Articles

Asymmetric Synthesis and Metalation of a Binaphthylcyclopentadiene, a C_2-Symmetric Chiral Cyclopentadiene

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The binaphthylcyclopentadiene **5**, abbreviated Binap-Cp, is a C_2-symmetric annulated cyclopentadiene possessing axial chirality. This diene is efficiently prepared in four steps via (1) the asymmetric coupling of 1-bromo-2-methylnaphthalene (**6**) with 1-(bromomagnesio)-2-methylnaphthalene (**16**) in the presence of catalytic amounts of nickel bromide and the chiral phosphine, (*R*)-1-[(*S*)-2-(diphenylphosphino)-ferrocenyl]ethyl methyl ether; (2) bromination of enantiomerically enriched 2,2′-dimethyl-1,1′-binaphthalene (**17**) with *N*-bromosuccinimide; (3) bisalkylation of cyclopentadiene to form the spiro-annulated binaphthylcyclopentadiene **15**; and (4) sigmatropic rearrangement in toluene at 220 °C to yield the fused diene **5**. The enantiomeric purity of **5** was confirmed with the use of a chiral lanthanide ^{1}H NMR shift reagent. The cyclopentadiene **5** was metalated to form the following complexes: the bis(Binap-Cp)dichlorotitanium **19**, the bis(Binap-Cp)dichlorozirconium **22**, the (Binap-Cp)dicarbonyliodoiron **26**, and the (Binap-Cp)dicarbonylmethyliron **27**. All complexes were identified by their spectral and physical data. The structure of the bis(Binap-Cp)dichlorotitanium complex **19** was determined by X-ray crystallography (1:1 racemic complex:hexane crystallized in the $C2/c$ space group, a = 29.611 Å, b = 10.902 Å, c = 15.868 Å, β = 108.41°, d = 1.101 (calcd, Z = 4) g cm^{-3}). The structure was resolved by direct methods and refined by least squares to R = 4.5% (R_w = 5.7%). The C_2-symmetrical nature of the complex was apparent from the 2-fold axis passing through the titanium.

Introduction

Organometallic complexes containing chiral cyclopentadienyl ligands are being used in an increasing number of asymmetric catalytic reactions, including hydrogenations,[1] hydroaminations,[2] and olefin polymerizations.[3] The wide range of potentially asymmetric reactions utilizing chiral cyclopentadienylmetal complexes motivates the development of new chiral cyclopentadienes and their application in new chiral organometallic complexes. Several types of known chiral cyclopentadienes are shown in Figure 1. These include cyclopentadienes containing a single chiral substituent,[1c,e,4] e.g., the menthylcyclopentadiene **1**; prochiral ligands where the chirality is formed upon metalation,[5] e.g., the bis(indenyl) **2**; annulated cyclopentadienes possessing diastereotopic faces,[1b-d,6] e.g., the camphor-derived **3**; and C_2-symmetric annulated cyclopentadienes containing homotopic faces,[1a,7] e.g., the bicyclooctane-fused cyclopentadiene **4**. The first three types of chiral cyclopentadienes have drawbacks—in the first case, the conformational ambiguity of the chiral appendage can lead to ill-defined transfer of asymmetry; in the second case, the organometallic compound must be resolved via diastereomeric complexes after the metalation has occurred; in the third case, the annulated ligand containing diastereotopic diene faces can and does form diastereomeric metal complexes that require separation. On the other hand, application of the last type of chiral cyclopentadiene, annulated ligands possessing C_2 symmetry, has several advantages. Since the chirality is already present in the ligand, resolution after metalation is unnecessary. The C_2-symmetry axis renders both faces of the

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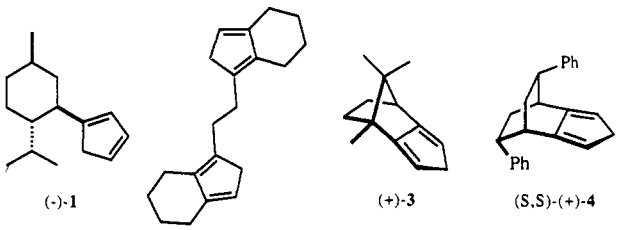
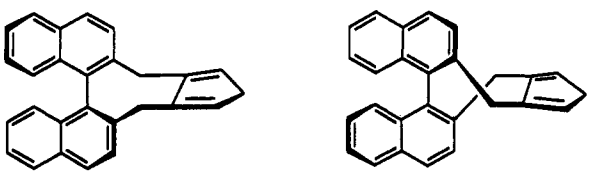


Figure 1. Chiral cyclopentadienes found in the literature: (1) Cp containing single chiral substituent, (2) prochiral bis(indenyl)Cp, (3) annulated Cp possessing diastereotopic faces, and (4) C_2-symmetric annulated Cp with homotopic faces.

diene equivalent, producing only one isomer upon metalation. The annulated nature of the ligand enables the fixed placement of sterically different groups in proximity to the metal. The judicious choice of synthetic scaffolding to hold the sterically different groups in place on either side of the metal allows the preparation of ligands having differing steric requirements. It is in this area of synthetic chiral cyclopentadienyl ligand design and synthesis that we have recently been active.

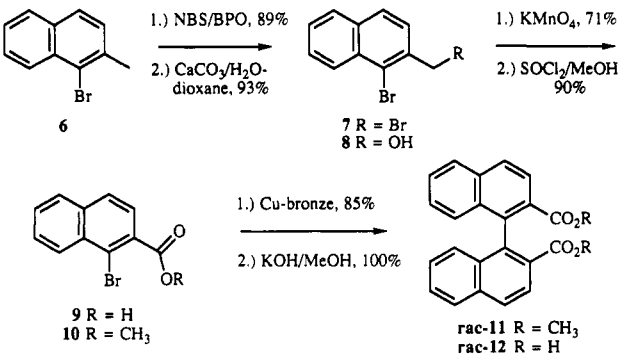
Based in part on the earlier success of the axially chiral binaphthyl backbone in highly selective chiral diol,[8] diamine,[9] and diphosphine ligands,[10] we undertook the synthesis of the binaphthylcyclopentadiene **5** (Binap-Cp),



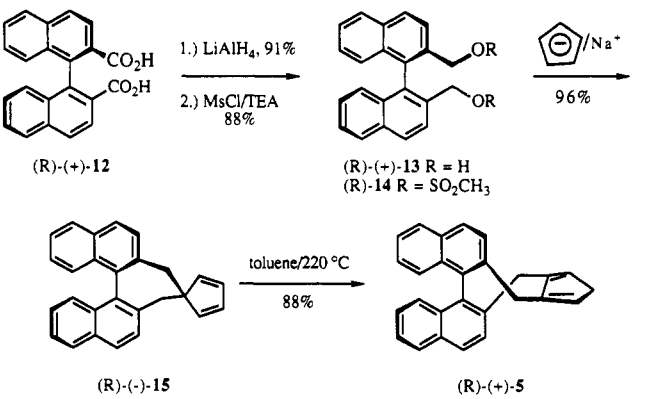
a ligand whose model indicated potentially advantageous placement of sterically large (C3 of the naphthyl) and small (equatorial hydrogen of the methylene) groups on either side of the cyclopentadiene. We have previously communicated[7a] the preparation of C_2-symmetric ligand **5** and give here a full account of the asymmetric synthesis of this cyclopentadiene and the formation of chiral cyclopentadienyltitanium, -zirconium, and -iron complexes containing this Binap-Cp ligand. In the following paper in this issue, we describe the asymmetric synthesis of the sterically more encumbered BCOCp ligands based on the bicyclo[2.2.2]octane framework and subsequent metalation of these C_2-symmetric ligands.[11]

The potential applications of chiral zirconocene and titanocene dichlorides in catalytic asymmetric reactions motivated our preparation of the Binap-Cp complexes of these metals. In order to establish the ability of this ligand to form complexes of metal carbonyls, we chose to prepare chiral cyclopentadienyliron dicarbonyls since cyclopentadienyliron dicarbonyls have been extensively used in stoichiometric organometallic reactions of potential interest to synthetic chemists.[12]

Scheme I. Synthesis of the Racemic Binaphthyl Diacid 12



Scheme II. Preparation of the Binaphthylcyclopentadiene 5 from the Resolved Diacid 12



Results and Discussion

Ligand Synthesis. We based our synthetic strategy for the synthesis of **5** on the established bisalkylation of cyclopentadiene[1a] by an appropriate binaphthyl moiety. Based on its presence in the literature, 1,1′-binaphthyl-2,2′-dicarboxylic acid (**12**) was chosen to provide one enantiomer of the binaphthyl skeleton (Scheme I). Using a modification of an earlier procedure,[13] we were able to synthesize multigram amounts of racemic diacid **12** in 45% yield from 1-bromo-2-methylnaphthalene (**6**) as compared to the literature yield of 12% in our hands. The key to this improved yield was the $CaCO_3$ hydrolysis of 1-bromo-2-(bromomethyl)naphthalene (**7**)[14] followed by complete oxidation of the alcohol **8** to the acid **9** with potassium permanganate.[15] This oxidation avoided the lower yielding Sommelet procedure cited in the literature.[13] An efficient esterification using $SOCl_2$/methanol transformed the acid **9** directly to its methyl ester **10**.[16] The copper-mediated Ullmann coupling of bromonaphthyl ester **10** followed by saponification of the resulting diester **11** according to the original procedure[13] provided the racemic binaphthyl diacid **12**. Brucine resolution[17] of the diacid **12** was found to be more efficient than the quinine resolution[13a] and afforded either enantiomer of the diacid

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(15) Jones oxidation of alcohol **8** in acetone at −10 °C gave clean 1-bromo-2-naphthaldehyde in 79% yield.

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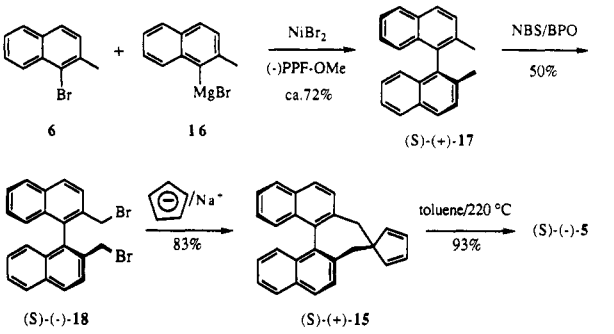
12 in roughly 40% yield for either the (*S*)-12 enantiomer or the (*R*)-12-enantiomer.

As our binaphthyl bisalkylating reagent, we initially utilized the bis(methanesulfonate ester) 14 (Scheme II), which was readily synthesized from resolved 12 in 80% yield by reduction with lithium aluminum hydride[18] followed by esterification with methanesulfonyl chloride and triethylamine.[19] Displacement of the methanesulfonate groups in intermediate (*R*)-14 by cyclopentadiene/sodium hydride at −30 °C rapidly formed the spiro-annulated diene (*R*)-(−)-15 in 96% yield. The desired C_2-symmetric fused cyclopentadiene (*R*)-(+)-5 was produced in 88% yield by the thermolysis[1a,20] of spirodiene (*R*)-(−)-15 in toluene containing a trace amount of anhydrous K_2CO_3 to prevent any acid-catalyzed decomposition of the product diene. Additional care such as using silylated glassware must be taken to prevent acid-promoted decomposition. The thermolysis is conducted under dilute conditions (0.01 M), and the solvent is removed in vacuo at 23 °C to prevent cycloaddition reactions from occurring. We have observed the formation of an undesired and uncharacterized product when the reaction is run at higher concentrations and/or the solvent is removed at elevated temperature. In addition to the C_2-symmetric diene 5, a small amount, ca. 5% of a diene isomer, was also observed in the ^1H NMR spectrum.[20] MM2 calculations using FMNR determine a thermodynamically favorable 8 kcal/mol decrease in energy proceeding from 15 to 5. The related 2,2′-dimethyl-1,1′-binaphthyl (17) has a calculated barrier to racemization of 35 kcal/mol[21] and experimentally is configurationally stable at 290 °C.[22] At higher temperatures, we find decomposition of 5, not racemization, most likely because 5 is an extremely rigid molecule locked into an eight-membered ring. The enantiomeric integrity of 5 was established by examining its ^1H NMR spectrum while titrating with a chiral lanthanide–silver shift reagent.[1a,23] No conversion of enantiomers was seen in the shift study of (*R*)-(+)-5 after (*R*)-(−)-15 was subjected to these standard thermolysis conditions. Although the resolved diacid 12 can be easily converted (four steps, 68% overall yield) to the desired parent ligand 5, the multistep (seven steps, 35% for both antipodes) synthesis and resolution of the diacid is a drawback and led us to develop an improved synthesis of 5 that is also more amenable to large-scale syntheses.

The highly enantioselective coupling of 1-bromo-2-methylnaphthalene (6), with its derived Grignard reagent 16 has been reported to be catalyzed by $NiBr_2$ in the presence of the chiral phosphine PPF-OMe[24] to produce 17 in 94% enantiomeric excess.[25] Although this chiral phosphine can be obtained commercially (Aldrich), its large-scale synthesis is well described and its recovery for reuse in the coupling reaction is routine. Racemic 17 can also be obtained (175 g) in 81% yield by a $NiCl_2$-catalyzed coupling of the bromide 6 and the Grignard reagent 16 in the presence of PPh_3.[26] By taking advantage of this very

Scheme III. Asymmetric Synthesis of the Binaphthylcyclopentadiene 5



easy access to the enantiomerically enriched 1,1′-binaphthyl skeleton, we were able to greatly shorten the synthesis of either enantiomer of the Binap-Cp 5 (Scheme III). We have prepared (*S*)-(+)-17 in 66% yield {$[\alpha]^{23}_D$ +39.3° (*c* 1.0, $CHCl_3$)} and 77% yield {$[\alpha]^{23}_D$ +31.8° (*c* 0.965, $CHCl_3$)}. The optical rotation of 17 in 99% enantiomeric excess is not known for this material but is reported[25] for (*R*)-(−)-17 in 94% enantiomeric excess {$[\alpha]^{23}_D$ −35.6° (*c* 1.0, $CHCl_3$)}. Bromination of the dimethylbinaphthyl 17 with *N*-bromosuccinimide was reported to produce the dibromide 18.[25] We have repeated the bromination reactions successfully on multigram scales to yield 75% of the enantiomerically enriched dibromide (*S*)-(−)-18. This was recrystallized in 66% yield, increasing the enantiomeric purity to 99% optical yield {$[\alpha]^{23}_D$ −162.3° (*c* 1.0, C_6H_6); lit.[27] $[\alpha]^{23}_D$ −159.2° (*c* 1.0, C_6H_6)}. Enantiomerically enriched 17 (75% optical yield) could also be obtained (ca. 50% yield) within a shorter reaction time by conducting the asymmetric coupling at room temperature. After subsequent bromination, this dibromide was recrystallized from hexane to increase the optical purity to 99%. The dibromide (*S*)-(−)-18 proved to be a suitable alkylating reagent, forming the spirodiene (*S*)-(+)-15 in 83% yield upon treatment with freshly cracked cyclopentadiene/sodium hydride. It was worthwhile to further purify the spirodiene with a dioxane/water solution of $CaCO_3$. Traces of organic bromides were thought to be the cause of lower yields in the following thermolysis and were completely removed by a simple hydrolysis workup. The spirodiene 15 so produced was identical in all respects with that produced starting from the brucine-resolved diacid 12.[28] Thermolysis of the spirodiene as before (0.01 M in toluene and anhydrous K_2CO_3 and careful solvent removal) gave (*S*)-(−)-5 in 93% yield, which was confirmed to be enantiomerically pure by using the previous method of chiral shift spectroscopy. The four-step synthesis described here produced (*S*)-(−)-5 in ca. 30% overall yield from commercially available 6.[29] The chiral phosphine needed for the asymmetric catalytic coupling reaction is available as either enantiomer, enabling a facile, large-scale synthesis of both enantiomers of the chiral cyclopentadiene ligand (*S*)-5 or (*R*)-5.

The C_2-symmetrical nature of the Binap-Cp ligand 5 is apparent from its spectroscopic characteristics, exhibiting in the ^1H NMR spectrum only one set of vinyl signals and

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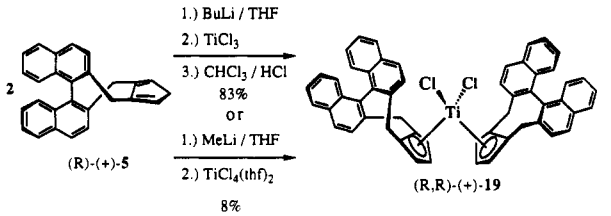
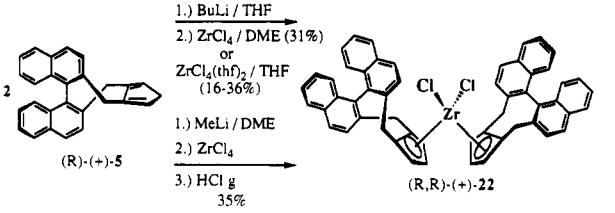
(28) We have been able to prepare *rac*-15 in a large-scale synthesis, isolating up to 31 g of this spirocycle, which we store at −30 °C as the precursor to 5.
(29) The preparation of 6 from 2-methylnaphthalene is also described in the literature: Adams, R.; Binder, L. O. *J. Am. Chem. Soc.* **1941**, *63*, 2773.

Scheme IV. Titanocene Formations with the Binaphthylcyclopentadiene 5

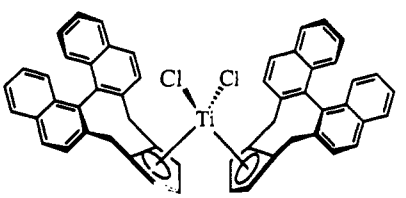


Scheme V. Zirconocene Formations with the Binaphthylcyclopentadiene 5



one signal for the bisallylic methylene hydrogens. In the ^{13}C NMR spectrum, the diene **5** shows the 14 signals expected for the C_2-symmetrical isomer. This ligand is seen by molecular modeling to be less sterically encumbering than the bicyclo[2.2.2]octane-derived cyclopentadiene ligands.[1a,7b,11] The preparation of a more hindered 3,3'-dimethyl-2,2'-binaphthylcyclopentadiene ligand should be possible by ortho methylation of oxazoline derivatives[30] of the diacid **12**, enabling the preparation of chiral cyclopentadienes spanning a range of steric requirements, and will be the subject of future work. Incorporating titanium and zirconium dichlorides and iron carbonyls, we have been successful in forming several new organometallic complexes by using the Binap-Cp **5**.

Metalation: Titanium and Zirconium Complexes. Starting from the racemic Binap-Cp **5**, both the *dl*-**19** and *meso*-**20** bis(Binap-Cp)dichlorotitanium complexes can potentially be formed, whereas using enantiomerically pure

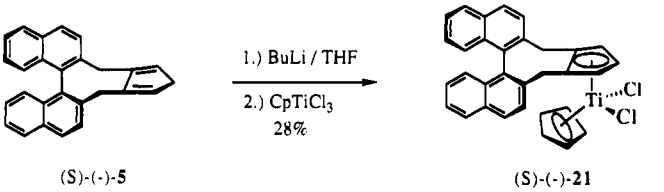


meso - **20**

5 produces only the C_2-symmetrical *d* or *l* metal complex **19**. Thus, treatment of the butyllithium-generated anion of enantiomerically pure (*R*)-(+)-**5** in THF (tetrahydrofuran) at −10 °C with trichlorotitanium–$(thf)_3$[1c,31] followed by heating under reflux for 6 h produced a brown solution. After removal of the ethereal solvent in vacuo and addition of chloroform, 6 M HCl was added to the solution at −78 °C followed by stirring open to air at room temperature for 3 h during which time the solution turned red. After removal of the solvent, the red titanium complex **19** was precipitated from methylene chloride by the addition of hexane (83% yield) (Scheme IV). C_2-Symmetric *dl*-**19** could be precipitated from *meso*-**19** by this method also. Complex **19** was also formed via $TiCl_4(thf)_2$,[3a] but the yields were consistently lower. The spectral and physical data for this dichlorotitanium complex support our formulation of the structure. The two substituted cyclopentadienyl ligands are identical in a C_2-symmetrical titanocene dichloride, and their ^1H NMR spectrum should show one set of cyclopentadienyl resonances; we observe the three expected signals at 6.05, 5.96, and 5.65 ppm. Since the expected ^1H NMR spectrum for *meso*-**20** or a (Binap-Cp)-$TiCl_3$ complex should also show three signals in this spectral region, we had to rely on additional data to confirm our structural assignment. The *meso*-**20** isomer is unlikely to have formed since we started with pure (*R*)-(+)-**5**. This supposition is confirmed since our metallocene **19** exhibits an optical rotation (+707°), a result not consistent with a meso isomer. The mass spectrum, high-resolution mass spectral analysis, and combustion analysis all indicate the presence of a titanium dichloride, precluding the final possibility of the (Binap-Cp)$TiCl_3$.

When an analogous metalation was performed with the racemic Binap-Cp **5**, the initial ^1H NMR spectrum indicated a 50:50 mixture of *dl*-**19** and *meso*-**20** diastereomers, where the resonances for one of the isomers was identical with the pure C_2-symmetrical bis(Binap-Cp)dichlorotitanium complex **19** formed above from enantiomerically pure (*R*)-(+)-**5**. The cyclopentadienyl ring signals in the ^1H NMR spectrum for the *meso*-**20** isomer were found at 6.53, 6.14, and 4.89 ppm distinguishable from the analogous signals of the C_2-symmetric **19** isomer. Although all efforts to grow a single crystal from the enantiomerically pure C_2-symmetrical complex failed, we were able to obtain a single crystal of the racemic C_2-symmetrical complex as a 1:1 hexane adduct. The solid-state structure of this complex was determined by X-ray crystallography and is discussed below.

Treatment of the butyllithium-generated anion of (*S*)-(−)-**5** in THF at 0 °C with cyclopentadienyltrichlorotitanium[1a] produced upon warming to room temperature overnight a deep red solution. After evaporation of the solvent, the red residue was dissolved in a minimal amount of chloroform to which hexane was added to precipitate the (Binap-Cp)cyclopentadienyldichlorotitanium **21**.



(S)-(-)-**5** (S)-(-)-**21**

The enantiomerically pure C_2-symmetrical (*R*,*R*)-(+)-$(Binap\text{-}Cp)_2ZrCl_2$ complex **22** (Scheme V) was synthesized from enantiomerically pure (*R*)-(+)-**5** following an established metalation procedure[32] that proved to be the most consistent of zirconocene formations. Addition of $ZrCl_4$ in DME to a THF solution of the *n*-butyllithium-generated anion of (*R*)-(+)-**5** at −10° followed by stirring at 23 °C overnight and at 50 °C for 2 h produced a light yellow heterogeneous reaction mixture. After solvent removal, the resulting solid was precipitated from methylene chloride upon addition of hexane to give a white powder of the zirconium complex **22** (31% yield). Since the metalation was performed on a single enantiomer of the Binap-Cp **5** ligand, only a C_2-symmetric isomer could be formed. The spectral characteristics of the product were found to be

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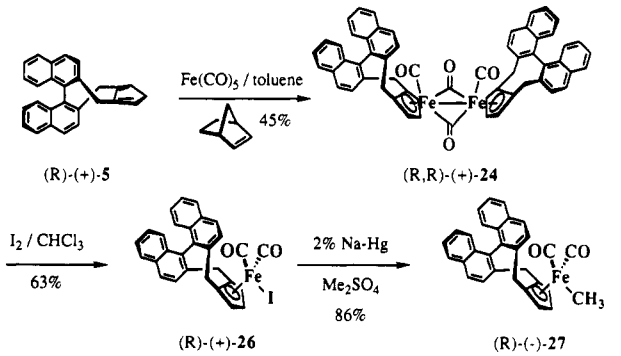
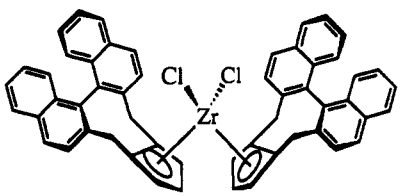
Scheme VI. Iron Carbonyl Formations with the Binaphthylcyclopentadiene 5



very similar to the C_2-symmetric titanocene complex **19**. The resonances for the cyclopentadienyl hydrogens appeared as doublets of doublets at 6.00, 5.83, and 5.63 ppm in the ^{1}H NMR spectrum. The optical rotation of this complex was +345°, confirming the formation of the C_2-symmetric zirconocene **22**.

When an analogous metalation was conducted by using the racemic Binap-Cp **5**, a mixture of *rac*-C_2-**22** and *meso*-**23** isomers was formed in a 46:54 ratio, respectively. The minor isomer was identified as *rac*-C_2-**22** since it exhibited identical signals in the ^{1}H NMR spectrum as the enantiomerically pure C_2-symmetrical isomer formed from (*R*)-(+)-**5**. Again the cyclopentadienyl ring ^{1}H NMR resonances for the *meso*-**23** isomer, 6.29, 6.08, and 4.91 ppm, were well-resolved from the analogous signals of the C_2-symmetric **22** isomer. The *dl*-**22** isomer could be separated by simply precipitating it from *meso*-**23** with CH_2Cl_2/hexane and/or recrystallization from 1-chlorobutane. The meso metal complex **23** was isolated either by washing out C_2-symmetric isomer *dl*-**22** with hot 1-chlorobutane or by recrystallization from 2% 1,2-dichloroethane in 1-chlorobutane. Using $ZrCl_4(thf)_2$[33] as the source of zirconium for these metalations in THF gave inconsistent yields (16–36%) and was not as clean as Petersen's $ZrCl_4$/DME preparation.



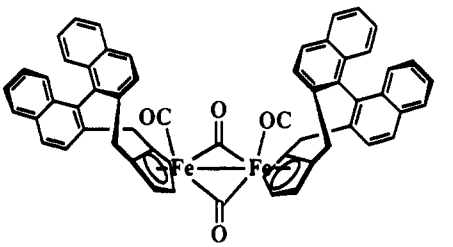
meso - **23**

When the zirconocene complex was synthesized from the racemic Binap-Cp **5** following Paquette's procedure,[31c] which requires heating the DME reaction mixture under reflux for 72 h, the *rac*-C_2-**22**/*meso*-**23** ratio was 75:25, respectively, possibly indicating lability of the cyclopentadienyl ligands under these forcing conditions.

In addition to the group 4 metallocene dichlorides, we have been able to prepare the (*R*)-(+)-(Binap-Cp)iodoiron dicarbonyl **26** and (*R*)-(−)-(Binap-Cp)methyliron dicarbonyl **27** complexes from the (*R*,*R*)-(+)-(Binap-Cp)Fe(CO)$_2$ dimer **24** (Scheme VI). Heating a mixture of (*R*)-(+)-**5**, norbornene, and $Fe(CO)_5$ in toluene for 40 h gave after filtration and solvent removal in vacuo a dark purple residue.[6b] Purification by alumina(I) chromatography gave dark purple crystals of the dimer **24** in 45% yield. When this same reaction was run with the racemic Binap-Cp **5**, a 72:28 mixture of C_2-**24**:C_s-**25** isomers was observed in the ^{1}H NMR spectrum.

Table I. Summary of Crystallographic Data for (Binap-Cp)$_2$TiCl$_2$ (19)

empirical formula	$C_{54}H_{38}TiCl_2 \cdot C_6H_{14}$
fw	891.877
cryst size, mm	0.02 × 0.15 × 0.15
cryst color	light red
T, K	293
space group	*C*2/*c* (No. 15)
cell dimension	25 rflns, 25–30° (2θ)
a, Å	29.611 (9)
b, Å	10.902 (5)
c, Å	15.868 (5)
β, deg	108.41 (2)
V, Å^3	4862.5 (2.6)
Z	4
d(calc), g/cm^3	1.218
radiation	Cu Kα (λ = 1.540 598 Å)
scan ratio, 2θ/ω	1.42
scan limit, deg	$5 \le 2\theta \le 110$
scan speed, deg min^{-1}	32
data collected	±31,±12,±17
no. of rflns collected	12 269
no. of unique intens	2581
R_{int}	5.6
abs cor (emp on F^2)	0.7095–1.2948
structure soln	direct methods (TEXSAN)
refinement	least squares
no. of variables	348
R	0.045
R_w	0.057
GOF	1.98
max param shift/esd	1.15
max resid e density, e Å^{-3}	0.24 (−0.21)



meso - **25**

The direct reduction of the iron dimer **24** with sodium amalgam, sodium sand, or sodium naphthalide followed by addition of dimethyl sulfate or iodomethane did not yield the expected (Binap-Cp)methyliron dicarbonyl **27**[34] but rather provided methylated Binap-Cp in 16–50% yield. This result indicated that the metal–ligand dissociation was competitive with metal–metal reductive bond cleavage. This difficulty was overcome by initially reacting the iron dimer **24** with iodine,[35] affording a 63% yield of the (Binap-Cp)iodoiron dicarbonyl **26**, followed by sodium amalgam reduction of the iodoiron species and trapping the iron anion with dimethyl sulfate. Using this two-step procedure, we could synthesize the (Binap-Cp)methyliron dicarbonyl **27** in 54% yield from the iron dimer **24**.[36]

X-ray Crystallographic Structure of 19. In an effort to gain further understanding of the chirality produced around metals coordinated to the Binap-Cp ligand, we sought to determine the solid-state structure of the (Bi-

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(36) Application of this complex in asymmetric migratory insertions has been studied. Colletti, S. L.; Halterman, R. L. Submitted for publication in *Organometallics*.

Table II. Intramolecular Distances (Å) for (Binap-Cp)$_2$TiCl$_2$ (19)

atom	atom	distance	atom	atom	distance
Ti	Cl	2.328 (1)	C(11)	C(12)	1.377 (5)
Ti	C(22)	2.509 (3)	C(11)	C(20)	1.431 (5)
Ti	C(23)	2.365 (3)	C(12)	C(13)	1.400 (5)
Ti	C(24)	2.330 (4)	C(12)	C(27)	1.515 (5)
Ti	C(25)	2.373 (4)	C(13)	C(14)	1.360 (5)
Ti	C(26)	2.477 (3)	C(14)	C(15)	1.410 (5)
C(1)	C(2)	1.375 (5)	C(15)	C(16)	1.406 (6)
C(1)	C(10)	1.428 (5)	C(15)	C(20)	1.410 (5)
C(1)	C(11)	1.488 (5)	C(16)	C(17)	1.356 (6)
C(2)	C(3)	1.412 (5)	C(17)	C(18)	1.389 (6)
C(2)	C(21)	1.516 (5)	C(18)	C(19)	1.365 (5)
C(3)	C(4)	1.366 (5)	C(19)	C(20)	1.419 (5)
C(4)	C(5)	1.406 (6)	C(21)	C(22)	1.500 (5)
C(5)	C(6)	1.433 (6)	C(22)	C(23)	1.400 (5)
C(5)	C(10)	1.416 (5)	C(22)	C(26)	1.417 (5)
C(6)	C(7)	1.341 (7)	C(23)	C(24)	1.406 (5)
C(7)	C(8)	1.396 (7)	C(24)	C(25)	1.386 (5)
C(8)	C(9)	1.368 (6)	C(25)	C(26)	1.424 (5)
C(9)	C(10)	1.412 (5)	C(26)	C(27)	1.503 (5)

Table III. Selected Intramolecular Bond Angles (deg) for (Binap-Cp)$_2$TiCl$_2$ (19)

atom	atom	atom	angle	atom	atom	atom	angle
Cl	Ti	Cl	95.88 (6)	C(22)	Ti	C(22)	165.1 (2)
C(23)	Ti	C(23)	99.3 (2)	C(24)	Ti	C(24)	77.6 (2)
C(25)	Ti	C(25)	142.9 (2)	C(26)	Ti	C(26)	171.2 (2)
C(1)	C(2)	C(3)	120.2 (3)	C(2)	C(3)	C(4)	120.6 (4)
C(3)	C(4)	C(5)	120.7 (4)	C(4)	C(5)	C(6)	122.0 (4)
C(5)	C(6)	C(7)	120.6 (5)	C(6)	C(7)	C(8)	121.0 (4)
C(7)	C(8)	C(9)	120.5 (5)	C(8)	C(9)	C(10)	120.4 (4)
C(1)	C(10)	C(9)	122.0 (4)	C(4)	C(5)	C(10)	119.4 (4)
C(1)	C(10)	C(5)	119.0 (4)	C(1)	C(11)	C(12)	120.6 (3)
C(1)	C(11)	C(20)	119.6 (3)	C(1)	C(2)	C(21)	120.5 (3)
C(2)	C(21)	C(22)	110.8 (3)	C(21)	C(22)	C(23)	125.7 (3)
C(21)	C(22)	C(26)	126.9 (3)	C(22)	C(23)	C(24)	109.3 (3)
C(23)	C(24)	C(25)	107.6 (3)	C(24)	C(25)	C(26)	108.6 (3)
C(25)	C(26)	C(27)	123.8 (3)				

nap-Cp)$_2$TiCl$_2$ complex **19** by X-ray diffraction of a single crystal. Unfortunately, we were unable to obtain single crystals of the enantiomerically pure titanocene complex **19**. Cooling a ca. 90:10 mixture of enantiomers of **19**, however, in 98:2 hexane:methylene chloride to −30 °C for several days did afford a small amount of red plates as single crystals. The crystal structure of these plates was solved and indicated the crystal to be comprised of racemic **19** and a disordered molecule of hexane (C_2/c space group; see Table I for a summary of crystallographic data). Thus, the minor amount of racemate (ca. 20%) preferentially crystallized in the presence of the major enantiomer.

The solid-state structure of one enantiomer of **19** is shown in Figure 2. Bond distances, bond angles, and atomic coordinates are listed in Tables II, III, and IV, respectively. The numbered monoview of **19** shown in Figure 2 is along the crystallographically imposed C_2 axis; the stereoview is approximately perpendicular to the Cp–Ti–Cp plane and accentuates the chiral cavity around the metal atom. The titanium atom is not located perpendicular above the Cp centroid but rather is shifted away from the substituted carbons (2.509 and 2.477 Å) and toward the unsubstituted carbons (2.365, 2.330, and 2.373 Å). The sterically asymmetric environment around the metal arises from the proximity of the naphthyl ring to one side of the titanium atom, Ti–C13 distance = 4.337 Å, and C24–Ti–C13 angle = 113.0°, versus, Ti–C21 distance = 3.656 Å and C24–Ti–C21 angle = 73.4°, the other side of the metal. The important parameter here is the much larger angle from the Cp carbon C24 through Ti to the naphthyl carbon C13 versus the acute angle to the methylene carbon C21, indicating the extension of the naphthyl ring over the titanium atom.

Table IV. Positional Parameters and *B*(eq) Values (Å^2) for (Binap-Cp)$_2$TiCl$_2$ (19)

atom	*x*	*y*	*z*	*B*(eq)
Ti	0	−0.00266 (7)	$^1/_4$	3.38 (4)
Cl	0.02394 (3)	0.14039 (8)	0.16378 (5)	4.11 (4)
C(1)	0.1371 (1)	0.1380 (3)	0.5478 (2)	4.0 (1)
C(2)	0.1121 (1)	0.0322 (3)	0.5495 (2)	3.8 (1)
C(3)	0.1340 (1)	−0.0658 (4)	0.6056 (2)	4.8 (2)
C(4)	0.1803 (2)	−0.0571 (4)	0.6588 (3)	5.5 (2)
C(5)	0.2074 (1)	0.0481 (4)	0.6566 (2)	5.2 (2)
C(6)	0.2568 (2)	0.0568 (5)	0.7072 (3)	7.5 (2)
C(7)	0.2824 (2)	0.1551 (6)	0.6995 (4)	8.6 (3)
C(8)	0.2618 (2)	0.2511 (5)	0.6420 (3)	7.5 (2)
C(9)	0.2144 (1)	0.2485 (4)	0.5942 (3)	5.7 (2)
C(10)	0.1861 (1)	0.1465 (3)	0.5997 (2)	4.5 (2)
C(11)	0.1126 (1)	0.2423 (3)	0.4914 (2)	3.9 (1)
C(12)	0.1011 (1)	0.2364 (3)	0.4003 (2)	4.0 (1)
C(13)	0.0767 (1)	0.3340 (4)	0.3481 (2)	5.0 (2)
C(14)	0.0633 (2)	0.4343 (4)	0.3853 (3)	5.7 (2)
C(15)	0.0734 (1)	0.4433 (3)	0.4781 (3)	5.2 (2)
C(16)	0.0594 (2)	0.5452 (4)	0.5181 (3)	6.8 (2)
C(17)	0.0697 (2)	0.5513 (4)	0.6075 (3)	7.9 (3)
C(18)	0.0941 (2)	0.4569 (4)	0.6618 (3)	6.7 (2)
C(19)	0.1083 (1)	0.3568 (3)	0.6249 (2)	5.2 (2)
C(20)	0.0985 (1)	0.3467 (3)	0.5317 (2)	4.2 (2)
C(21)	0.0613 (1)	0.0178 (3)	0.4889 (2)	4.1 (1)
C(22)	0.0603 (1)	−0.0326 (3)	0.4004 (2)	3.9 (1)
C(23)	0.0390 (1)	−0.1430 (3)	0.3632 (2)	4.3 (2)
C(24)	0.0518 (1)	−0.1692 (3)	0.2869 (2)	4.5 (2)
C(25)	0.0790 (1)	−0.0720 (3)	0.2737 (2)	4.2 (2)
C(26)	0.0844 (1)	0.0148 (3)	0.3432 (2)	3.9 (1)
C(27)	0.1153 (1)	0.1270 (3)	0.3556 (2)	4.3 (2)

Summary. The efficient synthesis of either enantiomer of the C_2-symmetrical binaphthyl annulated cyclopentadiene ligand **5** is possible by using a catalytic asymmetric nickel-coupling procedure. The formation of the enantiomerically pure C_2-symmetric titanocene **19** and zirconocene **22** dichlorides from enantiomerically pure **5** is possible. The racemic C_2-symmetrical **19**/**22** and *meso*-**20**/**23** metallocenes are available from racemic **5**. In the case of the racemic (Binap-Cp)$_2$TiCl$_2$ complex, the X-ray crystal structure was obtained and showed the C_2-symmetric cleft imposed around the metal atom by the chiral ligands. The preparation of the chiral cyclopentadienyliron dicarbonyls **26** and **27** was also demonstrated.

Experimental Section

General Methods. Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Copper bronze was purified by the literature preparation of Adams and Kleiderer.[37] Sodium amalgam was prepared as 2% by weight following Tischler's procedure and was stored in a drybox at room temperature.[38] THF, ether, toluene, DME, and hexane were distilled from sodium benzophenone ketyl. Other reaction, chromatographic, and recrystallizing solvents were purified and/or dried by standard methods.[39] All reactions involving air-sensitive or moisture-sensitive species were performed under argon or nitrogen atmospheres by utilizing standard Schlenk techniques or in a Vacuum Atmospheres Dri-Box, respectively. Routine solvent removal was performed with Büchi RE-111 rotary evaporators using water aspiration and warm water baths. Solvent removal in vacuo was accomplished on a vacuum line at <0.001 mmHg at ambient temperature. Abbreviations: DME, dimethoxyethane; THF, tetrahydrofuran; NBS, *N*-bromosuccinate.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-400 or JEOL JNM GSX-270 instrument. Data are reported

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(39) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, U.K., 1980.

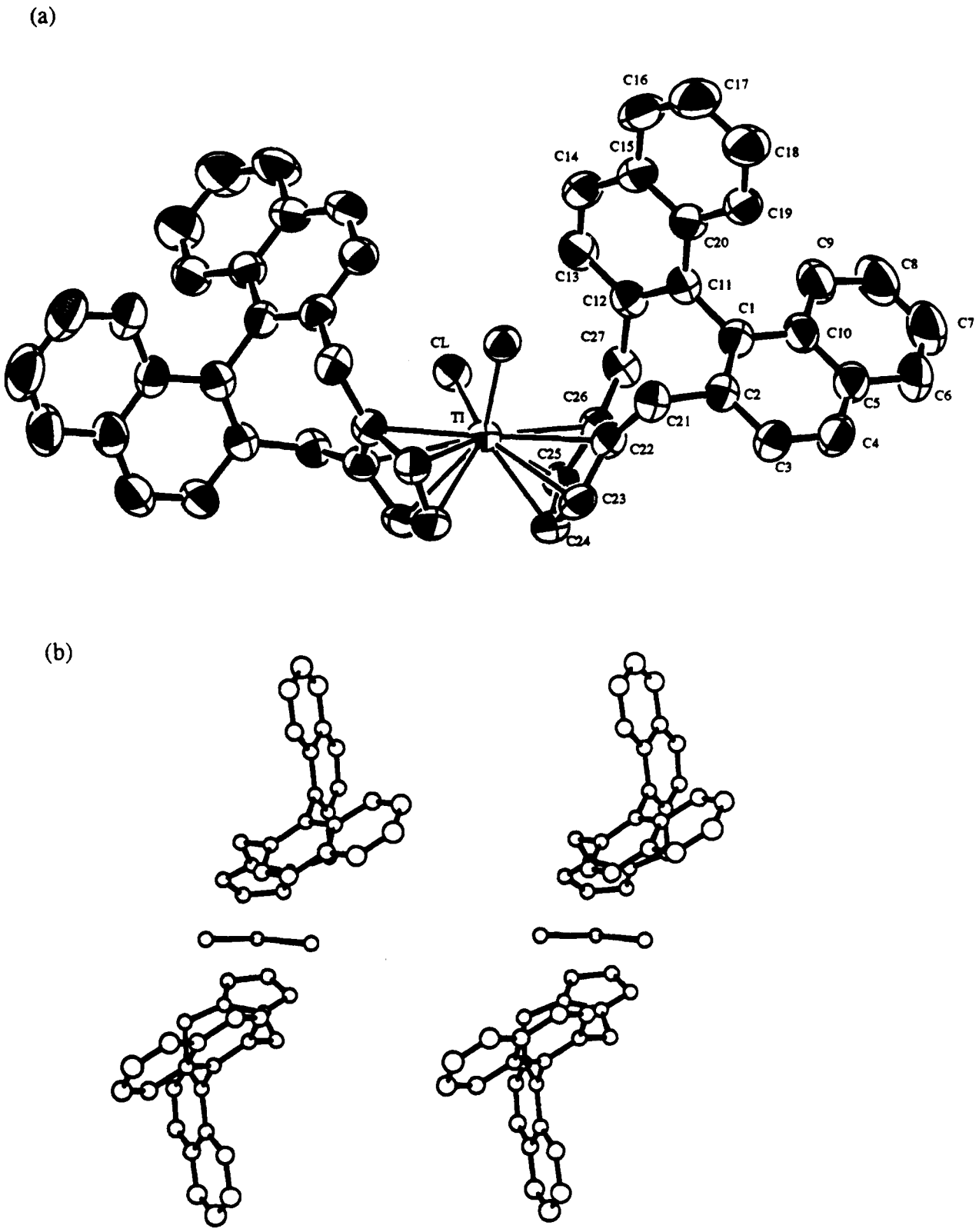

Figure 2. (a) ORTEP view of bis(Binap-Cp)$TiCl_2$ **19** showing 30% probability ellipsoids. (b) Stereoview of **19**.

as follows: chemical shifts (δ scale) in parts per million (ppm) relative to residual solvent peaks (multiplicity, coupling constants in hertz, number of hydrogens). For ^1H NMR spectra, the peaks due to residual $CHCl_3$, C_6H_6, or DMSO are listed at 7.24, 7.15, or 2.49 ppm, respectively, and for ^{13}C NMR spectra, the central peaks of the $CDCl_3$, C_6D_6, or DMSO-d_6 multiplets are assigned chemical shifts of 77.0, 128.0, or 39.5 ppm, respectively. Unless otherwise noted, multiplicities and compound ratios are deduced from the electronic integration by the XL-400 or the GSX-270. Infrared spectra were obtained on a Perkin-Elmer 1800 FT-IR or a Perkin-Elmer 1310 infrared spectrometer and were referenced to carbon dioxide or polystyrene, respectively. Only characteristic and/or strong signals are reported. Optical rotations were obtained on a Rudolph Research Autopol III polarimeter at 589 nm. Low-resolution mass spectra (reported as m/z (relative intensity at 40 or 70 eV)) and high-resolution mass spectra were recorded on a Finnegan MAT-90 instrument. Melting points were determined in open Pyrex capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Galbraith Analytical Laboratories (Knoxville, TN),

Schwarzkopf Microanalytical Laboratories (Woodside, NY), and Desert Analytics (Tucson, AZ).

Preparative column chromatography was performed on flash silica gel (E. Merck Reagents silica gel 60, 230–400-mesh ASTM) or neutral alumina (E. Merck Reagents activated alumina F-20, 80–200 mesh). Insoluble crude materials were applied to columns with a minimal amount of CH_2Cl_2. Preparative thin-layer chromatography was accomplished by using 500-μm E. Merck silica gel 60 F-254.

1-Bromo-2-(bromomethyl)naphthalene (7). 1-Bromo-2-methylnaphthalene (6; 80.8 g, 0.365 mol) was dissolved in dry CCl_4 (456 mL), and dry recrystallized NBS (65 g, 0.365 mol) was added under a steady purge of nitrogen. Benzoyl peroxide (230 mg, 0.950 mmol) was then added under a purge of nitrogen, and the reaction mixture was heated at reflux for 3 h while being irradiated with a standard 100-W bulb. The suspension of succinimide that formed was then removed via suction filtration of the hot solution. The precipitate was partitioned between hot CCl_4 and hot water. The filtrate and all organic extracts were combined and concentrated, yielding the white crystalline dibromide 7 (97.6 g, 89%), mp 100 °C (lit.[13b] mp 107–109 °C), which was sufficiently pure for the following hydrolysis. The pure dibromide obtained was spectroscopically and physically identical with that in the literature.[13b]

1-Bromo-2-(hydroxymethyl)naphthalene (8). $CaCO_3$ (116 g, 1.16 mol) and water (650 mL) were combined and heated as reflux. To this boiling solution was added 7 (68 g, 0.228 mol) in 1,4-dioxane (650 mL), and the reaction mixture was heated at reflux for 10 h. The solution was cooled to room temperature and the dioxane evaporated. CH_2Cl_2 (1 L) was added and, then in a separatory funnel, 2 N HCl was carefully added until both phases were homogeneous. The organic phase was separated and washed with $NaHCO_3$ (aqueous), dried over anhydrous $MgSO_4$, and concentrated. The white crystalline alcohol 8 obtained (50 g, 93%), mp 100 °C (lit.[14] mp 101–102 °C), was sufficiently pure for the following oxidation. The pure alcohol obtained was spectroscopically and physically identical with that in the literature.[14]

1-Bromo-2-naphthoic Acid (9). A hot solution of $KMnO_4$ (108.4 g, 0.686 mol) in a mixture of H_2O (235 mL) and acetone (1.6 L) was added over a period of 30 min to a refluxing mixture of 8 (47 g, 0.198 mol) in acetone (626 mL). The reaction mixture was then heated at reflux for 5 h during which the color changed from purple to brown. After cooling to room temperature, the residual MnO_2 was suction filtered on a bed of celite and washed with ether. The filtrate was evaporated, and the residue was partitioned between aqueous 3 M NaOH and ether. The aqueous extracts were combined, cooled in an ice bath at 0 °C, and carefully neutralized with concentrated HCl. The precipitated organic acid was then extracted back into ether and the organic phase dried over anhydrous Na_2SO_4. The product was concentrated, yielding the pure white crystalline acid 9 (35.4 g, 71%), mp 189–190 °C (lit.[13b] mp 189–190 °C). The acid obtained was spectroscopically and physically identical with that in the literature.[13b]

Methyl 1-Bromo-2-naphthoate (10). Freshly distilled $SOCl_2$ (32.7 mL, 0.448 mol) was added dropwise via an addition funnel to dry methanol (182 mL) at −30 °C. 9 (28.0 g, 0.112 mol) was dissolved in dry methanol (182 mL) and added to the $SOCl_2$/CH_3OH mixture in four portions over a period of 1 h at −30 °C. The reaction mixture was then slowly warmed to 35–40 °C for 2 h, after which it was cooled to room temperature and the methanol evaporated. The crude residue was purified by flash chromatography (SiO_2, 1:1 CH_2Cl_2/pentane), yielding the white crystalline ester 10 (26.6 g, 90%), mp 58 °C (lit.[13b] mp 53–55 °C, lit.[40] mp 58–59 °C). The ester obtained was spectroscopically and physically identical with that in the literature.[13b]

Dimethyl 1,1′-Binaphthyl-2,2′-dicarboxylate (11). Freshly activated and dry copper bronze (6.5 g, 97.68 mmol) was added to an oven-dried flask equipped with a condenser. 10 (3.32 g, 12.52 mmol) was dissolved in distilled DMF (50 mL), and the solution was transferred via cannula to the copper bronze. The reaction mixture was gently heated at 160 °C for 15 h and then cooled to room temperature, after which it was filtered through a glass frit. The residue was washed thoroughly with hot toluene, and the filtrate was extracted with 2 N HCl, H_2O, and brine, dried over anhydrous $MgSO_4$, and evaporated. The crude product was recrystallized from methanol, yielding colorless plates of 11 (1.97 g, 85%), mp 154 °C (lit.[13b] mp 157–158 °C, (lit.[13a] mp 158 °C). The diester obtained was spectroscopically and physically identical with that in the literature.[13b]

1,1′-Binaphthyl-2,2′-dicarboxylic Acid (12). 11 (16.0 g, 0.043 mol) was added to a warmed homogeneous solution of KOH (80.0 g, 1.43 mol) in distilled methanol (400 mL). The reaction mixture was then heated at reflux for 15 h. The solvent was evaporated, and water was continuously added to replace the volume. The basic aqueous solution was then cooled to 0 °C and carefully neutralized with concentrated HCl. After precipitation of the organic diacid, the product was suction filtered, washed with water, and vacuum dried to yield the white crystalline diacid 12 (14.8 g, 100%), mp 272 °C (lit.[13b] mp 272–274 °C). The diacid obtained was spectroscopically and physically identical with that in the literature.[13b]

Resolution of (*R*,*S*)-1,1′-Binaphthyl-2,2′-dicarboxylic Acid (12). The racemic diacid was recrystallized from acetone and then heated overnight under vacuum at 90 °C to remove residual acetone. The desolvated diacid 12 (mp 272 °C; 1.45 g, 4.24 mmol) was dissolved in acetone (22 mL) and added to a refluxing mixture of anhydrous brucine (1.67 g, 4.24 mmol) in acetone (48 mL), at which point crystals began to form. The mixture was allowed to stand at −4 °C overnight. The crystals were collected on a glass frit via suction filtration and washed with acetone. The crystalline material was air dried, $[\alpha]^{23}_D$ +150° (*c* 0.500, $CHCl_3$) (lit.[17] $[\alpha]^{25}_D$ +125° (*c* 0.500, $CHCl_3$)) and then dissolved in MeOH (48 mL), refluxed, and diluted with hot acetone (24 mL). Upon cooling, needles began to form. The crystals were filtered, washed with acetone, and dried for 3 h at 23 °C/0.1 mmHg. The (+)-brucine salt (1.27 g, 41%), mp 218 °C (lit.[17] mp 211–214 °C), $[\alpha]^{23}_D$ +226° (*c* 0.500, $CHCl_3$) (lit.[17] $[\alpha]^{25}_D$ +200° (*c* 0.500, $CHCl_3$)), was partitioned between ether and 6 M HCl. The aqueous phase was back-extracted twice with ether, and then all organic extracts were combined and washed with 1 N HCl and brine and dried over anhydrous sodium sulfate. After concentration of the product, crystalline (*R*)-(+)-12 was dried under vacuum at 90 °C (550 mg, 38%), $[\alpha]^{23}_D$ +230 ± 30° (*c* 1.0, 0.1 M KOH) (lit.[17] $[\alpha]^{25}_{546}$ +127° (*c* 1.0, 0.1 M NaOH); lit.[13a] $[\alpha]^{20}_{546}$ +124.2°, $[\alpha]^{20}_{579}$ +107.2° (*c* 1.115, approx. 0.1 N NaOH)). The mother liquors that contained the (−)-brucine salt was combined and evaporated. The crystalline material was desalted as before and then dissolved in ether (6 mL) with heating. The solution was cooled and filtered, and the mother liquor was concentrated to yield white crystals of (*S*)-(−)-12 (623 mg, 43%).

(*R*)-(+)-2,2′-Bis(hydroxymethyl)-1,1′-binaphthyl (13). A suspension of $LiAlH_4$ (755 mg, 19.86 mmol) in THF (21 mL) was warmed to 55 °C and stirred for 30 min under nitrogen. A solution of (*R*)-(+)-12 (3.40 g, 9.93 mmol) in THF (15 mL) was added dropwise via syringe. The reaction mixture was then stirred at 40 °C overnight. The reaction mixture was then cooled to 0 °C, carefully treated with H_2O, 10% NaOH, and H_2O, and then filtered over a moistened bed of celite. The precipitated salts were washed with ether, and the organic liquor was extracted with water and brine and dried over anhydrous $MgSO_4$. The product was concentrated to yield the white crystalline diol 13 (2.83 g, 91%), which was not purified, mp 168–170 °C (lit.[13a] mp 167–168 °C), $[\alpha]^{23}_D$ +65.5° (*c* 0.950, acetone) (lit.[13a] $[\alpha]^{21}_{546}$ +83.1°, $[\alpha]^{21}_{579}$ +72.2° (*c* 1.1495, acetone): ^1H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, J = 8.5 Hz, 2 H), 8.01 (d, J = 8.5 Hz, 2 H), 7.89 (d, J = 8.5 Hz, 2 H), 7.46 (dd, J = 7.5, 7.5 Hz, 2 H), 7.26 (dd, J = 7.5, 7.5 Hz, 2 H), 6.87 (d, J = 8.5 Hz, 2 H), 4.14 (d, J = 14.0 Hz, 2 H), 4.05 (d, J = 14.0 Hz, 2 H), 3.42 (s, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 60.70, 125.00, 125.34, 125.62, 126.46, 127.88, 128.18, 131.57, 131.84, 132.41, 138.25; IR (KBr) 3239, 3048, 2912, 1509, 1466, 1360, 1232, 1015, 979, 817, 755, 730, 542 cm^{-1}; MS, *m*/*z* (EI, 70 eV, rel intensity) 314 (M^+, 2.5%), 296 (40), 277 (100), 252 (28).

(*R*)-2,2′-Bis[(methylsulfonyl)methyl]-1,1′-binaphthyl (14). Distilled triethylamine (2.77 mL, 19.85 mmol) was added via syringe to a solution of dry (*R*)-(+)-13 (2.60 g, 8.27 mmol) in CH_2Cl_2 (33 mL) at −30 °C with stirring. A solution of distilled methanesulfonyl chloride (1.41 mL, 18.19 mmol) in CH_2CL_2 (8.3 mL) was added dropwise to the mixture at −30 °C. The reaction

(40) Bergmann, E. D.; Szmuskovicz, J. *J. Am. Chem Soc.* **1951**, *73*, 5153.

mixture was stirred for 10 min at −30 °C and warmed to room temperature. The reaction mixture was immediately worked up with 1 N HCl, H_2O, and brine, and the organic extracts were dried over anhydrous $MgSO_4$. Concentration of the product yielded white crystals of the pure dimesylate **14** (3.42 g, 88%), mp 97–100 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 2 H), 7.96 (d, J = 8.5 Hz, 2 H), 7.77 (d, J = 8.5 Hz, 2 H), 7.53 (dd, J = 7.5, 7.5 Hz, 2 H), 7.30 (dd, J = 7.5, 7.5 Hz, 2 H), 7.05 (d, J = 8.5 Hz, 2 H), 4.93 (d, J = 11.0 Hz, 2 H), 4.82 (d, J = 11.0 Hz, 2 H), 2.55 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.80, 69.68, 126.23, 126.64, 127.23, 127.30, 128.31, 129.49, 130.08, 132.56, 133.67, 134.87; MS, m/z (EI, 70 eV, rel intensity) 470 (M^+, 7%), 277 (100), 165 (79), 105 (83), 91 (70).

(*R*)-(−)-1-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-2,4-diene (15) from 14. NaH (60%) in mineral oil (740 mg, 18.40 mmol) was weighed into a dry round-bottom flask, deoiled by using dry pentane, and pumped dry to a gray powder, and THF (51 mL) was added. Freshly cracked cyclopentadiene (0.702 mL, 8.50 mmol) was syringed slowly to the NaH/THF slurry at room temperature. After complete formation of the anion, dry (*R*)-**14** (3.33 g, 7.08 mmol) in THF (17 mL) was added all at once to the pink slurry at −30 °C. The reaction mixture was allowed to stir at −30 °C for 6 h and was then quenched at −30 °C in a separatory funnel with ethyl acetate and water. The organic phase was extracted with saturated NH_4Cl, H_2O, and brine, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by flash chromatography (SiO_2, petroleum ether), leaving white crystalline **15** (2.34 g, 96%), mp 163–165 °C, $[\alpha]^{23}_D$ −219° (*c* 0.100, $CHCl_3$): ^{1}H NMR (400 MHz, C_6D_6) δ 7.75–7.80 (m, 4 H), 7.62 (d, J = 8.5 Hz, 2 H), 7.32 (d, J = 8.5 Hz, 2 H), 7.24 (dd, J = 7.5, 7.5 Hz, 2 H), 7.03 (dd, J = 7.5, 7.5 Hz, 2 H), 6.27 (d, J = 4.0 Hz, 2 H), 6.21 (d, J = 4.0 Hz, 2 H), 2.87 (d, J = 13.0 Hz, 2 H), 2.08 (d, J = 13.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.17, 67.91 (sp^3 quaternary), 124.97, 125.71, 127.15, 127.47, 128.22, 128.34, 128.69, 131.89, 132.80, 134.05, 137.56, 143.26; IR (neat film) 3060, 2940, 1620, 1600, 1510, 1450, 1370, 1260, 1030, 820, 750, 720 cm^{-1}; MS, m/z (EI, 70 eV, rel intensity) 344 (M^+, 68%), 279 (45), 84 (100). HRMS (EI, 70 eV) Calcd for $C_{27}H_{20}$: 344.1565. Found: 344.1567.

(*S*)-(+)-1-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-2,4-diene (15) from the Dibromide 18. This procedure was conducted similarly to the method described using **14** as the bisalkylating agent: Freshly distilled cyclopentadiene (2.35 mL, 0.0285 mol) was added slowly via syringe to a round-bottom flask containing a slurry of dry deoiled NaH (60% in mineral oil) (2.5 g, 0.0616 mol) in THF (169 mL) at 23 °C. (*S*)-(−)-2,2′-Bis(bromomethyl)-1,1′-binaphthyl (**18**, 10.39 g, 0.0237 mol) in THF (56 mL) was added all at once to the pink anion slurry at −30 °C. The reaction was allowed to stir at −30 °C for 2 h, after which it was quenched with ethyl acetate and water in a separatory funnel. The organic phase was worked up by using saturated NH_4Cl, H_2O, and brine, and the organic extracts were dried over anhydrous Na_2SO_4. After evaporation of organic solvents, the crude product was purified by flash chromatography (SiO_2, petroleum ether), yielding white crystalline **15** (6.8 g, 83%).

Purification of 15 with $CaCO_3$.[41] Crude (*S*)-(+)-**15** (0.440 g, 1.28 mmol) in 1,4-dioxane (6 mL) was added to $CaCO_3$ (13 mg, 0.1277 mmol) in H_2O (6 mL), and the mixture was heated at 100 °C for 4–6 h. The solution was then cooled and transferred to a separatory funnel where it was neutralized with 1 N HCl and extracted into CH_2Cl_2. The organic extracts were washed with $NaHCO_3$ and H_2O, dried over anhydrous sodium sulfate, and concentrated. The crude material was then chromatographed (SiO_2, petroleum ether), yielding white crystalline **15** (0.350 g, 80%), $[\alpha]^{23}_D$ +213° (*c* 0.185, $CHCl_3$). (*S*)-(+)-**15** was spectroscopically and physically identical with its (*R*)-(−)-**15** antipode.

(*S*)-(−)-2,3-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-diene (5). Dry (*S*)-(+)-**15** (1.50 g, 4.35 mmol) and anhydrous K_2CO_3 (60 mg, 0.436 mmol) were combined into a resealable vacuum thermolysis tube (washed with HMDS and oven dried at 150 °C overnight), and distilled toluene (435 mL) was added. This 0.01 M solution was bubbled through with nitrogen and then degassed with three successive freeze–pump–thaw cycles on a vacuum line. Upon the final thaw, the mixture was not purged, and the sealed vessel was heated under static vacuum at 220 °C for 30 h. The reaction vessel should be completely submerged into the oil bath to ensure that the temperature of the toluene is 220 °C. *Caution! One explosion (most likely due to weakening of glassware by drastic changes in temperature) has been experienced in this routine preparation (ca. 2.0 g). It is advised to conduct temperature changes from liquid nitrogen to 220 °C slowly and to follow safety precautions by caging the reaction vessel within two blast shields via aluminum rods.* The reaction mixture was then cooled to room temperature and freed of solvent at 23 °C/0.1 mmHg. Chromatographic purification (SiO_2, petroleum ether) afforded the white crystalline diene **5** (1.39 g, 93%), mp 80 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 4 H), 7.53 (d, J = 8.5 Hz, 2 H), 7.43 (ddd, J = 8.0, 6.0, 2.5 Hz, 2 H), 7.27 (m, 4 H), 6.11 (s, 2 H), 3.66 (d, J = 14.0 Hz, 2 H), 3.23 (dd, J = 14.0, 1.5 Hz, 2 H), 2.83 (d, J = 1.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.96 (2 C), 38.79 (1 C), 125.14, 126.04, 126.80, 127.97, 128.01, 128.20, 128.34, 132.29, 132.42, 135.29, 136.84, 144.69; IR (neat film) 3060, 2900, 1620, 1600, 1510, 1440, 1370, 1260, 1030, 960, 910, 820, 740 cm^{-1}; MS, m/z (EI, 70 eV, rel intensity) 344 (M^+, 100%), 279 (70), 265 (36). HRMS (EI, 70 eV) Calcd for $C_{27}H_{20}$: 344.1565. Found: 344.1558. Anal. Calcd for $C_{27}H_{20}$: C, 94.15; H, 5.85. Found: C, 94.20; H, 5.94. $[\alpha]^{23}_D$ −201° (*c* 0.115, $CHCl_3$); for (*R*)-(+)-**5** $[\alpha]^{23}_D$ +200° (*c* 0.125, $CHCl_3$).

Chiral Lanthanide–Silver ^{1}H NMR Shift Study of 5. In an NMR tube fitted with a septum, pure dry (*R*)-(+)-**5** (7 mg, 0.0203 mmol) was dissolved in $CDCl_3$ (500 μL) and purged with nitrogen. In a glovebox, Yb(tfc)$_3$ (26 mg, 0.0284 mmol) and Ag(FOD) (26 mg, 0.0645 mmol) were combined in a dry 1-dram vial fitted with septum and wrapped in aluminum foil to exclude light. At the time of ^{1}H NMR spectral analysis, $CDCl_3$ (300 μL) was syringed to this ytterbium–silver mixture. Six total spectra were recorded: one with no shift reagent and five titrated each with 60 μL of lanthanide–silver solution. For a prepared enantomerically enriched sample of the fused ligand, the proton spectrum is as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37, 3.65 [(*S*)-(−)-**5**], and 3.45, 3.71 [(*R*)-(+)-**5**].

(*R,R*)-(+)-Bis[2,3-(1,1′-binaphthyl-2,2′-diyldimethylene)-cyclopenta-1,3-dienyl]dichlorotitanium (19). A solution of (*R*)-(+)-**5** (350 mg, 1.02 mmol) in THF (3 mL) was cooled to −78 °C. A solution of butyllithium (2.0 M in pentane, 0.508 mL, 1.02 mmol) was introduced dropwise, and the resulting dark yellow solution was warmed to 0 °C over 0.5 h.[42] This anion was transferred via cannula to a round-bottom flask equipped with condenser/vacuum adapter and charged with $TiCl_3$ (75 mg, 0.4838 mmol) in THF (3 mL) at −10 °C with stirring. This dark purple mixture was stirred for 10 min at −10 °C and then heated a reflux for 6 h. The resulting red-brown heterogeneous solution was cooled to room temperature and the solvent removed in vacuo. The dry light brown residue was dissolved in distilled $CHCl_3$ (5 mL) and the temperature lowered to −78 °C. Then 6 M HCl (2.5 mL) was added, and the red mixture was stirred at 23 °C for 3 h open to air. The phase were separated and the aqueous layer was back-extracted with CH_2Cl_2. All the organic extracts were combined and partitioned with brine, dried over anhydrous Na_2SO_4, and concentrated. The crude red solid was triturated by dissolving in dry CH_2Cl_2 and slowly adding dry hexane until the product precipitated as a red powder **19** (325 mg, 83%), mp 265 °C; $[\alpha]^{23}_D$ +707° (*c* 0.080, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (m, 8 H), 7.62 (d, J = 8.5 Hz, 2 H), 7.40 (m, 6 H), 7.22 (m, 6 H), 7.11 (d, J = 8.5 Hz, 2 H), 6.05 (dd, J = 3.0, 3.0 Hz, 2 H), 5.96 (dd, J = 3.0, 3.0 Hz, 2 H), 5.65 (dd, J = 3.0, 3.0 Hz, 2 H), 4.14 (d, J = 15.5 Hz, 2 H), 3.92 (d, J = 14.0 Hz, 2 H), 3.47 (d, J = 15.5 Hz, 2 H), 3.36 (d, J = 14.0 Hz, 2 H); ^{13}C NMR (100 MHz,

(41) This may be omitted if the chromatographic purification of **15** is done carefully to remove all unreacted naphthylmethano bromides (^{1}H NMR: 2 doublets and/or 1 singlet at ca. δ 4.0 ppm). The hydrolysis purification may be run immediately upon crude **15** after the bisalkylation step, for example, yielding 1.9 g of (*R*)-**15** in 61% overall yield from (*R*)-**18**.

(42) General anion formation of **5** can also be conducted with the addition of *n*-BuLi at −78 °C and stirring at −78 °C for 0.5 h, after which a thick yellow slurry forms. Before reacting Li-**5**, it is warmed to 0 °C for ca. 5 min only. Allowing the anion of **5** to stand at room temperature for periods of time results in decomposition and color changes from yellow-brown to green-black.

$CDCl_3$) δ 35.50, 35.96, 109.68, 115.84, 123.95, 125.25, 125.47, 125.80, 126.33, 126.62, 126.97, 127.34, 127.98 (3 C), 128.13, 128.71, 130.13, 131.97, 132.32, 132.36, 132.63, 133.90, 135.21, 135.57, 135.73, 138.15; IR (neat film) 3053, 2927, 1593, 1507, 1487, 1420, 1260, 1100, 1024, 908, 821, 757, 731 cm^{-1}; MS, *m/z* (EI, 40 eV, rel intensity) 770 (M^+ - Cl + 1, 2%), 769 (M^+ - Cl) (3), 344 (100), 265 (97). HRMS (EI, 40 eV) Calcd for $C_{54}H_{38}Cl_2Ti$: 804.1830. Found: 804.1855. Anal. Calcd for $C_{54}H_{38}Cl_2Ti$: C, 80.50; H, 4.75. Found: C, 80.00; H, 4.85.

***C*$_s$-Symmetric *meso*-(Binap-Cp)$_2$TiCl$_2$ (20).** ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2 H), 7.89 (m, 8 H, 7.52 (d, *J* = 8.5 Hz, 2 H), 7.45 (m, 4 H), 7.26 (m, 4 H), 7.15 (m, 4 H), 6.53 (dd, *J* = 3.0, 3.0 Hz, 2 H), 6.14 (dd, *J* = 3.0, 3.0 Hz, 2 H), 4.89 (dd, *J* = 3.0, 3.0 Hz, 2 H), 4.09 (d, *J* = 16.0 Hz, 2 H), 3.88 (d, *J* = 14.0 Hz, 2 H), 3.52 (d, *J* = 14.0 Hz, 2 H), 3.36 (d, *J* = 16.0 Hz, 2 H).

Alternate Formation of 19. A solution of (*R*)-(+)-**5** (180 mg, 0.5226 mmol) in THF (1.5 mL) was cooled to −78 °C, and a solution of methyllithium (1.4 M in ether, 0.373 mL, 0.5226 mmol) was added dropwise. The resulting yellow solution was warmed to 0 °C over 0.5 h. The reaction mixture was recooled to −78 °C, and a solution of $TiCl_4(thf)_2$[43] (83 mg, 0.2489 mmol) in THF (1.5 mL) was added slowly. The dark brown reaction mixture was then heated at reflux for 18 h. After the reaction mixture was cooled to room temperature, the color turned red upon standing. The crude product solution was extracted with 1 N HCl, dried, and concentrated. The red titanocene **19** was obtained after recrystallization from CH_2Cl_2/hexane (15 mg, 8%). The product obtained was characterized as **19** by ^1H NMR.

(*S*)-(−)-Cyclopentadienyl[2,3-(1,1′-binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-dienyl]dichlorotitanium (21). A two-neck round-bottom flask, equipped with a powder addition side arm and cap was charged with cyclopentadienyltitanium trichloride (Strem, 155 mg, 0.706 mmol) and (*S*)-(−)-**5** (225 mg, 0.653 mmol). THF (7.1 mL) was introduced, and the solution was brought to −78 °C. A solution of butyllithium (1.99 M in hexanes, 0.355 mL, 0.706 mmol) was introduced dropwise, and the yellow solution of the anion was warmed to 0 °C over 0.5 h. The $CpTiCl_3$ was then slowly added at 0 °C and stirred for 2 h. The red reaction mixture was warmed to 23 °C and stirred overnight. The crude reaction mixture was concentrated, and dry CH_2Cl_2 (ca. 25 mL) was then added. The mixture was suction filtered through a glass frit to remove inorganics and the mother liquor concentrated. The red solid was then dissolved in dry $CHCl_3$ (ca. 50 mL), filtered, and evaporated to half volume (homogeneous), and dry hexane (ca. 50 mL) was added. The precipitated fine red powder was isolated as **21** (95 mg, 28%), mp 312–314 °C; $[\alpha]^{23}_D$ −13.3° (*c* 0.21, THF); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 4 H), 7.63 (d, *J* = 8.5 Hz, 1 H), 7.41 (m, 2 H), 7.38 (d, *J* = 8.5 Hz, 1 H), 7.20 (m, 3 H), 7.09 (d, *J* = 8.5 Hz, 1 H), 6.67 (dd, *J* = 3.0, 3.0 Hz, 1 H), 6.30 (s, 5 H), 6.23 (dd, *J* = 3.0, 3.0 Hz, 1 H), 5.77 (dd, *J* = 3.0, 3.0 Hz, 1 H), 4.16 (d, *J* = 16.0 Hz, 1 H), 3.90 (d, *J* = 14.0 Hz, 1 H), 3.48 (d, *J* = 14.0 Hz, 1 H), 3.45 (d, *J* = 16.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.52, 35.99, 110.43, 119.81 (5 C), 120.72, 124.92, 125.47, 125.65, 126.06, 126.49, 126.63, 126.92, 127.10, 128.03, 128.19, 128.36, 128.90, 129.54, 131.94, 132.22, 132,41, 132.61, 133.13, 133.66, 134.95, 135.20, 135.93, 136.95; IR (KBr) 3120, 3060, 2940, 1590, 1510, 1490, 1450, 1370, 1030, 960, 830, 760 cm^{-1}; MS, *m/z* (CI, NH_3CH_4, rel intensity) 547 ($M^+ + CH_4 + 5$, 3%), 546 ($M^+ + CH_4 + 4$) (9), 545 ($M^+ + CH_4 + 3$) (15), 544 ($M^+ + CH_4 + 2$) (38), 543 ($M^+ + CH_4 + 1$) (25), 542 ($M^+ + CH_4$) (51), 541 ($M^+ + CH_4 - 1$) (6), 540 ($M^+ + CH_4 - 2$) (4), 344 (43), 104 (100), 71 (49). HRMS (EI, 40 eV) Calcd for $C_{32}H_{24}Cl_2Ti$: 526.0735. Found: 526.0752.

(*R*,*R*)-(+)-Bis[2,3-(1,1′-binaphthyl-2,2′-diyldimethylene)-cyclopenta-1,3-dienyl]dichlorozirconium (22).[44] A solution of (*R*)-(+)-**5** (550 mg, 1.60 mmol) in THF (3.2 mL) was cooled to −78 °C. A solution of butyllithium (1.99 M in hexanes, 0.802 mL, 1.60 mmol) was added dropwise via syringe to form a deep yellow solution which was warmed to 0 °C over 0.5 h. The mixture was then cooled to −10 °C, and a chilled −10 °C solution of $ZrCl_4$ (177 mg, 0.760 mmol) in DME (1.5 mL) was slowly added to the lithium salts via syringe. The light brown reaction mixture was stirred overnight at room temperature and then gently heated at 50 °C for 2 h to afford a white yellow heterogeneous mixture. Solvents were evaporated in vacuo, and the white yellow solid was dissolved in an excess of dry CH_2Cl_2 and Schlenk filtered, and the light yellow mother liquor was triturated with dry hexane via syringe. The white precipitate was isolated under argon and washed further with hexane, yielding the white powder **22** (200 mg, 31%), mp 253–255 °C; $[\alpha]^{23}_D$ + 345° (*c* 0.380, $CHCl_3$). Pure needles of the white crystalline zirconocene **22** could also be grown from 1-chlorobutane with heating and cooling to −30 °C. These crystals were a 4:1 zirconocene:chlorobutane adduct as seen by ^1H NMR. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 3.5 Hz, 2 H), 7.90 (d, *J* = 3.5 Hz, 2 H), 7.85 (m, 4 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 7.40 (m, 4 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 7.20 (m, 4 H), 7.14 (d, *J* = 8.5 Hz, 2 H), 7.09 (d, *J* = 8.5 Hz, 2 H), 6.00 (dd, *J* = 3.0, 3.0 Hz, 2 H), 5.83 (dd, *J* = 3.0, 3.0 Hz, 2 H), 5.63 (dd, *J* = 3.0, 3.0 Hz, 2 H), 3.96 (d, *J* = 15.5 Hz, 2 H), 3.83 (d, *J* = 14.0 Hz, 2 H), 3.41 (d, *J* = 15.5 Hz, 2 H), 3.40 (d, *J* = 14.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.77, 35.32, 106.42, 112.22, 120.35, 125.27, 125.38, 125.88, 126.28, 126.65, 126.92, 127.15, 127.83, 127.96, 128.16, 128.19, 128.72, 129.81, 132.03, 132.25, 132.21, 132.58, 133.83, 133.99, 134.98, 135.89, 135.93; IR (neat film) 2923, 2852, 1592, 1508, 1440, 1427, 1376, 1259, 1227, 1107, 1020, 941, 863, 852, 818, 758, 703, 685 cm^{-1}; MS, *m/z* (EI, 70 eV, rel intensity) 850 (M^+ + 4, 6%), 849 (M^+ + 3) (5), 848 (M^+ + 2) (8), 847 (M^+ + 1) (5), 846 (M^+) (6), 505 (100), 467 (51), 344 (97), 265 (77). HRMS (EI, 70 eV) Calcd for $C_{54}H_{38}Cl_2Zr$: 846.1394. Found: 846.1379. Anal. Calcd for $C_{54}H_{38}Cl_2Zr$: C, 76.39; H, 4.51. Found: C, 76.00; H, 4.43.

***C*$_s$-Symmetric *meso*-(Binap-Cp)$_2$ZrCl$_2$ (23).** ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 10 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.42 (m, 4 H), 7.22 (m, 4 H), 7.13 (m, 4 H), 6.29 (dd, *J* = 3.0, 3.0 Hz, 2 H), 6.08 (dd, *J* = 3.0, 3.0 Hz, 2 H), 4.91 (s, 2 H), 3.93 (d, *J* = 15.5 Hz, 2 H), 3.80 (d, *J* = 14.0 Hz, 2 H), 3.52 (d, *J* = 14.0 Hz, 2 H), 3.34 (d, *J* = 15.5 Hz, 2 H).

Alternate Formation of 22. (*R*)-(+)-**5** (180 mg, 0.523 mmol) was dissolved in DME (3 mL) and the solution was cooled to −78 °C. A solution of methyllithium (1.4 M in ether, 0.373 mL, 0.523 mmol) was added dropwise, and the yellow solution was then warmed to 0 °C. The reaction mixture was recooled to −78 °C, and $ZrCl_4$ (58 mg, 0.249 mmol) was added via side arm with stirring. The reaction mixture was then heated under reflux for 72 h and the yellow heterogeneous mixture cooled to −78 °C, treated with gaseous HCl for 15 min, and stirred for 2 h at room temperature. The crude green yellow residue was dissolved in an excess of CH_2Cl_2 and filtered and the mother liquor triturated with hexane. The resulting yellow precipitate was found to be the C_2-symmetric product **22** (73 mg, 35%) and was spectroscopically and physically identical with the prior C_2-zirconocene dichloride **22**.

(*R*,*R*)-(+)-Bis[(2,3-(1,1′-binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-dienyl)dicarbonyliron] (24). A three-neck round-bottom flask equipped with condenser and Schlenk filter tube was chilled to −78 °C and charged with norbornene (8.6 g, 91.27 mmol). A solution of (*R*)-(+)-**5** (2.62 g, 7.61 mmol) in dry toluene (390 mL) was added via syringe to the norbornene, followed by the addition of $Fe(CO)_5$ (12.0 mL, 91.27 mmol) via syringe. The system was degassed via three successive freeze–pump–thaw cycles. The yellow mixture was then heated under reflux for 40 h, and the resulting black solution was hot filtered and stripped in vacuo of toluene, leaving a dark purple residue. Chromatography using alumina(I) and dry hexane/CH_2Cl_2 mixtures of 9:1 and 8:2 afforded organic material. A 1:1 mixture as eluent afforded the dimer **24** as dark purple crystals (1.57 g, 45%), mp 365–370 °C; $[\alpha]^{23}_D$ +700 ± 35° (*c* 0.40, $CHCl_3$): ^1H NMR (400 MHz, C_6D_6) δ 8.32 (d, *J* = 8.5 Hz, 2 H), 7.82 (m, 2 H), 7.69–6.99 (m, 20 H), 4.28 (s, 2 H), 3.92 (s, 2 H), 3.72 (d, *J* = 15.0 Hz, 2 H), 3.54 (d, *J* = 14.0 Hz, 2 H), 3.34 (s, 2 H), 3.22 (d, *J* = 15.0 Hz, 2 H), 3.00 (d, *J* = 14.0 Hz, 2 H); IR (KBr) 3052, 2959, 1986, 1944, 1767, 1508, 1428, 1260, 1095, 1024, 822, 758, 641, 545 cm^{-1}. Anal. Calcd for $[C_{29}H_{19}O_2Fe]_2$: C, 76.50; H, 4.21. Found: C, 75.59; H, 4.27.

***C*$_s$-Symmetric *meso*-[(Binap-Cp)Fe(CO)$_2$]$_2$ (25).** ^1H NMR (400 MHz, C_6D_6) δ 8.32 (d, *J* = 8.5 Hz, 2 H), 7.91 (d, *J* = 8.5 Hz,

(43) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(44) Formation of **22** with $ZrCl_4(thf)_2$[43] in THF (substituting for $ZrCl_4$/DME) was conducted in the same manner. **22** was formed as a *chalky* gray solid after precipitation in 16–36% yield (ca. 140 mg) and characterized by ^1H NMR.

2 H), 7.69–6.99 (m, 20 H), 3.87 (s, 2 H), 3.65 (d, J = 15.0 Hz, 2 H), 3.58 (d, J = 14.0 Hz, 2 H), 3.53 (s, 4 H), 3.18 (d, J = 15.0 Hz, 2 H), 2.98 (d, J = 14.0 Hz, 2 H).

(*R*)-(+)-[2,3-(1,1'-Binaphthyl-2,2'-diyldimethylene)cyclopenta-1,3-dienyl]dicarbonyliodoiron (26). **24** (264 mg, 0.2899 mmol) and a few crystals of iodine (103 mg, 0.4059 mmol) in dry $CHCl_3$ (3 mL) were heated under reflux for 0.5 h. The brown reaction mixture was cooled to room temperature and partitioned between $CHCl_3$ and $Na_2S_2O_3$(aq). The organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified on alumina(I) using dry hexane/CH_2Cl_2 mixtures as eluent. First washing with hexane and then with an 8:2 mixture afforded impurities. A 1:1 mixture afforded the pure iodoiron complex **26** as brown crystals (214 mg, 63%). This material was characterized as a 4:1 iodoiron:chloroform adduct as seen by ^{1}H NMR (C_6D_6), mp 135 °C freed of $CHCl_3$, 290 °C; $[\alpha]^{23}_D$ +483° (c 0.735, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1 H), 7.95 (d, J = 8.5 Hz, 1 H), 7.92 (d, J = 8.5 Hz, 1 H), 7.91 (d, J = 8.0 Hz, 1 H), 7.86 (d, J = 8.5 Hz, 1 H), 7.45 (dd, J = 8.0, 8.0 Hz, 2 H), 7.37 (d, J = 8.5 Hz, 1 H), 7.25 (m, 2 H), 7.19 (d, J = 8.5 Hz, 1 H), 7.06 (d, J = 8.5 Hz, 1 H), 5.12 (dd, J = 2.0, 2.0 Hz, 1 H), 4.93 (dd, J = 2.0, 2.0 Hz, 1 H), 4.53 (dd, J = 2.0, 2.0 Hz, 1 H), 3.52 (d, J = 15.5 Hz, 1 H), 3.43 (d, J = 14.0 Hz, 1 H), 3.29 (d, J = 15.5 Hz, 1 H), 3.24 (d, J = 14.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.31, 32.64, 79.79, 80.65, 91.88, 98.85, 104.45, 125.77, 125.94, 126.25, 126.42, 126.50, 126.70, 126.86, 128.09, 128.29, 128.78, 129.25, 129.50, 131.80, 132.10, 132.59, 132.83, 133.76, 134.56, 135.15, 135.52, 213.14, 213.53; IR (KBr) 3053, 2931, 2028, 1982, 1509, 1255, 1025, 824, 758, 609, 567, 545 cm^{-1}; MS, m/z (EI, 70 eV, rel intensity) 582 (M^+, 3.5%), 399 (22), 344 (11), 83 (100). HRMS (EI, 70 eV) Calcd for $C_{29}H_{19}O_2IFe$: 581.9778. Found: 581.9738. Anal. Calcd for $C_{29}H_{19}O_2IFe \cdot 0.20CHCl_3$: C, 57.92; H, 3.20. Found: C, 58.09; H, 3.46.

(*R*)-(−)-[2,3-(1,1'-Binaphthyl-2,2'-diyldimethylene)cyclopenta-1,3-dienyl]dicarbonylmethyliron (27). In a drybox, a flask was charged with 2% Na–Hg (143 mg, 0.1247 mmol) and at the bench top was combined with dry THF (0.5 mL) via syringe. In another flask, dry (*R*)-(+)-**26** (33 mg, 0.0567 mmol) was dissolved in dry THF (0.5 mL), and this solution was added via syringe to the amalgam solution all at once with vigerous stirring. The reaction mixture was stirred at room temperature for 25 min upon which the brown–yellow solution turned reddish brown. Distilled Me_2SO_4 (11 μL, 0.1134 mmol) was then added via syringe to the sodium salts, causing the color to turn yellow green instantly. This solution was stirred at room temperature for 15 min during which the color lightened. The mixture was quenched with wet hexane, filtered through a glass frit, washed with CH_2Cl_2, and concentrated excluding heat and light. The crude yellow oil was purified on alumina(I) by the first washing with dry hexane, and then a 9:1 hexane:CH_2Cl_2 mixture as eluent afforded the methyliron derivative **27** as a yellow crystalline compound (23 mg, 86%), which is heat, light, and acid sensitive, mp 145 °C freed of CH_2Cl_2, 170 °C; $[\alpha]^{23}_D$ −207° (c 0.4500, C_6D_6): ^{1}H NMR (400 MHz, C_6D_6) δ 7.82 (d, J = 8.5 Hz, 1 H), 7.70 (d, J = 4.5 Hz, 2 H), 7.68 (d, J = 4.5 Hz, 2 H), 7.30 (d, J = 8.5 Hz, 1 H), 7.26 (d, J = 8.5 Hz, 1 H), 7.16 (m, 3 H), 6.95 (m, 2 H), 3.92 (dd, J = 2.5, 2.5 Hz, 1 H), 3.90 (dd, J = 2.5, 2.5 Hz, 1 H), 3.73 (dd, J = 2.5, 2.5 Hz, 1 H), 3.01 (d, J = 14.0 Hz, 1 H), 2.96 (d, J = 15.0 Hz, 1 H), 2.89 (d, J = 15.0 Hz, 1 H), 2.67 (d, J = 14.0 Hz, 1 H), 0.003 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −17.22, 31.65, 33.13, 80.36, 81.02, 86.64, 99.30, 106.16, 125.46, 125.49, 126.18, 126.37, 126.66, 126.86, 127.01, 128.03, 128.18, 128.76, 128.88, 128.99, 131.96, 132.15, 132.37, 132.51, 134.44, 134.73, 135.48, 135.54, 217.48, 217.79; IR (KBr) 3045, 2962, 2929, 2361, 1995, 1934, 1507, 1261, 1096, 1023, 820, 800, 762, 593, 568 cm^{-1}; MS, m/z (EI, 70 eV, rel intensity) 470 (M^+, 1.9%), 414 (63), 399 (100), 344 (33). HRMS (EI, 70 eV) Calcd for $C_{30}H_{22}O_2Fe$: 470.0969. Found: 470.0934.

X-ray Structure Determination of 19. Suitable crystals of the red titanocene **19**, which contain 1 equiv of hexane, were grown from a ca. 90:10 mixture of enantiomers in hexane/CH_2Cl_2 by heating and cooling to −30 °C for several days. The intensity data were obtained at 20 °C with a Rigaku AFC5R four-circle autodiffractometer system using graphite monochromated Cu Kα radiation and a 12-kW rotating anode generator. The cell constants and an orientation matrix for data collection were obtained from a least-squares refinement by using the setting angles of 25 centered reflections in the range $25 \leq 2\theta \leq 30$. Scans were made at a speed of 32 deg/min in omega. The weak reflections ($I \leq 10.0\sigma$) were rescanned (maximum of two rescans). The intensities of three standard reflections were measured after every 150 refections and remained constant throughout the data collection; no decay correction was applied. The crystallographic calculations were performed by using the TEXSAN program.[45] Due to the average absorbance of 0.880, an emperical absorption correction, using the program DIFABS, was applied, which resulted in transmission factors ranging from 0.71 to 1.29. 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: Tables of positional parameters and anisotropic thermal parameters for **19** (6 pages); listings of h, k, l, F_o, F_c, and $\sigma(F_o)$ (17 pages). Ordering information is given on any current masthead page.

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