

lies 1.05 eV above the HOMOs and just 0.01 eV below the corresponding a_2'' orbital.

Calculations on C_8 [$Fe_3Co_3(C_2)(CO)_{18}$] $^-$ in the same geometry lead to analogous results, but with the degenerate e' and e'' sets slightly split because of the low symmetry of the heterometal triangles. However, the calculated splitting (0.07 eV) is too small to give a diamagnetic ground state at room temperature. Accordingly, we explored the possibility that the tilt of the two M_3 planes observed for 5 might increase the HOMO-LUMO separation. The distortion observed for 5 was modeled by tilting the metal planes of C_8 [$Fe_3Co_3(C_2)(CO)_{18}$] $^-$ and D_{3h} [$Co_6(C_2)(CO)_{18}$] $^{2+}$ as described above. This immediately lowers the symmetry of the latter to C_{2v} , but leaves the symmetry of the mixed-metal compound unchanged. The calculated total energy is virtually unaffected for both compounds, indicating such tipping is facile. Calculations performed on arrangements tilted up to 17.5° indicated a greatly increasing HOMO-LUMO separation with increasing tilt (Figure 6). Although this simple analysis ignores the rearrangement of carbonyl ligands, these results indicate that the observed diamagnetism results from the tilt of the two metal triangles. The gap results primarily from destabilization of the LUMO (Figure 7). The shifts of other frontier orbitals are minor by comparison, especially for those lacking involvement of the ligand π system.

These calculations also suggest 5 could display reversible redox behavior. Unfortunately, chemical reduction with

a variety of reagents leads to destructive cluster fragmentation. The opposite approach, reversible oxidation of $Co_6(C_2)(CO)_{18}$, may be more feasible.

Conclusions

Conversion of a cluster-bound ketenylidene ligand to dicarbides by cluster expansion of a metalated acetylide has been achieved, indicating that ketenylidenes might be general precursors to C_2 -containing metal clusters, just as they are useful precursors for metal cluster carbides. Analyses of metalate attack and $Co_2(CO)_8$ addition to the acetylide clusters indicate these reactions are mechanistically complex. NMR spectral properties of two dicarbide complexes have been recorded. A further distorted example of a rare structural type has been identified, and the electronic basis for this distortion has been described.

Acknowledgment. The contributions of Steve Gramsch to the structure determination of 5 and Mark Lonergan to the MO computations are appreciated. This work was supported by the NSF Synthetic Organometallic Program CHE-9014662.

Supplementary Material Available: Complete listings of thermal parameters and hydrogen atomic coordinates for 5 (4 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of Chiral Titanocene and Zirconocene Dichloride Complexes of a Chiral Ligand

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The ligand (*S,S*)-2,3-butylene-1,1'-bis(indene) was prepared from diindenylmagnesium and the dimesylate of (*R,R*)-2,3-butanediol after conventional synthetic methods had failed. Reaction of the dilithium salt of (*S,S*)-2,3-butylene-1,1'-bis(indene) with $TiCl_4 \cdot 2THF$ in THF under high-dilution conditions gave [$Ti((S,S)\text{-}2,3\text{-butylene-}1,1'\text{-bis(indenyl))Cl}_2$], which, upon PtO_2/H_2 reduction, gave [$Ti((S,S)\text{-chiracene})Cl_2$] as a mixture of kinetically formed isomers. These consisted of the *R,R*, *R,S*, and *S,S* diastereomers. Upon irradiation, a photostationary state consisting of 85% of the *R,R* isomer and 15% of the *R,S* isomer was obtained. The desired pure (*R,R*)-[$Ti((S,S)\text{-chiracene})Cl_2$] complex was isolated, and its crystal structure was determined by X-ray diffraction. It was found that this complex was configurationally stable under normal conditions, confirming our initial expectations. The circular dichroism spectra of the *R,R* and *R,S* isomers have been recorded and discussed, and a connection between the photostationary state and thermodynamic equilibrium of the isomers is suggested. The corresponding zirconium complexes were obtained in low yield. There is a strong kinetic preference for the (*R,S*)-[$Zr((S,S)\text{-chiracene})Cl_2$] isomer. This isomer was isolated, and its structure was determined by X-ray diffraction. The photostationary state is different from that of the titanium analogue. It consists of a mixture of *R,R* and *S,S* diastereomers.

With appropriate substitution cyclopentadienyl ligands form chiral complexes when bound to a metal. Of particular current interest are chiral species derived from [Cp_2MX_2] complexes (Cp = cyclopentadienyl; M = $Ti(IV)$, $Zr(IV)$, $Hf(IV)$). These chiral complexes have been employed as precursors for a variety of stereoselective transformations. Among these are asymmetric catalytic

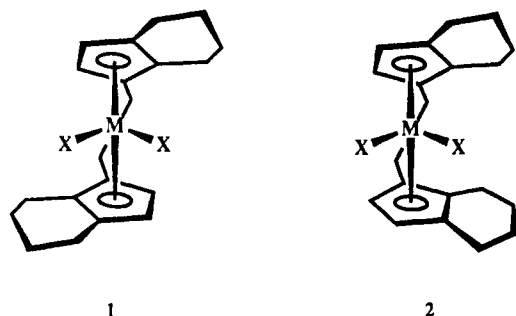
hydrogenation of olefins,¹ a variety of stoichiometric asymmetric transformations,^{2,5} and stereoselective polym-

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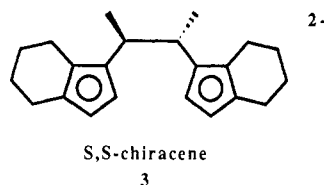
[‡] The University of Chicago.

erization of olefins.³ The most effective of these stereoselective precursors are complexes containing strapped ligand metallocenes, notably, the ethylenebis(1-indenyl) and ethylenebis(tetrahydro-1-indenyl) complexes of Ti(IV) and Zr(IV) first developed by Brintzinger.⁴ Complexes of this kind exist as meso and racemic forms and are illustrated as 1 (racemic) and 2 (meso). These two isomers



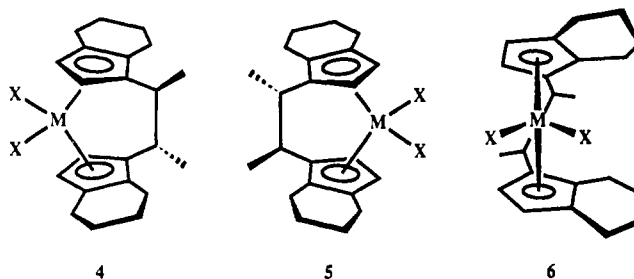
can be separated, and the racemic isomers have been resolved into their optical isomers. Although the Zr(IV) racemic species appears to be stable, the configurational integrity of the Ti(IV) analogue is lost photochemically,⁴ under circumstances⁵ which, as yet, are not understood. This configurational instability could present uncertainty in the validity of results obtained for stereoselective synthesis using the chiral Ti(IV) complexes.

Our interest in employing Ti(IV) complexes of type 1 for asymmetric catalysis prompted us to seek a solution to the problem of configurational instability and simultaneously to circumvent the necessity of resolution of the racemic compound. This paper describes the synthesis of the metal complexes of a chiral analogue of the ethylenebis(tetrahydro-1-indenyl) ligand, namely, the ligand (*S,S*)-chiracene (3). The syntheses of the Ti(IV) and Zr(IV) dichloro complexes of this ligand are described.



1. Diastereometric Preference

In principle the (*S,S*)-chiracene ligand can form three diastereomeric complexes, namely, (*R,R*)-[M((*S,S*)-chiracene) X_2] (4), (*S,S*)-[M((*S,S*)-chiracene) X_2] (5), and (*R,S*)-[M((*S,S*)-chiracene) X_2] (6). The first two isomers are chiral about the metal, whereas the last has the tetrahydroindenyl ligands disposed in a meso arrangement. Of these three structures, we expect 4 to be the most stable. Steric interactions are expected to be greatest for the meso

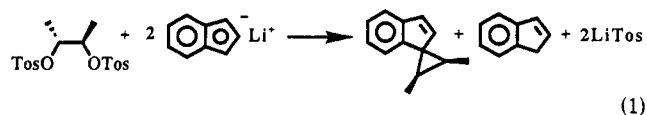


isomer 6 because of inter-ring interactions, and 4 is expected to be more stable than 5 because there appears to be less interaction between the methyl groups and the reduced rings in 4 than in 5, where the methyl groups are closer to these rings. These latter arguments depend on the assumption that the strap conformation will be δ in both 4 and 5 to allow the methyl groups to be equatorially disposed. This assumption is supported by the crystal structures we report here.

We note a recurring difficulty with chiral strapped metallocenes. The preparation of these species nearly always leads to mixtures of racemic and meso forms in similar proportions,^{4,6} despite the expectation that the meso forms would be less stable on steric grounds. The ratio of racemic to meso isomers is determined by the kinetics of formation. Although many variations in the preparative conditions have been investigated,^{4,6} no set of conditions has yet been devised which gives high selectivity for the generally preferred racemic isomer. The difficulties are compounded by the absence of a simple method of thermodynamic equilibration. The only effective method of racemic-meso interconversion is by irradiation to the photostationary state.^{4,7,8} Thus, although it is not possible to establish the metal isomer preference of the (*S,S*)-chiracene ligand, we may obtain the sense of the preference by assuming an approximate connection between the photostationary state and the thermodynamic equilibrium constant. We present later an argument which may plausibly connect the two for the [Ti((*S,S*)-chiracene) Cl_2] complex.

2. Ligand Synthesis

The reaction of lithium indenyl with α,ω -dihalides in tetrahydrofuran leads to the formation of the strapped bis(1-indene) ligands.⁴ Use of the ditosylate or dimesylate of (*R,R*)-2,3-butanediol under similar conditions gives none of the desired product; instead, the spiro compound is produced exclusively (eq 1). The formation of the spiro



compound could not be suppressed by changing the counterion to Na^+ , K^+ , or $MgBr^+$ under a variety of conditions and solvents. It thus appears that, after the first tosylate displacement, the relative rate of the second intramolecular tosylate displacement is much slower than that of proton abstraction followed by intramolecular cyclization (eq 2). In order to enhance double displacement

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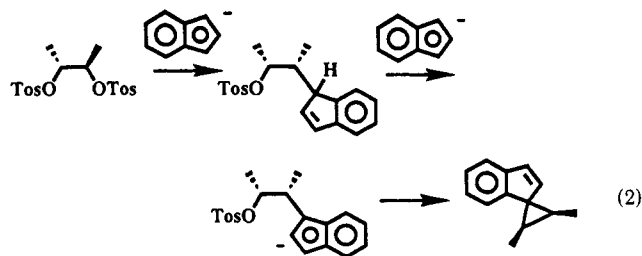
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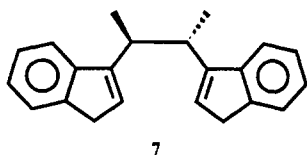
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over proton exchange, we sought conditions under which we expected the indenyl anion to be a less effective base. We chose the diindenylmagnesium compound⁹ as the source of indene anion, since we expected the anion to be effectively bound to the magnesium to suppress proton exchange and yet be sufficiently nucleophilic to cause displacement. Indeed, displacement of the insoluble dimesylate or soluble ditosylate of (*R,R*)-2,3-butanediol in nonpolar solvents such as benzene, toluene, and heptane led to the formation of the product in low yield (~10%) along with a variety of side products. No spiro compound was formed. The product from these solvents, however, consisted of a variety of (double-bond position) isomers and none of the thermodynamic isomer. The isomers could be converted to the thermodynamic isomer **7** by treatment



with potassium *tert*-butoxide in THF. Eventually, we found that the most efficient method of preparation of **7** involved adding the solid dimesylate to a suspension of Mg(indenyl)₂ in THF at 25 °C. The exothermic reaction was allowed to proceed without moderation, and the solution was refluxed to give exclusively the thermodynamic double-bond isomer of the product **7** as off-white crystals in 32% yield. The use of THF solvent does lead, however, to the production of some spiro compound, but the procedure has the advantage of giving a practical yield of the desired product, and double-bond equilibration is achieved in a single step.

3. Synthesis of Complexes

Various conditions and starting reagents were used to prepare compounds of the formula [Ti((*S,S*)-chiracene)Cl₂] and [Zr((*S,S*)-chiracene)Cl₂]. In the case of the synthesis of the Ti(IV) complex, use of either the lithium or potassium salt of the ligand precursor and the use of TiCl₄·2THF or TiCl₃·3THF in THF solutions caused variations in overall yield, but all permutations gave mixtures of diastereomers. In terms of yield, the most efficient method of preparation was found to occur under high-dilution conditions at 40 °C. Thus, the dilithio salt of **7** in THF and TiCl₄·2THF in THF were added very slowly to THF to suppress oligomerization to give, after PtO₂/H₂ reduction, the [Ti((*S,S*)-chiracene)Cl₂] isomers in ~40% yield. Under these conditions, the ratio of isomers was found to be *R,S*:*R,R*:*S,S* = 4.2:2.5:1. We found no efficient way of separating these isomers either by crystallization or by chromatography.

Irradiation of a THF solution of the isomers using a Hanovia 450-W mercury lamp in a Vycor sleeve filter (cutoff ~240 nm) caused redistribution of the isomers.

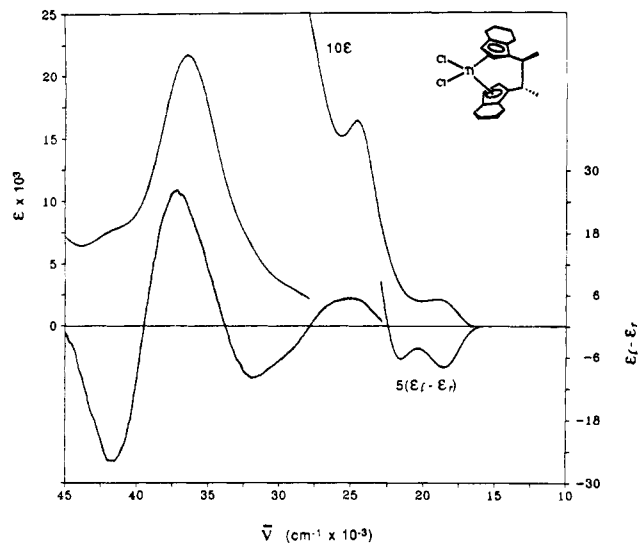


Figure 1. Electronic absorption and circular dichroism spectra of (*R,R*)-[Ti((*S,S*)-chiracene)Cl₂] in THF solution.

Early in the irradiation the *S,S* isomer disappeared, and thereafter the *R,S* to *R,R* isomer ratio slowly changed to give *R,R*:*R,S* = 5.9:1 after about 55 h. This ratio is close to that of the photostationary state. Even with this enhanced isomer ratio we found no clean method of separating the two dichloro isomers.

It is known that 1',1''-bi-2-naphtholate binds diastereoselectively to the racemic [Ti^{IV}(ethylenebis(tetrahydro-1-indenyl))] fragment, specifically, the (*R*)-binaphtholate binds only with the (*R,R*)-titanium isomer.⁴ We took advantage of this selectivity to separate the *R,R* isomer from the meso (*R,S*) form. Thus, reaction of the mixture of isomers, derived after photolysis, with the sodium salt of the (*R*)-binaphtholate gave the species (*R,R*)-[Ti((*S,S*)-chiracene)((*R*)-binaphtholate)] as pure red crystals after chromatography on silanized silica. The binaphtholate adduct of the meso titanium complex is probably oligomeric and can also be isolated in low yield. Addition of HCl gas to hexane solutions of these binaphtholate adducts gave the pure (*R,R*)-[Ti((*S,S*)-chiracene)Cl₂] and (*R,S*)-[Ti((*S,S*)-chiracene)Cl₂] isomers.

The synthesis of the [Zr((*S,S*)-chiracene)Cl₂] isomers followed a similar procedure to that described for the titanium analogues. The overall yield was lower (~18%), and the kinetic ratio of the isomers was *R,S*:*R,R*:*S,S* = 19:1:1. The meso (*R,S*) isomer is readily crystallized in pure form from this mixture. Photolysis of this isomeric mixture under conditions similar to those described for the titanium isomers was accompanied by extensive decomposition, but eventually a photostationary state consisting of *R,R*:*S,S* = 5.2:1 was obtained. No *R,S* isomer was detected. Since the yield of products was of little practical importance, we did not expend special effort to separate them. Our observations suggest, however, that if the yield could be improved, the two isomers could be separated by crystallization from a mixture of hexane and cyclohexane.

4. Circular Dichroism Spectra

The electronic absorption and circular dichroism spectra of (*R,R*)-[Ti((*S,S*)-chiracene)Cl₂] and (*R,S*)-[Ti((*S,S*)-chiracene)Cl₂] are shown in Figures 1 and 2, respectively. As expected, the absorption spectra of the *R,R* and *R,S* isomers are nearly identical but the circular dichroism spectra are quite distinct. The dissymmetry of these complexes arises from two major sources: the chiral arrangement of the tetrahydroindenyl rings and the chirality

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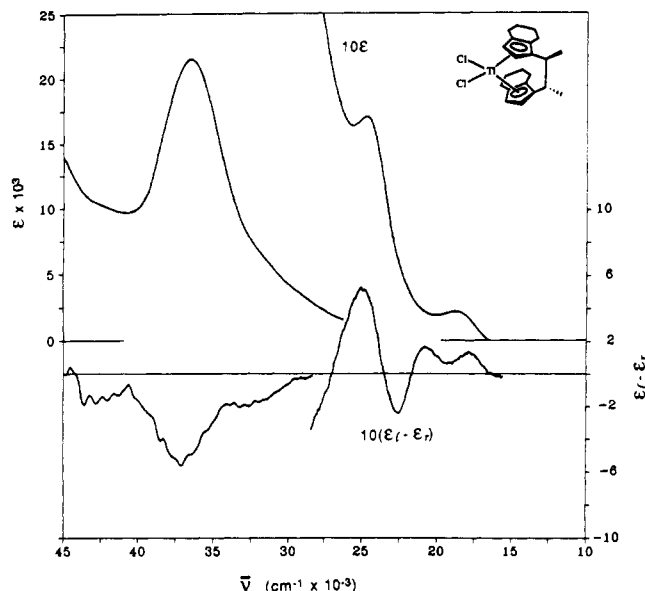


Figure 2. Electronic absorption and circular dichroism spectra of (R,S) -[Ti((S,S)-chiracene)Cl₂] in THF solution.

of the strap. To a first approximation, the R,R isomer possesses both sources of chirality, whereas the R,S isomer is chiral only because of the strap. Hence, we would expect¹⁰ that the former would display more intense circular dichroism than the latter. Inspection of Figures 1 and 2 shows that the circular dichroism for the R,R isomer is nearly 1 order of magnitude greater than for the R,S isomer. Moreover, the sign patterns are distinctly different for the two isomers.

The two lower energy transitions resolved in the linear absorption spectrum of the two isomers are almost certainly due to ligand to metal charge-transfer transitions.⁸ The circular dichroism reveals, however, that this absorption region is associated with at least four transitions. The electronic provenance of the high-energy transitions greater than 30 000 cm⁻¹ is uncertain, although it is likely that both ligand to metal charge-transfer and $\pi \rightarrow \pi^*$ transitions mainly localized on the cyclopentadienyl ligands¹¹ occur in these regions. The presence of ligand-localized $\pi \rightarrow \pi^*$ transitions at high energies suggests an explanation for the appearance of the strong circular dichroism couplet centered at $\sim 38\,000$ cm⁻¹, which is observed for the R,R isomer but which is absent in the R,S isomer. These strong equal and opposite couplets observed in circular dichroism spectra are characteristic of exciton coupling induced circular dichroism.¹² The localized ligand $\pi \rightarrow \pi^*$ transitions are polarized in the molecular plane, and the corresponding transitions of one ligand couple with those of the other to give symmetric and antisymmetric coupling modes which, to a first approximation, give equal but opposite circular dichroism. The degeneracy of the two coupling modes is removed by dipole-dipole interaction. In order to fully derive the absolute configuration, however, we require the structure of the complex and the polarization directions of the assigned $\pi \rightarrow \pi^*$ transitions. Although we know the geometry of the molecule, we are uncertain of the polarization directions and the energy positions of the ligand $\pi \rightarrow \pi^*$ transitions. Thus, we cannot unambiguously demonstrate the precise origins of the high-energy couplet observed in the

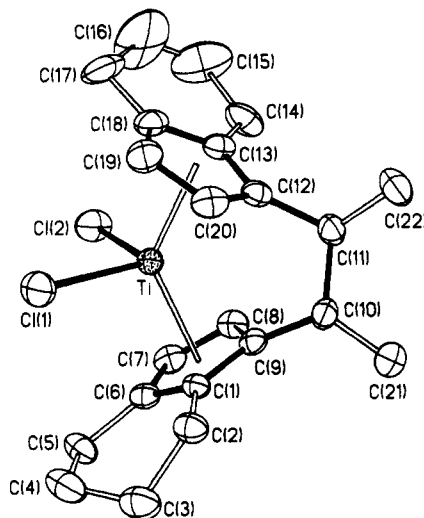


Figure 3. Molecular structure and labeling scheme for (R,R) -[Ti((S,S)-chiracene)Cl₂] (**4(Ti)**) drawn with 40% probability ellipsoids.

Table I. Crystallographic Data for **4(Ti) and **6(Zr)****

	4(Ti)	6(Zr)
(a) Crystal Parameters		
formula	C ₂₂ H ₂₆ Cl ₂ Ti	C ₂₂ H ₂₆ Cl ₂ Zr
fw	411.25	454.59
cryst syst	orthorhombic	monoclinic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁
a, Å	7.7046 (20)	9.751 (3)
b, Å	14.734 (3)	14.055 (3)
c, Å	18.140 (4)	15.100 (5)
β, deg		94.66 (2)
V, Å ³	2059.2 (8)	2062.6 (11)
Z	4	4
cryst dims, mm	0.28 × 0.40 × 0.42	0.40 × 0.40 × 0.46
cryst color	dark brown	pale yellow
D(calc), g cm ⁻³	1.466	1.421
μ(Mo Kα), cm ⁻¹	6.89	7.81
temp, K	297	297
(b) Data Collection		
diffractometer	Nicolet R3m	
monochromator	graphite	
radiation	Mo Kα (λ = 0.71073 Å)	
2θ scan range, deg	4–55	4–60
data collected (hkl)	±h, ±k, ±l	+h, +k, +l
no. of rflns collected	2745	6412
no. of indpt rflns	2718	6197
no. of indpt obsd rflns	2053 (n = 3)	5226 (n = 3)
F _o ≥ nσ(F _o)		
std rflns	3 std/197 rflns	3 std/197 rflns
var in stds	<1	~2
(c) Refinement		
R(F), %	5.25	4.78
R(wF), %	5.74	5.27
Δ/σ(max)	0.031	0.064
Δ(ρ), e Å ⁻³	0.38	1.17
N _o /N _v	9.00	11.56
GOF	1.165	1.162

circular dichroism spectrum of the R,R isomer but, if the spectroscopic details are established, the exciton method may provide a simple method of establishing the absolute configurations of chiral metal complexes formed with strapped-dicyclopentadienyl ligands.

5. Crystal Structures

The structures of (R,R) -[Ti((S,S)-chiracene)Cl₂] (**4(Ti)**) and (R,S) -[Zr((S,S)-chiracene)Cl₂] (**6(Zr)**) were crystallographically determined and are shown in Figures 3 and 4. Selected bond distances and angles are given in Table IV. As required, both compounds crystallize in chiral space

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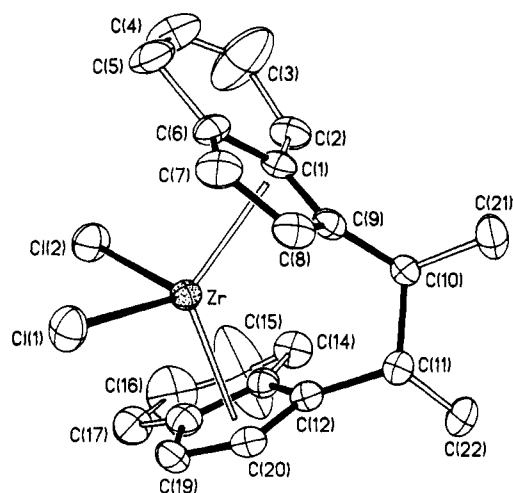


Figure 4. Molecular structure and labeling scheme for (*R,S*)-[Zr((*S,S*)-chiracene)Cl₂] (**6**(Zr)) drawn with 40% probability ellipsoids.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for **4**(Ti)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Ti	714.4 (10)	6671.6 (5)	2433.6 (4)	34.2 (2)
Cl(1)	-2279 (2)	6465 (1)	2595 (1)	76 (1)
Cl(2)	1259 (2)	5163 (1)	2108 (1)	65 (1)
C(1)	710 (6)	7448 (3)	3634 (2)	33 (1)
C(2)	-605 (7)	8121 (3)	3899 (3)	45 (2)
C(3)	-1536 (9)	7722 (4)	4577 (3)	64 (2)
C(4)	-2197 (8)	6767 (4)	4468 (3)	68 (2)
C(5)	-806 (7)	6104 (4)	4267 (3)	51 (2)
C(6)	608 (7)	6498 (3)	3795 (2)	38 (1)
C(7)	2091 (7)	6096 (4)	3526 (3)	45 (2)
C(8)	3126 (6)	6756 (3)	3173 (3)	43 (2)
C(9)	2289 (6)	7601 (3)	3268 (3)	36 (1)
C(10)	3001 (7)	8496 (3)	2981 (3)	43 (2)
C(11)	3642 (7)	8346 (3)	2187 (3)	45 (2)
C(12)	2196 (7)	7834 (3)	1795 (3)	39 (2)
C(13)	2403 (7)	7077 (3)	1326 (3)	44 (2)
C(14)	4037 (8)	6634 (4)	1060 (3)	67 (2)
C(15)	3734 (15)	6018 (7)	424 (5)	132 (5)
C(16)	2101 (18)	5817 (10)	174 (7)	218 (8)
C(17)	444 (12)	6089 (4)	494 (3)	84 (3)
C(18)	709 (8)	6832 (3)	1062 (3)	52 (2)
C(19)	-451 (8)	7415 (4)	1376 (3)	55 (2)
C(20)	406 (7)	8039 (3)	1833 (3)	47 (2)
C(21)	4416 (9)	8874 (4)	3483 (3)	74 (2)
C(22)	4114 (10)	9219 (4)	1782 (3)	78 (3)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

groups and the determination of the absolute configuration was possible for both structures. For **6**(Zr) the crystallographic asymmetric unit consists of two independent, but chemically similar, molecules.

The metal atom coordination geometry for both is that anticipated for a bent metallocene dihalide, i.e., a structure describable as either distorted tetrahedral, or, more correctly, as eight-coordinate dodecahedral, by the convention of assigning three coordination sites to each η^5 -Cp ligand.

The structures are constrained by the C₂ linkages joining the Cp rings, but the (C₅-ring centroid)-metal-(centroid) angles (126–129°) for both structures fall only at the lower end of the normal range for unconstrained group 4 bent metallocenes. However, in both molecules the Cp rings are slightly twisted (average 4–5°) from perpendicularity to the centroid-metal-centroid plane. In the case of **4**(Ti), the twist is conrotatory about the C(9)–C(10) and C(11)–C(12) axes, and in **6**(Zr), the twist is disrotatory and increases the separation between the six-membered rings.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for **6**(Zr)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Zr	781.2 (5)	5000	5888.2 (3)	32.9 (1)
Zr'	4103.3 (5)	3317.6 (4)	9184.4 (3)	32.6 (1)
Cl(1)	960 (2)	3383 (1)	6495 (1)	53 (1)
Cl(2)	-542 (2)	4590 (2)	4510 (1)	56 (1)
Cl(1')	3595 (2)	4959 (1)	8703 (1)	50 (1)
Cl(2')	5588 (2)	3702 (2)	10503 (1)	53 (1)
C(1)	-946 (5)	6324 (4)	6125 (3)	39 (1)
C(2)	-1585 (6)	6955 (5)	5385 (4)	52 (2)
C(3)	-3001 (11)	6661 (10)	5131 (10)	148 (7)
C(4)	-3543 (7)	5810 (9)	5221 (6)	87 (4)
C(5)	-2980 (6)	5151 (6)	5953 (5)	64 (2)
C(6)	-1614 (5)	5473 (5)	6372 (4)	42 (2)
C(7)	-826 (6)	5095 (6)	7120 (4)	54 (2)
C(8)	316 (6)	5693 (5)	7317 (3)	45 (2)
C(9)	244 (5)	6465 (4)	6696 (3)	37 (1)
C(10)	1208 (5)	7296 (4)	6671 (4)	42 (2)
C(11)	2685 (6)	6945 (5)	6689 (4)	47 (2)
C(12)	2782 (5)	6120 (4)	6045 (4)	39 (2)
C(13)	2414 (5)	6089 (4)	5113 (3)	38 (1)
C(14)	1975 (7)	6882 (5)	4485 (4)	55 (2)
C(15)	2143 (23)	6608 (10)	3566 (6)	200 (10)
C(16)	2219 (13)	5731 (10)	3257 (5)	106 (5)
C(17)	2601 (8)	4905 (7)	3838 (4)	65 (2)
C(18)	2695 (6)	5155 (6)	4796 (4)	48 (2)
C(19)	3202 (6)	4611 (4)	5540 (4)	46 (2)
C(20)	3239 (5)	5195 (4)	6291 (4)	41 (2)
C(21)	1040 (9)	7966 (6)	7453 (6)	76 (3)
C(22)	3710 (7)	7743 (6)	6497 (6)	72 (3)
C(1')	2769 (5)	2201 (4)	10152 (4)	41 (2)
C(2')	3332 (7)	1528 (6)	10859 (4)	53 (2)
C(3')	3307 (21)	1932 (8)	11739 (6)	163 (8)
C(4')	2810 (14)	2750 (12)	11948 (5)	120 (6)
C(5')	2336 (8)	3520 (6)	11260 (4)	70 (3)
C(6')	2273 (6)	3105 (5)	10332 (4)	45 (2)
C(7')	1644 (6)	3478 (5)	9558 (4)	47 (2)
C(8')	1729 (5)	2814 (5)	8870 (4)	41 (2)
C(9')	2431 (5)	2007 (4)	9242 (4)	37 (1)
C(10')	2722 (6)	1097 (4)	8742 (4)	43 (2)
C(11')	3374 (6)	1328 (5)	7888 (4)	43 (2)
C(12')	4488 (5)	2062 (4)	8064 (3)	38 (1)
C(13')	5679 (5)	2031 (4)	8664 (3)	38 (1)
C(14')	6265 (6)	1219 (5)	9242 (4)	45 (2)
C(15')	7815 (8)	1301 (7)	9430 (6)	72 (3)
C(16')	8266 (7)	2268 (7)	9701 (6)	73 (3)
C(17')	7837 (6)	3040 (6)	9045 (4)	57 (2)
C(18')	6440 (5)	2874 (5)	8582 (4)	42 (2)
C(19')	5687 (6)	3454 (5)	7959 (4)	49 (2)
C(20')	4510 (6)	2958 (5)	7635 (4)	43 (2)
C(21')	1398 (7)	491 (7)	8620 (6)	76 (3)
C(22')	3866 (8)	449 (5)	7394 (5)	63 (2)

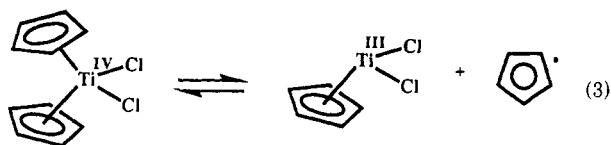
^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Such twisting is a normal feature of bent-metallocene structures of this type.⁴ The C(9)–C(10)–C(11)–C(12) torsion angles (average $\sim 46^\circ$) are similar in both structures. The methyl groups are equatorially disposed, and the strap adopts the δ conformation.

6. Photostationary State and Equilibrium Constant

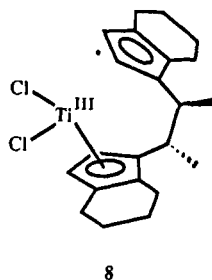
As was noted earlier, no convenient method has yet been found for establishing the equilibrium constant of the isomers of the present types of complexes. The only method of isomer interconversion is by irradiation to the photostationary state. We present here an argument which attempts to provide an approximate connection between the photostationary state and the equilibrium constant.

It has been established that the mechanism of cyclopentadienyl ion exchange from [Ti(cyclopentadienyl)₂Cl₂] ([Ti(Cp)₂Cl₂]) by irradiation involves the formation of cyclopentadienyl- and titanium-based radicals (eq 3). This



mechanism appears to obtain for all wavelengths of the visible and near-ultraviolet regions of the spectrum.⁷ We assume that this same mechanism is involved in generating the photostationary state of the [Ti((*S,S*)-chiracene)Cl₂] complexes.

After a few hours of irradiation, the three kinetically formed isomers *R,R*, *S,S*, and *R,S* convert to the two isomers *R,R* and *R,S*; none of the *S,S* isomer is detected. Thus, the photostationary state is essentially established between the *R,R* and *R,S* isomers. We find over all of the irradiation wavelengths that the integrated intensities of the absorptions of the *R,R* and *R,S* isomers are the same to within a few percent. Thus, the probability of absorption of these two isomers is essentially the same. In conformity with the experimental findings of the irradiation of [Ti(Cp)₂Cl₂], we assume that the common non-excited-state diradical intermediate **8** is formed from any of the



isomers; **8** can then either revert to the original isomer or convert to another isomer. Assuming that the quantum yields are approximately the same for the *R,R* and *R,S* isomers and invoking the Hammond postulate, we may illustrate the reaction profile as shown in Figure 5. According to the Hammond postulate, the thermodynamically more stable isomer will also have the more stable transition-state energy. Hence, the biradical **8** converts faster to the more stable product, in this case the *R,R* isomer. Because of the assumptions involved, this conclusion can, at best, only suggest which will be the preferred isomer. Even so, the conclusion conforms with our expectations based on reasonable steric arguments.

7. Discussion

At the outset, the chiracene ligand was prepared with three aims. First, we wished to prepare chiral [Ti((*S,S*)-chiracene)X₂] species which were configurationally stable. Second, we expected the chiracene ligand to strongly prefer one isomer. Third, because of this preference, we hoped to avoid a resolution step. These ambitions were partly fulfilled. The (*R,R*)-[Ti((*S,S*)-chiracene)Cl₂] complex is indeed configurationally stable under normal conditions. Chloroform solutions exposed to sunlight are configurationally stable for weeks. In tetrahydrofuran solutions under similar conditions, decomposition occurs but we observed no isomeric interconversion. Presumably, more extensive exposure to ambient light would cause isomerization, but handling of the solutions under normal conditions does not present difficulties. The (*S,S*)-chiracene appears to prefer the *R,R* isomer, but we have not been able to establish this unambiguously. The expectation of a simple diastereoselective synthesis of the desired (*R,R*)-[Ti((*S,S*)-chiracene)Cl₂] isomer was not observed under the reaction conditions. Because of the

Table IV. Selected Bond Distances and Angles for 4(Ti) and 6(Zr)

	4(Ti)	6(Zr)	
		molecule A	molecule B
(a) Bond Distances (Å)			
M-CNT(1)	2.085 (2)	2.211 (5)	2.218 (6)
M-CNT(2)	2.086 (2)	2.218 (5)	2.216 (5)
M-Cl(1)	2.344 (2)	2.451 (2)	2.457 (2)
M-Cl(2)	2.338 (2)	2.427 (2)	2.426 (2)
M-C(1)	2.460 (4)	2.554 (5)	2.569 (5)
M-C(6)	2.484 (4)	2.590 (5)	2.605 (6)
M-C(7)	2.402 (4)	2.531 (6)	2.518 (5)
M-C(8)	2.295 (5)	2.442 (5)	2.431 (5)
M-C(9)	2.375 (5)	2.471 (5)	2.467 (5)
M-C(12)	2.362 (5)	2.503 (6)	2.494 (6)
M-C(13)	2.467 (5)	2.560 (5)	2.539 (5)
M-C(18)	2.500 (5)	2.597 (6)	2.597 (5)
M-C(19)	2.384 (5)	2.520 (5)	2.512 (6)
M-C(20)	2.303 (5)	2.440 (5)	2.457 (5)
(b) Bond Angles (deg)			
CNT(1)-M-CNT(2)	128.9 (2)	125.8 (2)	126.3 (2)
Cl(1)-M-Cl(2)	94.8 (1)	96.7 (1)	97.3 (1)
(c) Torsion Angles (deg)			
C(9)-C(10)-C(11)-C(12)	47.3 (2)	45.2 (2)	45.1 (2)

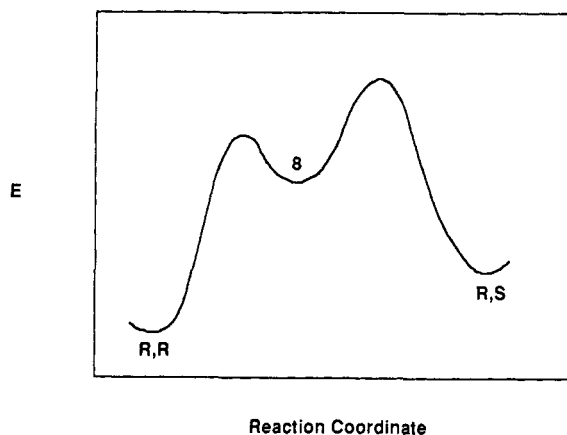


Figure 5. Reaction energy profile for the conversion of the diradical intermediate **8** formed from irradiation of (*R,R*)-[Ti((*S,S*)-chiracene)Cl₂] and (*R,S*)-[Ti((*S,S*)-chiracene)Cl₂].

number of steps required to obtain the pure *R,R* isomer, the present method of synthesis is cumbersome. Whereas the synthetic method is acceptable for obtaining material for our intended purpose of catalysis, it is not practical for stoichiometric reactions. We are currently investigating other synthetic routes to the desired *R,R*-isomer. We note that similar synthetic problems are encountered generally for analogous complexes.

After this work was completed, two reports appeared on chiral strapped bis(1-indenyl) ligand complexes of Ti(IV) and Zr(IV). In one case, the chiral strap contained an acid-sensitive acetonide group and the ligand gave only meso complexes of both titanium and zirconium.¹³ In the other case,¹⁴ a chiral binaphthyl strap was used and, although the arrangement of the indenyl groups was chiral, the conformation was not C₂ symmetric.

8. Experimental Section

The NMR spectra were obtained on a GE QE 300 and Chicago built 500-MHz spectrometers. Chemical shifts were referenced

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against internal CHCl_3 (δ 7.26) or CHDCl_2 (δ 5.32). UV-visible spectra were recorded on a Varian-Cary 2400 spectrometer. Circular dichroism spectra were measured with a Jasco J-600 instrument.

The following solvents were distilled under nitrogen immediately before use: tetrahydrofuran from potassium, methylene chloride from CaH_2 , and diethyl ether from LiAlH_4 . Unless otherwise noted, manipulations were carried out under an argon atmosphere using Schlenk techniques. The adducts $\text{TiCl}_4\cdot 2\text{THF}$, $\text{TiCl}_3\cdot 3\text{THF}$, and $\text{ZrCl}_4\cdot 2\text{THF}$ were prepared by established procedures.¹⁵ The ligand (*R*)-(+)-binaphthol was prepared by modification of the published procedure.¹⁶

(*S,S*)-2,3-Butylene-1,1'-bis(indene) (7). Dry, degassed THF (80 mL) was added at once to diindenylmagnesium⁹ (22.0 g, 86 mmol). The resulting warm, yellow mixture was stirred efficiently at room temperature for 1 h, whereafter the finely powdered dimesylate of (*2R,3R*)-2,3-butanediol¹⁷ (17.0 g, 69 mmol) was added in one portion. There followed an immediate vigorous exothermic reaction, giving a mobile amber red mixture. After it was stirred for 15 min, the reaction mixture was immersed in an 85 °C oil bath and refluxed for 3.5 h. The reaction mixture was cooled and then was quenched with a saturated aqueous solution of NH_4Cl (100 mL). The resultant mixture was poured into water (500 mL) and was extracted with benzene/ether (1/2, 3 × 200 mL). The combined organic layers were washed with water (6 × 150 mL) and brine (2 × 100 mL) and were dried (Na_2SO_4). On concentration on a rotary evaporator, a fluid brown oil remained. This was reduced further at 0.2 mmHg and 100 °C. The remaining residue, a gummy solid (11.5 g), was dissolved in hot cyclohexane (175 mL), this solution while still warm was loaded onto a basic alumina column (110 g, activity 1), and the material was eluted with cyclohexane. The combined eluates (~1 L) were concentrated, and the residue was dissolved in boiling cyclohexane (~25 mL). The solution stood at room temperature for 4 h, during which time crystals formed. Pentane (~1–2 mL) was then added, and the flask stood at -25 °C for 18 h. The off-white crystals (5.6 g) were collected and were washed with cold (-25 °C) pentane. A second crop (0.84 g) was similarly obtained from the filtrates for a total of 6.44 g (32%) of the chiracene precursor (*S,S*)-2,3-butylene-1,1'-bis(indene): $[\alpha]_D^{25} = +52.6^\circ$ (10 cm, $c = 0.6$ g/100 mL, CH_2Cl_2); mp 137–139 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.59 (d, $J = 7.5$ Hz, 2 H), 7.47 (d, $J = 7.3$ Hz, 2 H), 7.35 (t, $J = 7.3$ Hz, 2 H), 7.21 (t, $J = 7.4$ Hz, 2 H), 6.25 (s, 2 H), 3.40–3.25 (m, 2 H), 3.31 (s, 4 H), 1.20 (d, $J = 6.6$ Hz, 6 H). Anal. Calcd for $\text{C}_{22}\text{H}_{22}$: C, 92.3; H, 7.7. Found: C, 92.0; H, 7.9.

(*R,R*)-, (*S,S*)-, and (*R,S*)-[Ti((*S,S*)-2,3-butylene-1,1'-bis(indenyl))Cl₂]. A solution of the chiracene precursor 7 (4.006 g, 13.99 mmol) in THF (100 mL) was cooled to -78 °C and then was treated dropwise by syringe with a solution of *n*-butyllithium in hexane (1.6 M, 17.5 mL, 28 mmol) over 40 min. The bright yellow solution was stirred for 1 h and then was warmed to room temperature and cannulated into a constant-addition dropping funnel. The total solution volume was 145 mL. From a separate Schlenk flask, a solution of $\text{TiCl}_4\cdot 2\text{THF}$ (4.687 g, 14.03 mmol) in THF (120 mL) was cannulated into a second constant-addition dropping funnel and the solution was diluted to 145 mL.

The two solutions were simultaneously added dropwise to a 1000-mL three-neck flask containing THF (100 mL) maintained at 40 °C, over a period of 4.5 h. The resulting dark brown solution was stirred for a further 4 h and finally flushed with dry HCl gas for 30 s, during which time the color changed to dark green. The solvents were removed under reduced pressure. Diethyl ether (2 × 20 mL) was used to slurry the brown residue and was also evaporated under reduced pressure to ensure complete removal of THF. The dry residue was slurried with ether (50 mL), filtered, and washed with ether (50 mL). The solid was washed successively with aqueous HCl (4 N, 2 × 20 mL), H₂O (2 × 20 mL), EtOH (2 × 20 mL), and ether (20 mL) and was dried under a stream of nitrogen gas. The brown solid (2.702 g, 48%) was used in this crude form for hydrogenation. The Cp resonances were as follows. ^1H NMR (500 MHz, CDCl_3): *R,S* isomer, δ 7.17 (d, $J = 3.1$ Hz,

1 H), 6.66 (d, $J = 3.1$ Hz, 1 H), 6.43 (d, $J = 3.3$ Hz, 1 H), 6.07 (d, $J = 3.1$ Hz, 1 H); *R,R* isomer, δ 6.88 (d, $J = 3.3$ Hz, 2 H), 6.12 (d, $J = 3.3$ Hz, 2 H); *S,S* isomer, δ 6.56 (d, $J = 3.1$ Hz, 2 H), 5.70 (d, $J = 3.1$ Hz, 2 H). Variation of the conditions in terms of volume of solvent, temperature, and addition rate gave varying mixtures of isomers but did not improve the yield.

(*R,R*)-, (*S,S*)-, and (*R,S*)-[Ti((*S,S*)-2,3-butylene-1,1'-bis(tetrahydroindenyl))Cl₂]. A solution of the isomeric mixture of [Ti((*S,S*)-2,3-butylene-1,1'-bis(indenyl))Cl₂] (2.684 g, 6.6 mmol) and a suspension of PtO_2 (0.103 g, 0.453 mmol) in CH_2Cl_2 (100 mL) was stirred in a Parr pressure hydrogenator under 30 atm of H₂ gas for 20 h. The red solution was filtered through a pad of Celite, and the solvent was removed in vacuo to provide a red oil (*R,S*:*R,R*:*S,S* = 4.2:2.5:1). The titanocene dichlorides were purified by chromatography on silanized silica gel (20 g) with cyclohexane as eluent. The concentrated eluate was again chromatographed to provide a red solid (1.98 g, 72%) consisting of a mixture of [Ti((*S,S*)-chiracene)Cl₂] isomers.

(*R,R*)-[Ti((*S,S*)-chiracene)Cl₂]. A mixture of [Ti((*S,S*)-chiracene)Cl₂] isomers (1.98 g, 4.81 mmol) in THF (200 mL) was cannulated under argon into a water-jacketed 500-mL photolysis reactor containing a Hanovia 450-W mercury lamp surrounded by a Vycor cylindrical filter and a quartz cooling jacket. The solution was diluted further with THF (250 mL). The solution was vigorously stirred and irradiated over a period of 53 h at room temperature. NMR samples taken at 13-h intervals indicated that over the final 13 h the isomeric mixture had reached a photostationary state of *R,R*:*R,S* = 5.9:1. The solvent was removed in vacuo, and the resulting red oil was extracted with hot cyclohexane (200 mL), cooled, and filtered through a pad of Celite. Solvent removal in vacuo and chromatography on silanized silica gel (20 g, cyclohexane eluent) furnished a red-brown solid (1.53 g).

(*R,R*)-[Ti((*S,S*)-chiracene)(1,1'-bi-2-naphtholate)]. Sodium hydride (80% mineral oil emulsion, 0.283 g, 9.43 mmol) was introduced into a capped three-neck flask fitted with an argon inlet. The solid was washed with dry hexane (2 × 10 mL) by careful addition and removal with a syringe. A solution of (*R*)-(+)-binaphthol (1.066 g, 3.72 mmol) in THF (50 mL) was cannulated onto the NaH, causing H₂ evolution and the formation of a yellow solution. The isomeric mixture of (*R,R*)- and (*R,S*)-[Ti((*S,S*)-chiracene)Cl₂] (1.53 g, 3.72 mmol) dissolved in THF (60 mL) was similarly cannulated into the three-neck flask, and the flask was fitted with a reflux condenser. The mixture was heated at 80 °C for 1 h, cooled, and filtered through Celite, and the solvents were removed in vacuo. The red oil was slurried with benzene (50 mL) and the mixture filtered through Celite, and the solvents were removed. Chromatography on silanized silica (20 g, cyclohexane eluent) separated a faster running red band from a dark band. The clear red band, after solvent evaporation, was crystallized from CH_2Cl_2 /hexane (1/16, 85 mL) by gentle warming on a steam bath to remove CH_2Cl_2 . The red needles (1.00 g, 51% based on 85% presence of *R,R*) of (*R,R*)-[Ti((*S,S*)-chiracene)(binaphtholate)] were collected and washed with pentane (2 × 10 mL). ^1H NMR (500 MHz, CDCl_3): δ 7.78 (d, $J = 8.7$ Hz, 2 H), 7.76 (d, $J = 7.8$ Hz, 2 H), 7.16 (pseudo-t, $J = 7.4$ Hz, 2 H), 7.08 (d, $J = 8.7$ Hz, 2 H), 7.01 (pseudo-t, $J = 7.8$ Hz, 2 H), 6.89 (d, $J = 8.4$ Hz, 2 H), 5.68 (d, $J = 2.9$ Hz, 2 H), 5.51 (d, $J = 2.9$ Hz, 2 H), 3.31–3.29 (m, 2 H), 2.51–2.46 (m, 4 H), 1.77–1.69 (m, 2 H), 1.68–1.65 (m, 3 H), 1.57–1.45 (m, 5 H), 1.41 (d, $J = 5.7$ Hz, 6 H), 1.22–1.15 (m, 2 H). Anal. Calcd for $\text{C}_{42}\text{H}_{40}\text{O}_2\text{Ti}$: C, 80.76; H, 6.45. Found: C, 80.74; H, 6.46.

(*R,S*)-[Ti((*S,S*)-chiracene)Cl₂]. The slower moving dark red band was eluted, and the solvent was evaporated to dryness to give a dark solid. This fraction was further purified by chromatography on silanized silica gel with hexane eluent. Various attempts to crystallize the material were unsuccessful. A hexane solution (50 mL) of the purified eluate was flushed with dry HCl gas for 15 s, during which time the color changed from black to light red. The evaporated residue was slurried with cyclohexane (5 mL), and the precipitated solids were collected on a fine frit. Recrystallization from hot cyclohexane/hexane (7.5/1, 8.5 mL) provided spectroscopically pure orange square plates of (*R,S*)-[Ti((*S,S*)-chiracene)Cl₂] (0.013 g, 14%). ^1H NMR (300 MHz, CDCl_3): δ 6.60 (d, $J = 3.1$ Hz, 1 H), 6.30 (d, $J = 3.1$ Hz, 2 H), 5.80 (d, $J = 2.9$ Hz, 1 H), 3.45–3.16 (m, 4 H), 2.73–2.55 (m, 3 H), 2.43–2.13 (m, 4 H), 2.12–1.95 (m, 2 H), 1.79–1.71 (m, 1 H), 1.66–1.48

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(m, 4 H), 1.42 (d, $J = 6.8$ Hz, 3 H), 1.26 (d, $J = 6.5$ Hz, 3 H). Anal. Calcd for $C_{22}H_{28}Cl_2Ti$: C, 64.25; H, 6.86. Found: C, 64.60; H, 6.94. $[\alpha]_{436}^{25^\circ C} = -480^\circ$ (10 cm, $c = 2.5$ mg/100 mL, $CHCl_3$).

(*R,R*)-[Ti((*S,S*)-chiracene)Cl₂]. A solution of (*R,R*)-[Ti((*S,S*)-chiracene)((*R*)-binaphtholate)] (0.4972 g, 0.796 mmol) in hexane (200 mL) was flushed with dry HCl gas for 30 s. The solution stood for 2 h at room temperature, during which time free binaphthol precipitated (0.161 g, 71%). After filtration, the filtrate was evaporated in vacuo, the red-brown solid was dissolved in hot cyclohexane (30 mL) and cooled, and the crystallized red prisms (0.1178 g) were collected and were washed with hexane (20 mL). Successive crystallizations produced a further crop of red prisms (0.1741 g, total yield 89%). ¹H NMR (500 MHz, $CDCl_3$): δ 6.66 (d, $J = 3.1$ Hz, 2 H), 5.49 (d, $J = 3.1$ Hz, 2 H), 3.21–3.13 (m, 4 H), 2.69–2.64 (m, 2 H), 2.51–2.45 (m, 2 H), 2.33–2.27 (m, 2 H), 2.05–1.99 (m, 2 H), 1.96–1.89 (m, 2 H), 1.63–1.52 (m, 4 H), 1.36 (d, $J = 6.2$ Hz, 6 H). Anal. Calcd for $C_{22}H_{28}Cl_2Ti$: C, 64.25; H, 6.86; Cl, 17.24. Found: C, 64.56; H, 6.81; Cl, 17.27. $[\alpha]_{436}^{25^\circ C} = +3440^\circ$ (10 cm, $c = 2.5$ mg/100 mL, $CHCl_3$).

(*R,R*)-, (*S,S*)-, and (*R,S*)-[Zr((*S,S*)-2,3-butylene-1,1'-bis(indenyl))Cl₂]. The procedure outlined for the titanium analogue was followed with 3.769 g (13.16 mmol) of (*S,S*)-2,3-butylene-1,1'-bis(indene), 16.6 mL of *n*BuLi (1.6 M, 26.56 mmol) in hexane, and 4.957 g of $ZrCl_4 \cdot 2THF$ (13.14 mmol) with the following changes. The temperature was maintained at 25 °C throughout the reaction. The simultaneous addition of 125-mL THF solutions of the dilithium ligand salt and $ZrCl_4 \cdot 2THF$ was to 250 mL of THF over 3 h. The resultant solution was then stirred for 18 h. After workup by the method described for the titanium analogue, there was obtained 1.08 g (18%) of a bright yellow solid consisting mainly of the *R,S* isomer. ¹H NMR (*R,S* isomer; 500 MHz, $CDCl_3$): δ 7.75 (d, $J = 8.7$ Hz, 1 H), 7.46 (pseudo-t, $J = 9.9$ Hz, 2 H), 7.28 (d, $J = 8.7$ Hz, 1 H), 7.18 (pseudo-t, $J = 7.2$ Hz, 1 H), 7.12 (pseudo-t, $J = 7.4$ Hz, 1 H), 7.01 (t, $J = 7.4$ Hz, 2 H), 6.87 (d, $J = 3.8$ Hz, 1 H), 6.54 (d, $J = 3.8$ Hz, 1 H), 6.49 (d, $J = 3.8$ Hz, 1 H), 6.22 (d, $J = 3.8$ Hz, 1 H), 4.28–4.22 (m, 1 H), 3.80–3.72 (m, 1 H), 1.72 (d, $J = 6.7$ Hz, 3 H), 1.56 (d, $J = 6.7$ Hz, 3 H).

(*R,S*)-[Zr((*S,S*)-chiracene)Cl₂]. The procedure outlined for the titanium analogue was followed with 1.077 g (2.41 mmol) of the zirconocene isomeric mixture, 0.0394 g (0.173 mmol) of PtO_2 , and CH_2Cl_2 (80 mL) under 20 atm of H_2 over 15 h. Filtration, solvent removal in vacuo, and chromatography (silanized silica gel, 14 g, cyclohexane eluent) provided a white solid (0.55 g, 50%) with the isomeric composition *R,S*:*R,R*:*S,S* = 18.8:1:1. Crystallization of the meso compound was effected by dissolution of the isomeric mixture (0.38 g) in hot toluene (3 mL) and cooling to -20 °C. The off-white hexagonal prisms (0.058 g) were washed with pentane (5 mL) and dried under a stream of argon. ¹H NMR (500 MHz, CD_2Cl_2): δ 6.38 (d, $J = 3.4$ Hz, 1 H), 6.05 (d, $J = 3.7$ Hz, 1 H), 6.03 (d, $J = 2.9$ Hz, 1 H), 5.74 (d, $J = 2.9$ Hz, 1 H), 3.31–3.19 (m, 2 H), 3.11–3.05 (m, 1 H), 3.00–2.94 (m, 1 H), 2.69–2.59 (m, 3 H), 2.51–2.41 (m, 2 H), 2.37–2.32 (m, 1 H), 2.13–2.05 (m, 1 H), 2.03–1.92 (m, 2 H), 1.79–1.72 (m, 1 H), 1.65–1.50 (m, 4 H), 1.39 (d, $J = 6.3$ Hz, 3 H), 1.26 (d, $J = 5.7$ Hz, 3 H). Anal. Calcd for $C_{22}H_{28}Cl_2Zr$: C, 58.13; H, 6.21; Cl, 15.60. Found: C, 58.53; H, 6.15; Cl, 15.47.

(*R,R*)- and (*S,S*)-[Zr((*S,S*)-chiracene)Cl₂]. The procedure described previously for the titanium analogue was followed with 0.55 g (1.21 mmol) of the isomeric zirconium complexes in THF (450 mL) and irradiation over 14 h. During the last 8 h of photolysis, the concentration of (*S,S*)-zirconocene remained static, resulting in a photostationary state of *R,R*:*S,S* = 5.2:1. Isolation in the usual manner provided a yellow oil, which was slurried with EtOH (10 mL), filtered, and washed with EtOH (5 mL). The collected white solid was chromatographed (silanized silica, 2 g; cyclohexane eluent) to furnish a white solid (0.050 g, 9%). Various attempts to recrystallize the material from hot cyclohexane (3 mL) did not separate isomers. ¹H NMR (500 MHz, $CDCl_3$): *R,R* isomer, δ 6.46 (d, $J = 3.0$ Hz, 2 H), 5.53 (d, $J = 3.0$ Hz, 2 H), 3.14–3.08 (m, 4 H), 2.99–2.93 (m, 2 H), 2.65–2.59 (m, 2 H), 2.53–2.47 (m, 2 H), 2.42–2.36 (m, 2 H), 2.05–1.98 (m, 2 H), 1.96–1.89 (m, 2 H), 1.68–1.62 (m, 2 H), 1.33 (d, $J = 6.1$ Hz, 6 H); *S,S* isomer, δ 6.19 (d, $J = 2.8$ Hz, 2 H), 5.50 (d, $J = 2.9$ Hz, 2 H), 3.42–3.40 (m, 2 H), 2.84–2.78 (m, 2 H), 2.65–2.59 (m, 2 H), 2.58–2.54 (m, 2 H), 1.96–1.89 (m, 2 H), 1.85–1.78 (m, 2 H), 1.68–1.62 (m, 2 H), 1.60–1.50 (m, 4 H), 1.37 (d, $J = 6.1$ Hz, 6 H).

Crystal Structure Determinations. Crystal structure determinations for (*R,R*)-[Ti((*S,S*)-chiracene)Cl₂] (4(Ti)) and (*R,S*)-[Zr((*S,S*)-chiracene)Cl₂] (6(Zr)). Crystallographic data are summarized in Table I. Preliminary photographic characterization revealed *mmm* and *2/m* Laue symmetry for 4(Ti) and 6(Zr), respectively. The orthorhombic space group $P2_12_12_1$ was uniquely determined from systematic absences in the data for 4(Ti), and for 6(Zr), either of the monoclinic space groups $P2_1$ and $P2_1/m$ were indicated. Since the presence of mirror-plane symmetry is incompatible with this chiral molecule (without disorder), processing was confined to the noncentrosymmetric alternative. The results of refinement were well-behaved. No corrections for absorption were applied to the data; for 4(Ti) and 6(Zr) the maximum/minimum transmission ratios were less than 1.1.

Heavy-atom methods were used to locate the metal atoms in each. The crystallographic asymmetric unit for 4(Ti) contains two chemically similar independent molecules. All non-hydrogen atoms in both were refined with anisotropic thermal parameters; hydrogen atoms were treated as idealized contributions and not refined. For both structures the correctness of the enantiomorph reported was tested by refinement of a multiplicative term for $\Delta f''$: for 4(Ti), 1.09 (15); for 6(Zr), 1.11 (13).

All calculations used SHELXTL (version 5.1) software developed for the Siemens (Nicolet) Corp. (Madison, WI) by G. Sheldrick. Atomic coordinates for 4(Ti) and 6(Zr) are provided in Tables II and III, respectively, and selected bond distances and angles are given in Table IV.

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for 4(Ti) and 6(Zr) (12 pages). Ordering information is given on any current masthead page.

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