

Photochemical Isomerization of Me₂Si-Bridged Zirconocene Complexes. Application to Stereoselective Syntheses of *ansa*-Zirconocene Binaphtholate Stereoisomers^{†,1}

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Upon irradiation in toluene solution, *meso*-racemate mixtures of Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂-ZrCl₂ or Me₂Si(2-Me-4-phenyl-C₅H₂)₂ZrCl₂ react with 1 equiv of the dilithium salt of racemic binaphthol quantitatively to the racemic binaphtholate complex. Analogous reactions with 1 equiv of the *R*(+) enantiomer of dilithium binaphtholate give a near-quantitative yield of the enantiomerically pure *ansa*-zirconocene binaphtholate complex. The structures of the racemic binaphtholate complex, Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂Zr(binaphtholate), and of a monodentate binaphtholate complex with a *meso* configured zirconocene moiety, Me₂Si(3-*t*Bu-C₅H₃)₂Zr(binaphtholate) chloride, were crystallographically determined.

Introduction

Racemic *ansa*-metallocene complexes continue to be of interest as catalysts for the stereospecific polymerization of α -olefins;² their separate enantiomers are presently gaining interest also as precatalysts for enantioselective hydrogenation³ and C–C bond formation reactions.⁴ A problem in the synthesis of these complexes is the formation of *meso* and racemic isomers in the reaction of a prochiral ligand unit with the appropriate metal halide. While methods have been devised to minimize the formation of unwanted *meso* isomers⁵ or to eliminate the possibility of their formation altogether,⁶ the overall yields of the reaction sequences required for this purpose are generally relatively low.

In an earlier study in our group, ethylenebis(tetrahydroindenyl)titanium dichloride had been found to undergo an efficient photoinduced *meso*-to-*rac* isomerization.⁷ By a combined irradiation/evaporation technique, *meso*-racemate mixtures of this complex were almost completely converted to the pure racemate due to the much lower solubility of the latter.⁸ This technique is not applicable to *ansa*-metallocene complexes in general, as solubilities for their *meso* and racemic isomers are usually not sufficiently different to drive their photoisomerization anywhere close to completion.⁹ In a study on photoisomerizations of ethylene-bridged bis(cyclopentadienyl)titanium complexes in THF solutions, Collins and co-workers observed that the photo-stationary *rac*/*meso* ratios depend on the substitution patterns of the cyclopentadienyl rings. Unspectacular *rac*/*meso* ratios of ≤ 1 were obtained for complexes containing only substituents in the β -position; complexes carrying substituents in the α as well as in the β -position, however, yielded *rac*/*meso* ratios up to 15:1.¹⁰

We now report on a high-yield synthesis of racemic Me₂Si-bridged zirconocene binaphtholate complexes and their isolated enantiomers, which is based on a combined photoisomerization and complex formation with 1,1'-bi-2-naphthol.

[†] Dedicated to Professor Walter Siebert on the occasion of his 60th birthday.

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Table 1. Irradiation of the Complexes

Me₂Si(1-Cp-3-*t*Bu)₂ZrCl₂ (1),
Me₂Si(1-Cp-2-Me-4-*t*Bu)₂ZrCl₂ (2),
Me₂Si(1-Cp-2-Me-4-*i*Pr)₂ZrCl₂ (3),
Me₂Si(1-Cp-2-Me-4-Ph)₂ZrCl₂ (4)

time/min	1 ^a	2 ^a	2 ^b	3 ^a	3 ^b	4 ^a
0	75:25 ^b	100:0	100:0	100:0	100:0	0:100
15		72:28	100:0	64:36	100:0	
20	61:39					41:59
45	56:44	56:44	90:10	58:42	96:4	56:44
105		56:44	72:28	56:44	90:10	
465			43:57		70:30	
1905			42:58		56:44	

^a Rac/meso ratios in benzene-*d*₆ at room temperature. ^b Rac/meso ratios, in toluene-*d*₈ at -40 °C.

Results and Discussion

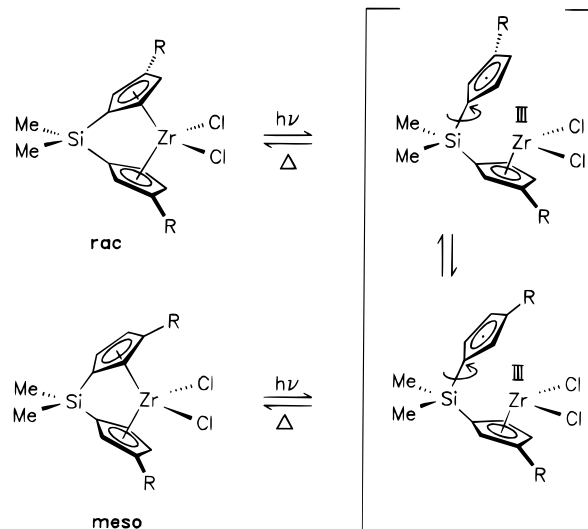
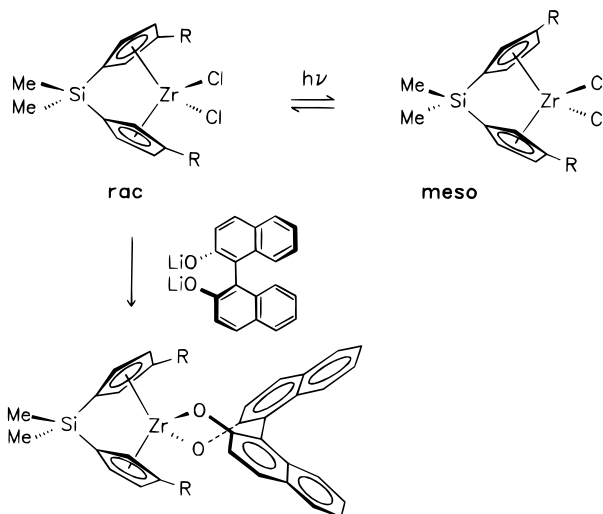
Irradiation of benzene-*d*₆ or toluene-*d*₈ solutions containing an arbitrary mixture of the racemic and meso isomers of the Me₂Si-bridged zirconocene dichlorides Me₂Si(3-*t*Bu-C₅H₃)₂ZrCl₂ (1),⁹ Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂ZrCl₂ (2),⁹ Me₂Si(2-Me-4-*i*Pr-C₅H₂)₂ZrCl₂ (3),⁹ or Me₂Si(2-Me-4-Ph-C₅H₂)₂ZrCl₂ (4)¹¹ with a 125 W high-pressure Hg lamp causes a rather rapid photoisomerization. In the course of 1–2 h, one obtains in each case photostationary reaction mixtures with meso/racemate ratios close to 1 (Table 1).

Even the presence of α -methyl substituents in the Me₂Si-linked C₅ rings, which had been found to lead to meso/racemate ratios of 1:6 for Me₂Si(2-Me-4-*i*Pr-C₅H₂)₂ZrCl₂ and 1:2 for Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂ZrCl₂ in the thermal synthesis of these complexes, does not affect the photostationary isomer ratios in any comparable manner. In this regard, the Me₂Si-bridged zirconocene complexes studied here yield results distinctly different from the C₂H₄-bridged titanocene complexes studied by Collins and co-workers.¹⁰

In accord with previous studies,¹² we assume that this photoisomerization occurs by way of a homolytic photodissociation of one of the C₅ ring ligands, rotation of the resulting cyclopentadienyl radical about the Si–C(1) bond, and its reattachment to the Zr(III) center (Scheme 1). Apparently, the extinction coefficients of the two isomers, the quantum yields for their conversion to the diradical intermediates and the reaction rates along the alternative recombination paths are all sufficiently similar to generate practically identical stationary concentrations of the two isomers under the conditions employed.

In an attempt to trap the racemic isomers from each of these photostationary reaction systems by a selective reaction with a binaphthol ligand, we have tried to conduct analogous photoisomerization reactions in toluene solutions containing the dilithium salt of racemic 1,1'-bi-2-naphthol (Scheme 2).¹³

A first experiment of this kind with a meso-racemate mixture of Me₂Si(3-*t*Bu-C₅H₃)₂ZrCl₂, where the C₅ rings

Scheme 1**Scheme 2**

of 1 carry only a single substituent, proved fruitless: Addition of dilithium binaphtholate to this solution causes the generation of exactly that fraction of the binaphtholate chelate *rac*-Me₂Si(3-*t*Bu-C₅H₃)₂Zr-(C₂₀H₁₂O₂) (*rac*-1-BIN) to which *rac*-1-Cl₂ was present in the initial isomer mixture. The meso isomer, on the other hand, is quantitatively converted to an asymmetric binaphtholate complex Me₂Si(3-*t*Bu-C₅H₃)₂Zr-(C₂₀H₁₂O₂Li)Cl (*meso*-1-Cl-BIN-Li). NMR data of this complex (see Experimental Section) indicate monodentate bonding of the binaphtholate ligand.^{5b,14} A complex *meso*-1-Cl-BINH, derived from *meso*-1-Cl-BIN-Li by hydrolysis, was isolated by crystallization. Its molecular structure, represented in Figure 1 and Table 2, reveals a monodentate coordination of the binaphtholate ligand at the unobstructed coordination site of the meso *ansa*-zirconocene. The chloride ligand shielded by the two *tert*-butyl groups is apparently retained due to its steric inaccessibility. The torsion angle between the two naphthyl ring planes (75.8°) is relatively large compared to bidentate binaphtholate complexes. The Zr–O distance of 1.98 Å is somewhat shorter, the Zr–O–C angle (154°) somewhat larger, than the respective parameters

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(13) In similar experiments with en(3-*t*Bu-C₅H₃)TiCl₂ or en(thind)-TiCl₂ and racemic or enantiomerically pure 1,1'-bi-2-naphthol in THF solution, Kuntz and Collins obtained the respective binaphtholate complexes in low yields only. Kuntz, R. A. Ph.D. Thesis, University of Waterloo, 1991.

(14) A related complex Me₄C₂(3-*t*Bu-C₅H₃)₂TiCl-BINH has been described by McLaughlin et al.^{5b}

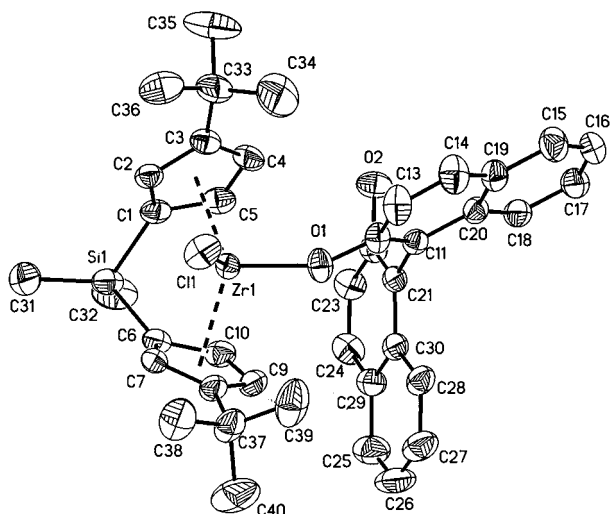


Figure 1. Molecular structure of *meso*-1-Cl-BINH (30% probability thermal ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\text{Me}_2\text{Si}(3\text{-}t\text{Bu-C}_5\text{H}_3)_2\text{ZrCl-Binaphtholate (1-Cl-BINH)}$

Zr(1)–O(1)	1.967 (2)	Zr(1)–Cl(1)	2.446 (2)
Zr(1)–C(1)	2.481 (3)	Zr(1)–C(2)	2.556 (4)
Zr(1)–C(3)	2.668 (4)	Zr(1)–C(4)	2.583 (4)
Zr(1)–C(5)	2.452 (4)	Zr(1)–C(6)	2.486 (4)
Zr(1)–C(7)	2.531 (3)	Zr(1)–C(8)	2.640 (4)
Zr(1)–C(9)	2.592 (4)	Zr(1)–C(10)	2.476 (4)
Zr(1)–Cp(1) ^a	2.248	Zr(1)–Cp(2) ^a	2.243
Si(1)–C(1)	1.876 (3)	Si(1)–C(6)	1.859 (3)
Si(1)–C(31)	1.845 (4)	Si(1)–C(12)	1.852 (4)
C(1)–Si(1)–C(6)	95.0 (1)	O(1)–Zr(1)–Cl(1)	97.8 (1)
Naph(1)–Naph(2) ^b	75.8	Zr(1)–O(1)–C(12)	154.6 (2)

^a Cp(1) and Cp(2) are the centroids of the C(1)–C(5) and C(6)–C(10) cyclopentadienyl rings. ^b Naph(1) and Naph(2) are the planes of C(11)–C(20) and C(21)–C(30) binaphtholate rings.

in chlorine-free, bidentate binaphtholate complexes. *meso*-1-Cl-BINH as well as its unprotonated precursor *meso*-1-Cl-BIN-Li are totally insensitive to irradiation. Apparently, the lowest-lying ligand-to-metal charge-transfer absorption, which appears to be antibonding with respect to the Zr–C₅ ring bond in the dichloride complexes 1-Cl₂, 2-Cl₂, 3-Cl₂, and 4-Cl₂, is replaced by an even lower-lying binaphtholate-to-metal charge transfer which is expected to leave the Zr–C₅ ring bond unaffected.

These observations suggest that a successful sequence of photoisomerization and complex formation reactions requires that the *meso* isomer is protected from formation of a monodentate binaphtholate complex, e.g., by steric restraints. The Me₂Si-bridged zirconocene complexes 2-Cl₂ and 4-Cl₂, which carry an α -methyl substituent at each C₅ ring ligand, do indeed conform to this expectation. Upon irradiation of a mixture of *meso* and racemic isomers of one of these complexes (or even of the pure *meso* isomer) in the presence of 1 equiv of dilithium binaphtholate, we observe the formation of the corresponding racemic zirconocene binaphtholate complexes, *rac*-2-BIN and *rac*-4-BIN. Although the reaction mixtures are not homogeneous, due to the low solubility of Li₂BIN in toluene, the zirconocene binaphtholate complexes can be isolated, after removal of the LiCl precipitate, in near-quantitative yields by crystallization from hexane (*rac*-2-BIN) or diethyl ether (*rac*-4-BIN) solutions.

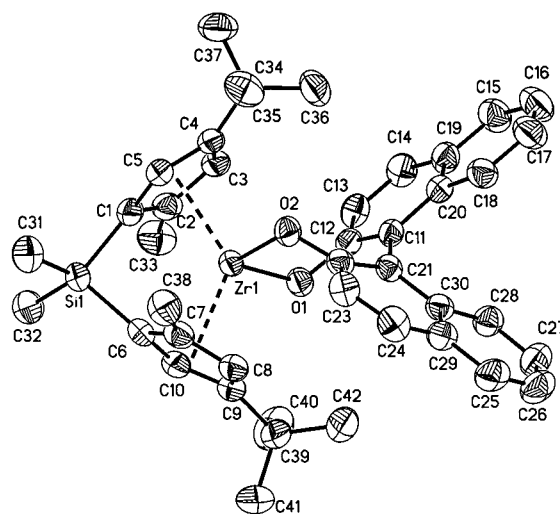


Figure 2. Molecular structure of *rac*-2-BIN (30% probability thermal ellipsoids).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\text{Me}_2\text{Si}(2\text{-Me-4-}t\text{Bu-C}_5\text{H}_2)_2\text{Zr-Binaphtholate (2-BIN)}$

Zr(1)–O(1)	2.010 (2)	Zr(1)–O(2)	2.019 (2)
Zr(1)–C(1)	2.502 (3)	Zr(1)–C(2)	2.514 (3)
Zr(1)–C(3)	2.603 (3)	Zr(1)–C(4)	2.668 (3)
Zr(1)–C(5)	2.544 (3)	Zr(1)–C(6)	2.489 (4)
Zr(1)–C(7)	2.511 (3)	Zr(1)–C(8)	2.606 (3)
Zr(1)–C(9)	2.681 (4)	Zr(1)–C(10)	2.540 (4)
Zr(1)–Cp(1) ^a	2.264	Zr–Cp(2) ^a	2.265
Si(1)–C(1)	1.872 (4)	Si(1)–C(6)	1.873 (3)
Si(1)–C(31)	1.857 (3)	Si(1)–C(32)	1.852 (4)
C(1)–Si(1)–C(6)	95.8	Zr(1)–O(1)–C(12)	120.8 (2)
Naph(1)–Naph(2) ^b	64.9	Zr(1)–O(2)–C(22)	120.5 (2)

^a Cp(1) and Cp(2) are the centroids of the C(1)–C(5) and C(6)–C(10) cyclopentadienyl rings. ^b Naph(1) and Naph(2) are the planes of C(11)–C(20) and C(21)–C(30) binaphtholate rings.

The molecular structure of complex *rac*-2-BIN (Figure 2 and Table 3) documents the tight fit of the binaphtholate ligand into the helical groove of the chiral *ansa*-zirconocene framework. The torsion angle between the naphthyl ring planes (64.5°) and the Zr–C–O angles (120–121°) are comparable to other bidentate binaphtholate complexes.⁸

Analogous procedures, in which racemic 1,1'-bi-2-naphthol is replaced by its *R* enantiomer, give enantiomerically pure (*S*)-2-(*R*)-binaphtholate and (*S*)-4-(*R*)-binaphtholate. Optical rotation values of these binaphtholates indicate a substantial enantiomeric excess. Independent control experiments show that the binaphtholate auxiliary is configurationally stable under the conditions of the procedure employed.

The conversion of the racemic zirconocene binaphtholate complexes thus obtained, either to a dihalide or to a dimethyl derivative, proved unexpectedly difficult. Reacting Me₂Si(2-Me-4-Ph-C₅H₂)₂Zr-BIN (4-BIN) with acids HX, with Lewis acidic metal halides such as BX₃, AlX₃, or ZrX₄ (X = Cl, Br), and with methyl-transferring nucleophiles such as CH₃Li or CH₃MgX produced varying amounts of the *meso* configured products along with the expected *R* and/or *S* compounds from the racemic zirconocene binaphtholates (Table 4). Apparently, the Zr–C₅ ring bonding is sufficiently labile in comparison to the Zr–O bonds to be cleaved at least to some degree when the Zr–O bonds in these complexes are attacked by nucleophilic or electrophilic reagents.

Table 4. Racemate Meso Ratios for Reaction Products Obtained from *rac*-4-BIN with Various Nucleophiles or Electrophiles

BBr ₃	9:1 ^a	HCl	3:1 ^b
BCl ₃	5:1 ^b	MeLi	9:1 ^c
AlCl ₃	4:1 ^b	MgCl ₂	3:1 ^b
ZrCl ₄	3:1 ^b	MeMgCl	3:1 ^c

^a 4-Br₂, ^b 4-Cl₂, ^c 4-Me₂.

Racemic Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂Zr-BIN (**2**-BIN), on the other hand, reacts with methyllithium to produce only the racemic dimethyl complex **2**-Me₂ in a clean reaction. We conclude, therefore, that the phenyl substituent in complex **4**-BIN is responsible for the partial isomerization to the unwanted meso complex, possibly by stabilizing a negative charge of the Cp ring in the transition state of the side reaction, which does not occur with *tert*-butyl-substituted cyclopentadienyl rings. The same observations were made with the enantiomerically pure complexes (*S*)-**2**-(*R*)-BIN and (*S*)-**4**-(*R*)-BIN. While methylation of (*S*)-**4**-(*R*)-BIN gave a mixture of the 4-Me₂ isomers, only (*S*)-**2**-Me₂ is obtained when (*S*)-**2**-(*R*)-BIN is reacted with methyllithium.

The enantiomeric purity of (*S*)-**2**-Me₂ was determined by reaction with *D*-(−)-acetylmandelic acid.¹⁵ Although a clean reaction to the bisacetylmandelate complex was not feasible—probably because of steric hindrance between the *tert*-butyl groups and the acetylmandelate ligands—we were able to generate a monomethylmonoacetylmandelate species, which gave rise to well-separated ¹H-NMR signals for the two possible diastereomers in the case of racemic **2**-BIN as starting material. With (*S*)-**2**-Me₂ derived from enantiomerically pure (*S*)-**2**-(*R*)-BIN we did indeed detect only resonances of a single diastereomer after reaction with acetylmandelic acid.

These results show that photoassisted complex formation with binaphtholate converts *ansa*-metallocene complexes, which are susceptible to photoisomerization,⁷ to any desired chiral stereoisomer in practically quantitative yields.

Experimental Section

All reactions were carried out under Ar or N₂ atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on Bruker WM 250 MHz, Bruker DRX 600 MHz, and Jeol FX 90Q spectrometers with residual C₆HD₅ (7.15 ppm) and CHCl₃ (7.24 ppm) as internal standards.

Irradiation of Complexes 1–4. A sample of 5 mg of each of these complexes was dissolved in 0.4 mL of benzene-*d*₆ or toluene-*d*₈ in an NMR tube. The tube was sealed and placed adjacent to the cooling jacket of a high-pressure mercury lamp (125 W). For low-temperature reactions, the lamp and the tube were placed into a cooling bath. The photoreaction was monitored by ¹H NMR; the *rac*/*meso* ratios were calculated from the integrals of the appropriate Me₂Si, *tert*-butyl, and α -methyl signals. The results are summarized in Table 1.

Me₂Si(3-*t*Bu-C₅H₃)₂ZrCl-Binaphtholate (1-Cl-BINH). To a mixture of 488 mg (1.2 mmol) of complex **1** with a *rac*/*meso* ratio of 1:1.3 and 410 mg (1.4 mmol) dilithium 1,1'-bi-2-naphtholate was added 20 mL of CH₂Cl₂. This suspension was stirred overnight at room temperature and filtered, and the filtrate evaporated to dryness. According to its ¹H-NMR spectrum, the residue is a 1:1.3 mixture of the racemic complex Me₂Si(3-*t*Bu-C₅H₃)₂Zr-binaphtholate (**1**-BIN) and of an asym-

metric binaphtholate complex (**1**-Cl-BIN-Li), formed from the *meso* isomer. Complex (**1**-Cl-BINH) was isolated after several recrystallizations from diethyl ether, yielding 42 mg (9% based on *meso*-**1**) of light yellow crystals, of which a crystal structure was obtained. ¹H NMR of **1**-Cl-BINH (C₆D₆, 250 MHz, δ in ppm): 0.1 (s, 3H, Si(CH₃)₂), 0.27 (s, 3H, Si(CH₃)₂), 1.37 (s, 9H, C(CH₃)₃), 1.47 (s, 9H, C(CH₃)₃), 4.49 (br s, 1H, OH), 4.41, 5.29, 5.56, 5.72 (each dd, 1H, α -C₅H₂H and β -C₅H₂H), 6.8–7.8 (m, C₂₀H₁₂O₂). Complex **1**-BIN was enriched in the mother liquor but could not be isolated in pure form. ¹H NMR of **1**-BIN (C₆D₆, 250 MHz, δ in ppm): 0.49 (s, 6H, Si(CH₃)₂), 0.74 (s, 18H, C(CH₃)₃), 5.65 (dd, 2H, α -C₅H₂H), 5.80 (dd, 2H, α -C₅H₂H), 6.11 (dd, 2H, β -C₅H₂H), 6.8–7.8 (m, C₂₀H₁₂O₂).

Reaction of Complex 1 with Dilithium 1,1'-Bi-2-naphthol upon Irradiation. A reaction was set up as described above, and 1 mL of the well-mixed suspension was transferred into an NMR tube, evaporated to dryness, and suspended in benzene-*d*₆. The tube was irradiated with the high-pressure mercury lamp. The same two products, **1**-BIN and **1**-Cl-BINLi, were formed in a ratio identical to the original *rac*/*meso* ratio. This result documents that the irradiation does not affect the product distribution in this case.

Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂Zr-BIN (*rac*-2**-BIN).** In a Schlenk tube, 248 mg (0.51 mmol) of complex **2** (*rac*/*meso* 1:1) and 160 mg (0.51 mmol) dilithium 1,1'-bi-2-naphtholate were suspended in 60 mL of toluene. The tube was stirred and irradiated at 80 °C for 24 h. The reaction mixture was evaporated to dryness and the resulting residue taken up in toluene again, salts were removed by filtration, the solvent was evaporated, and the residue recrystallized from 5 mL of pentane to yield 316 mg (0.45 mmol, 88%) of complex *rac*-**2**-BIN as a clean yellow powder. Crystals were obtained from toluene or hexane. ¹H NMR (C₆D₆, 600 MHz, δ in ppm): 0.59 (s, 6H, Si(CH₃)₂), 0.76 (s, 18H, C(CH₃)₃), 2.11 (s, 6H, C₅H₂CH₃), 5.59 (2H, d, *J* = 2.17 Hz, α -C₅H₂H), 5.96 (2H, d, *J* = 1.99 Hz, β -C₅H₂H), 6.91 (2H, t, HC(17,27)), 7.09 (2H, t, HC(16,26)), 7.20 (2H, d, *J* = 8.75 Hz, HC(13,23)), 7.27 (2H, d, *J* = 8.59 Hz, HC(18,28)), 7.73 (2H, d, *J* = 7.99 Hz, HC(15,25)), 7.80 (2H, d, *J* = 8.75 Hz, HC(14,24)). ¹³C NMR (C₆D₆, 600 MHz, δ in ppm): −1.85 (Si(CH₃)₂), 16.07 (C₅H₂CH₃), 29.44 (C(CH₃)₃), 33.08 (C(CH₃)₃), 106.08 (C(1,6)), 108.96 (C(5,10)), 118.72 (C(11,21)), 119.06 (C(3,8)), 122.08 (C(13,23)), 122.77 (C(16,26)), 126.06 (C(17,27)), 126.29 (C(2,7)), 127.72 (C(18,28)), 127.84 (C(15,25)), 129.43 (C(19,29)), 129.7 (C(14,24)), 136.33 (C(20,30)), 154.01 (C(4,9)), 160.14 (C(12,22)). Anal. Calcd for C₄₂H₄₆O₂SiZr: C, 71.85; H, 6.60. Found: C, 71.68; H, 6.63.

In an analogous experiment with enantiomerically pure *R*(+)-dilithium 1,1'-bi-2-naphtholate the reaction time had to be extended to six days to obtain the enantiomerically pure complex (*S*)-**2**-(*R*)-BIN in 87% yield. [α]_D = −780°; [α]₄₃₆ = −2620° (*c* = 1 g/100 mL, toluene).

Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂Zr-Me₂ (2**-Me₂).** A 120 mg (0.171 mmol) sample of **2**-BIN was dissolved in 20 mL of diethyl ether, and 0.22 mL of a 1.6 M solution of methyllithium in diethyl ether (0.342 mmol) was added via syringe. After 1 h, during which Li₂BIN precipitated and the yellow color of the solution had disappeared, the solvent was evaporated and the residue taken up in pentane. Li₂BIN was removed by filtration and the filtrate evaporated to dryness. The white residue consisted—according to its ¹H-NMR spectrum—only of racemic **2**-Me₂. Enantiomerically pure (*S*)-**2**-(*R*)-BIN was converted to (*S*)-**2**-Me₂ following the same procedure. In both cases, **2**-Me₂ was not further purified before reaction with *D*-(−)-acetylmandelic acid to avoid enrichment of one enantiomer. ¹H NMR (CDCl₃, 250 MHz, δ in ppm): −0.26 (s, 6H, Zr(CH₃)₂), 0.56 (s, 6H, Si(CH₃)₂), 1.31 (s, 18H, C(CH₃)₃), 1.96 (s, 6H, C₅H₂CH₃), 5.28 (2H, d, *J* = 2.35 Hz, C₅HH), 6.48 (2H, d, *J* = 2.28 Hz, C₅HH).

Reaction of 2-Me₂ with *D*-(−)-Acetylmandelic Acid. A solution of complex *rac*-**2**-Me₂ (10.7 mg, 0.024 mmol) in CDCl₃ was treated in one portion with 1 equiv of *D*-(−)-acetylmandelic acid (4.6 mg, 0.024 mmol) at room temperature. After gas

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Table 5. Crystallographic and Experimental Data for $\text{Me}_2\text{Si}(\text{3-}i\text{Bu-C}_5\text{H}_3)_2\text{ZrCl-Binaphtholate}$ (*meso*-1-Cl-BINH) and $\text{Me}_2\text{Si}(\text{2-Me-4-}i\text{Bu-C}_5\text{H}_2)_2\text{Zr-Binaphtholate}$ (*rac*-2-BIN)

compound	<i>meso</i> -1-Cl-BINH	<i>rac</i> -2-BIN
formula	$\text{C}_{44}\text{H}_{53}\text{ClO}_3\text{SiZr}$	$\text{C}_{42}\text{H}_{46}\text{O}_2\text{SiZr}$
fw	784.6	702.1
color, habit	yellow rhombohedron	yellow cube
crystal size	$0.2 \times 0.2 \times 0.3$	$0.3 \times 0.3 \times 0.3$
crystal system	triclinic	triclinic
space group	<i>P</i> 1	<i>P</i> 1
unit cell dimensions		
<i>a</i> , Å	10.061(8)	10.019(4)
<i>b</i> , Å	10.501(7)	10.407(5)
<i>c</i> , Å	19.901(14)	19.719(8)
α , deg	99.39(5)	78.25(3)
β , deg	92.96(6)	75.35(3)
γ , deg	92.71(6)	67.94(3)
volume	2068(3)	1830(1.4)
<i>Z</i>	2	2
density (calcd), g/cm ³	1.260	1.274
abs coeff (μ), mm ⁻¹	0.389	0.359
temp, K	233	296
2θ range, deg	4.0–54	4.0–54
no. of rflns collected	8038	8462
no. of independent rflns	7512	7994
no. of obsd rflns	6145 ($F > 4\sigma(F)$)	6325 ($F > 5\sigma(F)$)
soln	direct methods	direct methods
weighting scheme	$\sigma^2(F) + 0.0004F^2$	$\sigma^2(F) + 0.0004F^2$
R_F , %	3.68	3.89
R_{wF} , %	4.36	4.50
goodness of fit	1.34	1.29
residual density, e Å ⁻³	0.69	0.38

evolution had ceased (10 min), a ¹H-NMR spectrum (250 MHz) was recorded. With **2-Me₂** derived from racemic **2-BIN** as starting material, we observed eight doublets in the cyclopentadienyl region (δ in ppm: 5.1, 5.3, 5.67, 5.75, 5.99, 6.0, 6.14, and 6.33), which are assignable to two diastereomers of a monomethylmonoacetylmandelate complex. Only four doublets were observed when (*S*)-**2-Me₂**, derived from enantiomerically pure (*S*)-**2-(R)**-BIN as starting material, was reacted with 1 equiv of *D*(–)-acetylmandelic acid (δ in ppm: 5.1, 5.67, 5.99, 6.33); signals of the other diastereomer were not detectable here. This corresponds to an optical purity of ee > 95% for the dimethyl complex (*S*)-**2-Me₂**.

Me₂Si(2-Me-4-Ph-C₅H₂)₂Zr-BIN (4-BIN). **4-BIN** was obtained by a procedure similar to that described above for **2-BIN**. A 528 mg (1 mmol) sample of *meso*-**4** was reacted under irradiation with 328 mg (1.2 mmol) of racemic dilithium 1,1'-bi-2-naphtholate in 60 mL of toluene. In contrast to the procedure described above, this reaction was already complete after 4–6 h at 40 °C. The toluene suspension was evaporated to dryness and redissolved in toluene; precipitated LiCl was removed by filtration and the residue evaporated again. The resulting yellow powder was suspended in diethyl ether, where impurities were dissolved; the racemic complex **4-BIN** was collected by filtration and washed with pentane to yield 690

mg (0.93 mmol, 93%) *rac*-**4-BIN** as a yellow powder. ¹H NMR (C_6D_6 , 600 MHz, δ in ppm):¹⁶ 0.66 (s, 6H, Si(CH₃)₂), 2.07 (s, 6H, C₅H₂CH₃), 5.92 (2H, d, $J = 2.3$ Hz, α -C₅HH), 6.22 (2H, d, $J = 2.06$ Hz, β -C₅HH), 6.48 (4H, m, *o*-C₆H₃H₂), 6.49 (4H, m, *m*-C₆H₃H₂), 6.68 (2H, t, *p*-C₆H₄H), 6.92 (2H, t, HC(17,27)), 6.97 (2H, d, $J = 8.08$ Hz, HC(13,23)), 7.11 (2H, m, HC(18,28)), 7.12 (2H, m, HC(16,26)), 7.65 (2H, d, $J = 8.8$ Hz, HC(14,24)), 7.7 (2H, d, $J = 8.81$ Hz, HC(15,25)). ¹³C NMR (C_6D_6 , 600 MHz, δ in ppm): –1.73 (Si(CH₃)₂), 16.05 (C₅H₂CH₃), 107.41 (C(1,6)), 108.95 (C(5,10)), 118.44 (C(11,21)), 120.48 (C(3,8)), 122.18 (C(13,23)), 122.8 (C(16,26)), 126.07 (C(17,27)), 126.75 (*o*-CC₅H₅), 126.86 (C(2,7)), 127.24 (*p*-CC₅H₅), 127.68 (C(18,28)), 128.08 (C(15,25)), 128.16 (*m*-CC₅H₅), 129.22 (C(19,29)), 129.37 (C(14,24)), 133.592 (Cp-CC₅H₅), 136.06 (C(20,30)), 141.77 (C(4,9)), 160.14 (C(12,22)). Anal. Calcd for $\text{C}_{46}\text{H}_{38}\text{O}_2\text{SiZr}$: C, 74.45; H, 5.16. Found: C, 74.41; H, 5.64.

Reacting 37 mg (0.125 mmol) of *R*(+)-dilithium 1,1'-bi-2-naphtholate with 53 mg (0.1 mmol) of *meso*-**4** yields 65 mg (0.088 mmol, 88%) of (*S*)-**4-(R)**-BIN. $[\alpha]_D = -750^\circ$; $[\alpha]_{436} = -2100^\circ$ ($c = 0.05$ g/100 mL, toluene).

Crystal Structures of Complexes 2-BIN and 1-Cl-BINH. Crystals were obtained by slow crystallization from hexane (**2-BIN**) or diethyl ether (**1-Cl-BINH**). Intensity data were measured on a Syntex/Siemens-P3 four-circle diffractometer with graphite-monochromated Mo K α radiation (0.71073 pm). Crystallographic and experimental data are summarized in Table 5. Both structures were solved by direct methods and refined by least-squares methods using the SHELXTL (VMS) program. All non-H-atoms were refined anisotropically. Hydrogen atom positions were calculated and refined with fixed isotropic *U* using riding model techniques. The resulting structures are represented in Figures 1 and 2 and Tables 2 and 3.

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Supporting Information Available: Tables of additional crystallographic data for complexes **1-Cl-BINH** and **2-BIN**, final positional parameters, bond distances, and bond angles (18 pages). Ordering information is given on any current masthead page. This information is also available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen 2, upon quotation of the depository numbers 406317 and 406318, the authors, and the journal reference for this article.

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(16) Assignments are based on DEPT, COSY, ROESY, HMQC, and HMBC spectra. Labels of the binaphtholate carbons in complexes **2-BIN** and **4-BIN** are analogous to those of complex **2-BIN** in Figure 2.