Preparation of [2,5-Diisopropylcyclohexane-1,4-bis(indenyl)]titanium Dichloride and [2,5-Diisopropylcyclohexane-1,4-bis(tetrahydroindenyl)]-titanium Dichloride and Their Comparison as Catalysts for the Enantioselective Pinacol Coupling of Benzaldehyde†

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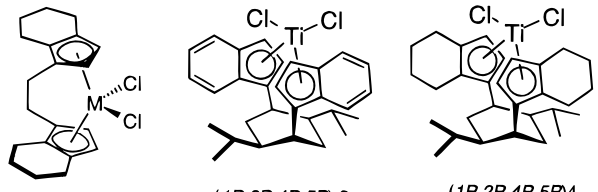
The nonracemic bis(indene) (+)-(1*R*,2*R*,4*R*,5*R*)-1,4-bis(3′-indenyl)-2,5-diisopropylcyclohexane (**10**) was synthesized in 60% yield from the addition of indenyllithium to the corresponding bis(methanesulfonate) ester of 2,4-diisopropyl-1,4-cyclohexanediol. Deprotonation of bis(indene) **10** with *n*-BuLi followed by metalation with $TiCl_3$ and oxidative workup (HCl, air, chloroform) gave the single stereoisomeric 2,5-diisopropylcyclohexane-1,4-diyl-bridged bis(indenyl)titanium dichloride **3** in 80% yield. Attempts to form the corresponding bis(indenyl)zirconium dichloride were unsuccessful. Catalytic hydrogenation of bis(indenyl)-titanium dichloride **3** gave the 2,5-diisopropylcyclohexane-1,4-diyl-bridged bis(tetrahydroindenyl)titanium dichloride **4** in 76% yield. The solid-state structure of **4** was determined by X-ray crystallographic methods. Nonracemic mixtures of chiral bis(indenyl)titanium dichloride **3** and bis(tetrahydroindenyl)titanium dichloride **4** were examined as catalysts for the pinacol coupling of benzaldehyde in the presence of manganese metal. The enantioselectivities for dihydrobenzoin were 0% with bis(indenyl) **3** and 32% with bis(tetrahydroindenyl) **4** to give the first comparison of enantioselectivities with corresponding bis(indenyl) and bis-(tetrahydroindenyl) complexes.

Introduction

Chiral *ansa*-bis(indenyl)metal and *ansa*-bis(tetrahydroindenyl)metal complexes have been used as catalysts in a number of enantioselective reactions[1] such as hydrogenations,[2] reductions,[3] epoxidations,[4] carbomagnesations,[5] and pinacol couplings.[6] Direct comparisons of enantioselectivity using corresponding chiral bis-(indenyl) and bis(tetrahydroindenyl) complexes, however, have been lacking due to poor access to resolved catalysts. For example, the most widely used chiral *ansa*-metallocenes, Brintzinger's chiral ethylene bis-(tetrahydroindenyl)titanium and zirconium dichlorides **1** and **2**,[7] can be resolved while the facile resolution of



1 M = Ti
2 M = Zr

(1*R*,2*R*,4*R*,5*R*)-**3**

(1*R*,2*R*,4*R*,5*R*)**4**

the corresponding bis(indenyl) complexes has not been developed. Comparisons between the stereoselectivity of racemic *ansa*-bis(tetrahydroindenyl)zirconium and *ansa*-bis(indenyl)zirconium complexes have been possible in the isotactic polymerization of propylene,[8] but

† Dedicated to Professor Herbert Schumann, TU-Berlin, on the occasion of his 65th birthday.

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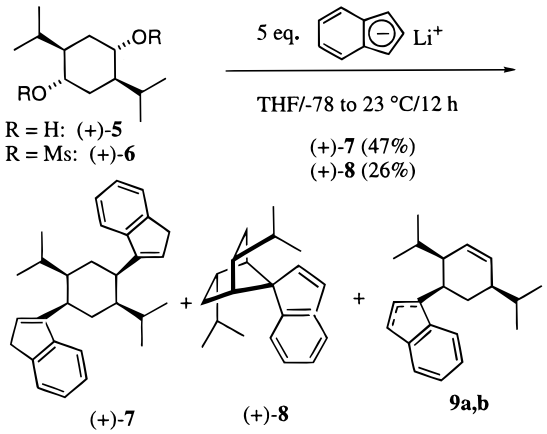
such comparisons have not been made for enantioselective reactions. We have been active in developing new methods for the preparation of ligands for incorporation into chiral metallocenes[9] and have used chiral bridging groups to enable the enantioselective preparation of bis(indenyl)metal complexes.[10] We report here that the use of a chiral bridging group enables us to obtain enantiomerically enriched samples of both the chiral *ansa*-bis(indenyl)titanium dichloride complex **3** and its corresponding *ansa*-bis(tetrahydroindenyl) analogue **4**.

We have previously communicated the preparation of **3** along with its X-ray structure.[10a] We now report the full details for the preparation of *ansa*-bis(tetrahydroindenyl)titanium dichloride **4**, its characterization, including a solid-state X-ray structure, and a comparison of bis(indenyl) **3** with bis(tetrahydroindenyl) **4** in the catalytic enantioselective pinacol coupling of benzaldehyde. Recent studies, including those in one of our laboratories,[6c] have established the effectiveness of titanocene derivatives as catalysts for *dl*-diastereoselective pinacol coupling. Gansäuer has reported the use of Brintzinger's [ethylenebis(tetrahydroindenyl)]titanium dichloride in racemic form[6] for the pinacol coupling of aromatic aldehydes,[6] and we have achieved moderate enantioselectivity in the pinacolization of benzaldehyde using this complex in chiral, nonracemic form. However, no comparison can be made with the corresponding bis(indenyl)titanium complex, since its resolution has not been accomplished.

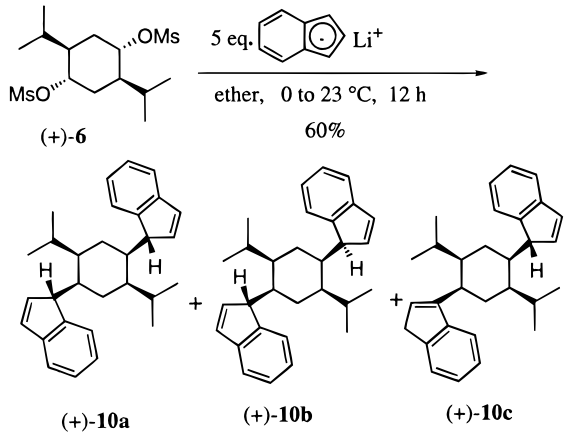
Results and Discussion

Ligand Synthesis. The enantioselective preparation of diol **5** and bis(mesylate) **6** was carried out by a hydroboration method according to our previously published procedure.[9c] Initially, the reaction between bis(mesylate) **6** and 5 equiv of indenyllithium in THF produced a 1.3:1 mixture of the desired bis(indene) ligand (+)-**7**, the spiro-annulated indene (+)-**8**, and the elimination products **9**, which were readily separable through SiO_2 chromatography (Scheme 1). The more substituted alkene position in **7** could be formed through an indenyllithium-promoted facile deprotonation/protonation isomerization of the initially formed 1-substituted indenes.

Scheme 1



Scheme 2



Considerable variation of the reaction conditions was undertaken in an attempt to improve the formation of the desired bis(indene) ligand. With 5 equiv of indenylpotassium in THF, (+)-**7** was isolated in 29% yield, whereas with 5 equiv of indenylmagnesium bromide in THF, the yield was increased to about 50%, but the product mixture was very complicated. The side products in these reactions not only included the spiro-fused indene (+)-**8**, but also the elimination products such as **9**. We examined the solvent effects on the reactions with 5 equiv of the indenyllithium reagents. Using DME, the ratio of (+)-**7** to (+)-**8** was 1:2. Using hexane or toluene or a hexane/THF mixture, the yields of the desired bis(indene) were 27%, 34%, and 22%, respectively. When HMPA was added as a cosolvent, the spiro-fused indene **8** was formed as the only detectable product in high yield. Diethyl ether proved to be most satisfactory for our purposes, giving a 60% yield of the bis(indene) ligands (+)-**10a**−**c** as an inconsequential mixture of double-bond isomers. The exact distribution of these isomers varied somewhat from run to run, depending on the manner of workup, but in all cases the C_2-symmetric isomer (+)-**10a** was always the predominant component (Scheme 2). In no case did we see evidence for the formation of a second C_2-symmetrical isomer. We have assigned the stereochemistry at the 1-indenyl position in **10a**,**c** as the isomer showing the least amount of steric interaction between the indenyl and isopropyl groups. While we have no specific spectral

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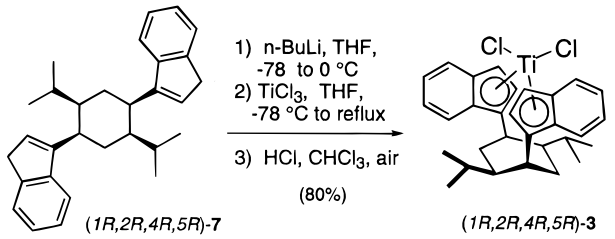
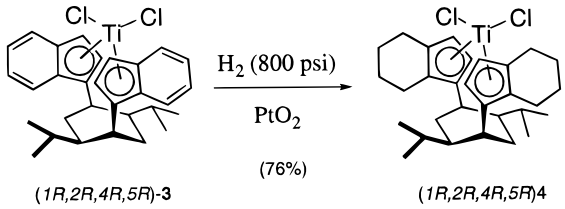
Scheme 3



Scheme 4



proof for this assignment, the orientation of the indenyl groups in the titanocene complexes **3** and **4** supports our assignment. We could isomerize this mixture of double-bond isomers through a deprotonation by *n*-BuLi and protonation by water sequence to give only bis(indene) **7**.

Preparation of (+)-(Diisopropyl-C6)In_2TiCl_2 (3). The dianion derived from either ligand (+)-**7** or the bis(indene) mixture of (+)-**10** was mixed with $TiCl_3$ in a concentrated THF solution. After oxidative workup with aqueous HCl in air, bis(indenyl)titanium dichloride complex **3** was observed as the only compound in the crude product (Scheme 3). Recrystallization from hexane provided (+)-**3** as analytically pure crystals in 80% yield. We have confirmed the structure of this complex through X-ray diffraction methods and have previously communicated the solid-state structure of (±)-**3**.[9c] Although the solid-state structure is twisted away from the ideal C_2 symmetry shown in the line drawing, the complex exhibits averaged C_2 symmetry in its NMR spectra, presumably due to rapid interconversion of the C_1-symmetrical conformations seen in the solid-state structure. The lack of coalescence in the variable-temperature NMR to −60 °C indicates that the barrier for this interconversion is low.

We unsuccessfully attempted to prepare the zirconium analogue of complex **3**. The reaction between $ZrCl_4$ and the dianion of bis(indene) **7** generated from various reagents (*n*-BuLi, NaH, EtMgCl)[11] always produced sparingly soluble, presumably polymeric metal complexes, as indicated by the broad signals in the crude ^{1}H NMR spectrum. Collins' high concentration method,[11a] Buchwald's double dilute addition method,[11b] and Jordan's method for using $Zr(NMe_2)_4$ under equilibration conditions[12] did not offer any success in providing the desired zirconium complex.

Hydrogenation of 3 to 4. Following the established procedure for the hydrogenation of bis(indenyl)metal dichlorides,[7] green bis(indenyl)titanium dichloride **3** was hydrogenated over PtO_2 at 800 psi of hydrogen at room temperature to give red bis(tetrahydroindenyl)titanium dichloride **4** in good yield (Scheme 4). The NMR spectra of **4** were consistent with a C_2-symmetric structure, and the solid-state structure was confirmed by X-ray diffraction. The crystallographic details are summarized in Table 1, and the ORTEP structure of **4** is shown in Figure 1. The tetrahydroindenyl rings are not symmetrically disposed about the Cl−Ti−Cl bisector but rather have a C_1-symmetric conformation in which Cl(1) is between the tetrahydroindenyl rings and Cl(2) is underneath the C(1)−C(6) ring. The titanium−cyclopentadienyl centroid lengths (2.093 and 2.094 Å) and bite angle (133.4°) are typical for bis(tetrahydroindenyl)titanium dichloride compounds (Table 2).

Table 1. Crystal Data and Structure Refinement for 4

empirical formula	$C_{30}H_{42}Cl_2Ti$
fw	521.44
temp	173(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1$
unit cell dimens	
a	9.6968(11) Å
b	12.4194(11) Å
c	11.0353(10) Å
α	90°
β	91.217(7)°
γ	90°
V, *Z*	1328.7(2) Å^{-3}, 2
density (calcd)	1.303 Mg m^{-3}
abs coeff	0.540 mm^{-1}
F(000)	556
cryst size	0.44 × 0.42 × 0.38 mm
θ range for data collecn	1.85−25.99°
limiting indices	$-11 \le h \le 11$, $-15 \le k \le 15$, $-13 \le l \le 13$
no. of rflns collected	4250
no. of indep rflns	3679 (R(int) = 0.0393)
abs cor	semiempirical from *ψ*-scans
max and min transmissn	0.4620 and 0.4193
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3675/1/302
goodness of fit on F^2	1.036
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0280, wR2 = 0.0729
R indices (all data)	R1 = 0.0304, wR2 = 0.0793
abs structure param	−0.02(2)
largest diff peak and hole	0.272 and −0.292 e Å^{-3}

Pinacol Coupling Catalyzed by Chiral Titanocene Dichlorides. To provide a unique comparison of the reactivity and enantioselectivity of corresponding chiral bis(indenyl) and bis(tetrahydroindenyl) complexes, we examined complexes **3** and **4** as catalysts for the pinacol coupling of benzaldehyde. Gansäuer has reported the use of Brintzinger's [ethylenebis(tetrahydroindenyl)]titanium dichloride in similar pinacol couplings,[6] but no comparison can be made with the corresponding bis(indenyl)titanium complex, since its resolution has not been accomplished. When the pinacol coupling is run using manganese metal as the stoichiometric reductant and TMSCl in THF at room temperature, it is catalytic in titanocene dichloride,[13] producing a mixture of unreacted aldehyde and *meso*- and *dl*-silyl ethers **11a**,**b** (Scheme 5). The silyl ethers can be desilylated using tetrabutylammonium fluoride to give a *meso*/*dl* mixture of diols **12a**,**b**. These diols can be

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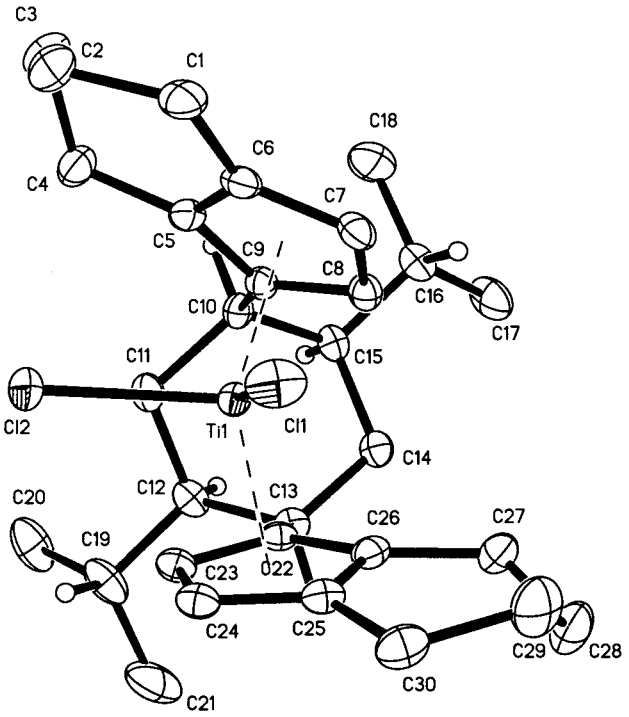
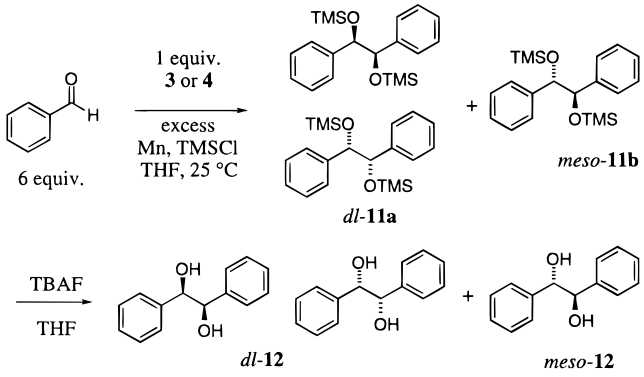


Figure 1. ORTEP drawing of **4** (shown with 50% probability ellipsoids).

Scheme 5



analyzed by HPLC using a chiral column to give the enantiomeric purity of the *dl* isomer. The results from employing bis(indenyl)- and bis(tetrahydroindenyl)titanium dichlorides **3** and **4** in the coupling of benzaldehyde are presented in Table 3. Both complexes gave 3 or 4 turnovers in 24 h. The bis(indenyl) complex **3** was slightly more selective for the *dl* isomer (4.6:1) than was the bis(tetrahydroindenyl) complex **4** (3.4:1), but only the bis(tetrahydroindenyl) complex produced enantiomerically enriched diol (32% ee). Following the precedent of isotactic propylene polymerizations using racemic bis(indenyl) versus bis(tetrahydroindenyl)zirconium complexes,[8] one can postulate that the tetrahydroindenyl ligand provides more steric hindrance in the vicinity of the active site than does the indenyl ligand. Although the selectivities are low, we have now provided an example in which a chiral bis(tetrahydroindenyl)metal complex gives higher enantioselectivity than its bis(indenyl)metal counterpart.

Experimental Section

General Considerations. All reactions involving air- or moisture-sensitive reagents or intermediates were performed under nitrogen or argon using drybox and Schlenk-line techniques. Ethereal and aromatic solvents were distilled under nitrogen from sodium benzophenone ketyl. NMR solvents (Aldrich or Merck Isotopes) were stored over 4 Å molecular sieves for routine samples. NMR solvents for air or moisture samples were vacuum-distilled (chloroform from P_2O_5, benzene from sodium benzophenone ketyl) and stored under nitrogen. Additional details about experimental procedures and equipment can be found in ref 14.

Table 2. Selected Bond Lengths (Å) and Angles(deg) for 4

Ti(1)−C(8)	2.322(2)	Ti(1)−C(22)	2.446(2)
Ti(1)−C(23)	2.330(2)	Ti(1)−C(6)	2.470(2)
Ti(1)−C(24)	2.332(2)	Ti(1)−C(25)	2.471(2)
Ti(1)−Cl(2)	2.3457(6)	Ti(1)−C(26)	2.502(2)
Ti(1)−Cl(1)	2.3495(6)	Ti(1)−C(5)	2.514(2)
Ti(1)−C(7)	2.365(2)	Ti···Cp(1)	2.093(2)
Ti(1)−C(9)	2.405(2)	Ti···Cp(2)	2.094(2)
Cl(2)−Ti(1)−Cl(1)	93.01(2)	Cl(2)−Ti(1)−Cl(1)	93.01(2)
Cp−Ti−Cp	133.4(1)		

Table 3. Pinacol Coupling of Benzaldehyde

titanocene	product:aldehyde	*dl*:*meso*	% ee
3	1:3	4.6:1	0
4	1:4	3.4:1	32

(+)-(1*R*,2*R*,4*R*,5*R*)-1,4-Bis((1*R*)-indenyl)-2,5-diisopropylcyclohexane (10a). To indene (4.16 mL, 35.0 mmol) in diethyl ether (120 mL) at 0 °C was added *n*-butyllithium (2.5 M in hexane, 14.0 mL, 35.0 mmol). After 30 min, the mixture was warmed to room temperature for 30 min. At −78 °C solid bis(mesylate) **6** (3.56 g, 10.0 mmol) was added from a sidearm. The cold bath was removed, and a pink slurry formed as the mixture was warmed to room temperature. After 12 h at room temperature, ice water (20 mL), saturated NH_4Cl (20 mL), and petroleum ether (20 mL) were sequentially added. The aqueous portion was separated and extracted with petroleum ether (3 × 20 mL). The combined organic portion was dried ($MgSO_4$), concentrated by rotary evaporation, and purified by column chromatography (SiO_2, petroleum ether) to give first unreacted indene, *spiro*-indene **8**, and the elimination product **9** as colorless oils and then bis(indene) **10** as a mixture of double-bond isomers as a white powder in a ratio of 7:2:1 (2.34 g, 60% yield); mp 115−130 °C. $[\alpha]^{23}_D$ = +77.9° (*c* 0.945, CH_2Cl_2). HRMS (EI, 70 eV): calcd for $C_{30}H_{36}$ 396.2817, found 396.2825. Anal. Calcd for $C_{30}H_{36}$: C, 90.84, H, 9.16. Found: C, 90.18, H, 9.30. Data for the C_2-symmetric isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.5 Hz, 2 H), 7.23−7.15 (m, 4 H), 6.87 (dd, J = 5.5, 2.0 Hz, 2 H), 6.32 (dd, J = 5.5, 1.5 Hz, 2 H), 3.57 (br s, 2 H), 2.73 (m, 2 H), 1.61 (m, 2 H), 1.38 (m, 2 H), 1.14 (m, 2 H), 1.04 (d, J = 6.5 Hz, 6 H), 0.74 (d, J = 6.5 Hz, 6 H), 0.32 (ddd, J = 14.0, 13.5, 10.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 144.2, 137.9, 131.8, 126.0, 124.6, 122.1, 120.8, 50.9, 41.4, 36.9, 28.4, 22.3, 22.2, 21.7. Diagnostic signals for the C_1-symmetic isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, J = 5.5, 2.0 Hz, 1 H), 6.52 (dd, J = 5.5, 2.0 Hz, 1 H), 6.38 (dd, J = 5.5, 2.0 Hz, 1 H), 5.82 (dd, J = 5.5, 2.0 Hz, 1 H). Diagnostic signals for the unsymmetrical isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (dd, J = 5.5, 2.0 Hz, 1 H), 6.56 (dd, J = 5.5, 2.0 Hz, 1 H), 6.16 (br s, 1 H). Data for the elimination Products **9**: MS (*m*/*z* (relative intensity); EI, 70 eV) 281 (M^+ + 1, 10%), 280 (M^+, 50), 265 (8), 237 (17), 168 (40), 115 (35), 109 (39); HRMS (EI, 70 eV) calcd for $C_{21}H_{28}$ 280.2191, found 280.2191; ^{1}H NMR (400 MHz, $CDCl_3$) **9a**, δ 6.84 (dd, J = 5.5, 2.0 Hz, 1 H), 5.74 (m, 1 H), 5.68 (m, 1 H); ^{1}H NMR (400 MHz, $CDCl_3$) **9b**, δ 6.29 (br s, 1 H), 5.79 (br s, 2 H).

(+)-(1*R*,2*R*,4*R*,5*R*)-2,5-Diisopropylbicyclo[2.2.1]heptane-7-spiro-1′-indene (8). In addition to forming as a side product

(14) Halterman, R. L.; Ramsey, T. M.; Pailes, N. A.; Khan, M. A. *J. Organomet. Chem.* **1995**, *497*, 43−53.

under conditions given for the formation of **10**, *spiro*-indene **8** could be produced as the major product under the following conditions. To indene (3.0 mL, 25 mmol) in THF was added *n*-butyllithium (2.1 M in hexane, 11.9 mL, 25 mmol) over 10 min at −78 °C. The resulting yellow slurry was stirred at 0 °C for 30 min and at room temperature for 30 min. The resulting yellow solution was cooled to −78 °C; HMPA (8.8 mL, 50 mmol) was added, followed by bis(mesylate) **6** (3.56 g, 10 mmol) from a sidearm. The mixture was stirred for 12 h at room temperature. The reaction mixture was worked up and purified as for the preparation of **10** to give a mixture of indene and **8**. The indene was removed in vacuo to give spiro-annulated **8** as a colorless oil (2.71 g, 96% yield). $[\alpha]^{23}_D$ = +77.9° (*c* 0.945, hexane). IR (KBr): 3064, 2956, 2889, 2867, 1468, 1453, 1384, 1366, 781, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 1 H), 7.26 (m, 1 H), 7.20 (d, J = 7.5 Hz, 1 H), 7.08 (d, J = 7.5 Hz, 1 H), 6.68 (m, 2 H), 2.54 (ddd, J = 13.0, 7.5, 4.0 Hz, 1 H), 2.05 (t, J = 3.5 Hz, 1 H), 2.03−1.91 (m, 2 H), 1.96 (dd, J = 2.0, 2.0 Hz, 1 H), 1.74−1.32 (m, 5 H), 0.95 (d, J = 6.5 Hz, 3 H), 0.89 (d, J = 6.0 Hz, 3 H), 0.87 (d J = 6.5 Hz, 3 H), 0.83 (d, J = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 145.5, 141.7, 129.1, 126.8, 126.4, 123.6, 121.0, 68.7, 54.1, 53.8, 48.7, 48.5, 40.3, 37.7, 32.4, 29.2, 23.7, 23.1, 20.8, 19.9. MS (*m*/*z* (relative intensity); EI, 70 eV): 280 (M^+, 9%), 265 (2), 237 (10), 167 (100), 141 (9). HRMS (EI, 70 eV): calcd for $C_{21}H_{28}$ 280.2191, found 280.2196. Anal. Calcd for $C_{21}H_{28}$: C, 89.93; H, 10.07. Found: C, 90.07; H, 9.83.

(+)-(1*R*,2*R*,4*R*,5*R*)-1,4-Bis(3′-indenyl)-2,5-diisopropylcyclohexane (7). Method A. Following the procedure for the preparation of **10**, but using THF in place of diethyl ether, gave after chromatographic removal of *spiro*-indene **8** (26%) bis(indene) **7** as a white powder in 47% yield; mp 50−55 °C. $[\alpha]^{23}_D$ = +42.1° (*c* 1.11, CH_2Cl_2). IR (KBr): 3067, 3017, 2954, 2868, 1606, 1574, 1458, 1395, 1365, 1283, 1020, 769 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.5 Hz, 2 H), 7.43 (d, J = 7.5 Hz, 2 H), 7.30 (dd, J = 7.5, 7.5 Hz, 2 H), 7.20 (dd, J = 7.5, 7.5 Hz, 2 H), 6.34 (br s, 2 H), 3.35 (br s, 4 H), 3.20 (br s, 2 H), 2.11 (m, 2 H), 1.95 (m, 2 H), 1.75 (m, 2 H), 0.70 (d, J = 6.5 Hz, 6 H), 0.59 (d, J = 6.5 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 146.3, 143.9, 127.5, 126.0, 124.4, 123.7, 119.2, 44.4, 37.9, 36.6, 28.6, 28.5, 22.5, 20.2. MS (*m*/*z* (relative intensity); EI, 70 eV): 396 (M^+, 40%), 353 (12), 199 (17), 198 (100), 185 (15), 142 (23), 117 (25). HRMS (EI, 70 eV): calcd for $C_{30}H_{36}$ 396.2817, found 396.2815.

Method B. A sample of **10** (5 mg, 0.013 mmol) in THF (10 mL) at −78 °C was treated with *n*-butyllithium (2 M in hexane, 0.1 mL, 0.2 mmol). The reaction mixture was warmed to room temperature and 30 min later was hydrolyzed with water (2 mL). After the mixture was extracted with petroleum ether (2 × 2 mL), the organic portion was dried ($MgSO_4$) and concentrated by rotary evaporation to give **7** as the only isomer (5 mg, 100% yield) as a yellow oil.

(+)-(1*S*,2*R*,4*R*,5*R*)-[2,5-Diisopropylcyclohexane-1,4-bis(indenyl)]titanium Dichloride (3). A 500 mL three-necked flask containing (+)-bis(indene) **10** (2.33 g, 5.64 mmol) was equipped with a reflux condenser, a magnetic stirrer, and a sidearm containing $TiCl_3$ (0.932 g, 5.92 mmol). THF (113 mL) was added to the flask and the solution cooled to −78 °C. *n*-Butyllithium (2.25 M in hexane, 5.14 mL, 11.55 mmol) was added by syringe over 10 min. The resulting solution was stirred at 0 °C and at room temperature for 30 min each to yield an orange solution. At −78 °C the $TiCl_3$ was added from the sidearm in one portion. The cold bath was removed, and the mixture was stirred for 30 min and then heated under reflux for 18 h to give a greenish solution. The solvent was removed in vacuo, and the resulting greenish residue was taken up in $CHCl_3$ (70 mL). A 70 mL portion of 6 N HCl was added at −78 °C over 10 min. The mixture was warmed to room temperature and vigorously stirred in air for 2 h. The greenish organic portion was separated and the aqueous portion extracted with CH_2Cl_2 (3 × 20 mL). The combined organic portion was washed with brine (30 mL), dried over $CaCl_2$, filtered, and concentrated by rotary evaporation to give a dark green solid (3.01 g). This crude product was taken up in hot hexane (ca. 300 mL) and filtered. The filtrate was concentrated to ca. 200 mL and cooled to −25 °C. The crystals that formed overnight were collected to yield the first crop of titanocene dichloride **3** as a dark green solid. The filtrate was further concentrated to 20 mL and cooled to −25 °C to yield a second crop of crystals of **3** (total 0.56 g, 80% yield), mp 264−265 °C. Anal. Calcd for $C_{30}H_{34}TiCl_2$: C, 70.16; H, 6.68. Found: C, 69.94; H, 6.66. $[\alpha]^{23}_D = (2.9 \times 10^3)°$ (*c* 0.0202, CH_2Cl_2). IR (KBr): 3058, 2957, 2866, 1611, 1535, 1384, 1367, 843, 813, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.5 Hz, 2 H), 7.71 (d, J = 8.5 Hz, 2 H), 7.39 (dd, J = 8.5, 6.5 Hz, 2 H), 7.23 (dd, J = 8.5, 6.5 Hz, 2 H), 6.56 (d, J = 3.5 Hz, 2 H), 5.79 (d, J = 3.5 Hz, 2 H), 3.86 (dd, J = 9.0, 2.0 Hz, 2 H), 2.67−2.54 (m, 4 H), 1.97−1.83 (m, 4 H), 1.08 (d, J = 6.5 Hz, 6 H), 0.83 (d, J = 6.5 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3, 129.6, 128.9, 128.2, 126.9, 126.2, 122.3, 120.2, 111.9, 43.4, 33.2, 32.3, 31.2, 22.3, 21.1. MS (*m*/*z* (relative intensity); EI, 70 eV): 516 (M^+ + 4, 13%), 514 (M^+ + 2, 50), 513 (M^+ + 1, 31), 512 (M^+, 68), 477 (M^+ − Cl, 86), 476 (M^+ − HCl, 100), 440, (31), 141 (50), 115 (36).

(+)-(1*S*,2*R*,4*R*,5*R*)-[2,5-Diisopropylcyclohexane-1,4-bis(4′,5′,6′,7′-tetrahydroindenyl)]titanium Dichloride (4). (+)-(1*S*,2*R*,4*R*,5*R*)-[2,5-Diisopropylcyclohexane-1,4-bis(indenyl)]-titanium dichloride (**3**; 1.22 g, 2.38 mmol), PtO_2 (0.090 g, 0.40 mmol), and dichloromethane (150 mL) were charged in a 500 mL autoclave. While the mixture was stirred, the autoclave was pressurized with hydrogen (800 psi) at room temperature. After 12 h, the reaction was found to be complete, as evidenced by an ^1H NMR spectrum of an aliquot. The autoclave was carefully vented, the reaction mixture was filtered, and the residue was washed with dichloromethane (30 mL). The solvent was removed by rotary evaporation to give a red solid that was recrystallized from hexane at −30 °C to give titanocene dichloride **4** as red crystals (0.94 g, 76% yield), mp 273−274 °C. $[\alpha]^{23}_D$ = 246.4° (*c* 1.06, CH_2Cl_2). Anal. Calcd for $C_{30}H_{42}TiCl_2$: C, 69.10; H, 8.12. Found: C, 68.94; H, 8.32. ^1H NMR (300 MHz, $CDCl_3$): δ 6.22 (d, J = 3 Hz, 2 H), 5.90 (d, J = 3 Hz, 2 H), 3.22 (m, 4 H), 2.55−2.70 (m, 6 H), 2.19−2.29 (ddd, J = 15, 6.5, 6.5 Hz, 2 H), 1.85−2.05 (m, 4 H), 1.81 (dd, J = 15, 14 Hz, 2 H), 1.50−1.65 (m, 8 H), 0.96 (d, J = 7 Hz, 6 H), 0.81 (d, J = 7 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.2, 111.9, 109.8, 101.7, 101.5, 55.8, 49.4, 49.0, 48.4, 45.9, 45.4, 43.5, 43.1, 42.5. MS (*m*/*z* (relative intensity); 70 eV): 484 (M^+ − Cl, 4%), 448 (M^+ − 2Cl, 100), 149 (13), 177 (41).

X-ray Data for 4. The data were collected on a Siemens P4 diffractometer,[15] using Mo Kα (=0.710 73 Å) radiation. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans[16] was applied. The structure was solved by the heavy-atom method using the SHELXTL system[17] and refined by full-matrix least squares on F using all reflections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement with idealized parameters. The final R1 = 0.028 is based on 3557 "observed reflections" ($I > 2\sigma(I)$), and the final wR2 = 0.079 is based on all reflections (3679 unique data). Figures depicting the molecule used thermal ellipsoids at the 50% level.

Pinacol Coupling Reactions. A round-bottom flask equipped with a sidearm was charged with the chiral titanocene dichloride complex **3** or **4** (0.20 mmol) and manganese powder (50 mesh, 1.2 mmol, 66 mg) under nitrogen. THF (20 mL) was added, and the mixture was stirred for 15 min while

(15) XSCANS: X-ray Single-Crystal Analysis System, Version 2.1; Siemens Analytical X-ray instruments Inc., Madison, WI, 1994.
(16) North, A. T. C.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351−359.
(17) SHELXTL, Release 5.03; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.

changing from red to green. Chlorotrimethylsilane (2.2 mmol, 0.28 mL) and benzaldehyde (2.0 mmol, 0.20 mL) were sequentially added by syringe. After 24 h, the volatiles were removed under vacuum, and the residue was triturated with 4:1 petroleum ether/diethyl ether. The washings were passed through Celite and concentrated as a yellow oil that was further purified by column chromatography (SiO_2, 4:1 petroleum ether/diethyl ether) to give hydrobenzoin bis(silyl) ethers **11** as a colorless oil. The product mixture was characterized by ^{1}H NMR (400 MHz, $CDCl_3$): *dl* isomer **11a**, δ 7.20−7.31 (m 10 H), 4.63 (s, 2 H), −0.09 (s, 18 H); *meso* isomer **11b**, δ 7.00−7.18 (m, 10 H), 4.42 (s, 2 H), −0.29 (s, 18 H). ^{13}C NMR ($CDCl_3$, 100 MHz): mixture, δ 143.1, 141.8, 127.3, 127.1, 126.9, 79.8, 79.4, −0.05, −0.50. GCMS (*m*/*z* (relative intensity); 12 eV, EI): *m*/*z* 179 (M^+, 100) for both GC peaks.

Desilylation of 1,2-Bis(trimethylsiloxy)-1,2-diphenylethane. In a typical procedure, bis(silyl) ether **11** (0.34 mmol, 0.12 g) was combined with THF (10 mL) in a round-bottom flask equipped with a reflux condenser. Once the compound dissolved, tetrabutylammonium fluoride (1.0 M in THF, 0.30 mL, excess) was added by syringe to give a dark brown solution. After it was heated under reflux for 4 h, the reaction mixture was hydrolyzed with water (10 mL) and extracted with diethyl ether (3 × 5 mL). The combined organic portion was dried (Na_2SO_4), concentrated by rotary evaporation, and filtered through a silica gel pipet column using ether as the eluent to give after concentration diol **12** (55% yield), confirmed by comparison with an authentic sample of *dl*-dihydrobenxoin obtained commercially. ^{1}H NMR (400 MHz, $CDCl_3$): *dl* isomer **12a**, δ 7.10−7.45 (m, 10 H), 4.80 (s, 2 H), 1.6 (br s, 2 H); *meso* isomer **12b**, δ 7.10−7.45 (m, 10 H), 4.70 (s, 2 H), 2.81 (br s, 2 H). The *dl*-hydrobenzoin **12a** was resolved analytically using a 250 × 4.6 mm Chiracel OJ column packed with cellulose tris(4-methylbenzoate) on 10 μm silica gel.

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Supporting Information Available: Crystallographic tables for bis(2-menthyl-4,7-dimethylindenyl)titanium dichloride (**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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