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Preparation and Structural Characterization of an Enantiomerically Pure, C_2-Symmetric, Single-Component Ziegler−Natta α-Olefin Polymerization Catalyst

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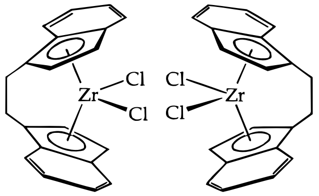
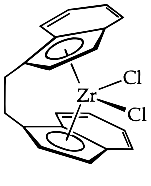
Abstract: A new linked bis(cyclopentadienyl) ligand, $\{(C_5H_3\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2Si(OC_{10}H_6C_{10}H_6O)\}$ ($BnBpH_2$), has been designed to coordinate to transition metals to afford a single enantiomeric C_2-symmetric *ansa*-metallocene. The syntheses of its dipotassium salt and (BnBp)YCl(THF) are described. Steric interactions between the 3- and 3′-methine positions of the 1,1′-binaphth-2,2′-diolate rings of the chiral linker with the α-trimethylsilyl substituents on the cyclopentadienyl rings force enantioselective metalation of this ligand. Thus, coordination to yttrium occurs in an entirely diastereoselective manner: the ligand prepared from (*R*)-(+)-1,1′-bi-2-naphthol directs formation of the (*S*)-yttrocene, (*R*,*S*)-(BnBp)YCl(THF), while that from (*S*)-(−)-1,1′-bi-2-naphthol directs formation of the (*R*)-yttrocene, (*S*,*R*)-(BnBp)YCl(THF). Removal of coordinated tetrahydrofuran allows the preparation of (BnBp)$YCH(SiMe_3)_2$. Treatment of *rac*-(BnBp)$YCH(SiMe_3)_2$ with H_2 yields a kinetic mixture of both heterochiral and homochiral dimers (*e.g.* (*R*,*S*)-(BnBp)$Y(\mu_2\text{-}H)_2$-(*S*,*R*)-(BnBp) and (*R*,*S*)-(BnBp)$Y(\mu_2\text{-}H)_2$-(*R*,*S*)-Y(BnBp), respectively). Over several hours this mixture undergoes conversion to the pure homochiral dimers. As anticipated, hydrogenolysis of enantiopure (BnBp)$YCH(SiMe_3)_2$ (*e.g.* *R*,*S*-(BnBp)$YCH(SiMe_3)_2$) affords directly only enantiopure homochiral dimer (*e.g.* (*R*,*S*)-(BnBp)$Y(\mu_2\text{-}H)_2$-(*R*,*S*)-Y(BnBp)). The hydride, generated *in situ* from (*R*,*S*)-(BnBp)$YCH(SiMe_3)_2$, polymerizes 1-pentene to highly isotactic poly-1-pentene ($M_n = 119\,000$, PDI = 1.44, *mmmm* >95%). The much higher solubility of the enantiopure homochiral dimers was used to grow crystals of the racemate at the interface of layered solutions of the pure optical isomers. *rac*-(BnBp)$Y(\mu_2\text{-}H)_2$(BnBp) crystallizes in the centrosymmetric space group $P\bar{1}$ (#2) with $a = 11.925(4)$ Å, $b = 19.461(8)$ Å, $c = 23.814(10)$ Å and $\alpha = 82.80(3)°$, $\beta = 84.64(4)°$, $\gamma = 81.30(3)°$, with a volume of $5404(4)$ Å^3 and $Z = 2$.

Although Ziegler−Natta polymerization of olefins has been investigated extensively since its discovery in the early 1950's,[1] soluble, relatively well-defined catalysts have been developed only recently. When combined with methylaluminoxane cocatalyst a C_2-symmetric *ansa*-zirconocene dichloride first developed by Brintzinger is capable of carrying out stereospecific propylene insertions to give highly isotactic polypropylene. This observation has stimulated a resurgence of research activity into the mechanistic basis for the remarkable selectivity and productivity of this catalytic process.[2] The amazingly high enantioselectivity in the carbon−carbon bond forming step exhibited in α-olefin polymerizations by some of these metallocene-based catalyst systems has also motivated research into other types of enantioselective reactions utilizing these same chiral metallocenes as catalysts.[3]

Unfortunately, these types of studies are encumbered by lengthy, tedious, often low-yield syntheses of enantiopure, C_2-symmetric metallocene catalyst or pre-catalyst. For example, formation of the ethylene-linked bis(indenyl) (EBI) derivatives of zirconium typically proceeds to give a kinetic distribution of desired *racemo* isomer (**1**) and undesired *meso* isomer (**2**), which must then be separated. Procedures for these separations and subsequent resolution of the *rac* isomer are well developed,[4,5] but its resolution requires first a catalytic hydrogenation to the $(EBTHI)ZrCl_2$ (EBTHI = ethylenebis(tetrahydroindenyl) derivatives.



racemo
1



meso
2

The challenges associated with the preparation of enantiopure C_2-symmetric metallocenes are 2-fold: (1) maximizing the

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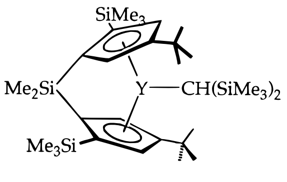
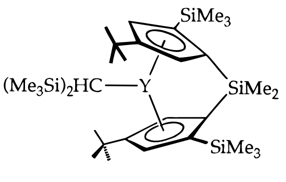
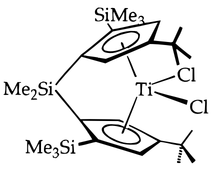
amount of the desired *racemo* isomer during coordination of the linked bis(cyclopentadienyl) ligand to the metal, and (2) resolving the racemate into its component enantiomers. With regard to the former, we have developed a ligand that coordinates to a variety of early transition metals to yield the pure *racemo* isomers, *e.g. rac*-BpMCH$(SiMe_3)_2$ (Bp = $\{(\eta^5$-C_5H_2-2-$SiMe_3$-4-$CMe_3)_2SiMe_2\}$; M = Sc, Y) and *rac*-BpMCl_2 (M = Ti, Zr).[6] The key design features of this linked ligand system are based on the original requirements discussed by Brintzinger and Collins[7] and include (a) incorporation of bulky trimethylsilyl substituents in the narrow portion of the metallocene wedge (α to the dimethylsilylene linker) and (b) use of *tert*-butyl groups in the 4-positions to direct steric interactions in the reactive (open) part of the wedge. The steric bias exerted by this substitution pattern, especially unfavorable trimethylsilyl−trimethylsilyl interactions for an eclipsed *meso* coordination, allows for formation of only the desired *racemo* product upon metalation. Moreover, the yttrium hydride derivative $[BpY]_2$-$(\mu_2$-$H)_2$ functions as a single component catalyst for the production of highly isotactic poly-α-olefins.[6a]



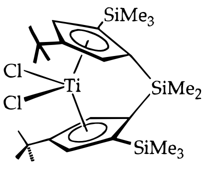
S-BpY-CH$(SiMe_3)_2$



R-BpY-CH$(SiMe_3)_2$



S-Bp$TiCl_2$



R-Bp$TiCl_2$

Jordan has recently reported a high-yield synthesis of *rac*-(EBI)-bis(dimethylamido)zirconium(IV) that operates by equilibrating *racemo* and *meso* products, and thus minimizes the amount of the less stable *meso* isomer.[8] Herrmann and co-workers have reported a route to pure *racemo* C_2 metallocenes, but at the expense of the remaining coordination sites at the group 4 metal.[9] Several groups have incorporated two linkers between the two cyclopentadienyl groups, hoping to impart sufficient rigidity to force formation of only the *racemo*, C_2-symmetric metallocene. Brintzinger's strategy does indeed succeed, and only doubly bridged, C_2-symmetric, racemic zirconocenes *rac*-1,2-$(SiMe_2)_2(\eta^5$-C_5H-4,5-$Me_2)_2ZrCl_2$ and *rac*-1,2-$(SiMe_2)_2(\eta^5$-$C_9H_9)_2ZrCl_2$ are obtained.[10] By using biaryl-based linkers attached to the two indenyl groups at the 2-position rather than the 1-position, both faces of the coordinating Cp are rendered stereochemically equivalent. Thus, Halterman[11] and Bosnich[12] were successful in avoiding formation of the *meso* isomer by incorporating a biaryl linker to direct the indenyl groups into a staggered, C_2-symmetric array around the metal center. Brintzinger and Katz have used a similar approach to obtain diastereomerically pure metallocenes.[13] Buchwald and co-workers have recently synthesized a cleverly designed doubly bridged bis(cyclopentadienyl) ligand which can metalate only as the *racemo* isomer.[14] Thus, a variety of strategies have been used to direct coordination of linked bis(cyclopentadienyl) ligands to early transition metal centers to yield the desired *racemo ansa* metallocenes.

Even the most successful scheme for preparing pure *racemo ansa* metallocene requires subsequent resolution of the racemate in order to obtain the enantiopure *ansa* metallocene that is needed to effect asymmetric catalytic transformations. Such resolved metallocenes may also serve as powerful stereochemical probes of the mechanistic aspects of Ziegler−Natta polymerization of α-olefins.[15] The most desirable ligand design would produce *only one enantiomer* upon coordination to the metal.[16] Not only would the wasteful and tedious separation of the *racemo* and *meso* isomers be avoided, but the subsequent resolution of the racemate would also be obviated. Use of an enantiopure stereogenic linking group could, in principle, provide only one enantiomer of the C_2-symmetric metallocene. Indeed, Green, Halterman, Bosnich, Buchwald, and Nantz have pointed out this possibility, and some success has been realized.[10,11,13,17] Problems encountered with these systems, however, are insufficient diasteromeric control in complexation,[16c] lack of C_2 symmetry in the final product, and greatly reduced catalytic activity, due, at least in part, to the flexibility of the linker groups, which contain as many as six atoms.[18]

We report herein that modification of the [Bp] ligand system with a stereogenic linking group cleanly affords a single diasteromeric yttrocene. Thus, with an enantiopure linker enantiomerically pure catalysts based on the [Bp] ligand system may be obtained. Such "self-resolving" ligand systems, in addition to providing powerful mechanistic probes of Ziegler−Natta catalysis, are also promising candidates for use in a variety of other catalytic asymmetric transformations.

Results and Discussion

Syntheses of $BnBpH_2$, *rac*-(BnBp)YCl(THF), and *rac*-(BnBp)YCH$(SiMe_3)_2$. It occurred to us that the very features of the [Bp] ligand framework that prevent formation of the *meso* isomer upon coordination to the metal center, the α-(trimethylsilyl) substituents, would be particularly well-suited to direct coordination to a single diastereomer, if the achiral $[SiMe_2]$

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[16] Although some examples of diastereomerically enriched or pure group III and lanthanide metallocene systems employing enantiopure cyclopentadienyl substituents have been reported, none possess C_2-symmetry. See for example: Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y.; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc* **1992**, *114*, 2671.

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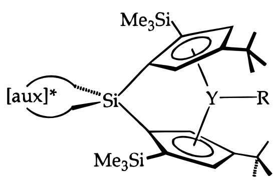
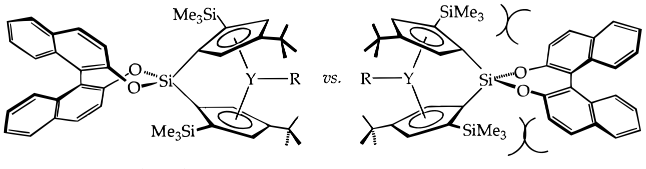
linker is substituted with a silylene linking group bearing a chiral auxiliary:



The situation would be optimized with a stereogenic auxiliary having groups extending toward the [$SiMe_3$] substituents arranged in C_2 symmetry. Furthermore, the single atom silylene linker should provide rigidity, thus avoiding the problems previously encountered with flexible, many-atom linking groups.

Along these lines, the synthesis of a new ligand, $\{(C_5H_2\text{-}2\text{-}SiMe_3\text{-}4\text{-}CMe_3)_2Si(OC_{10}H_6C_{10}H_6O)\}^{2-}$ ($[BnBp]^{2-}$), has been undertaken. This derivative of $[Bp]^{2-}$ has the two methyl groups on the silylene linker replaced by the C_2-symmetric 1,1′-binaphth-2,2′-diolate group. Simple molecular models and preliminary molecular mechanics calculations suggested that steric interactions between the 3- and 3′-methine positions of the naphthol rings of the chiral linker with the α-(trimethylsilyl) substituents on the cyclopentadienyl rings might be sufficient to force enantioselective metalation of this ligand.[19]



R,S-(BnBp)Y-R
(preferred)

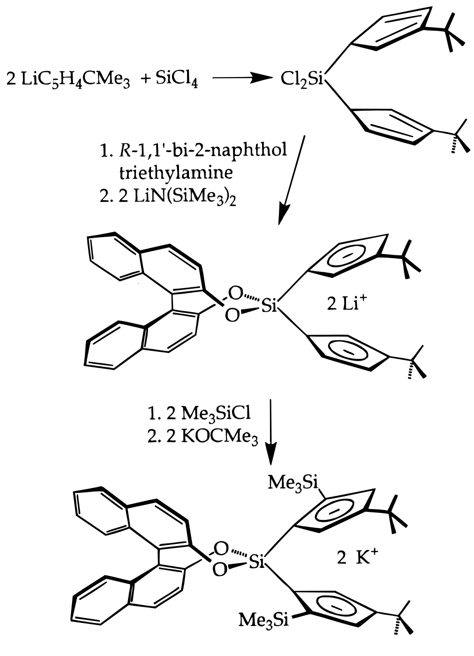
R,R-(BnBp)Y-R

Both *R* and *S* enantiomers of 1,1′-bi-2-naphthol are readily available. Thus, in principle, either diastereomer (or the enantiomeric pair of diastereomers from (±)-1,1′-bi-2-naphthol) could easily be synthesized.

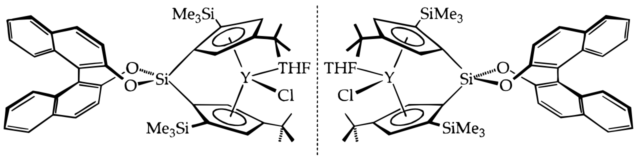
This (binaphtholato)silylene-linked ligand, $K_2(BnBp)$, can be conveniently prepared in high overall yield (*ca.* 70% based on 1,1′-bi-2-naphthol) according to the procedure shown in Scheme 1. As indicated, 1,1′-bi-2-naphthol is incorporated onto the ligand framework after linking of the two *tert*-butylcyclopentadienes to dichlorosilylene. The alternative sequence wherein $Si(OC_{10}H_6C_{10}H_6O)Cl_2$ is treated with 2 equiv of *tert*-butylcylopentadienide failed. The subsequent reactions are analogous to those used for the preparation of $K_2(Bp)$.[6] All reactions can be carried out in multigram quantities, and a serendipitous benefit from the introduction of the binaphtholate moiety is the increased crystallinity of the ligand and its precursors.

$YCl_3(THF)_3$ and *rac*-$K_2(BnBp)$ react cleanly in THF to yield (BnBp)YCl(THF) (**3**). Significantly, ^1H NMR (Table 1) and ^{13}C NMR spectroscopy indicate formation of a single isomeric form for **3**. Multidimensional NMR studies have allowed complete ^1H- and ^{13}C-spectral assignments for **3** in THF-d_8 (see Experimental Section). Particularly indicative of a single pair of enantiomeric diastereomers is observation of only 15 aromatic carbon signals in the ^{13}C NMR spectrum.[20] We have subsequently determined (*vide infra*) that it is indeed the preferred pair of enantiomeric diastereomers predicted by molecular modeling, *i.e.* (*R*)-(+)-1,1′-bi-2-naphthol directs formation of the (*S*)-yttrocene and (*S*)-(−)-1,1′-bi-2-naphthol directs formation of the (*R*)-yttrocene. Use of optically pure ligand yields the corresponding enantiomerically pure metallocenes.

Scheme 1



$K_2[R\text{-}BnBp]$



R,S-(BnBp)YCl(THF)
R,S-**3**

S,R-(BnBp)YCl(THF)
S,R-**3**

The preparations of alkyl and hydride derivatives (BnBp)Y-R (R = $CH(SiMe_3)_2$, H) from **3** are plagued by problems associated with non-stoichiometric amounts of coordinated THF lingering in the desired products. Fortunately we have found that the THF-free species, which is presumably the dimer $[(BnBp)Y]_2(\mu_2\text{-}Cl)_2$ (**4**) analogous to the hydride dimer described below, can be obtained from **3** in either of two ways. The first method involves repeated cycles of refluxing **3** in toluene followed by removal of volatiles *in vacuo*. Two such cycles are sufficient for removal of >95% (^1H NMR) of the THF from **3** to give the THF-free species **4**. Alternatively, selective removal of THF by Soxhlet extraction of the volatile components of a toluene solution of **3** is accomplished by placing 10× molecular sieves in the thimble of the extraction apparatus; a toluene solution of THF-free **4** (in the lower flask) is so obtained.[21] The alkyl derivative $(BnBp)YCH(SiMe_3)_2$ (**5**) is readily prepared from **4** by treatment with $LiCH(SiMe_3)_2$. As expected, **5** is a competent (pre)catalyst for α-olefin hydrogenation and polymerization. For example, neat 1-pentene is readily polymerized when **5** is exposed to H_2 at 0 °C. The resulting

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[19] Although these models suggest that one diastereomer of the final *yttrocene* product should be more stable, the formation of the first yttrium−cyclopentadienyl bond on complexation of $BnBp^{2-}$ to $YCl_3(THF)_3$ may be irreversible. Hence, it would be this step that ultimately determines the preferred diasteromeric yttrocene. Although neither the identities of the other ligands for this *mono*-cyclopentadienyl yttrium intermediate nor its geometry are known, simple molecular models also suggest that yttrium should prefer to coordinate to only one face of the $BnBp^{2-}$ ligand.

[20] Rapid interchange of the tetrahydrofuran ligand between the two sides of the [BnBpY] wedge (either by dissociation/reassociation or by associative substitution), commonly observed for these group 3 metallocene derivatives, is required to effect time-averaged C_2 symmetry.

[21] Herzog, T. A.; Bercaw, J. E. Unpublished results.

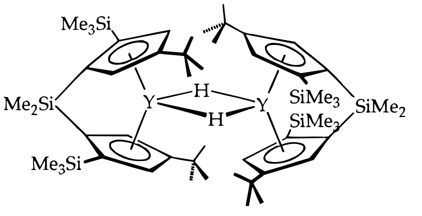
Table 1. ^1H NMR Data[a]

compd	assignment	δ (ppm); coupling, Hz
$(C_{20}H_{12}O_2)Si[C_5H_3(C(CH_3)_3]_2Li_2$ Li_2[BnDp][b]	$(C_{20}\boldsymbol{H}_{12}O_2)Si$	7.86 (d, 2H); $^3J_{H-H} = 8.7$ Hz
		7.85 (d, 2H); $^3J_{H-H} = 7.8$ Hz
		7.46 (d, 2H); $^3J_{H-H} = 8.8$ Hz
		7.25 (m, 2H)
		7.17 (d, 2H); $^3J_{H-H} = 8.3$ Hz
		7.08 (m, 2H)
	$[\eta^5\text{-}C_5\boldsymbol{H}_3(C(CH_3)_3]_2$	5.79 (m, 2H)
		6.00 (br, 2H)
		6.04 (br, 2H)
	$[\eta^5\text{-}C_5H_3(C(C\boldsymbol{H}_3)_3]_2$	1.21 (s, 18H)
$(C_{20}H_{12}O_2)Si[C_5H_2(C(CH_3)_3(Si(CH_3)_3)]_2K_2$ K_2[BnBp][b]	$(C_{20}\boldsymbol{H}_{12}O_2)Si$	7.77 (d, overlapping, 4H)
		7.62 (d, 2H); $^3J_{H-H} = 8.7$ Hz
		7.19 (m, 2H)
		7.12 (d, 2H); $^3J_{H-H} = 8.5$ Hz
		7.04 (m, 2H)
	$[\eta^5\text{-}C_5\boldsymbol{H}_2(C(CH_3)_3(Si(CH_3)_3)]_2$	6.57 (d, 2H); $^4J_{H-H} = 2.0$ Hz
		6.00 (d, 2H); $^4J_{H-H} = 2.0$ Hz
	$[\eta^5\text{-}C_5H_2(C(C\boldsymbol{H}_3)_3(Si(CH_3)_3)]_2$	1.23 (s, 18H)
	$[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(C\boldsymbol{H}_3)_3)]_2$	0.14 (s, 18H)
$(C_{20}H_{12}O_2)Si[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(CH_3)_3)]_2YCl$ BnBpYCl[b]	$(C_{20}\boldsymbol{H}_{12}O_2)Si$	7.92 (d, 2H); $^3J_{H-H} = 8.8$ Hz
		7.85 (d, 2H); $^3J_{H-H} = 8.1$ Hz
		7.65 (d, 2H); $^3J_{H-H} = 8.8$ Hz
		7.28 (m, 2H)
		7.17 (d, 2H); $^3J_{H-H} = 8.7$ Hz
		7.12 (m, 2H)
	$[\eta^5\text{-}C_5\boldsymbol{H}_2(C(CH_3)_3(Si(CH_3)_3)]_2$	6.54 (m, 4H)
	$[\eta^5\text{-}C_5H_2(C(C\boldsymbol{H}_3)_3(Si(CH_3)_3)]_2$	1.31 (s, 18H)
	$[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(C\boldsymbol{H}_3)_3)]_2$	0.22 (s, 18H)
$(C_{20}H_{12}O_2)Si[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(CH_3)_3)]_2YCH(Si(CH_3)_3)_2$ $BnBpYCH(TMS)_2$[c]	$(C_{20}\boldsymbol{H}_{12}O_2)Si$	7.77 (d, 1H); $^3J_{H-H} = 6.8$ Hz
		7.74 (d, 1H); $^3J_{H-H} = 6.8$ Hz
		7.63 (m, 2H, overlapping)
		7.58 (d, 1H); $^3J_{H-H} = 7.8$ Hz
		7.57 (d, 1H); $^3J_{H-H} = 7.8$ Hz
		7.45 (d, 1H); $^3J_{H-H} = 8.5$ Hz
		7.44 (d, 1H); $^3J_{H-H} = 8.5$ Hz
		7.09 (m, 2H, overlapping)
		6.91 (m, 2H, overlapping)
	$[\eta^5\text{-}C_5\boldsymbol{H}_2(C(CH_3)_3(Si(CH_3)_3)]_2$	7.30 (d, 1H); $^4J_{H-H} = 1.9$ Hz
		6.96 (d, 1H); $^4J_{H-H} = 1.9$ Hz
		6.85 (d, 1H); $^4J_{H-H} = 1.9$ Hz
		6.70 (d, 1H); $^4J_{H-H} = 1.9$ Hz
	$[\eta^5\text{-}C_5H_2(C(C\boldsymbol{H}_3)_3(Si(CH_3)_3)]_2$	1.40 (s, 9H)
		1.31 (s, 9H)
	$[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(C\boldsymbol{H}_3)_3)]_2$	0.36 (s, 9H)
		0.34 (s, 9H)
	$YC\boldsymbol{H}(Si(CH_3)_3)_2$	0.46 (d, 1H); $^2J_{Y-H} = 2.3$ Hz
	$YCH(Si(C\boldsymbol{H}_3)_3)_2$	0.25 (s, 9H)
		0.19 (s, 9H)
$\{(R,S)\text{-}(C_{20}H_{12}O_2)Si[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(CH_3)_3)]_2Y\}_2(\mu_2\text{-}H)_2$ and enantiomer homochiral hydride dimer[c]	$(C_{20}\boldsymbol{H}_{12}O_2)Si$	7.78 (d, 4H); $^3J_{H-H} = 8.8$ Hz
		7.70 (d, 4H); $^3J_{H-H} = 8.9$ Hz
		7.63 (d, 4H); $^3J_{H-H} = 7.8$ Hz
		7.50 (d, 4H); $^3J_{H-H} = 8.5$ Hz
		7.12 (m, 4H)
		6.94 (m, 4H)
	$[\eta^5\text{-}C_5\boldsymbol{H}_2(C(CH_3)_3)(Si(CH_3)_3)]_2$	6.97 (d, 4H); $^4J_{H-H} = 1.8$ Hz
		6.84 (d, 4H); $^4J_{H-H} = 1.8$ Hz
	$[\eta^5\text{-}C_5H_2(C(C\boldsymbol{H}_3)_3)(Si(CH_3)_3)]_2$	1.44 (s, 36H)
	$[\eta^5\text{-}C_5H_2(C(CH_3)_3)(Si(C\boldsymbol{H}_3)_3)]_2$	0.30 (s, 36H)
	$Y_2(\mu_2\text{-}H)_2$	4.98 (t, 2H); $^1J_{Y-H} = 31.4$ Hz
$\{(R,S)\text{-}(C_{20}H_{12}O_2)Si[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(CH_3)_3)]_2Y\}(\mu_2\text{-}H)_2\{(S,R)\text{-}(C_{20}H_{12}O_2)Si[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(CH_3)_3)]_2Y\}$ and enantiomer heterochiral dimer	$(C_{20}\boldsymbol{H}_{12}O_2)Si$	7.79 (d, 4H); $^3J_{H-H} = 8.8$ Hz
		7.70 (d, 4H); $^3J_{H-H} = 8.9$ Hz
		7.62 (d, 4H); $^3J_{H-H} = 7.8$ Hz
		7.50 (d, 4H); $^3J_{H-H} = 8.5$ Hz
		7.12 (m, 4H)
		6.94 (m, 4H)
	$[\eta^5\text{-}C_5\boldsymbol{H}_2(C(CH_3)_3(Si(CH_3)_3)]_2$	7.00 (d, 4H); $^4J_{H-H} = 1.8$ Hz
		6.87 (d, 4H); $^4J_{H-H} = 1.8$ Hz
	$[\eta^5\text{-}C_5H_2(C(C\boldsymbol{H}_3)_3(Si(CH_3)_3)]_2$	1.45 (s, 36H)
	$[\eta^5\text{-}C_5H_2(C(CH_3)_3(Si(C\boldsymbol{H}_3)_3)]_2$	0.36 (s, 36H)
	$Y_2(\mu_2\text{-}\boldsymbol{H})_2$	5.97 (t, 2H); $^1J_{Y-H} = 31.4$ Hz

[a] All spectra were recorded at 500 MHz at ambient temperature. [b] THF-d_8 solvent. [c] Benzene-d_6 solvent.

polymer has a relatively narrow molecular weight distribution and moderate molecular weight (PDI = 1.44; M_n = 119 000), and ^{13}C NMR spectra reveal >95% *mmmm* pentads.[22]

Syntheses and Characterization of Homochiral and Heterochiral Hydride Dimers [(BnBp)Y]$_2$(μ_2-H)$_2$. As reported earlier,[6,23] reaction of *rac*-BpYCH(SiMe$_3$)$_2$ with dihydrogen allows isolation of the enantiomeric pairs of homochiral hydride dimers, one of which is shown below. The racemic compound, *rac*-[BpY]$_2$(μ_2-H)$_2$, characterized by X-ray crystallography, displays a diagnostic triplet in its ^1H NMR spectrum for the Y(μ_2-H)$_2$Y unit due to hydrogen coupling with two ^{89}Y (100% abundance, $I = ^1/_2$) centers ($^1J_{YH}$ = 30 Hz).

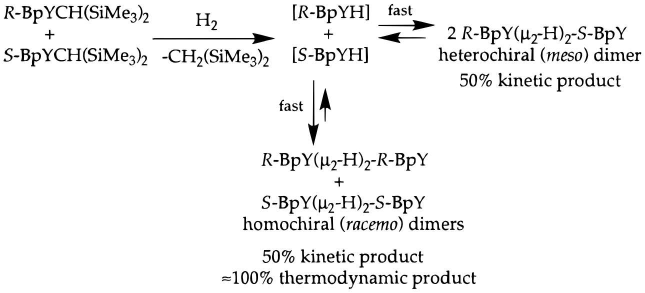


[*R*-(Bp)Y]$_2$(μ_2-H)$_2$
D_2 symmetry

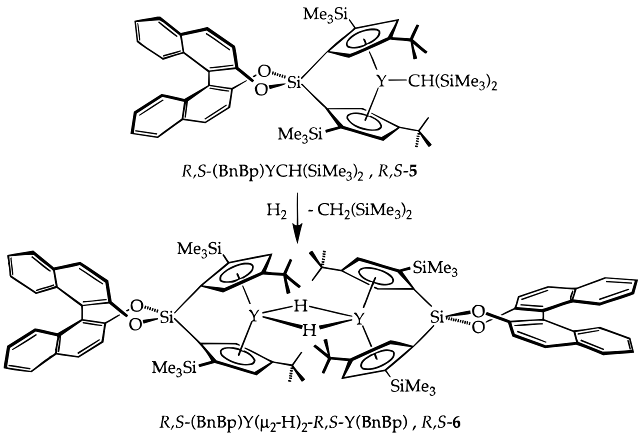
Hydrogenolysis of **5** proceeds analogously to the reaction of BpYCH(SiMe$_3$)$_2$ with H$_2$, proceeding cleanly and quantitatively by σ bond metathesis. Like the [Bp] analog, the hydride dimer [(BnBp)Y]$_2$(μ_2-H)$_2$ (**6**) can be cleanly isolated as a white solid or generated quantitatively from **5** *in situ*. Some interesting characteristics of the hydride dimers have been discovered during the course of these investigations with racemic and enantiopure **5**. Careful ^1H NMR observation of the reaction of *rac*-**5** with H$_2$ reveals an unexpected sequence of transformations. Immediately upon addition of H$_2$, the ^1H NMR spectrum reveals that not one but rather equal amounts of *two different* yttrium hydride species have been formed. Moreover, both are (effectively) highly symmetric dimers as evidenced by the observation of triplets attributable to the hydride ligands of each and the minimum number of resonances for the [BnBp] ligands for each dimer, indicative of equivalent [η^5-C$_5$H$_2$-2-(SiMe$_3$)-4-(CMe$_3$)] and bi-2-naphthyl groups. With time, the set of resonances for one of the dimers grows in at the expense of the other set, and eventually the spectrum is that observed for the isolated homochiral dimer (*vide infra*). The fact that equal amounts of these two hydride dimers are immediately formed suggests that both homochiral and heterochiral dimers are generated. Significantly, no free monomeric hydride (which should exhibit a characteristic doublet rather than triplet) is observed.

In light of these new findings, we undertook a similar, careful study of the original [Bp] system. Close investigation of BpYCH(SiMe$_3$)$_2$ hydrogenolysis under the same conditions as above reveals that it, too, initially forms equimolar amounts of two symmetric dimers which then yield the thermodynamically more stable homochiral form over time (Scheme 2).

Scheme 2



Scheme 3



If the [BnBp] yttrium derivatives are formed cleanly as single diastereomers, then the analogous hydrogenolysis reaction using the resolved alkyl (*R,S*)-**5**, prepared from enantiopure (*R*)-(+)-1,1′-bi-2-naphthol, may only form the homochiral hydride dimer (*R,S*)-**6**. Indeed, only one species is observed immediately upon reaction of (*R,S*)-**5** with dihydrogen (Scheme 3). The differences between the racemic and resolved complexes are illustrated in Figure 1, which shows the time course of the characteristic hydride triplets for all three reactions.

There are several possibilities for the solution structures of the homochiral and heterochiral dimers. The complementary steric interactions of BnBp ligand, like those for the original Bp ligand, allow the homochiral dimer to assume an eclipsed arrangement, as was established by X-ray crystallography for D_2-symmetric [BpY]$_2$(μ_2-H)$_2$. Thus, the eclipsed, D_2-symmetric arrangement, *e.g.* (*R,S*)-**6** shown in Figure 2a, is a likely structure for the homochiral dimer. Moreover, even if the monomeric units are arranged in a skewed, rather than eclipsed, manner, *i.e.* twisted somewhat from perfectly eclipsed, D_2 symmetry still may be retained. Thus, the NMR data do not distinguish between two possible structures for the homochiral hydride, a or b in Figure 2.

Less obvious is the manner by which the heterochiral dimer avoids apparently prohibitive steric interactions, yet preserves its high symmetry. Thus, whereas the analogous eclipsed, C_{2h}-symmetric dimer (Figure 3a) would exhibit a ^1H NMR spectrum having a single set of [η^5-C$_5$H$_2$-2-(SiMe$_3$)-4-(CMe$_3$)] resonances and a single set of bi-2-naphthyl resonances, the close proximity of the *tert*-butyl substituents makes this arrangement seem unlikely. A staggered structure with the yttrocene units twisted 90° (Figure 3b) would have effective S_4 symmetry (hence equivalencing the [η^5-C$_5$H$_2$-2-(SiMe$_3$)-4-(CMe$_3$)] and bi-2-naphthyl resonances), if the hydrides are rapidly rotating or flipping 90° to alternate between equatorial planes of the two yttrocene units. Alternatively, the structure in Figure 3b may be rapidly oscillating via the eclipsed C_{2h} structure in Figure 3a. Finally, a skewed arrangement (Figure 3c) could lead to minimal steric congestion for the heterochiral dimer. Such a structure (rapidly oscillating via the structure in Figure 3a) seems most likely, since it compromises good orbital overlap between

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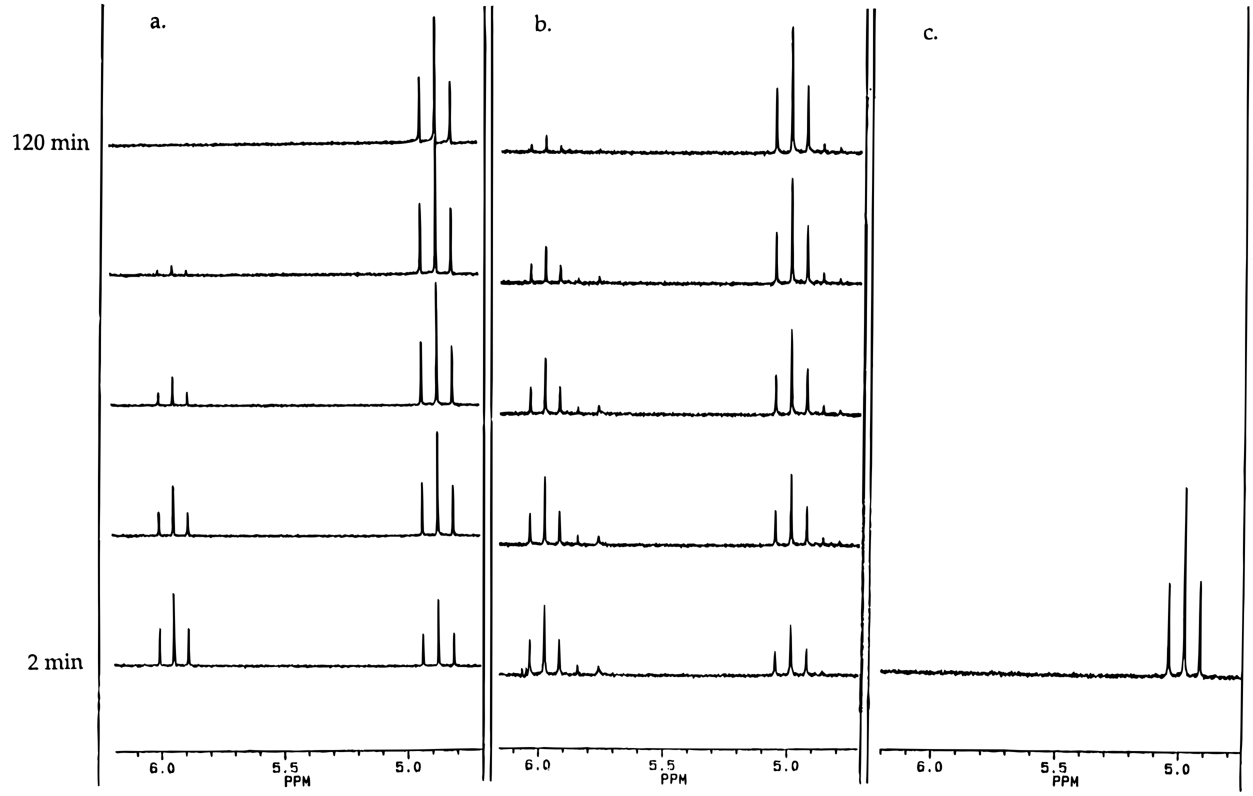
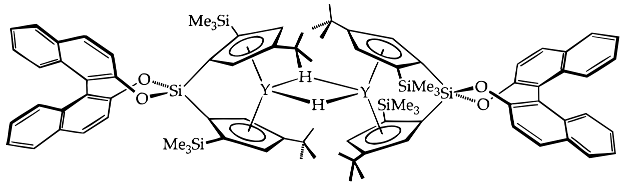
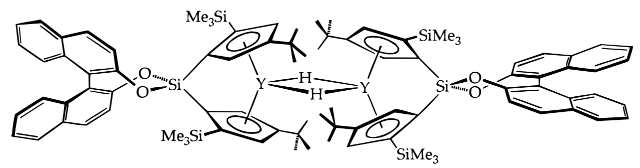


Figure 1. Y(μ_2-*H*)$_2$Y region of the 500-MHz ^{1}H NMR spectra for [BpY]$_2$(μ_2-H)$_2$ (a) and [(BnBp)Y]$_2$(μ_2-H)$_2$ (b and c) following H$_2$ addition at 2 min, at 120 min, and at regular intervals in between: (a) *rac*-BpYCH(SiMe$_3$)$_2$; (b) *rac*-(BnBp)YCH(SiMe$_3$)$_2$ (prepared from (±)-1,1′-bi-2-naphthol); (c) (*R*,*S*)-(BnBp)YCH(SiMe$_3$)$_2$ (prepared from (*R*)-(+)-1,1′-bi-2-naphthol).



a. eclipsed, D_2 homochiral hydride dimer, *R,S*-(BnBp)Y(μ_2-H)$_2$-*R,S*-(BnBp)Y

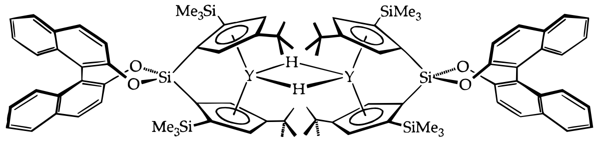


b. skewed, D_2 homochiral hydride dimer, *R,S*-(BnBp)Y(μ_2-H)$_2$-*R,S*-(BnBp)Y

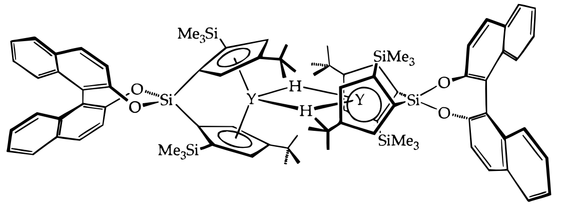
Figure 2. Possible solution structures for homochiral dimer (*R,S*)-(BnBp)Y(μ_2-H)$_2$-(*R,S*)-(BnBp)Y.

the two yttrocene units and the μ_2-hydride ligands, thus maintaining good Y−H bonding, while at the same time reducing the steric crowding of *tert*-butyl groups of the eclipsed C_{2h} isomer.

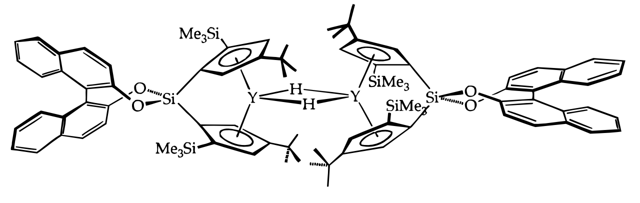
Crystallization and X-ray Crystal Structure Determination for *rac*-[(BnBp)Y]$_2$(μ_2-H)$_2$. During the course of our experimental work with hydride dimers **6**, we have noted an additional significant difference: the racemic dimer, *rac*-[(BnBp)Y]$_2$(μ_2-H)$_2$ (*rac*-**6**), is markedly less soluble in hydrocarbon and ether solvents than either of the two corresponding resolved complexes. The implication is that the racemate readily crystallizes in a centrosymmetric manner.[24] This phenomenon has also been reported originally by Brintzinger,[25] and more recently by Bosnich[12] and by Collins.[26] All three groups found that racemic titanocene derivatives are less soluble than the resolved compounds.



a. eclipsed, C_{2h}-symmetric heterochiral hydride dimer, *R,S*-(BnBp)Y(μ_2-H)$_2$-*S,R*-(BnBp)Y



b. staggered, ≈S_4-symmetric heterochiral hydride dimer, *R,S*-(BnBp)Y(μ_2-H)$_2$-*S,R*-(BnBp)Y



c. skewed, C_2-symmetric heterochiral hydride dimer, *R,S*-(BnBp)Y(μ_2-H)$_2$-*S,R*-(BnBp)Y

Figure 3. Possible solution structures for heterochiral dimers (*R,S*)-(BnBp)Y(μ_2-H)$_2$-(*S,R*)-(BnBp)Y.

X-ray quality crystals of *rac*-**6** have been obtained by taking advantage of these solubility differences. Thus, by layering a solution of (*R,S*)-**6** in petroleum ether carefully over a solution of (*S,R*)-**6** in toluene, crystals of the racemic mixture grow slowly at the interface in the form of long, colorless needles. Crystallographic studies confirm the centrosymmetry of the space group $P\bar{1}$, and that the [BnBp] ligand is indeed coordinated to the metal as the predicted diastereomer (*vide supra*). As

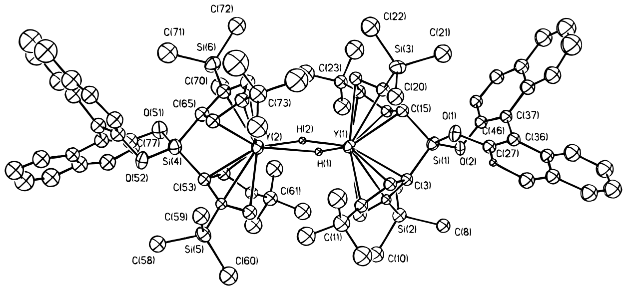


Figure 4. A drawing (of the (*S*,*R*)-(BnBp)Y(μ_2-H)$_2$-(*S*,*R*)-(BnBp)Y enantiomer) of the homochiral dimer *rac*-[(BnBp)Y]$_2$(μ_2-H)$_2$ shown at the 50% probability level, showing the numbering system. The only hydrogen atoms shown (as spheres of arbitrary size) are on the two hydride ligands bridging yttrium centers.

shown in Figure 4, the individual C_2-symmetric yttrocene units of the dimer are symmetrically bridged by the hydride ligands. However, unlike *rac*-[BpY]$_2$(μ_2-H)$_2$, which has nearly ideal D_2-symmetry, and thus maximum overlap of yttrium and hydride orbitals for the Y(μ_2-H)Y moiety, *rac*-**6** exhibits a twisted, *i.e.* skewed (Figure 2b), rather than eclipsed (Figure 2a) arrangement. Thus, the dimer has overall D_2-symmetry. The dihedral angle for the equatorial planes of the individual yttrocene units of each dimer is approximately 40°. Apparently, substantial overlap with the spherically symmetric hydrogen 1s valence orbitals is maintained, despite the skewed arrangement of yttrocene frontier orbitals. Indeed, an even more dramatic twisting (53° dihedral angle) has recently been reported for related C_2-symmetric [(EBTHI)Ti^{III}]$_2$(μ_2-H)$_2$, a feature that was reconciled on the basis of the apparent steric demands of the tetrahydroindenyl ligands.[27] The differences in the crystal structures of *rac*-[BpY]$_2$(μ_2-H)$_2$ (eclipsed, D_2) and *rac*-[(BnBp)Y]$_2$(μ_2-H)$_2$ (skewed, D_2) must therefore be due to differences in crystal packing forces, since both dimers have identically substituted cyclopentadienyls projecting toward the opposite yttrocene fragment. The barrier must be quite small for twisting the yttrocene units relative to each other by this amount, in agreement with the ^{1}H NMR spectra that indicate either an eclipsed solution structure (Figure 2a) or a rapidly oscillating skewed structure (Figure 2b) (*vide supra*).

Conclusions

The new ligand described above, {(η^{5-}C$_5$H$_2$-2-SiMe$_3$-4-CMe$_3$)$_2$Si(OC$_{10}$H$_6$C$_{10}$H$_6$O)} ([BnBp]), exhibits sufficient diasteromeric control to direct coordination of the bis(cyclopentadienyl) unit onto the yttrocene unit in a completely stereospecific manner. Hence, by incorporating commercially available enantiopure (*R*)-(+)-1,1′-bi-2-naphthol or (*S*)-(−)-1,1′-bi-2-naphthol, either enantiopure (*S*)- or (*R*)-, C_2-symmetric yttrocene derivatives can been prepared.

The monomeric hydride derivative (BnBp)YH, prepared via hydrogenolysis of (BnBp)YCH(SiMe$_3$)$_2$, exhibits a strong tendency to dimerize. Indeed, when *rac*-(BnBp)YH is generated, both the homochiral and heterochiral dimers are observed to rapidly form, the latter only slowly converts to the more stable homochiral dimer. Reexamination of the hydrogenolysis of *rac*-BpYCH(SiMe$_3$)$_2$ revealed this same sequence of events. This propensity for the monomeric hydrides to rapidly dimerize to much more stable dimers greatly reduces their activity as catalysts for hydrogenation or polymerization of α-olefins. In fact, the (homochiral) dimers are the thermodynamic “sinks” after these catalytic reactions are complete, being generated, if need be, even by β-H elimination from the yttrocene alkyls. The solid state structures of the homochiral hydride dimers *rac*-[BpY]$_2$(μ_2-H)$_2$ and *rac*-[(BnBp)Y]$_2$(μ_2-H)$_2$ differ, the former adopting an eclipsed D_2 structure, the latter a skewed, D_2 structure with a dihedral angle between the equatorial planes of the yttrocene units of 40°. Apparently, good overlap of hydride orbitals with the frontier orbitals of the yttrocenes is maintained, even in this twisted conformation. A similar skewed arrangement (Figure 3c) is thus the most likely structure for the less stable heterochiral dimers, since by moderately twisting yttrocene units adequate Y(μ_2-H)$_2$Y bonding would be retained and unfavorable steric interactions between *tert*-butyl substituents would be avoided.

We are presently utilizing these enantiopure yttrocenes to define the absolute configurations for α-olefin insertion into Y−H and Y−alkyl bonds.[28] We are also exploring the scope of this approach whereby the stereogenic linker, [Si(1,1′-binaphth-2,2′-diolate)] directs coordination of similarly substituted cyclopentadienyl ligands to afford a single diasteromeric *ansa*-metallocene.

Experimental Section

General Considerations. All air and/or moisture sensitive compounds were manipulated using standard high-vacuum line, Schlenk, or cannula techniques, or in a glovebox under a nitrogen atmosphere, as described previously.[29] Argon and hydrogen gases were purified and dried by passage through columns of MnO on vermiculite and activated 4 Å molecular sieves. Solvents were stored under vacuum over titanocene[30] or sodium benzophenone ketyl. The preparations of 6,6-dimethylfulvene[31] and *tert*-butylcyclopentadienyllithium[32] were carried out as previously reported. LiN(SiMe$_3$)$_2$ and KOCMe$_3$ (Aldrich) were purified by sublimation prior to use. (*R*)-(+)-, (*S*)-(−)-, and *rac*-(±)-1,1′-bi-2-naphthol were purchased (Aldrich) and used as received. The same procedures were followed for racemic or resolved 1,1′-bi-2-napthol.

NMR spectra were recorded on General Electric QE300 (300 MHz for ^{1}H) and Bruker AM500 (500.13 MHz for ^{1}H) spectrometers. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey. Many of the compounds failed to give satisfactory carbon/hydrogen analyses, even when combusted with added V$_2$O$_5$ oxidant. Moreover, in many cases the results were inconsistent from run to run.

{C$_5$H$_4$(CMe$_3$)}$_2$SiCl$_2$. In a dinitrogen-filled glovebox, to a stirring solution of 31.5 g of SiCl$_4$ in 700 mL of THF was added 47.4 g (2 equiv) of *tert*-butylcyclopentadienyllithium over 20 min, giving a clear yellow solution. After the solution was stirred overnight, the flask was fitted with a Kugelrohr bulb and taken out of the box. All volatiles were removed *in vacuo*, followed directly by a Kugelrohr distillation

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(24) Of course, the enantiomerically pure hydride dimers, (*R*,*S*)-(BnBp)Y-(μ_2-H)$_2$-(*R*,*S*)-(BnBp)Y and (*S*,*R*)-BnBp)Y(μ_2-H)$_2$-(*S*,*R*)-(BnBp)Y, must crystallize in a chiral space group, rather than a racemic one. We have not yet established whether the enantiomerically pure hydride dimer must form a thermodynamically less stable crystal, or (more likely) that its crystal is kinetically less accessible than that for the racemate. For a discussion of the relative occurrences and stabilities of racemic versus homochiral crystals, see: Brock, C. P.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 9811.

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at 60 °C. The product was stored in the glovebox freezer. Yield: 31.5 g of yellow oil, 57%.

BnDpH$_2$. In a dinitrogen-filled glovebox, 11.78 g of $\{C_5H_4(CMe_3)\}_2SiCl_2$ was stirred with 350 mL of THF. A solution of 9.89 g of (±)-1,1′-bi-2-naphthol (or (*R*)-(+)-1,1′-bi-2-naphthol or (*S*)-(−)-1,1′-bi-2-naphthol) and 10.47 g (3 equiv) of triethylamine in 200 mL of THF was added dropwise over several hours. The initially clear solution became cloudy and pale green after several minutes. After the solution was stirred overnight, the flask was removed from the glovebox and the THF removed *in vacuo*. Petroleum ether (300 mL) was condensed in, the mixture was stirred briefly, and then the petroleum ether was removed *in vacuo*. The reaction flask was fitted with a standard fine frit assembly, and 250 mL of diethyl ether was condensed onto the mixture and stirred. Filtration and washing with diethyl ether yielded a large amount of a white solid ($NEt_3{\cdot}HCl$) and a clear yellow filtrate. All volatiles were removed *in vacuo*, leaving a shiny yellow solid foam. Yield 17.9 g of fine yellow powder, 93%. Elemental analysis calcd for $C_{38}H_{38}O_2Si$: C 82.25; H 6.92. Found (with V_2O_5 added): For *rac* (±) C 81.61, 81.47; H 7.48, 7.57. For (*R*)-(+) C 79.19, 80.85; H 6.40, 6.57. For (*S*)-(−) C 82.77; H 6.93. Found (without added oxidant): For (*R*)-(+) C 81.25, 81.39; H 7.18, 7.14. For (*S*)-(−) C 74.65, 73.50; H 7.07, 7.09.

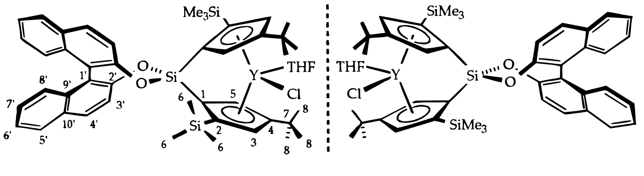
[BnDp]Li$_2$. An extra large swivel frit assembly equipped with two 1-L round-bottom flasks was loaded in the glovebox with 17.7 g of [(±)-Bn]DpH$_2$ (or one of the resolved materials) and 10.7 g (2 equiv) of $LiN(SiMe_3)_2$. The assembly was transferred to a vacuum line and evacuated and 600 mL of THF was condensed in at −78 °C. The solution was stirred for 15 min at −78 °C and then allowed to warm slowly to room temperature. The solution was stirred for 3 h at room temperature. All volatiles were removed *in vacuo*, leaving a pasty beige solid. Diethyl ether (150 mL) was condensed in at −78 °C, the mixture was warmed to room temperature and stirred, and diethyl ether was removed *in vacuo*, leaving a foamy yellow paste which was pumped on under dynamic vacuum overnight. Approximately 200 mL of petroleum ether was condensed onto the paste, and the mixture was stirred vigorously at room temperature for 20 min to produce a white solid and light yellow supernatant. The solid was filtered off, washed with additional petroleum ether, and dried *in vacuo* to yield 18.34 g (86%) of off white [BnDp]Li$_2$·(THF). Elemental analysis calcd for $C_{42}H_{44}O_3SiLi_2$: C 78.97; H 6.94. Found (with V_2O_5 added): For (*R*)-(+) C 77.06, 79.01; H 7.51, 7.30. For (*S*)-(−) C 76.87; H 6.91. Found (without added oxidant): For (*R*)-(+) C 77.56, 77.35; H 7.50, 7.46. For (*S*)-(−) C 74.86, 75.96; H 7.21, 7.31.

BnBpH$_2$. An extra large swivel frit assembly fitted with a 500-mL Kjeldahl flask and a 1-L round-bottom flask was loaded with 18.1 g of [(±)-Bn]DpLi$_2$ in a dinitrogen-filled glovebox. The assembly was moved to a vacuum line and evacuated and 600 mL of THF was condensed on at −78 °C. $SiMe_3Cl$ (11 mL, 3 equiv) was condensed into the solution at −78 °C. The reaction was allowed to warm to room temperature and stirred overnight. All volatiles were removed *in vacuo*, leaving a light yellow foamy solid. After pumping on the solid for 2 h under dynamic vacuum, 200 mL of diethyl ether was condensed in at −78 °C, allowed to warm to room temperature, and stirred for 15 min before being pumped off, leaving a light yellow foamy solid. Petroleum ether (400 mL) was condensed in at −78 °C, giving a light yellow solution and a white precipitate (LiCl). After the solution was stirred at room temperature for 2 h, the LiCl was filtered off and washed, giving a clear yellow filtrate. When volatiles were removed, a yellow foamy solid remained. Yield: 16.62 g (87%) of BnBpH$_2$ as a microcrystalline white powder. Elemental analysis calcd for $C_{44}H_{54}O_2Si_3$: C 75.59; H 7.78. Found (with V_2O_5 added): For (*S*)-(−) C 69.15; H 8.15. Found (without added oxidant): For (*R*)-(+) C 74.42, 74.23; H 8.11, 8.20. For (*S*)-(−) C 74.35; H 8.15.

[BnBp]K$_2$. An extra large swivel frit assembly fitted with a 1-L round-bottom flask and a 500-mL Kjeldahl flask was loaded with 16.22 g of BnBpH$_2$ and 5.19 g (2 equiv) of $KOCMe_3$ in a dinitrogen-filled glovebox. The assembly was transferred to a vacuum line and evacuated, and 500 mL of THF was condensed onto the solids at −78 °C. The brownish-yellow solution was warmed to room temperature, all solids were dissolved, and the solution was allowed to stir overnight. All volatiles were removed *in vacuo*, leaving a light brown foamy paste. Diethyl ether (200 mL) was condensed in at −78 °C and warmed to room temperature. All volatiles were removed *in vacuo* leaving a light brown solid. Diethyl ether (100 mL) was condensed in at −78 °C, giving a yellow solution with a white precipitate. Petroleum ether (400 mL) was condensed in, and the solution was warmed to room temperature and stirred for 1 h. The yellow supernatant was filtered away from the solid. The solid was washed once with the volatile components of the filtrate, and then all volatiles were removed *in vacuo*. Its ^{1}H NMR spectrum indicates 0.5 equiv of THF. Yield 17.62 g (92%) of [BnBp]K$_2$·0.5(THF) as a free-flowing yellow powder. Elemental analysis calcd for $C_{46}H_{56}O_{2.5}Si_3K_2$: C 68.09; H 6.96. Found (with V_2O_5 added): For *rac* (±) C 66.43, 66.29; H 7.02, 7.08. For (*R*)-(+) C 67.49, 66.75; H 7.19, 7.16. For (*S*)-(−) C 67.79, 68.08; H 7.07, 7.32. Found (without added oxidant) for *rac* (±) C 67.30, 66.90; H 7.30, 7.22. For (*S*)-(−) C 66.97, 66.99; H 7.23, 7.39.

(BnBp)YCl(THF) (3) and [(BnBp)Y]$_2$(μ_2-Cl)$_2$ (4). In a round-bottom flask attached to a vacuum line 3.00 g of [BnBp]K$_2$ and 1.59 g (1 equiv) of $YCl_3(THF)_3$ were refluxed overnight in 150 mL of THF under argon. After the mixture was cooled to room temperature, all volatiles were removed *in vacuo*, and 100 mL of diethyl ether were condensed in at −78 °C. Filtration and concentration of the filtrate at this stage results in precipitation of THF adduct **3** in approximately 75% yield as an off-white solid. As the THF-free chloride **4** is normally desired, the mixture was warmed to room temperature and stirred briefly and then all volatiles were removed *in vacuo*. The residue was pumped on at high vacuum for another 8 h. Toluene (100 mL) was condensed onto the residue at −78 °C. This mixture was refluxed under an argon atmosphere for several hours. All volatiles were again pumped away at high vacuum. Diethyl ether was condensed on at −78 °C and pumped away at room temperature under high vacuum. The reaction apparatus was then transferred to the dinitrogen-filled glovebox where the flask containing the products was fitted with a large swivel frit apparatus. After transferring the apparatus back to the vacuum line, it was evacuated and 100 mL of Et_2O was condensed on at −78 °C. After the mixture was warmed to room temperature, the orange supernatant was filtered away from the white solid (KCl). The filter cake was washed once with fresh Et_2O, and the volatiles were removed from the filtrate *in vacuo*, leaving an orange foam. Petroleum ether (100 mL) was condensed in and the mixture stirred vigorously for 2 h. The orange supernatant was filtered away from the white solid, which was washed twice with fresh petroleum ether. The solid was dried *in vacuo*. White solid **4** (1.74 g, 55%) was obtained. Elemental analysis calcd for $C_{44}H_{52}O_2Si_3ClY$: C 64.33; H 6.38. Found (without added oxidant): For *rac* (±) C 55.57; H 5.77. For (*S*)-(−) C 56.54, 56.49; H 6.10, 5.91.

^{1}H and ^{13}C NMR Characterization of *rac*-BnBpYCl·THF. Multidimensional NMR studies have allowed thorough ^{1}H- and ^{13}C-spectral assignments for **2** in THF-d_8. The C2′ carbon was assigned on the basis of its upfield chemical shift. H,C-COSY established the carbon−hydrogen connectivities, and H,H-COSY spectra were used to distinguish H3′ and H4′ from H5′−H8′. Cross peaks found from long-range HETCOR studies then allowed unambiguous connectivities to be established for the binaphthyl fragment as follows: C2′ with H3′; C10′ with H4′ and H5′; C9′ with H8′; and thus C1′ by elimination. The cyclopentadienyl fragment was similarly assigned; however, due to the coincident chemical shifts of H3 and H5, their respective carbon atoms could not be distinguished.



C1 (δ 114.93); C2 (δ 125.47); C3 (δ 127.69 or 116.81); C4 (δ 147.07); C5 (δ 116.81 or 127.69); C6 (δ 1.96); C7 (δ 33.29); C8 (δ 31.91); C1′ (δ 122.34); C2′ (δ 152.04); C3′ (δ 130.61); C4′ (δ 123.26); C5′ (δ 127.77); C6′ (δ 126.35); C7′ (δ 124.53); C8′ (δ 128.85); C9′ (δ 134.69); C10′ (δ 131.42); H3 (δ 6.54, m, 1H); H5 (δ 6.54, m, 1H); H6 (δ 0.22, s, 9H); H8 (δ 1.31, s, 9H); H3′ (δ 7.92, d, J = 8.7 Hz, 1 H); H4′ (δ 7.65, d, J = 8.4 Hz, 1 H); H5′ (δ 7.17, ∼d, J = 8.4 Hz, 1 H); H6′ (δ 7.12, ∼t, J = 7.1 Hz, 1 H); H7′ (δ 7.28, ∼d, J = 7.1 Hz, 1 H); H8′ (δ 7.85, ∼d, J = 8.1 Hz, 1 H).

(BnBp)YCH(SiMe$_3$)$_2$ (5). In a dinitrogen-filled glovebox, 1.60 g of [(BnBp)Y]$_2$(μ_2-Cl)$_2$ and 0.324 g of LiCH(SiMe$_3$)$_2$ (1 equiv) were loaded into a flask and fitted with a large swivel frit. The assembly was evacuated and 150 mL of toluene condensed in at −78 °C. The mixture was warmed to room temperature and stirred for 2 days. All volatiles were removed *in vacuo* and 75 mL of petroleum ether was condensed in, the solution was warmed to room temperature, and petroleum ether was removed *in vacuo*. The remaining solid was pumped on under dynamic vacuum for 2 h. Petroleum ether (150 mL) was then condensed in, and the mixture was warmed to room temperature and stirred vigorously. The orange supernatant was filtered away from the white solid (LiCl), which was washed twice with fresh petroleum ether. All volatiles were removed *in vacuo*, and the remaining orange foam was pumped on for 3 h at high vacuum. Light brownish-orange free-flowing solid **5** (1.15 g, 62%) was obtained. {^{1}H}^{13}C NMR (benzene-d_6): δ 151.7, 151.1, 134.7, 131.5, 131.3, 129.0, 127.9, 127.8, 127.1, 127.0, 126.9, 126.8, 125.0, 122.6, 125.0, 122.6, 122.5, 121.5, 121.3, 120.0, 199.8, 32.8, 32.5, 33.8, 32.5, 2.2, 1.9, 1.8. Elemental analysis calcd for $C_{51}H_{71}O_2Si_5Y$: C 64.78; H 7.58. Found (with V_2O_5 added): For (*R*)-(+) C 64.18, 64.13; H 7.49, 7.49. Found (without added oxidant): For *rac* (±) C 57.92, 57.32; H 6.61, 6.64.

[(BnBp)Y]$_2$(μ_2-H)$_2$ (6). (*R*,*S*)-(BnBp)YCH(SiMe$_3$)$_2$ (700 mg) was loaded into a high-pressure glass bomb. After evacuating, approximately 50 mL of toluene was condensed in at −78 °C. H_2 (4 atm) was then admitted. The reaction was stirred at room temperature for 2 h. The solution was transferred into a 100-mL Kjeldahl flask fitted with a medium-sized swivel frit assembly. Toluene was removed *in vacuo*, and 30 mL of petroleum ether was condensed into the evacuated assembly at −78 °C. The mixture was stirred vigorously at room temperature. The orange filtrate was filtered away from the white solid, which was washed twice with fresh petroleum ether. All volatiles were removed *in vacuo* from the filtrate, and the residual solid was pumped on at high vacuum overnight. Recrystallization from petroleum ether yielded 269 mg (46%) of white solid **6** in two crops. {^{1}H}^{13}C NMR (benzene-d_6): δ 147.9, 143.9, 134.8, 131.5, 131.2, 129.3, 127.0, 125.0, 123.2, 122.8, 122.7, 120.1, 120.0, 34.5, 33.4, 2.4. Elemental analysis calcd for $C_{44}H_{53}O_2Si_3Y$: C 67.15; H 6.79. Found (with V_2O_5 added): For *rac* (±) C 68.58, 65.54; H 7.35, 7.07.

^{1}H NMR Studies of the Hydrogenolysis of BpYCH(SiMe$_3$)$_2$ and 5. Approximately 10 mg of the appropriate bis(trimethylsilyl)methyl complex, BpYCH(SiMe$_3$)$_2$, *rac*-(BnBp)YCH(SiMe$_3$)$_2$, or (*R*,*S*)-(BnBp)YCH(SiMe$_3$)$_2$, was loaded into a J. Young NMR tube. The tube was filled with benzene-d_6 , frozen by cooling to with liquid nitrogen, and evacuated at that temperature. H_2 (1 atm) was admitted into the tube at that temperature. The tube was sealed and kept at −78 °C until just before putting it into the spectrometer, at which point it was quickly thawed and shaken vigorously. Spectra were taken immediately, and then at regular time intervals over several hours.

1-Pentene Polymerization with (*R*,*S*)-BnBpYH. A 50-mL flask was charged with 12 mg of **5** and approximately 6 mL of 1-pentene, which was vacuum transferred from $LiAlH_4$. At 0 °C with stirring the flask was opened to a manifold containing H_2 (740 Torr). Stirring continued for at least 2.5 h at 0 °C, but after 11 h at 0 °C stirring had stopped. The yellow solid poly-1-pentene was dissolved in 20 mL of chloroform and reprecipitated by addition to 200 mL of methanol containing 2 mL 12 M HCl. The white solid was washed with 200 mL of boiling methanol and dried *in vacuo* for 12 h. Yield was 2.73 g of hard white solid (ca. 70% based on 1-pentene). ^{13}C NMR spectra (9:1 *o*-dichlorobenzene−benzene-d_6, 10% w/v solution of polymer, 50 °C, 12 000 scans, inverse gated decoupling, 2-s relaxation delay) revealed >95% *mmmm* pentad.[22] GPC (methylene chloride vs polystyrene standards) indicated M_n = 119 000, PDI = 1.44.

X-ray Crystal Structure Determination for 6. Most of the crystals examined were of very poor X-ray quality. One acceptable crystal of **6**, obtained from a toluene/petroleum ether solution, was secured in a glass capillary with grease, placed in a goniometer head on the Enraf-Nonius CAD4 diffractometer, and centered optically. Unit cell parameters and an orientation matrix for data collection were obtained by using the centering program of the CAD4 system. Details of the crystal data are given in the supporting information. For each crystal, the actual scan range was calculated by scan width = scan range + 0.35 tan θ, and backgrounds were measured by using the moving-crystal−moving-counter technique at the beginning and end of each scan. Two representative reflections were monitored every 150 min as a check on the instrument and crystal stability. Lorentz, polarization, and decay corrections were applied, as was an empirical absorption correction based on a series of ψ scans. The weighting scheme used during refinement was $1/\sigma^2(F_o^2)$ based on counting statistics, plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term $(0.014\bar{I})^2$.

The structure was solved by direct methods using SHELXL-86,[33] which revealed the positions of most of the non-hydrogen atoms. All other non-hydrogen atoms were found by successive difference Fourier syntheses. The bridging hydride positions were located in a final difference Fourier map and their positions fixed; all other hydrogens were placed at their expected chemical positions using the program HFIX in SHELXL-93[34] and were included in the final least-squares refinement cycles as riding atoms with *U*'s related to the atoms ridden upon. The yttrium, silicon, and oxygen atoms were refined anisotropically; all other non-hydrogen atoms were refined isotropically.

There were several solvent molecules present in the crystal lattice: two toluene molecules which could only be modeled as benzene-like moieties as the methyl groups were completely disordered, and two other smaller solvent fragments which could not be modeled successfully. Scattering factors were taken from Cromer and Waber.[35] Anomalous dispersion corrections were those of Cromer.[36] All data processing was carried out on a Micro VAX 3100 computer using the CRYM[37] system and structure solution, refinement, and preparation of figures and tables for publication were carried out on PC's using SHELXL-86,[33] SHELXL-93,[34] and XP/PC.[38]

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Supporting Information Available: Details of the structure determinations, including listings of final atomic coordinates, thermal parameters and bond distances and angles (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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