	2.371 (3)	C(2)	C(6)	1.43 (1)
Ti	C(2)	2.50 (1)	C(3)	C(4)	1.43 (1)
Ti	C(3)	2.35 (1)	C(4)	C(5)	1.41 (1)
Ti	C(4)	2.336 (9)	C(5)	C(6)	1.41 (1)
Ti	C(5)	2.38 (1)	C(6)	C(7)	1.48 (1)
Ti	C(6)	2.516 (9)	C(14)	C(15)	1.48 (1)
Ti	C(15)	2.478 (9)	C(14)	C(22)	1.54 (1)
Ti	C(16)	2.37 (1)	C(14)	C(23)	1.53 (1)
Ti	C(17)	2.27 (1)	C(15)	C(16)	1.44 (1)
Ti	C(18)	2.392 (9)	C(15)	C(19)	1.37 (1)
Ti	C(19)	2.53 (1)	C(16)	C(17)	1.42 (1)
C(1)	C(2)	1.49 (1)	C(17)	C(18)	1.37 (1)
C(1)	C(9)	1.52 (1)	C(18)	C(19)	1.38 (1)
C(1)	C(11)	1.54 (1)	C(19)	C(20)	1.48 (1)

Table IV. Selected Bond Angles (deg) for 14

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Ti	Cl(2)	92.2 (1)	C(2)	C(1)	C(9)	104.7 (8)
C(3)	Ti	C(16)	132.6 (3)	C(3)	C(2)	C(6)	107.1 (9)
C(4)	Ti	C(17)	148.0 (4)	C(3)	C(4)	C(5)	106.7 (9)
C(5)	Ti	C(18)	135.0 (3)	C(4)	C(5)	C(6)	108.5 (9)
C(2)	Ti	C(15)	130.7 (3)	C(2)	C(3)	C(4)	109.4 (9)
C(6)	Ti	C(19)	128.7 (3)	C(5)	C(6)	C(7)	134.8 (9)
C(9)	C(1)	C(11)	106.4 (8)	C(2)	C(6)	C(7)	112.8 (9)
C(2)	C(1)	C(9)	104.7 (8)	C(6)	C(7)	C(8)	100.5 (7)
C(1)	C(2)	C(3)	136 (1)	C(6)	C(7)	C(10)	116.2 (8)
C(2)	C(1)	C(11)	107.6 (8)	C(8)	C(9)	C(12)	111.4 (9)

fluorocamphorato, HMPA, hexamethylphosphoric triamide; BCO-Cp, bicyclooctylcyclopentadiene.

(1*S*,2*R*,4*S*,5*R*)-(+)-2,5-Diisopropylcyclohexane-1,4-diol (4). A 1-L flask fitted with a rubber septum and a magnetic stirring bar was charged with IPCBH$_2$[6] [assumed 0.524 M in ether, 250 mL, 131 mmol, derived from (1*R*)-(+)-α-pinene, 98%, 91+% ee, Aldrich] and cooled to −25 °C. 1,4-Diisopropylcyclohexa-1,4-diene (3) (87.7%, 10.27 g, 54.9 mmol, the rest was 1,4-diisopropylcyclohexene, 6.9%, and 1,4-diisopropylbenzene, 5.4%) was added

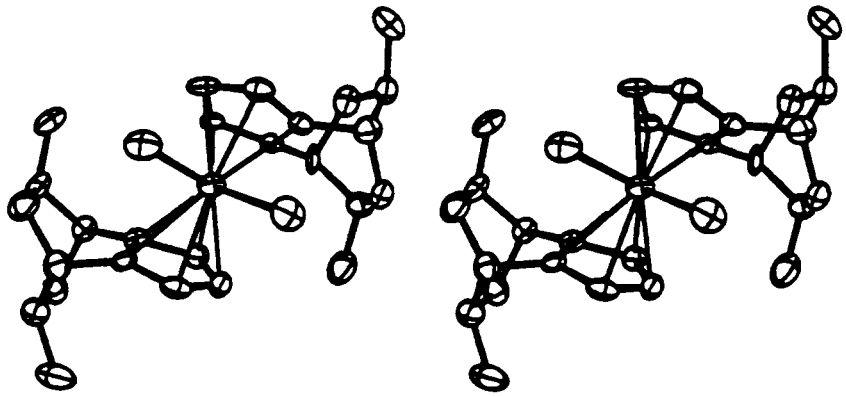


Figure 2. Stereoview of (dimethyl-BCO-Cp)$_2$TiCl$_2$ (14).

over 5 min. The reactants were mixed together well and left at −25 °C without stirring for 24 h and then at 0 °C for another 24 h. The mixture was then treated with methanol (9.2 mL, 228 mmol) dropwise at −25 °C (H_2 evolved!) and then warmed to room temperature. The solution of organoboranes was recooled to 0 °C and oxidized by successive slow addition of sodium hydroxide (4 M, 86 mL, 342 mmol) and hydrogen peroxide (30%, 35 mL, 342 mmol, heat evolved!). The contents were maintained at 34 °C for 2 h to ensure complete oxidation. Two layers separated after cooling and the addition of anhydrous potassium carbonate. The aqueous layer was extracted with portions of ether (3 × 100 mL). The combined organic portion was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The oily residue was subjected to vacuum distillation (water aspirator, 110–120 °C) to remove most of the pinanol, leaving a white solid (10.27 g) that contained a 6:1 mixture of the C_2- and C_i-symmetrical diols by ^{1}H NMR analysis. Flash chromatography (SiO_2, 30% ethyl acetate in hexane) gave first the remaining pinanol, the C_i-symmetrical diol, and other byproducts and then the (ethyl acetate) diol 4 (6.04 g, 55.0%, 83.5% ee by Mosher ester analysis). The purified C_2-symmetrical diol 4 was dissolved in a mixture of absolute ethanol (24 mL) and 1,2-dichloroethane (480 mL), and the solution was stored at −25 °C for 3 days to induce self-resolution by crystallization. After filtration, the filtrate, upon removal of the solvent by rotary evaporation, afforded the diol 4 as white crystals (4.773 g, 43.5%, >96% ee by Mosher ester analysis): rf 0.23 (SiO_2, 1:1 ethyl acetate/petroleum ether); mp 119–120 °C; $[\alpha]^{25}_D$ +35.4° (*c* 0.605, CH_2Cl_2); IR (KBr) 330, 2950, 1465, 1370, 1055, 1020, 1000, 980, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (br s, 2 H), 1.79 (m, 2 H), 1.61 (m, 4 H), 1.47 (ddd, *J* = 12.5, 6.0, 6.0 Hz, 2 H), 1.36 (br s, 2 H), 0.89 (d, *J* = 8.0 Hz, 6 H), 0.87 (d, *J* = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.51, 46.08, 29.11, 26.66, 21.04, 18.77; MS, *m*/*z* (EI, 70 eV, rel intensity) 200 (M^+, 3.8%), 167 (5.3), 139 (20), 123 (4.8), 100 (100), 83 (28), 69 (23). HRMS (EI, 70 eV) Calcd for $C_{12}H_{24}O_2$: 200.1776. Found: 200.1776. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.92; H, 12.08. Found: C, 71.71; H, 11.91.

(1*S,2*R*,4*S**,5*R**)-2,5-Diisopropylcyclohexane-1,4-diol [(±)-4].** A dry 1-L flask, fitted with a magnetic stirring bar and a refluxing condenser, was charged with 1,4-diisopropylcyclohexa-1,4-diene (3) (84%, 15.6 g, 80 mmol, the rest was 1,4-diisopropylcyclohexene and 1,4-diisopropylbenzene) in THF (400 mL). A BH_3·THF complex (1 M in THF, 112 mL, 112 mmol) was added dropwise over 10 min to the stirred solution at 0 °C. The mixture was warmed to room temperature and heated to reflux for 2 h. After the reaction solution was cooled to room temperature, MeOH (14 mL, 320 mmol) was added slowly (hydrogen evolved!). The resulting organoboranes were oxidized at 0 °C by rapid addition of NaOH (5 M, 48 mL, 240 mmol), followed by slow addition of hydrogen peroxide (30% in water, 25 mL, 240 mmol). The mixture was warmed to 50 °C for 2 h and brought back to room temparature. Anhydrous K_2CO_3 was added, the aqueous layer was extracted with ether (2 × 100 mL), and the combined organic portion was dried over anhydrous Na_2SO_4. Removal of solvent via rotary evaporation gave a white solid residue that contained a 1.5:1 mixture of the C_2- and C_i-symmetrical diols by ^{1}H NMR analysis. Flash chromatography (SiO_2, 30% ethyl acetate in petroleum ether) gave first the C_i-symmetrical diol and then (ethyl acetate) the desired C_2-symmetrical diol 4 as white crystals (8.764 g, 55%): mp 139–140 °C; ^{1}H NMR (C_i-symmetrical diol; 400 MHz, $CDCl_3$) δ 3.44 (m, 2 H), 2.12 (m, 2 H), 1.87 (ddd, *J* = 12.5, 4.0, 4.0 Hz, 2 H), 1.29 (m, 4 H), 1.05 (ddd, *J* = 12.5, 12.5, 11.0 Hz, 2 H), 0.92 (d, *J* = 7.0 Hz, 6 H), 0.81 (d, *J* = 7.0 Hz, 6 H).

Mosher Ester Analysis of the Diol 4. To a mixture of the racemic diol 4 (5.0 mg, 0.025 mmol), molecular sieves (4 Å), and 4-(dimethylamino)pyridine (0.5 mg) was added pyridine (0.4 mL) and α-methoxy-α-(trifluoromethyl)phenylacetic chloride [0.2 M in CH_2Cl_2, 0.4 mL, 0.08 mmol, prepared from (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid, 99+% ee, Aldrich]. After being stirred overnight, the mixture was filtered through silica gel with dichloromethane and then filter paper. The solvent was removed by rotary evaporation, and the residue was further dried in vacuo. The esters from (+)-4 and (−)-4 were prepared by this same procedure. Several diagnostic signals were observed in the ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, C_6D_6) δ 3.50 (s, 6 H), 0.85 (d, *J* = 7.0 Hz, 6 H), 0.79 (d, *J* = 7.0 Hz, 6 H) [correspond to the diester from (+)-diol 4], and 3.45 (s, 6 H), 0.91 (d, *J* = 6.0 Hz, 6 H), 0.82 (d, *J* = 6.0 Hz, 6 H) [correspond to the diester from (−)-diol 4].

(1*S*,2*R*,4*S*,5*R*)-(+)-2,5-Diisopropylcyclohexanyl-1,4-diol Bis(methanesulfonate) (5). To a stirred solution of the diol 4 (5.00 g, 25.0 mmol) and dry trimethylamine (9.06 mL, 65.0 mmol) in CH_2Cl_2 (200 mL) at 0 °C was added dropwise a solution of methanesulfonyl chloride (4.33 mL, 53.8 mmol) in CH_2Cl_2 (24 mL). The mixture was stirred at 0 °C for 30 min and then at room temperature for another 30 min and was quenched with saturated NH_4Cl solution in ice–water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation. Further drying in vacuo afforded **5** as a light yellow solid (8.89 g, 100%): mp 128–129 °C; $[\alpha]^{22}_D$ +39.3° (*c* 0.570, CH_2Cl_2); IR (KBr) 3020, 2940, 1455, 1355, 1170, 900 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (m, 2 H), 3.01 (s, 6 H), 1.98 (m, 2 H), 1.91 (m, 2 H), 1.82 (m, 4 H), 0.95 (d, *J* = 6.5 Hz, 6 H), 0.93 (d, *J* = 6.5 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 78.51, 43.95, 38.89, 27.33, 26.34, 20.66, 18.26; MS, *m*/*z* (EI, 150 eV, rel intensity) 164 ($C_{12}H_{20}$, 40%), 149 (12), 121 (100), 108 (11), 78 (6).

(1*R*,2*R*,4*R*,5*R*)-(+)-2,5-Diisopropylbicyclo[2.2.1]heptane-7-spiro-1'-2',4'-cyclopentadiene (6). A solid mixture of the dimesylate **5** (11.7 g, 32.9 mmol), lithium cyclopentadienylide (97%, 4.74 g, 65.7 mmol, Aldrich), and sodium hydride [60% in mineral oil, 2.63 g, 65.7 mmol, washed with hexane (3 × 20 mL) prior to use] was placed in a 1-L flask equipped with a stirring bar and refluxing condenser. To the reactants was added at 0 °C via cannula THF (320 mL), followed by HMPA (23 mL, 131 mmol, distilled over BaO_2). The resulting pink slurry was heated to reflux for 18 h and then cooled to room temperature followed by slow addition of ice–water (125 mL). The mixture was diluted with petroleum ether (125 mL). The aqueous portion was washed with petroleum ether (3 × 125 mL). The combined organic extracts were washed with brine (125 mL) and then dried over anhydrous $MgSO_4$. Removal of solvent by rotary evaporation gave brown oily material that was purified by flash chromatography

(SiO_2, petroleum ether) to afford spiro-annulated diene **6** as a clear oil (7.22 g, 95%): rf 0.66 (SiO_2, petroleum ether); $[\alpha]^{22}_D$ +64.8° (*c* 1.14, CH_2Cl_2); IR (thin film) 3120, 3050, 2960, 2870, 1645, 1470, 1385, 1370, 1266, 988 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.46 (m, 2 H), 6.34 (m, 2 H), 1.93 (br m, 2 H), 1.78 (ddd, *J* = 12.0, 7.0, 3.5 Hz, 2 H), 1.59 (m, 4 H), 1.24 (m, 2 H), 0.87 (d, *J* = 5.5 Hz, 6 H), 0.85 (d, *J* = 6.5 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.01, 129.19, 70.95, 53.34, 48.80, 40.31, 32.69, 22.89, 20.79; MS, *m/z* (EI, 70 eV, rel intensity) 231 (M^+ + 1, 11%), 230 (M^+, 56), 187 (22), 161 (15), 160 (99), 134 (11), 117 (100). HRMS (EI 70 eV) Calcd for $C_{17}H_{26}$: 230.2035. Found: 230.2033.

(1*R*,7*R*,8*R*,10*R*)-(+)-8,10-Diisopropyltricyclo[5.2.2.0^{2,6}]-2,5-undecadiene (Diisopropyl-BCO-Cp) (1a). A solution of spiro-annulated diene **6** (4.841 g, 21.05 mmol) in toluene (702 mL) was degassed by four freeze–pump–thaw cycles in a resealable tube and then heated to 220 °C for 22 h. Upon being cooled to room temperature, the solvent was removed in vacuo, and the resulting residue was purified by flash chromatography (SiO_2, petroleum ether) to give the title diene **1a** as a clear oil (4.60 g, 95%, >95% ee by chiral shift reagent): rf 0.77 (SiO_2, petroleum ether); $[\alpha]^{22}_D$ +21.3° (*c* 1.44, hexane); IR (thin film) 3070, 2974, 1610, 1470, 1448, 1385, 1370, 900 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (br s, 2 H), 2.88 (s, 2 H), 2.75 (br d, *J* = 2.5 Hz, 2 H), 1.85 (ddd, *J* = 13.0, 5.5, 3.0 Hz, 2 H), 1.28 (m, 2 H), 1.11 (ddd, *J* = 13.0, 5.5, 3.0 Hz, 2 H), 0.94 (m, 2 H), 0.84 (d, *J* = 6.0 Hz, 6 H), 0.77 (d, *J* = 6.5 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.80, 119.19, 44.14, 40.99, 34.89, 33.28, 33.07, 20.84, 20.61; MS, *m/z* (EI, 70 eV, rel intensity) 230 (M^+, 65%), 187 (58), 160 (60), 131 (25), 116 (100), 105 (30). HRMS (EI, 30 eV) Calcd for $C_{17}H_{26}$: 230.2035. Found: 230.2039. Anal. Calcd for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.40; H, 11.25.

Determination of the Enantiomeric Purity of 1a. To a solution of racemic **1a** (5.0 mg, 0.04 M in $CDCl_3$) was added portionwise a solution of Yb(tfc)$_3$ (0.10 M) and Ag(FOD) (0.20 M) in $CDCl_3$. The ^1H NMR spectra were recorded. Optimal resolution of several peaks was achieved at 0.39 equiv of added shift reagent based on Yb(tfc)$_3$. The same procedure was followed using (+)-**1a** and (−)-**1a**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.76, 2.90, 2.74 [correspond to (−)-1], and 5.69, 2.82, 2.77 [correspond to (+)-1]. In the cases where the enantiomerically enriched diene was used, the signals corresponding to the minor enantiomer were not observed.

(1*R*,2*R*,4*R*,5*R*)-(−)-2,5-Dimethylcyclohexane-1,4-diol (8). A 100-mL flask fitted with a rubber septum and a magnetic stirring bar was charged with a solution of IpcBH$_2$[6] [assumed 0.524 M, 220 mL, 115 mmol, derived from (1*S*)-(−)-α-pinene, 98+%, 87+% ee, Aldrich) in ether and cooled to −25 °C. 1,4-Dimethylcyclohexa-1,4-diene (**7**) (80%, 6.0 g, 44 mmol, the rest was 1,4-dimethylcyclohexene, 9%, and 1,4-dimethylbenzene, 11%) was added via cannula over 5 min. The reactants were stirred at −25 °C for 10 min and then left at −25 °C without stirring for 24 h and at 0 °C for another 24 h. The mixture was then treated with methanol (8.1 mL, 200 mmol) dropwise at −25 °C (H_2 evolved!) and then warmed to room temperature. The septum was replaced by a refluxing condenser capped with a septum. The solution of organoboranes was recooled to 0 °C and oxidized by successive slow addition of sodium hydroxide (4 M, 75 mL, 300 mmol) and hydrogen peroxide (30%, 31 mL, 300 mmol, heat evolved!). The contents were maintained at 34 °C for 3 h to ensure complete oxidation. Two layers separated after cooling and addition of anhydrous potassium carbonate. The aqueous layer was extracted with portions of ether (3 × 100 mL). The combined organic portion was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The oily residue was subjected to vacuum distillation (water aspirator, 110 °C) to remove most of the pinanol, leaving a white residue that contained a 3.6:1 mixture of the C_2- and C_i-symmetrical diols by ^1H NMR analysis. Flash chromatography (SiO_2, 1:1 ether/petroleum ether) gave first the remaining pinanol, the C_i-symmetrical diol, and other byproducts and then (ethyl acetate) the desired C_2-symmetrical diol **8** as a white solid (3.45 g, 54.5%, >97% ee by Mosher ester analysis): rf 0.24 (SiO_2, ether); mp 121–122 °C; $[\alpha]^{26}_D$ −32.8° (*c* 0.525, CH_2Cl_2); IR (KBr) 3290, 2920, 1450, 1420, 1080, 1040, 990 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.53 (m, 2 H), 1.88 (m, 2 H), 1.74 (ddd, *J* = 13.5, 7.5, 4.5 Hz, 2 H), 1.54 (ddd, *J* = 13.5, 7.5, 3.5 Hz, 2 H), 1.45 (br s, 2 H), 1.23 (d, *J* = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.39, 35.48, 35.23, 17.89; MS, *m/z* (EI, 70 eV, rel intensity) 144 (M^+, 3.8%), 126 (3.0), 111 (10), 97 (9.0), 82 (25), 72 (100). HRMS (EI, 70 eV) Calcd for $C_8H_{16}O_2$: 144.1150. Found: 144.1153. Anal. Calcd for $C_8H_{16}O_2$: C, 66.61; H, 11.19. Found: C, 66.13; H, 10.85.

(*R,2*R**,4*R**,5*R**)-2,5-Dimethylcyclohexane-1,4-diol [(±)-8].** A dry 500-mL flask, fitted with a magnetic stirring bar and a refluxing condenser, was charged with 1,4-dimethylcyclohexa-1,4-diene (**7**) (88.4%, 6.12 g, 50 mmol, the rest was 1,4-dimethylcyclohexene and 1,4-dimethylbenzene) in THF (250 mL). The flask was immersed in an ice bath, and then a BH_3·THF complex (1 M in THF, 77 mL, 77 mmol) was added dropwise over 10 min to the stirred solution. The mixture was warmed to room temperature and heated to reflux for 2 h. After the reaction solution was cooled to room temperature, MeOH (8 mL, 200 mmol) was added slowly (hydrogen evolved!). The resulting organoboranes were recooled to 0 °C and oxidized by rapid addition of NaOH (5 M, 30 mL, 150 mmol), followed by slow addition of hydrogen peroxide (30% in water, 15.3 mL, 150 mmol). The mixture was warmed to 50 °C for 2 h and brought back to room temperature. Anhydrous K_2CO_3 was added, the aqueous layer was extracted with ether (2 × 50 mL), and the combined organic portion was dried over anhydrous Na_2SO_4. Removal of solvent via rotary evaporation gave a white residue that contained a 1:1 mixture of the C_2- and C_i-symmetrical diols by ^1H NNR analysis. Flash chromatography (SiO_2, 1:1 Et_2O/CH_22Cl_2) gave first the C_i-symmetrical diol and then (ethyl acetate) the desired C_2-symmetrical diol **8** as white crystals (1.75 g, 24.3%): mp 95–97 °C; ^1H NMR (C_i-symmetrical diol; 400 MHz, $CDCl_3$) δ 3.19 (m, 2 H), 1.91 (ddd, *J* = 13.0, 4.0, 4.0 Hz, 2 H), 1.45 (m, 4 H), 1.09 (ddd, *J* = 12.5, 12.5, 11.0 Hz, 2 H), 1.01 (d, *J* = 6.5 Hz, 6 H). For larger scale reactions, an initial crystallization of the 1:1 C_2-/C_i-diol mixture from benzene (1 g/120 mL) gave a 9:1 mixture of C_2-/C_i-diols in the mother liquor and essentially pure crystals of the C_1-diol. The C_2-diol **8** was further purified as above.

Mosher Ester Analysis of the Diol 8. Following the procedure above for the analysis of the diol **4**, racemic diol **8**, (+)-**8**, and (−)-**8** were derivatized by using the acid chloride derived from (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid. Several diagnostic ^1H NMR signals were observed: ^1H NMR (400 MHz, C_6D_6) δ 3.54 (s, 6 H), 0.93 (d, *J* = 7.0 Hz, 6 H) [correspond to the diester from (+)-diol **8**], and 3.52 (s, 6 H), 1.00 (d, *J* = 7.0 Hz, 6 H) [correspond to the diester from (−)-diol **8**].

(1*R*,2*R*,4*R*,5*R*)-(−)-2,5-Dimethylcyclohexane-1,4-diol Bis(methanesulfonate) (9). To a stirred solution of the diol **8** (3.194 g, 22.18 mmol) and dry trimethylamine (8 mL, 57.7 mmol) in CH_2Cl_2 (177 mL) at 0 °C was added dropwise a solution of methanesulfonyl chloride (3.77 mL, 47.69 mmol) in CH_2Cl_2 (22 mL). The mixture was stirred at 0 °C for 30 min and then at room temperature for another 30 min and quenched with saturated NH_4Cl solution in ice–water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic portion was dried over anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation. Further drying in vacuo afforded **9** as a light yellow solid (6.609 g, 99.3%): mp 68–77 °/; $[\alpha]^{26}_D$ −33.1° (*c* 0.995, CH_2Cl_2); IR (KBr) 3020, 2940, 1460, 1335, 1170, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.57 (ddd, *J* = 7.0, 7.0, 3.5 Hz, 2 H), 3.03 (s, 6 H), 2.22 (m, 2 H), 2.07 (ddd, *J* = 14.0, 7.0, 4.5 Hz, 2 H), 1.08 (ddd, *J* = 14.0, 7.5, 3.5 Hz, 2 H), 1.07 (d, *J* = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.41, 38.72, 33.36, 33.12, 17.35; MS, *m/z* (CI ammonia, rel intensity) 318 (M + NH_4^+, 100%), 108 (23), 93 (2.6).

(1*S*,2*R*,4*S*,5*R*)-(−)-2,5-Dimethylbicyclo[2.2.1]heptane-7-spiro-1′-2′,4′-cyclopentadiene (10). Following the same procedure as for the synthesis of **6** using the dimesylate **9** (52.4 g, 174.6 mmol), lithium cyclopentadienylide (97%, 38.9 g, 523.8 mmol) and sodium hydride (60%, 21.0 g, 523.8 mmol) in two 3-L flasks with ether (3500 mL) and HMPA (375.4 mL, 2095 mmol) gave after chromatography (SiO_2, petroleum ether) spiro-annulated cyclopentadiene **10** as a colorless oil (23.1 g, 76.1%). Due to its thermal liability, this compound was stored at −25 °C and converted to the fused diene within 1–2 days: rf 0.54 (SiO_2, petroleum ether); $[\alpha]^{23}_D$ −35.6° (*c* 1.15, CH_2Cl_2); IR (thin film) 3120, 3020, 2920, 1640, 1460, 1370, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.52 (m, 2 H), 6.38 (m, 2 H), 1.85 (m, 2 H), 1.75 (m, 2 H), 1.63 (m, 4 H), 1.13 (d, *J* = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 138.86, 129.08, 65.26, 53.32, 42.62, 38.19; MS, m/z (EI, 70 eV, rel intensity) 174 (15%), 132 (100), 117 (20), 84 (14), 57 (26). HRMS (EI, 70 eV) Calcd for $C_{13}H_{18}$: 174.1409. Found: 174.1406.

(1*S*,7*S*,8*R*,10*R*)-(−)-8,10-Dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadiene (Dimethyl-BCO-Cp) (1b). A solution of spiro-annulated diene **10** (4.90 g, 28.2 mmol) in toluene (600 mL) was degassed by four freeze–pump–thaw cycles in a resealable tube and then heated to 220 °C for 22 h. Upon being cooled to room temperature, the solvent was removed in vacuo and the resulting residue was purified by flash chromatography (SiO_2, petroleum ether) to afford the title diene **1b** as a clear oil (3.590 g, 73.3%): rf 0.77 (SiO_2, petroleum ether); $[\alpha]^{22}_D$ −14.5° (*c* 1.05, CH_2Cl_2); IR (thin film) 3070, 2930, 1610, 1450, 1370, 900 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (br s, 2 H), 2.91 (br s, 2 H), 2.37 (ddd, *J* = 2.5, 2.5, 2.5 Hz, 2 H), 1.98 (ddd, *J* = 13.0, 10.0, 3.0 Hz, 2 H), 1.89 (m, 2 H), 0.91 (ddd, *J* = 12.5, 5.0, 2.5 Hz, 2 H), 0.74 (d, *J* = 6.5 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.47, 120.22, 40.98, 37.31, 37.14, 30.46, 22.21; MS, m/z (EI, 70 eV, rel intensity) 174 (M^+, 100%), 167 (4), 132 (3), 84 (5). HRMS (EI, 30 eV) Calcd for $C_{13}H_{18}$: 174.1409. Found: 174.1404. Anal. Calcd for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.43; H, 10.11.

(1*R,6*R**)-3,6-Dimethylcyclohex-3-en-1-ol (11).** A 3-L flask, fitted with a rubber septum and a magnetic stirring bar, was charged with 1,4-dimethylcyclohexa-1,4-diene (**7**) (2.658 g, 24.6 mmol) in THF (185 mL), to which was added at 0 °C slowly a BH_3·THF complex (1 M, 8.19 mL, 8.19 mmol) over 5 min. The reactants were mixed together well and left in a freezer (−25 °C) overnight. After being warmed to room temperature and stirred for 1 h, the mixture was hydrolyzed slowly with water (0.443 mL, 24.6 mmol) and then recooled to 0 °C. The organoboranes were oxidized by adding sodium hydroxide (5 M, 12.3 mL, 49.2 mmol) and then hydrogen peroxide (30% in water, 1.5 mL, 49.2 mmol) slowly. The mixture was warmed to 50 °C for 1 h and then cooled to room temperature. Two layers separated after the addition of anhydrous K_2CO_3. The organic portion was dried over anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation to give an oily residue. Flash chromatography (Si_2O, 5% ether in CH_2Cl_2) gave the desired alcohol **11** as a colorless oil (1.025 g, 33%). For larger scale reactions, the product was separated by distillation (water aspiration, 75–95 °C) to afford **11** in the same yield: rf 0.20 (60% CH_2Cl_2 in petroleum ether); IR (thin film) 3390, 2960, 2910, 2840, 1630, 1450, 1440, 1275, 1265, 1040, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (br s, 1 H), 3.51 (m, 1 H), 2.20 (m, 2 H), 1.93 (m, 1 H), 1.66 (m, 3 H), 1.63 (s, 3 H), 0.99 (d, *J* = 6.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.48, 120.09, 72.78, 38.65, 35.00, 32.45, 23.17, 17.47; MS, m/z (EI, 70 eV, rel intensity) 126 (M^+, 32%), 108 (64), 97 (17), 93 (83), 82 (33), 72 (65). HRMS (EI,70 eV) Calcd for $C_8H_{14}O$: 126.1045. Found: 126.1050.

(1*R,6*R**)-3,6-Dimethylcyclohex-3-en-1-yl Acetate (12).** To a solution of the alcohol **11** (15.14 g, 120 mmol) in pyridine (375 mL, distilled over BaO) was added acetic anhydride (11.6 mL, 156 mmol, distilled azeotropically with toluene) and 4-(dimethylamino)pyridine (50 mg, 0.41 mmol). After being stirred for 9 h at room temperature, the mixture was quenched with water (400 mL), diluted with ether (300 mL), and acidified with HCl (6 N) to pH 4. The aqueous layer was extracted with ether (2 × 200 mL). The combined organic portion was dried with anhydrous Na_2SO_4. Removal of solvent by rotary evaporation gave the acetate **12** as a light yellow liquid (20.05 g, 99.5%): rf 0.55 (SiO_2, 60% CH_2Cl_2); IR (thin film) 2940, 2910, 2830, 1730, 1430, 1370, 1240, 1025, 840 cm^{-1}; ^{1}H NMR δ 5.30 (br s, 1 H), 4.72 (ddd, *J* = 9.0, 8.5, 5.5 Hz, 1 H), 2.30 (m, 1 H), 2.19 (m, 1 H), 2.06 (s, 3 H), 1.96 (m, 1 H), 1.78 (m, 2 H), 1.63 (s, 3 H), 0.93 (d, *J* = 5.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.84, 131.04, 119.93, 75.02, 35.21, 32.22, 32.19, 22.96, 21.18, 17.30; MS, m/z (EI, 70 eV, rel intensity) 168 (M^+, 1%), 125 (8), 110 (12), 108 (100), 94 (20), 92 (15), 83 (11). HRMS (EI, 70 eV) Calcd for $C_{10}H_{16}O_2$: 168.1151. Found: 168.1130.

Enzymatic Kinetic Resolution of (1*R,6*R**)-3,6-Dimethylcyclohex-3-en-1-yl Acetate [(±)-12].** To a solution of the racemic acetate **12** (1.2 g, 7.1 mmol) in a sodium phosphate buffer (0.1 M, pH 7.0, 510 mL) was added at 20 °C pig liver esterase (120 μL, 6365 units/19 mg protein/mL, 764 units, Sigma). The mixture was stirred at 20 °C, and the hydrolysis was monitored by GC. An aliquot (0.5 mL) was taken out the reaction solution and extracted with ether (5 × 1.5 mL). The GC analysis of the ether extract was performed on a Hewlett-Packard 5890 chromatograph using a cross-linked 5% phenyl methyl silicone capillary column (25 m × 0.20 mm i.d.). The temperature was programmed as initial 65 °C/2 min, rate 10 °C/min, final 250 °C/10 min. The retention times were 1.30 min for the alcohol **11** and 3.34 min for the acetate **12**. At 41 h, a 53% conversion of the acetate to alcohol was detected. The hydrolysis was stopped by extracting the reaction mixture with ether (4 × 300 mL). The organic phase was dried over anhydrous Na_2SO_4 and then concentrated by rotary evaporation to afford an oily residue that contained a 59:41 mixture of the alcohol and the acetate by ^{1}H NMR analysis. Separation by flash chromatography (Si_2O, CH_2Cl_2/Et_2O) gave first the (+)-acetate **12** (528 mg, 44%, 88% ee by Mosher ester analysis after being hydrolyzed to the alcohol with KOH/MeOH/H_2O/reflux/2 h) and then the (−)-alcohol **11** (475 mg, 53%, 72% ee by Mosher ester analysis, $[\alpha]^{25}_D$ −87° (*c* 0.65, CH_2Cl_2) for 78% ee in another experiment where the corresponding acetate showed $[\alpha]^{25}_D$ +75° (*c* 0.70, CH_2Cl_2)).

Asymmetric Hydroboration of (1*R,6*R**)-3,6-Dimethylcyclohex-3-en-1-yl Acetate [(+)-12] from Enzymatic Kinetic Resolution.** A 10-mL two-necked flask, fitted with a rubber septum, a refluxing condenser, and a magnetic stirring bar, was charged with (+)-**12** (170 mg, 1.01 mmol, 88% ee) from the enzymatic kinetic resolution and cooled to −25 °C. Then $IPCBH_2$[6] [assumed 0.723 M in ether, 1.5 mL, 1.3 mmol, derived from (1*R*)-(+)-α-pinene, 98%, 91+% ee, Aldrich] was added through a syringe. The reactants were mixed together well and left at −25 °C without stirring for 12 h before they were treated with water (0.04 mL, 2 mmol) dropwise at 0 °C and then warmed to room temperature. The solution of organoboranes was recooled to 0 °C and oxidized by successive rapid addition of sodium hydroxide (4 M, 0.75 mL, 3 mmol) and slow addition of hydrogen peroxide (30% in water, 0.4 mL, 3 mmol). The contents were maintained at 34 °C for 1.5 h to ensure complete oxidation. Two layers separated after cooling and addition of anhydrous potassium carbonate. The aqueous layer was extracted with portions (3 × 2 mL) of ether. The combined organic portion was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The oily residue was subjected to hydrolysis with KOH (112 mg, 2 mmol) in methanol (6 mL) and water (0.8 mL) under refluxing for 2 h. After being cooled to room temperature, the mixture was diluted with water (10 mL) and extracted with ether (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation to afford an oily residue (450 mg), some of which (262 mg) was subjected to preparative TLC (SiO_2, 90% ether in petroleum ether) to give pure desired C_2-symmetrical diol (1*R*,2*R*,4*R*,5*R*)-(−)-2,5-dimethylcyclohexane-1,4-diol (**8**, 24.3 mg, 29% for the whole reaction sequence, >96% ee by Mosher ester analysis).

Mosher Ester Analysis of the Alcohol 11. To a mixture of the racemic alcohol **11** (12.6 mg, 0.10 mmol, prepared from a hydroboration reaction with BH_3), molecular sieves (4 Å), and 4-(dimethylamino)pyridine (0.5 mg) was added pyridine (0.3 mL) and α-methyl-α-(trifluoromethyl)phenylacetic chloride[7] (35 mg, 0.14 mmol, prepared from (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid, 99+% ee, Aldrich) in CH_2Cl_2 (0.3 mL). After being stirred overnight, the mixture was filtered through silica gel, washed with CH_2Cl_2, and then refiltered through filter paper. The solvent was removed by rotary evaporation, and the residue was further dried in vacuo. Several diagnostic signals were observed in the ^{1}H NMR spectrum: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (s, 3 H), 1.64 (s, 3 H), 0.82 (d, *J* = 6.5 Hz, 3 H) [correspond to the ester from (+)-alcohol **11**], and 3.53 (s, 3 H), 1.61 (s, 3 H), 0.95 (d, *J* = 7.0 Hz, 3 H) [correspond to the ester from (−)-alcohol **11**].

Hydroboration of (1*R,6*R**)-3,6-Dimethylcyclohex-3-en-1-ol (11).** A representative procedure for hydroboration using thexylborane is as follows: A 25-mL flask, equipped with a stirring bar and a refluxing condenser, was charged with BH_3 (1 M in THF, 3 mL, 3 mmol) and then immersed in an ice–acetone bath. 2,3-Dimethyl-2-butene (1 M in THF, 3 mL, 3 mmol) was added slowly via a syringe. The mixture was stirred at −5 to 0 °C for 3 h to complete the formation of the boranes. The racemic alcohol **11** (189 mg, 1.5 mmol) in THF (3 mL) was added at 0 °C, and the

mixture was warmed to room temperature, stirred for 2 h, and then quenched carefully with water (0.164 mL, 9 mmol). After being recooled to 0 °C, the organoboranes were oxidized by adding sodium hydroxide (5 M, 0.5 mL, 3 mmol) rapidly and hydrogen peroxide (30% in water, 1.19 mL, 9 mmol) slowly. The mixture was kept at about 40 °C for 2 h and then cooled to room temperature and saturated with anhydrous K_2CO_3. The aqueous portion was extracted ether (3 × 2 mL), and the combined organic portion was dried over anhydrous Na_2SO_4. Removal of the solvent through rotary evaporation gave an oily residue (255 mg) that contained a 1.5:1 mixture of the C_2- and C_i-symmetrical diols 8 by ^1H NMR analysis. The ratios of the C_2- and C_i-symmetrical diols from other borane reagents are 1:1 from BH_3, 1:1 from $(disamyl)_2BH$, and 1.5:1 from $(cyclohexyl)_2BH$.

Hydroboration of (1*R,6*R**)-3,6-Dimethylcyclohex-3-en-1-yl Acetate (12).** A representative procedure for hydroboration using thexylborane is as follows: A 25-mL flask equipped with a stirring bar and a refluxing condenser, was charged with BH_2 (1 M in THF, 8 mL, 8 mmol) and then immersed in an ice–acetone bath. 2,3-Dimethyl-2-butene (1 M in THF, 8 mL, 8 mmol) was added slowly via a syringe. The mixture was stirred at −5 to 0 °C for 3 h to complete formation of the boranes. The racemic acetate **12** (336 mg, 2 mmol) in THF (4 mL) was added at 0 °C, and the mixture was warmed to room temperature, stirred for 2 h, and then quenched carefully with water (0.432 mL, 24 mmol). After being recooled to 0 °C, the organoboranes were oxidized by adding sodium hydroxide (5 M, 1.5 mL, 7.5 mmol) rapidly and hydrogen peroxide (30% in water, 3.17 mL, 24 mmol) slowly. The mixture was kept at about 40 °C for 2 h and then cooled to room temperature and saturated with anhydrous K_2CO_3. The aqueous portion was extracted ether (3 × 2 mL), and the combined organic portion was dried over anhydrous Na_2SO_4. Removal of the solvent through rotary evaporation gave an oily residue that was deacylated with KOH (224 mg, 4 mmol) in MeOH (8 mL) and water (2 mL) under refluxing for 2 h. The reaction mixture was diluted with water (15 mL) and then extracted with ether (3 × 15 mL). The organic portion was dried over anhydrous Na_2SO_4. The oily residue, after removal of organic solvent, contained a 1.5:1 mixture of the C_2- and C_i-symmetrical diols 8 by ^1H NMR analysis. The ratios of the C_2- and C_i-symmetrical diols from other borane reagents are 1.2:1 from BH_3 and 1:1 from $(disamyl)_2BH$.

(+)-Bis[(1*R*,7*R*,8*R*,10*R*)-8,10-Diisopropyltricyclo-[5.2.2.0^{2,6}]-2,5-undecadienyl]dichlorotitanium (13). To a solution of the (+)-diisopropyl-BCO-Cp **1a** (690 mg, 3.00 mmol) in THF (12 mL) was added at −78 °C via syringe *n*-butyllithium (2.5 M in hexane, 1.44 mL, 3.60 mmol). The cooling bath was removed, and the mixture was stirred for 45 min during which time the temperature rose to −10 to 0 °C. The resulting solution of yellow lithio salts was added at −10 °C via a cannula to a slurry of trichlorotitanium (241 mg, 1.53 mmol) and sodium hydride [60% in mineral oil, 18 mg, 0.459 mmol, washed with petroleum ether (3 × 4 mL) prior to use] in THF (3 mL). The dark blue solution was stirred at room temperature for 10 min and then heated under reflux for 4 h. After being cooled to room temperature, the solvent was removed in vacuo. To the resulting dark blue residue was added chloroform (20 mL) and then concentrated hydrochloric acid (10 mL) at −78 °C. The biphasic mixture was warmed to room temperature and stirred vigorously for 40 min. The organic layer was washed with brine (10 mL), and the combined aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic portion was dried over anhydrous $CaCl_2$, and the solvent was removed by rotary evaporation. Recrystallization of the dark brown residue from CH_2Cl_2 and hexane gave the titanocene dichloride **13** as dark red crystals (386 mg, 45%): mp 165–166 °C (hexane/CH_2Cl_2); $[\alpha]^{23}_D$ +482° (*c* 0.0224, CH_2Cl_2); IR (KBr) 2960, 2875, 1470, 1380, 1340, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 (br s, 2 H), 6.31 (br s, 2 H), 5.77 (t, *J* = 2.5 Hz, 2 H), 3.36 (br s, 2 H), 3.22 (br s, 2 H), 1.95 (ddd, *J* = 12.0, 8.5, 3.5 Hz, 2 H), 1.67 (ddd, *J* = 13.5, 10.0, 4.0 Hz, 2 H), 1.43 (m, 4 H), 1.21 (m, 2 H), 1.08 (br s, 6 H), 0.91 (d, *J* = 6.5 Hz, 6 H), 0.86 (dd, *J* = 6.5, 6.5 Hz, 2 H), 0.77 (br d, *J* = 4.5 Hz, 6 H), 0.65 (d, *J* = 6.5 Hz, 6 H), 0.46 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.53, 135.32, 123.53, 117.25, 108.21, 45.65, 45.38, 41.67, 36.09, 34.72, 32.64, 32.48, 31.45, 21.89, 21.02, 20.75, 20.53; MS, *m*/*z* (EI, 70 eV, rel intensity) 543 (M^+ − Cl + 2, 43%), 541 (M^+ − Cl, 100), 347 (29), 331 (19), 229 (12), 159 (16), 117 (18). HRMS (EI, 70 eV) Calcd for $C_{34}H_{50}TiCl_2$: 576.2769. Found: 576.2712. HRMS (EI, 70 eV) Calcd for $C_{34}H_{50}TiCl$: 541.3091. Found: 541.3086. Anal. Calcd for $C_{34}H_{50}TiCl_2$: C, 70.69; H, 8.73; Cl, 12.28. Found: C, 71.30; H, 8.99; Cl, 11.71.

(−)-Bis-[(1*S*,7*S*,8*R*,10*R*)-(−)-8,10-Dimethyltricyclo-[5.2.2.0^{2,6}]-2,5-undecadienyl]dichlorotitanium (14). Following the procedure for the synthesis of **13** using the (−)-dimethyl-BCO-Cp **1b** (637 mg, 3.66 mmol) in THF (15 mL), a slurry of *n*-butyllithium (2.5 M in hexane, 1.76 mL, 4.40 mmol), trichlorotitanium (305 mg, 1.94 mmol), and sodium hydride (60% in mineral oil, 16 mg, 0.40 mmol) in THF (3.5 mL) produced after recrystallization of the dark crude residue from CH_2Cl_2/hexane the desired titanocene dichloride **14** as dark red crystals (463 mg, 54.5%): mp 189–190 °C (hexane/CH_2Cl_2); $[\alpha]^{23}_D$ −534° (*c* 0.0232, CH_2Cl_2); IR (KBr) 2930, 2880, 1450, 1140, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.51 (s, 1 H, H-5), 6.44 (s, 1 H, H-3), 5.91 (br t, *J* = 2.5 Hz, 1 H, H-4), 3.00 (s, 1 H, H-7), 2.82 (s, 1 H, H-1), 2.00 (m, 2 H, H-11a and H-10), 1.88 (m, 1 H, H-8), 1.77 (ddd, *J* = 13.0, 9.5, 4.0 Hz, 1 H, H-9b), 1.37 (dd, *J* = 13.0, 8.0 Hz, 1 H, H-9a), 0.93 (d, *J* = 7.0 Hz, 3 H, H-12), 0.54 (d, *J* = 6.5 Hz, 3 H, H-13), 0.27 (dd, *J* = 11.5, 4.5 Hz, 1 H, H-11b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.73, 134.60, 123.74, 118.14, 108.30, 43.15, 40.67, 39.48, 34.59, 31.89, 31.28, 21.17, 20.84; MS, *m*/*z* (EI, 70 eV, rel intensity) 431 (M^+ − Cl + 2, 39%), 429 (M^+ − Cl, 100), 394 (15), 253 (16), 212 (11), 131 (14). HRMS (EI, 70 eV) Calcd for $C_{26}H_{34}TiCl_2$: 464.1517. Found: 464.1520.

(+)-Bis[(1*S*,7*S*,8*R*,10*R*)-(−)-8,10-Dimethyltricyclo-[5.2.2.0^{2,6}]-2,5-undecadienyl]dichlorozirconium (15). To a solution of the (−)-dimethyl-BCO-Cp **1b** (348 mg, 2 mmol) in DME (10 mL) in a 25-mL flask was added dropwise at −78 °C *n*-butyllithium (2.2 M in hexane, 1.0 mL, 2.2 mmol). The resulting mixture was allowed to rise to 0 °C and was stirred for 30 min and then at room temperature for another 30 min to afford a pink slurry that was added at 0 °C to a second 50-mL flask containing $ZrCl_4$ (99.6%, Strem, 234 mg, 1 mmol). The resulting yellow slurry was heated under reflux for 12 h. Upon being cooled to room temperature, the solvent was removed in vacuo to give a yellow residue that was extracted with CH_2Cl_2 (2 × 15 mL). Removal of the solvent from the filtrate via rotary evaporation gave a yellow orange solid (515 mg). A portion (121 mg) of the crude product was sublimed (10^{-4} Torr, 175 °C, dry ice–acetone cooling) to afford the title compound **15** as yellow crystals (77 mg, 64.5%): mp 229–230 °C; $[\alpha]^{22}_D$ +138° (*c* 0.555, CH_2Cl_2); IR (KBr) 2920, 2860, 1450, 1375, 1150, 1030, 880, 830, 805 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.23 (m, 4 H), 6.10 (m, 2 H), 2.93 (br s, 2 H), 2.77 (br s, 2 H), 1.98 (m, 4 H), 1.85 (m, 4 H), 1.67 (m, 2 H), 1.02 (d, *J* = 7.0 Hz, 6 H), 0.48 (d, *J* = 6.5 Hz, 6 H), 0.20 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.61, 132.70, 117.85, 111.82, 107.85, 42.88, 40.39, 39.03, 34.50, 32.33, 31.04, 21.74, 20.91; MS, *m*/*z* (EI, 70 eV, rel intensity) 510 (M^+ + 4, 12%), 509 (M^+ + 3, 7), 508 (M^+ + 2, 18), 507 (M^+ + 1, 8), 506 (M^+, 16), 475 (7), 474 (6), 473 (13), 472 (10), 471 (18), 337 (64), 336 (25), 335 (100), 334 (33), 333 (98). HRMS (EI, 70 eV) Calcd for $C_{26}H_{34}ZrCl_2$: 506.1081. Found: 506.1077. Anal. Calcd for $C_{26}H_{34}ZrCl_2$: C, 61.37; H, 6.74. Found: C, 61.24; H, 6.75.

(−)-Bis[(1*R*,7*R*,8*R*,10*R*)-(+)-8,10-Diisopropyltricyclo-[5.2.2.0^{2,6}]-2,5-undecadienyl]dichloroniobium (16). To a solution of the (+)-diisopropyl-BCO-Cp **1a** (1.380 g, 6.0 mmol) in THF (12 mL) in a 50-mL flask was added dropwise at −78 °C *n*-butyllithium (2.5 M in hexane, 2.52 mL, 6.3 mmol). The resulting mixture was stirred at −10 °C for 1 h to afford a yellow solution that was added at −10 °C to a second 50-mL flask containing a suspension of $NbCl_4(thf)_2$ (1.249 g, 3.3 mmol)[19] and sodium hydride [60% in mineral oil, 40 mg, 0.9 mmol, washed with petroleum ether (3 × 10 mL) prior to use] in THF (12.5 mL). After being stirred at room temperature for 3 h, the resulting dark blue solution was concentrated by rotary evaporation to dryness. The dark brown residue was washed with petroleum ether (20 mL) to remove any unreacted diene ligand **1a**. The residue was then taken up by CH_2Cl_2 (100 mL). The filtrate, upon removal of solvent by rotary evaporation, gave the niobium complex **16** as a greenish blue parametic solid (1.749 g, 95%, fairly air and moisture stable): mp 131–132 °C; $[\alpha]^{26}_D$ −660° (*c* 0.022, CH_2Cl_2); IR (KBr) 2980, 2960, 2930, 1690, 1615, 1460, 1385, 1365, 1030, 810, 795 cm^{-1}; MS, *m*/*z* (EI, 70 eV, rel intensity) 625 (M^+ + 4, 12%), 624 (M^+ + 3, 21), 623 (M^+ + 2, 68), 622 (M^+ + 1, 33), 621

(M^+, 100), 587 (8), 586 (18). HRMS (EI, 70 eV) Calcd for $C_{34}H_{50}NbCl_2$: 632.2350. Found: 621.2364.

(−)-Bis[(1*S*,7*S*,8*R*,10*R*)-(−)-8,10-Dimethyltricyclo-[5.2.2.0^{2,6}]-2,5-undecadienyl]dichloroniobium (17). Following the procedure for the synthesis of **16** using the (−)-dimethyl-BCO-Cp **1b** (522 mg, 3.0 mmol) in THF (6 mL), a slurry of *n*-butyllithium (2.5 M in hexane, 1.32 mL, 3.30 mmol), $NbCl_4(thf)_2$[19] (625 mg, 1.65 mmol), and sodium hydride (60% in mineral oil, 18 mg, 0.45 mmol) in THF (6.3 mL) gave **17** as a dark greenish parametic solid (621 mg, 81.3%, 90.2% based on the ligand actually consumed) that was more air and moisture unstable than **16**: mp 200 °C dec; $[\alpha]^{26}_D$ +1000° (*c* 0.018, CH_2Cl_2); IR (KBr) 2920, 2860, 1620, 1480, 1450, 1375, 1145, 1030, 910, 800 cm^{-1}; MS, *m/z* (EI, 70 eV, rel intensity) 513 (M^+ + 4, 10%), 512 (M^+ + 3, 15), 511 (M^+ + 2, 67), 510 (M^+ + 1, 24), 509 (M^+, 100), 475 (6.5), 474 (21), 258 (9), 131 (6). HRMS (EI, 70 eV) Calcd for $C_{26}H_{34}NbCl_2$: 509.1098. Found: 509.1083.

(+)-Bis[(1*R*,7*R*,8*R*,10*R*)-(+)-8,10-Diisopropyltricyclo-[5.2.2.0^{2,6}]-2,5-undecadienyl]chloroniobium(V) Oxide (18). To a solution of the niobium dichloride **16** (240 mg, 0.390 mmol) in deoxgenated CH_2Cl_2 (20 mL, bubbling through N_2 for 20 min prior to use) was added dropwise hydrogen peroxide (30%, 1.1 mL, 9.9 mmol). After vigorous stirring for 30 min, the solution became clear yellow. The organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic portion was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The resulting yellow residue (200 mg, 85%) showed a clean ^{1}H NMR spectrum for the title compound. Recrystallization from absolute ethanol gave pure **18** as yellow needles: mp 118–119 °C; $[\alpha]^{23}_D$ +55.6° (*c* 0.30, CH_2Cl_2); IR (KBr) 2970, 2930, 2872, 1550, 1450, 1380, 1360, 880, 863, 820, 750, 625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, *J* = 1.5 Hz, 1 H, H-5), 6.14 (dd, *J* = 3.5, 1.5 Hz, 1 H, H-22), 6.03 (d, *J* = 2.0 Hz, 1 H, H-20), 5.84 (d, *J* = 2.5 Hz, 1 H, H-3), 5.42 (m, 1 H, H-4), 5.37 (dd, *J* = 3.5, 2.0 Hz, 1 H, H-21), 3.30 (br s, 1 H, H-7), 3.25 (br s, 1 H, H-24), 3.20 (br s, 1 H, H-1), 2.97 (br s, 1 H, H-18), 2.24 (m, 2 H, H-9b and H-26b), 1.99 (ddd, *J* = 12.5, 8.5, 3.5 Hz, 1 H, H-11a), 1.92 (ddd, *J* = 12.0, 8.5, 3.5 Hz, 1 H, H-28a), 1.84 (m, 1 H, H-12), 1.63 (m, 1 H, H-29), 1.45 (ddd, *J* = 21.5, 10.5, 3.5 Hz, 1 H, H-9a), 1.42 (ddd, *J* = 21.5, 10.5, 3.5 Hz, 1 H, H-26a), 1.31 (m, 3 H, H-8, H-10, and H-27), 1.21 (m, 1 H, H-25), 1.12 (d, *J* = 6.5 Hz, 3 H, H-31), 0.94 (d, *J* = 6.5 Hz, 3 H, H-13), 0.88 (d, *J* = 6.5 Hz, 3 H, H-34), 0.85 (d, *J* = 6.5 Hz, 3 H, H-16), 0.77 (d, *J* = 6.5 Hz, 3 H, H-30), 0.67 (d, *J* = 7.9 Hz, 6 H, H-17 and H-33), 0.66 (d, *J* = 7.0 Hz, 3 H, H-14), 0.62 (m, 1 H, H-9b), 0.54 (ddd, *J* = 12.0, 6.0, 2.0 Hz, 1 H, H-28b), 0.43 (m, 1 H, H-15), 0.36 (m, 1 H, H-32); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.85, 141.59, 132.48, 125.90, 123.68, 113.08, 111.63, 109.23, 107.58, 91.25, 47.24, 46.87, 46.36, 45.20, 39.98, 39.35, 34.90, 34.60, 34.04, 33.78, 33.27, 32.97, 30.55, 29.42, 27.35, 27.19, 22.22, 22.18, 21.22, 20.93, 20.90, 20.61, 20, 53, 20.32; MS, *m/e* (EI, 70 eV, rel intensity) 605 (M^+ + 2, 0.23%), 604 (M^+ + 1, 0.45), 603 (M^+, 0.54), 568 (M^+ − Cl, 7), 566 (100), 373 (9), 301 (6), 206 (39), 174 (53), 117 (48), 102 (39), 90 (38). HRMS (EI, 70 eV) Calcd for $C_{34}H_{50}NbOCl$: 602.2610. Found: 602.2608. Anal. Calcd for $C_{34}H_{50}NbClO$: C, 67.69; H, 8.36. Found C, 67.10; H, 7.89.

X-ray Structure Determination of 14. Suitable crystals of the red titanocene **14** were grown from a 90:10 mixture of hexane/CH_2Cl_2 by slow evaporation at room temperature for several days. The intensity data were obtained at 20 °C with a Syntex $P2_1$ four-circle autodiffractometer system using graphite monochromated Mo Kα radiation at 20 kV and 50 mA. The cell constants and an orientation matrix for data collection were obtained from the setting angles of 15 centered reflections. Scans were made at a maximum speed of 20 deg/min in omega (automatically determined for each reflection). The intensities of 3 standard reflections were measured after every 150 reflections and remained constant throughout the data collection; no decay correction was applied. The crystallographic calculations were performed by using the TEXSAN program.[20] A ψ scan of one reflection indicated ≤5% variation of intensity and no absorption correction was used. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions for the final full-matrix least-squares refinement cycles but were not refined.

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Supplementary Material Available: Complete tables of bond lengths, angles, positional parameters, and anisotropic thermal parameters for both modifications of **14** (22 pages); listings of *h*, *k*, *l*, F_o, F_c, and $\sigma(F_o)$ (19 pages). Ordering information is given on any current masthead page.

(20) TEXSAN program. TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.