Synthesis of ansa-titanocenes via a double-Skattebol rearrangement

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Synthesis of *ansa*-Titanocenes *via* a Double-Skattebøl Rearrangement

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Novel synthetic approaches to chiral ethylene-bridged *ansa*-titanocenes possessing stereogenic centers on the bridging carbon chain are described. A key step in the preparation of these compounds is the double-Skattebøl rearrangement of bis(vinyldibromocyclopropane) intermediates derived from 1,4-disulfones. The influence of tether substitution on the diastereoselection in *ansa*-titanocene formation has been examined through stereospecific 2,3-dimethyl substitution on the ethylene bridge of β-methyl-substituted bis(cyclopentadienyl) ligands. The ethylene-bridged bis(cyclopentadienes) were converted to their dilithium salts and treated with $TiCl_3$·3THF to afford mixtures of *meso* and racemic *ansa*-titanocenes. Several isomers were isolated, and their structures were determined by X-ray diffraction. The *meso* configuration of tether-methyl substituents was found to promote the formation of a racemic configuration of β-methyl cyclopentadienide ligands whereas the racemic configuration of tether-methyl substituents was found to have little effect on the racemic to *meso* ratio relative to ethylenebis[η^5-1-(3-methylcyclopentadienyl)]titanium dichloride. The spectral and physical characteristics of these compounds are discussed.

Introduction

Investigations toward the preparation of chiral *ansa*-metallocenes of group 4 transition metals have been driven by the use of these compounds as precursors to soluble Ziegler–Natta catalysts[1–7] and by the use of these compounds as reagents and catalysts in asymmetric syntheses.[8] Studies of asymmetric syntheses using chiral *ansa*-metallocenes have been limited by the availability of enantiomerically pure complexes. With the exception of several recent examples,[9–11] the literature syntheses of chiral *ansa*-metallocenes deliver racemates. Consequently, an optical resolution process[12] is required to obtain enantiomerically pure material. This process is often further complicated by the presence of a *meso* diastereomer which must be removed prior to optical resolution.

Efforts to circumvent the problems associated with optical resolution have led to the development of a promising new strategy for enantioselective synthesis of *ansa*-metallocenes. The introduction of asymmetry on the bridging carbons of a tethered bis(cyclopentadienide) ligand has been used to promote a distereoselective complexation of the cyclopentadienide (Cp) rings. This strategy has been applied in the synthesis of complexes 1–4 (Chart I).[4d,9,10] For example, titanocene 1 was obtained as the sole diastereomer on complexation of the corresponding C_2-symmetric binaphthyl-bridged bis(indenyl) ligand.[9]

The potential advantages in using tether asymmetry as a control mechanism led us to develop a novel synthetic approach to chiral ethylene-bridged *ansa*-titanocenes. Previous preparations of *ansa*-metallocenes have relied on a common strategy in which the cyclopentadienyl anion or indenyl anion is reacted with an electrophilic tether component. Application of this strategy to the synthesis of asymmetrically substituted ethylene-bridged systems would require the reaction of a cyclopentadienyl or indenyl anion with a carbon bearing a secondary leaving group. The problems associated with the formation of Cp regioisomers, racemization[13] of the electrophilic component and formation of spirocyclic rings,[10b] have limited the

(1) (a) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* 1992, *31*, 1347. (b) Hermann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W. *Ibid.* 1989, *28*, 1511.

(2) (a) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* 1988, *110*, 6255. (b) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *Ibid.* 1987, *109*, 6544. (c) Ewen, J. A. Ligand Effects on Metallocene Catalyzed Polymerizations. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1986; p 271. (d) Ewen, J. A. *J. Am. Chem. Soc.* 1984, *106*, 6355.

(3) (a) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* 1992, *114*, 9679. (b) Waymouth, R. M.; Coates, G. W. *J. Am. Chem. Soc.* 1991, *113*, 6270.

(4) (a) Llinas, G. H.; Dong, S. H.; Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* 1992, *25*, 1242. (b) Chien, J. C. W.; Llinas, G. H.; Rausch, M. D.; Lin, G.-Y.; Winter, H. H. *J. Am. Chem. Soc.* 1991, *113*, 8569. (c) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* 1991, *113*, 8570. (d) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* 1990, *112*, 2030. (e) Rieger, B.; Chien, J. C. W. *Polym. Bull.* 1989, *21*, 159.

(5) (a) Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* 1990, *29*, 279. (b) Brintzinger, H. H. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerisation*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 249. (c) Pino, P.; Cioni, P. Galimberti, M.; Wei, J.; Piccolrovazzi, N. *Ibid.*, p 269.

(6) (a) Pino, P.; Galimberti, M. *J. Organomet. Chem.* 1989, *1*, 370. (b) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* 1987, *109*, 6189.

(7) (a) Kaminsky, W.; Ahlers, A.; Moller-Lindehof, N. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 1216. (b) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* 1987, *8*, 305. (c) Kaminsky, W. *Angew. Makromol. Chem.* 1986, *145/146*, 149. (d) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 507.

(8) (a) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *Tetrahedron Lett.* 1992, *33*, 6423. (b) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* 1992, *114*, 7562. (c) Colletti, S. L.; Halterman, R. L. *Tetrahedron Lett.* 1992, *33*, 1005. (d) Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* 1991, *113*, 2321. (e) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* 1990, *112*, 4911. (f) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* 1989, *54*, 4154.

(9) Burk, M. J.; Colletti, S. L.; Halterman, R. L. *Organometallics* 1991, *10*, 2998.

(10) (a) Hollis, T. K.; Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* 1992, *11*, 2812. (b) Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* 1992, *11*, 1869.

(11) Bandy, J. A.; Green, M. L. H.; Gardiner, I. M.; Prout, K. *J. Chem. Soc., Dalton Trans.* 1991, 2207.

(12) For procedures detailing *ansa*-metallocene optical resolution, see: (a) Reference 8f. (b) Schafer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1987, *328*, 87.

(13) Cesarotti, E.; Ugo, R.; Vitiello, R. *J. Mol. Catal.* 1981, *12*, 63.

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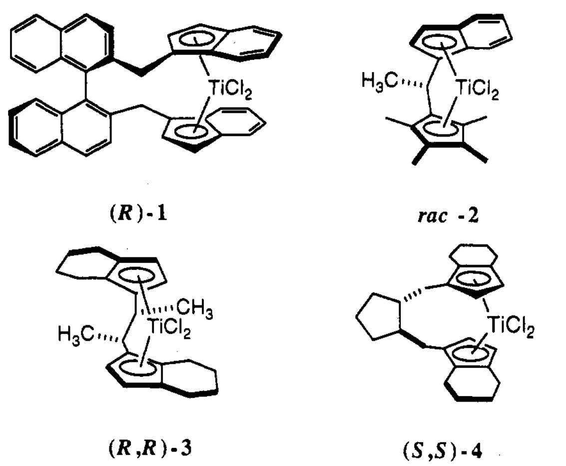
Chart I



flexibility of this approach. To avoid these problems, we selected a strategy which involves a (4 + 1) construction of the Cp rings around two carbon centers which are tethered by a substituted ethylene bridge. A 2,3-disubstituted 1,4-disulfone is used as a template on which the Cp carbons are introduced via alkylation α to the sulfone groups. A subsequent sulfone elimination then sets the stage for the (4 + 1) synthesis of the cyclopentadienyl rings. We envisioned that a double-Skattebøl rearrangement[14,15] would be well suited in this instance to prepare the ethylene-bridged ligands *meso*-**11** and DL-**11** (Scheme I).

Synthesis

Our previous work with 2,3-dimethylsuccinic acid[16] resulted in a convenient synthesis of *meso*-2,3-dimethylsuccinic acid and DL-2,3-dimethylsuccinic anhydride (see Experimental Section). Consequently, *meso*-**5**[17] was prepared by borane–dimethyl sulfide reduction of *meso*-2,3-dimethylsuccinic acid and DL-**5** was prepared by $LiAlH_4$ reduction of DL-2,3-dimethylsuccinic anhydride. Conversion of the diols to the corresponding disulfones *meso*-**8** and DL-**8** (Scheme I) was readily achieved in good yield. The optimized procedure for the sulfone alkylation–elimination sequence (**8** to **9**) involved the formation of a diastereomeric mixture of homoallylic sulfones which were treated with KOtBu in THF at −10 °C to afford the tetraenes *meso*-**9** and DL-**9**. During the alkylation step, we observed the elimination of phenyl sulfinate from the α-alkylated products, a process induced by unreacted α-sulfonyl anions and resulting in lower yields. The inverse addition of the dianion derived from **8** to an excess of 3-bromo-2-methylpropene at 25 °C helped to ameliorate this problem. The two step alkylation–elimination process afforded *meso*-**9** in 94% yield as a single 3*E*,7*E* isomer. Similarly, DL-**9** was obtained in 84% yield as a 20:1 mixture of 3*E*,7*E* and 3*E*,7*Z* isomers. Subsequent cyclopropanation using Doering–Hoffmann conditions[18] afforded a diastereomeric mixture of the thermally unstable tetrabromides *meso*-**10** and DL-**10** in nearly quantitative yield. ^{1}H NMR decoupling experiments confirmed that the dibromocarbene addition had occurred with the regiochemistry as depicted. The double-Skattebøl rearrangement was induced by treatment of the tetrabromides **10** with 4 equiv of CH_3Li in Et_2O at −78 °C. Crystallization of the resultant product mixtures from hexane at low temperatures afforded single isomers[19] of *meso*-**11** and DL-**11** in 48% and 22% yields, respectively. The modest yields in this case may be attributed to a competing process involving terminal allene formation.[14] GC and ^{1}H NMR analysis of the crude product mixture containing DL-**11** indicated that the ratio of bis(cyclopentadiene) to mono(allene) and bis(allene) side products was approximately 2:1. This ratio is consistent with results obtained from a model study involving the Skattebøl rearrangement of a similarly substituted vinyl dibromocyclopropane.[20]

As shown in Scheme II, the titanocene dichlorides **12a–c** and **13a–c** were prepared from the dianions of *meso*-**11** and DL-**11** (2 equiv of nBuLi, THF, 0 °C) and $TiCl_3{\cdot}3THF$[21] (−40 °C to reflux, 4 h) followed by the addition of 12 M HCl (−40 to +25 °C) and stirring for 1 h open to the ambient atmosphere. Compounds **12a–c** were isolated in 98% yield as a 2.6:1:1 mixture of **12a**:**12b**:**12c**. The effect of the reflux period on the diastereoselection was found to be negligible in the case of *meso*-**11**. When the dianion of *meso*-**11** was treated at −40 °C with $TiCl_3{\cdot}3THF$ followed by stirring at 25 °C for 8 h and workup in the usual manner, a similar ratio (**12a**:**12b**:**12c** = 2.8:1:1) was obtained. The ratios were determined by integration of the Cp-methyl singlets in the ^{1}H NMR spectrum of the titanocenes. Compound **12a** gives two Cp-methyl singlets at 2.27 and 2.37 ppm. Compounds **12b** and **12c** are axially symmetric and yield ^{1}H NMR spectra with one methyl singlet. The ^{1}H NMR spectra of **12b** and **12c** remain unassigned with respect to stereochemistry. Titanocene **12a** was obtained in enriched form after precipitation from toluene–hexane (**12a**:**12b**:**12c** = 20:2.4:1). Recrystallization of this material from benzene–isooctane gave well-formed crystals of **12a**. The structural assignment was confirmed by X-ray crystallography (Figure 1).

Compounds **13a–c** were isolated in 83% yield as a 4.6:2.8:1 mixture of **13a**:**13b**:**13c**. The ^{1}H NMR spectrum of the unsymmetrical titanocene, **13a**, was readily assigned by the presence of two singlets (2.37 and 2.40 ppm) attributed to the nonequivalent Cp-methyl groups. Compounds **13b** and **13c** are axially symmetric and each gives a ^{1}H NMR spectrum having one methyl singlet. To correlate the structures of **13b** and **13c** with the ^{1}H NMR

(14) (a) Boche, G.; Walborsky, H. M. In *Cyclopropane Derived Reactive Intermediates*; Pati, S., Rappaport, Z., Eds.; John Wiley and Sons: New York, 1990; p 195. (b) Holm, K. H.; Skattebøl, L. *Acta Chem. Scand.* **1984**, *38*, 183. (c) Holm, K. H.; Skattebøl, L. *Tetrahedron Lett.* **1977**, 2347. (d) Reinarz, R. B.; Fonken, G. J. *Tetrahedron Lett.* **1973**, 4591. (e) Skattebøl, L. *Tetrahedron* **1967**, *23*, 1107. (f) Skattebøl, L. *Chem. Ind.* **1962**, 2146.

(15) The usefulness of the Skattebøl rearrangement in the synthesis of optically pure cyclopentadienes has been demonstrated: (a) Paquette, L. A.; McLaughlin, M. L. *Org. Synth.* **1989**, *68*, 220. (b) McLaughlin, M. L.; Paquette, L. A. *Tetrahedron Lett.* **1986**, *27*, 5595.

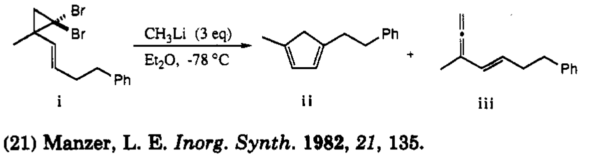
(16) Sutton, S. C.; Nantz, M. H.; Hitchcock, S. R. *Org. Prep. Proced. Int.* **1992**, *24*, 39.

(17) McCasland, G. E.; Proskow, S. *J. Am. Chem. Soc.* **1954**, *76*, 3486.

(18) (a) *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 3, p 876. (b) Doering, W. E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162.

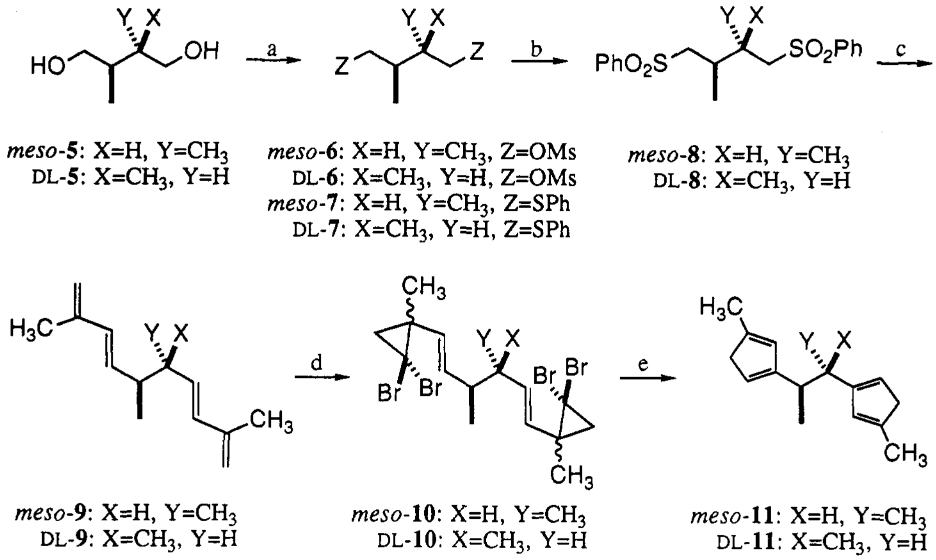
(19) The structure of **11** has been arbitrarily assigned as one of two possible stereoisomers which are in accord with ^{1}H NMR decoupling experiments and literature coupling constants.

(20) The Skattebøl rearrangement was examined for dibromocyclopropane i and was found to afford a 5:1 ratio of ii:iii. To our knowledge, the substitution pattern present in i has not been previously examined in the Skattebøl rearrangement.



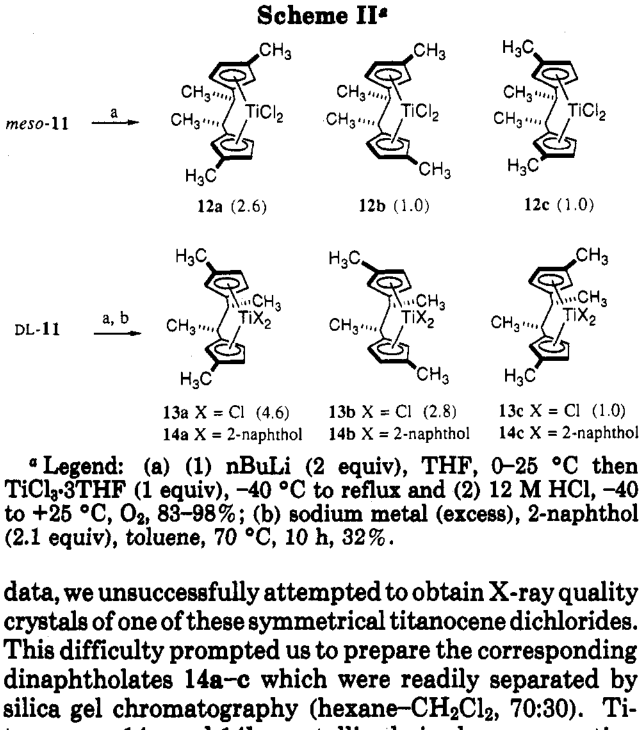
(21) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

Scheme I[a]



[a] Legend: (a) (1) MsCl (2.3 equiv), Et_3N, CH_2Cl_2, −78 °C, 1 h, 80–90% and (2) PhSK (2.1 equiv), DMF, 25 °C, 5 h, ~100%; (b) mCPBA (4.3 equiv), CH_2Cl_2, 0–25 °C, 4.5 h, 67–80% recrystallized yield; (c) (1) nBuLi (2.1 equiv), THF, −78 °C then 3-bromo-2-methylpropene, 25 °C, 3 h and (2) KOtBu (3 equiv), THF, −10 to 0 °C, 2 h, 84–94%; (d) Br_3CH (2.4 equiv), KOtBu (2.8 equiv), pentane, 0 °C, 2 h; (e) MeLi (4 equiv), THF, −78 °C, 1 h, 22–48% from **9**.

Scheme II[a]



[a] Legend: (a) (1) nBuLi (2 equiv), THF, 0–25 °C then $TiCl_3{\cdot}3THF$ (1 equiv), −40 °C to reflux and (2) 12 M HCl, −40 to +25 °C, O_2, 83–98%; (b) sodium metal (excess), 2-naphthol (2.1 equiv), toluene, 70 °C, 10 h, 32%.

data, we unsuccessfully attempted to obtain X-ray quality crystals of one of these symmetrical titanocene dichlorides. This difficulty prompted us to prepare the corresponding dinaphtholates **14a–c** which were readily separated by silica gel chromatography (hexane–CH_2Cl_2, 70:30). Titanocenes **14a** and **14b** crystallized via slow evaporation from a CH_2Cl_2–cyclohexane solution to give crystals which were satisfactory for structure determination by X-ray diffraction. The structures so obtained (Figures 2 and 3) enabled us to correlate the titanocene structures with the ^1H NMR data.

Diastereoselection in *ansa*-Titanocene Formation

Comparison of the ratios obtained in the formation of compounds **12a–c** (*rac*:*meso* = 1.3:1) to those obtained by Collins[22] (*rac*:*meso* = 1:1.3) for the closely related ethylenebis[η^5-1-(3-methylcyclopentadienyl)]titanium dichloride reveals an interesting difference. In the present example, a *meso* configuration on the ethylene bridge promotes a racemic arrangement of β-methylcyclopentadienyl rings during complexation. This racemic preference is unusual in that ethylene-bridged β-substituted *ansa*-titanocenes typically exhibit a bias toward formation of a *meso* complex,[22] a bias which has been explained in part using thermodynamic considerations.[23]

In the formation of compounds **13a–c**, a slight preference for formation of the *meso* isomers is observed (*rac*:*meso* = 1:1.2). Interestingly, the compound which has the *anti–anti*[24] arrangement of the Cp-methyl groups (**13b**) is formed in preference to the compound which has the *syn–syn* arrangement (**13c**) by a ratio of 2.8:1. It is not clear why this is so, particularly, considering that no difference in the formation of the *anti–anti* (**12b**) and *syn–syn* (**12c**) complexes is observed when the ethylene bridge has a *meso* configuration of substituents. A comparison of the results obtained in the formation of **13a–c** with those reported by Bosnich[10b] reveals some interesting similarities. An identical *rac*:*meso* ratio is reported (1:1.2) in the synthesis of complex **3** and its isomers. Furthermore, the ratio of racemic isomers formed in the complexation leading to **3** (*anti–anti*:*syn–syn* = 2.5:1) is similar to the **13b**:**13c** ratio (2.8:1). These similarities are striking considering that the comparison is made between β-substituted *ansa*-titanocenes and α,β-disubstituted *ansa*-titanocenes, each possessing asymmetric substitution on an ethylene bridge. The intuitive expectation that tether substitution might influence the magnitude of diastereoselection with α-substituted Cp ligands more so than with β-substituted Cp ligands is surprisingly not supported by the above comparisons. Further investigations are required to clarify the thermodynamic and kinetic aspects of *ansa*-metal-

(22) Collins, S.; Hong, Y.; Taylor, N. *Organometallics* **1990**, *9*, 2695.

(23) For a discussion regarding the steric interactions between ring substituents and chloride ligands and their effect on the racemic to *meso* isomer ratio see ref 22, also see: (a) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359. (b) Gutmann, S.; Burger, P.; Hund, H.-U.; Hofmann, J.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 343.

(24) The descriptors *anti* and *syn* are used here to denote the stereochemical relationship between a Cp-methyl substituent and its proximal tether-methyl substituent relative to the bisector of the $TiCl_2$ angle in the plane defined by the ethylene bridge carbons.

Table I. ^{1}H NMR Chemical Shifts of Cyclopentadienyl Protons for Compounds 12a–c and 13a–c[a]

racemic[b] compd	δ, ppm[c] ring A	δ, ppm[c] ring B	meso[b] compd	δ, ppm[c] ring A	δ, ppm[c] ring B
12a	5.82	5.88	**12b** or c	5.73	
	6.27	6.02		6.21	
	6.57	6.44		6.36	
13b	5.42		**12b** or c	5.76	
	6.02			6.48	
	6.35			6.50	
13c	5.64		**13a**	5.60	5.64
	5.85			6.24	5.91
	6.43			6.54	6.64

[a] All spectra were recorded in $CDCl_3$, and shifts are reported with respect to the $CHCl_3$ peak at 7.26 ppm. [b] Racemic and *meso* is used to denote the configuration of the β-methyl Cp ligands. [c] See Experimental Section for coupling constants.

locene formation in relation to the stereochemical outcome of complexation.[25]

^{1}H NMR Spectra

The ^{1}H NMR chemical shifts for the cyclopentadienyl protons of compounds **12a–c** and **13a–c** are shown in Table I. For β-substituted *ansa*-metallocenes, the relative spacing of the cyclopentadienyl protons has been used to facilitate the identification of the *meso* and racemic isomers in lieu of crystallographic data.[22,23b] In a mixture of the two isomers, the racemic isomer usually has two closely spaced triplets with the remaining triplet at lowest field whereas the corresponding *meso* isomer has three somewhat evenly spaced triplets with one of them at highest field. Compounds **12a–c** are not in agreement with this trend and show no obvious correlation between the ^{1}H NMR chemical shifts of the cyclopentadienyl protons and structure. The asymmetrically substituted *ansa*-titanocenes, **13a–c**, show a correlation that is different from the previously observed trend noted for β-substituted *ansa*-metallocenes.

We have noted that the relative spacing of the cyclopentadienyl protons in **13a–c** correlates with the stereochemical relationship of the Cp-methyl substituent to the proximal tether-methyl substituent. When the Cp methyl is *syn* to the proximal tether methyl, as is the case for both rings of compound **13c**, the ^{1}H NMR signals occur as two closely spaced triplets with the remaining signal at low field. When the Cp methyl is *anti* to the proximal tether methyl, as is the case for both rings of compound **13b**, the ^{1}H NMR signals occur as two closely spaced triplets with the remaining triplet at highest field. It should be noted that compound **13b** is a racemic β-substituted *ansa*-titanocene having ^{1}H NMR spectral characteristics which, using the earlier trend, would be associated with a *meso* arrangement of β-substituents. Compound **13a** has both a *syn* and an *anti* arrangement of Cp methyls. The Cp protons were assigned to their respective Cp rings using decoupling experiments. As expected, one ring has a pattern similar to **13b** and the other ring parallels **13c** (Table I) thus following the general *anti–syn* trend. It is well documented that the α-proton resonances of *ansa*-metallocenes with a 16-electron configuration appear at a higher field than those for the β-protons.[26] Thus, we can assign the triplet at 5.42 ppm in **13b** to one of the α-protons. Comparison of this value to the α-proton resonance (5.49 ppm) in (*R,R*)-[Ti((*S,S*,)-chiracene)Cl_2] (**3**) leads to a possibly useful trend. Both **3** and **13b** have an *anti–anti* arrangement of Cp substituents, and each exhibits the highest field resonance of their respective isomers. It remains to be seen whether these trends are general in asymmetrically substituted ethylene-bridged metallocenes.

Crystal Structures

Single crystals of compound **12a** were well-formed transparent prisms belonging to the space group *C*2/*c*. The structure was solved using direct methods and refined by full-matrix least squares with the use of Siemens SHELXTL PLUS software[27] to an *R* value of 0.0414 and R_w = 0.0388. Atomic coordinates and isotropic thermal parameters, bond lengths, and selected bond angles are shown in Tables III–V, respectively. A thermal ellipsoid plot of this structure is depicted in Figure 1; the structural data confirm the ^{1}H NMR identification of this complex as the unsymmetrical isomer.

The interannular bridge of **12a** is misaligned relative to the $TiCl_2$ bisector axis. This is perhaps best appreciated from the projection perpendicular to the $TiCl_2$ plane. This misalignment has been observed in *ansa*-titanocenes with bulky groups in the β-position of the Cp rings[22,23b] and more recently in complexes without Cp substitution.[28] Brintzinger describes this distortion as arising from a rotation of the Cp rings about the respective metal–centroid axes, away from an idealized C_{2v} symmetric geometry by some torsional angle θ. For the two rings of **12a**, we find θ = +30 and −39°, i.e. |θ| = 35 ± 5°. The consymmetric rotation of the ligand framework relative to the metal places one of the Cp-methyl groups, C(101), between the chlorides (3.68 Å from Cl(1) and 3.35 Å from Cl(2)) and the other Cp-methyl group, C(21), 3.11 Å away from Cl(1). This rotation is presumed[23,26,28] to reduce the interaction between the β-methyl groups and the chloride ligands, although it has also been recognized that crystal packing effects may contribute to this distortion.[29] In addition, the chelate adopts a twisted conformation which reduces the eclipsing interaction between the methyl groups on the ethylene bridge. The C(61)–C(6)–C(7)–C(71) torsion angle is 40° and the C(6)–C(7) bond of the ethylene bridge is inclined approximately 27° from the perpendicular line which bisects the Cl–Ti–Cl plane. This twisted conformation places one methyl group in a pseudoequatorial position and the other in a pseudoaxial position.

Slow evaporation of a concentrated solution of compound **14a** in CH_2Cl_2–cyclohexane led to the deposition of **14a** as clusters of small needles. Most of these crystals were irregular in shape and not well formed. Due to the small size and poor quality of the crystals, diffraction was

(25) Photochemical isomerization experiments have not yet been conducted on complexes 12 and 13. Although the photoisomerization of titanocene complexes without α-substituents has been shown to be unsuccessful,[22] the presence of tether substituents might influence the photostationary state in these complexes.

(26) Gutmann, S.; Burger, P.; Prosenc, M.-H.; Brintzinger, H. H. *J. Organomet. Chem.* **1990**, *397*, 21.

(27) Sheldrick, G. M. *SHELXTL PLUS, A Program for Crystal Structure Determination*, Version 4.0; Siemens Analytical X-ray Instruments: Madison, WI, 1989.

(28) Burger, P.; Diebold, J.; Gutmann, S.; Hund, H. U.; Brintzinger, H. H. *Organometallics* **1992**, *11*, 1319.

(29) Collins[22] reported the occurrence of axially symmetric and nonaxially distorted forms in different crystal modifications of the same compound, *rac*-$C_2H_4(1\text{-}C_5H_3\text{-}3\text{-}C(CH_3)_3)_2TiCl_2$.

Table II. Crystal Data for Compounds 12a, 14a, and 14b

	12a	14a	14b
formula	$C_{16}H_{20}Cl_2Ti$	$C_{36}H_{34}O_2Ti$	$C_{36}H_{34}O_2Ti \cdot 1.6C_6H_{12}$
color, habit	red block	orange-red block	orange-red block
fw	331.1	546.56	654.8
cryst syst	monoclinic	orthorhombic	monoclinic
cell constants			
a, Å	15.925(2)	16.414(3)	12.165(4)
b, Å	12.730(2)	9.148(2)	23.156(6)
c, Å	16.864(2)	18.473(4)	15.435(3)
β, deg	117.68(1)		112.72(2)
V, Å^3	3027.5(7)	2773.8(10)	4010(2)
space group	$C2/c$	$Pca2_1$	$P2_1/c$
Z	8	4	4
ρ, g cm^{-3}	1.453	1.309	1.084
$F(000)$	1376	1152	1354
λ, Å	0.710 73	1.541 78	0.710 73
T, K	130	120	130
cryst size, mm	0.40 × 0.15 × 0.15	0.10 × 0.08 × 0.06	0.60 × 0.50 × 0.40
diffractometer	Syntex $P2_1$	Siemens P4RA	Syntex $P2_1$
scan method	ω	θ–2θ	ω
2θ range, deg	0.0–50.0	0–108.9	0.0–50.0
scan width, deg	1.00	●1.00 + Kα separation	2.00
scan speed, deg min^{-1}	20	20	15 in ω (2θ = 0–35°) 4 in ω (2θ = 35–50°)
std reflns	2 measured every 198 reflections	2 measured every 198 reflections	2 measured every 198 reflections
no. of measd data	2800	3870	7623
no. of unique data	2680	1770	7084
no. of obsd data	2122 ($F > 4.0\sigma(F)$)	1770 ($F > 4.0\sigma(F)$)	3773 ($F > 6.0\sigma(F)$)
no. of params	184	352	475
R[a]	0.0414 ($F > 4.0\sigma(F)$)	0.0503 ($F > 4.0\sigma(F)$)	0.0933 ($F > 6.0\sigma(F)$)
R_w[b]	0.0388	R_w2[d] = 0.1131	0.1027
GOF[c]	1.27	1.078[c]	1.96

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum||F_o| - |F_c||(w)^{1/2}/\sum|F_o|(w)^{1/2}$. [c] $GOF = [\sum(w||F_o| - |F_c||^2)/(M - N)]^{1/2}$ where M is the number of observed data and N is the number of parameters refined. [d] $R_w2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [e] $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ where M is the number of observed data and N is the number of parameters refined.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 12a

	x/a	y/b	z/c	U(eq)[a]
Ti	2727(1)	1506(1)	3068(1)	18(1)
Cl(1)	2682(1)	2057(1)	1722(1)	23(1)
Cl(2)	3285(1)	3142(1)	3813(1)	27(1)
C(1)	1265(2)	590(3)	2422(2)	23(1)
C(2)	1008(2)	1626(3)	2090(2)	25(1)
C(21)	517(3)	1956(3)	1122(2)	36(2)
C(3)	1250(2)	2292(3)	2832(2)	26(2)
C(4)	1609(2)	1659(3)	3608(2)	22(1)
C(5)	1600(2)	601(3)	3362(2)	19(1)
C(6)	1909(2)	−355(3)	3963(2)	24(1)
C(61)	1295(3)	−502(3)	4438(3)	30(2)
C(7)	2987(2)	−308(3)	4616(2)	24(1)
C(71)	3260(3)	306(3)	5475(2)	27(2)
C(8)	3476(2)	124(3)	4099(2)	21(1)
C(9)	4135(2)	952(3)	4344(2)	21(1)
C(10)	4400(2)	1126(3)	3656(2)	22(1)
C(101)	5070(3)	1948(3)	3652(3)	29(2)
C(11)	3893(2)	387(3)	2978(2)	23(2)
C(12)	3313(2)	−211(3)	3230(2)	22(1)

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

weak but data collection using Cu Kα radiation (rotating anode) proved possible. The structure was solved by direct methods (SHELXS-92) and refined by full-matrix least squares on F^2 (SHELXL-92).[30] Additional atomic coordinates and isotropic thermal parameters, bond lengths, and bond angles for **14a** are included in the supplementary material. Thermal ellipsoid plots of this structure are depicted in Figure 2. The conformation adopted by the *ansa* ligand in compound **14a** is aligned relative to the

(30) Sheldrick, G. M. *SHELXS-92, SHELXL-92, Programs for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1992.

Table IV. Bond Lengths (Å) for 12a[a]

Ti–Cl(1)	2.345(1)	Ti–Cl(2)	2.381(1)
Ti–C(1)	2.368(3)	Ti–C(2)	2.458(3)
Ti–C(3)	2.413(4)	Ti–C(4)	2.355(5)
Ti–C(5)	2.370(4)	Ti–C(8)	2.369(3)
Ti–C(9)	2.382(3)	Ti–C(10)	2.420(4)
Ti–C(11)	2.400(4)	Ti–C(12)	2.342(4)
C(1)–C(2)	1.417(5)	C(1)–C(5)	1.418(5)
C(2)–C(21)	1.505(5)	C(2)–C(3)	1.409(5)
C(3)–C(4)	1.413(5)	C(4)–C(5)	1.407(5)
C(5)–C(6)	1.512(5)	C(6)–C(61)	1.536(7)
C(6)–C(7)	1.551(4)	C(7)–C(71)	1.522(5)
C(7)–C(8)	1.516(6)	C(8)–C(9)	1.408(5)
C(8)–C(12)	1.430(5)	C(9)–C(10)	1.425(6)
C(10)–C(101)	1.496(6)	C(10)–C(11)	1.410(5)
C(11)–C(12)	1.407(6)	Cent^{syn}–Ti	2.056(5)
Cent^{anti}–Ti	2.070(5)		

[a] Cent^{anti} and Cent^{syn} are the two centroids of the cyclopentadienyl rings with the *anti* and *syn* arrangement, respectively.

Ti(2-naphtholate)$_2$ bisector axis. A dissymmetric rotation of both rings with $\theta = 28 \pm 1°$ places both tether methyls in pseudoequatorial positions with a C(61)–C(6)–C(7)–C(71) torsion angle of 60°.

Single crystals of compound **14b** were obtained by the procedure described above leading to small needles or larger "cubic" crystals depending on the duration of the crystallization period. Two partial occupancy disordered cyclohexane molecules were present in the crystal. Furthermore, one of the 2-naphtholate ligands was disordered in two orientations flipped 180° relative to each other. The inherent disorder led to very weak diffraction at $2\theta > 35°$ and a rather poorly defined structure. The structure was solved and refined using the same techniques as used for compound **12a**. Additional atomic coordinates and isotropic thermal parameters, bond lengths, and bond angles for **14b** are included in the supplementary material,

Table V. Selected Bond Angles (deg) for 12a[a]

Cl(1)–Ti–Cl(2)	94.9(1)	C(2)–C(1)–C(5)	108.8(3)
C(1)–C(2)–C(21)	126.7(3)	C(1)–C(2)–C(3)	107.4(3)
C(21)–C(2)–C(3)	125.8(3)	C(2)–C(3)–C(4)	107.8(3)
C(3)–C(4)–C(5)	109.2(3)	C(1)–C(5)–C(4)	106.6(3)
C(1)–C(5)–C(6)	125.3(3)	C(4)–C(5)–C(6)	128.0(3)
C(5)–C(6)–C(61)	111.1(3)	C(5)–C(6)–C(7)	110.6(3)
C(61)–C(6)–C(7)	113.4(3)	C(6)–C(7)–C(71)	115.3(4)
C(6)–C(7)–C(8)	107.5(3)	C(71)–C(7)–C(8)	111.4(3)
C(7)–C(8)–C(9)	128.0(3)	C(7)–C(8)–C(12)	125.7(3)
C(9)–C(8)–C(12)	106.3(4)	C(8)–C(9)–C(10)	109.9(3)
C(9)–C(10)–C(101)	126.4(3)	C(101)–C(10)–C(11)	127.2(4)
C(9)–C(10)–C(11)	106.4(3)	C(10)–C(11)–C(12)	109.0(4)
C(8)–C(12)–C(11)	108.4(3)	Cent^{anti}–Ti–Cent^{syn}	129.2(4)

[a] Cent^{anti} and Cent^{syn} are the two centroids of the cyclopentadienyl rings.

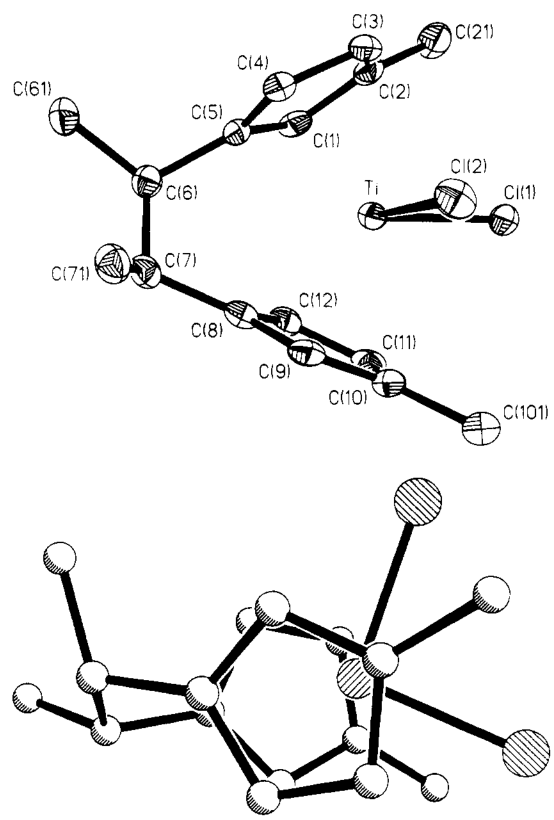


Figure 1. Molecular structure of compound **12a** with 50% probability ellipsoids depicted and H atoms removed for clarity: (a, top) side view; (b, bottom) projection perpendicular to the $TiCl_2$ plane.

and the structure is depicted in Figure 3. The *ansa* ligand framework deviates from C_{2v} symmetry by a dissymmetric rotation of both rings with $\theta = 29 \pm 2°$ with the C(61)–C(6)–C(7)–C(71) torsion angle at 62°.

The energy difference between the conformation depicted in Figure 1 and one in which the ligand framework bisects the Cl–Ti–Cl angle is expected to be small. It is presumed that in solution a fluctuation of the ligand framework relative to the $TiCl_2$ unit occurs rapidly relative to the NMR time scale. Indeed, low temperature ^1H NMR experiments (−80 °C, 300 MHz, CD_2Cl_2) did not provide evidence for a significant energy barrier between non-equivalent conformations of compound **12a**. This fluctuation is potentially an undesirable liberty in catalysts designed for asymmetric synthesis. In this regard, the flexibility of the double-Skattebøl approach demonstrated in the present syntheses should facilitate the preparation of a variety of tether- and Cp-substituted *ansa*-metallocenes in which both conformational and stereochemical relationships may be examined. We are currently studying modifications of the synthetic route which will enable the placement of substituents in the α positions of *ansa*-metallocenes and will report on this work in due course.

Table VI. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 14a

	x/a	*y/b*	*z/c*	*U*(eq)[a]
Ti	2535.1(10)	2068(2)	2163.6(10)	33.9(7)
O(1)	1701(4)	3118(8)	1713(3)	56(4)
O(2)	1872(4)	893(7)	2794(4)	50(4)
C(1)	3387(6)	49(12)	1933(6)	49(6)
C(2)	2619(6)	−383(10)	1653(6)	48(6)
C(21)	2109(7)	−1641(11)	1931(6)	69(7)
C(3)	2407(7)	550(11)	1118(5)	52(7)
C(4)	3067(8)	1525(11)	1033(6)	61(10)
C(5)	3680(7)	1186(14)	1530(6)	58(7)
C(6)	4497(7)	1933(16)	1597(8)	97(9)
C(61)	5029(6)	1657(13)	956(6)	59(6)
C(7)	4471(6)	3287(13)	1939(6)	71(7)
C(71)	5210(5)	3967(9)	2262(6)	52(6)
C(8)	3730(6)	3468(11)	2412(5)	47(5)
C(9)	3558(5)	2661(12)	3048(6)	47(5)
C(10)	2828(5)	3206(10)	3349(5)	36(5)
C(101)	2427(6)	2685(11)	4050(5)	54(7)
C(11)	2518(6)	4258(10)	2891(5)	39(5)
C(12)	3093(5)	4448(10)	2328(6)	48(5)
C(201)	1163(6)	3386(12)	1168(5)	42(6)
C(202)	412(6)	2754(10)	1164(5)	35(6)
C(203)	−175(6)	3230(9)	649(5)	34(6)
C(204)	−982(6)	2709(11)	666(5)	43(6)
C(205)	−1543(6)	3188(12)	182(6)	51(6)
C(206)	−1328(6)	4146(11)	−337(7)	61(7)
C(207)	−565(7)	4703(11)	−386(6)	54(8)
C(208)	45(6)	4255(10)	119(5)	40(6)
C(209)	836(6)	4813(12)	116(5)	47(7)
C(210)	1402(6)	4394(11)	618(5)	47(6)
C(211)	1168(5)	793(11)	3156(5)	38(5)
C(212)	546(6)	1795(12)	3098(5)	43(6)
C(213)	−191(5)	1630(12)	3492(5)	38(6)
C(214)	−856(6)	2600(11)	3402(5)	42(7)
C(215)	−1567(6)	2386(12)	3793(6)	52(6)
C(216)	−1632(6)	1191(11)	4282(6)	47(6)
C(217)	−1010(5)	235(11)	4360(5)	41(5)
C(218)	−269(5)	421(10)	3973(5)	32(5)
C(219)	381(6)	−596(12)	4030(5)	44(6)
C(220)	1080(5)	−402(11)	3628(5)	44(5)

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

Table VII. Selected Bond Lengths (Å) for 14a[a]

Ti–O(1)	1.868(6)	Ti–O(2)	1.922(6)
Ti–C(1)	2.355(10)	Ti–C(2)	2.436(9)
Ti–C(3)	2.388(10)	Ti–C(4)	2.317(10)
Ti–C(5)	2.356(11)	Ti–C(8)	2.387(10)
Ti–C(9)	2.404(9)	Ti–C(10)	2.471(9)
Ti–C(11)	2.412(9)	Ti–C(12)	2.381(9)
C(1)–C(2)	1.418(13)	C(1)–C(5)	1.367(15)
C(2)–C(21)	1.513(12)	C(2)–C(3)	1.352(14)
C(3)–C(4)	1.412(14)	C(4)–C(5)	1.397(15)
C(5)–C(6)	1.510(15)	C(6)–C(61)	1.493(14)
C(6)–C(7)	1.391(15)	C(7)–C(71)	1.488(13)
C(7)–C(8)	1.508(13)	C(8)–C(9)	1.415(14)
C(8)–C(12)	1.386(13)	C(9)–C(10)	1.412(12)
C(10)–C(101)	1.530(12)	C(10)–C(11)	1.378(12)
C(11)–C(12)	1.415(12)	Cent^{syn}–Ti	2.096(5)
Cent^{anti}–Ti	2.057(5)		

[a] Cent^{anti} and Cent^{syn} are the two centroids of the cyclopentadienyl rings with the *anti* and *syn* arrangement, respectively.

Experimental Section

All solvents and chemicals were reagent grade and were purified as required. THF and diethyl ether were distilled from NaK–benzophenone. All reactions were performed under an atmosphere of dry argon. CH_2Cl_2 was distilled from CaH_2. Pentane

Table VIII. Selected Bond Angles (deg) for 14a[a]

O(1)–Ti–O(2)	98.2(3)	C(6)–C(7)–C(71)	122.0(10)
C(5)–C(1)–C(2)	109.0(10)	C(6)–C(7)–C(8)	112.6(9)
C(3)–C(2)–C(1)	108.7(9)	C(71)–C(7)–C(8)	112.3(9)
C(3)–C(2)–C(21)	125.8(10)	C(12)–C(8)–C(9)	106.3(9)
C(1)–C(2)–C(21)	125.5(10)	C(12)–C(8)–C(7)	127.9(10)
C(2)–C(3)–C(4)	106.4(10)	C(9)–C(8)–C(7)	125.8(10)
C(5)–C(4)–C(3)	109.9(10)	C(8)–C(9)–C(10)	108.2(9)
C(1)–C(5)–C(4)	105.9(10)	C(11)–C(10)–C(9)	108.5(9)
C(1)–C(5)–C(6)	127.7(12)	C(11)–C(10)–C(101)	125.4(8)
C(4)–C(5)–C(6)	126.4(13)	C(9)–C(10)–C(101)	126.1(9)
C(7)–C(6)–C(61)	121.8(11)	C(10)–C(11)–C(12)	106.9(8)
C(7)–C(6)–C(5)	114.4(10)	C(8)–C(12)–C(11)	109.9(9)
C(61)–C(6)–C(5)	112.2(10)	Cent^{anti}–Ti–Cent^{syn}	127.9(4)

[a] Cent^{anti} and Cent^{syn} are the two centroids of the cyclopentadienyl rings.

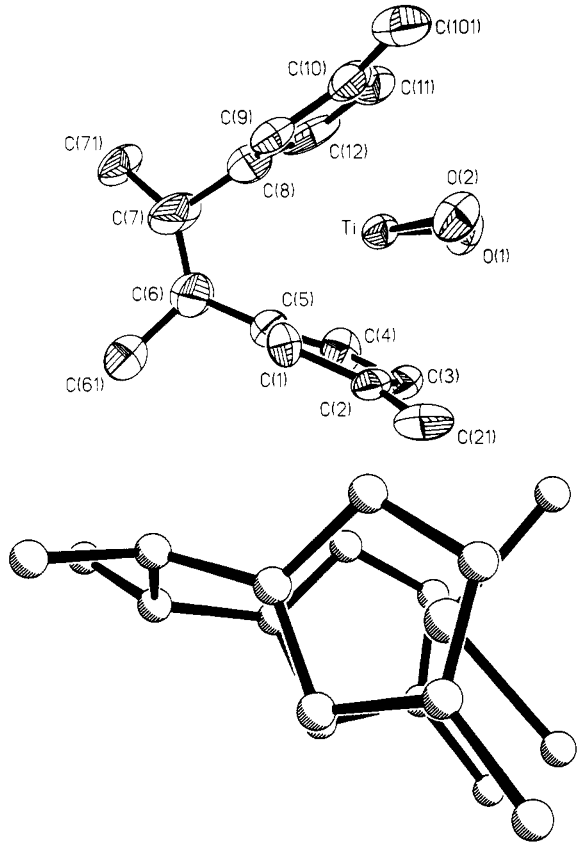


Figure 2. Molecular structure of compound **14a** with 50% probability ellipsoids depicted: (a, top) side view; (b, bottom) projection perpendicular to the $TiCl_2$ plane. The naphthalene portion of the 2-naphtholate ligands and the H atoms were removed for clarity.

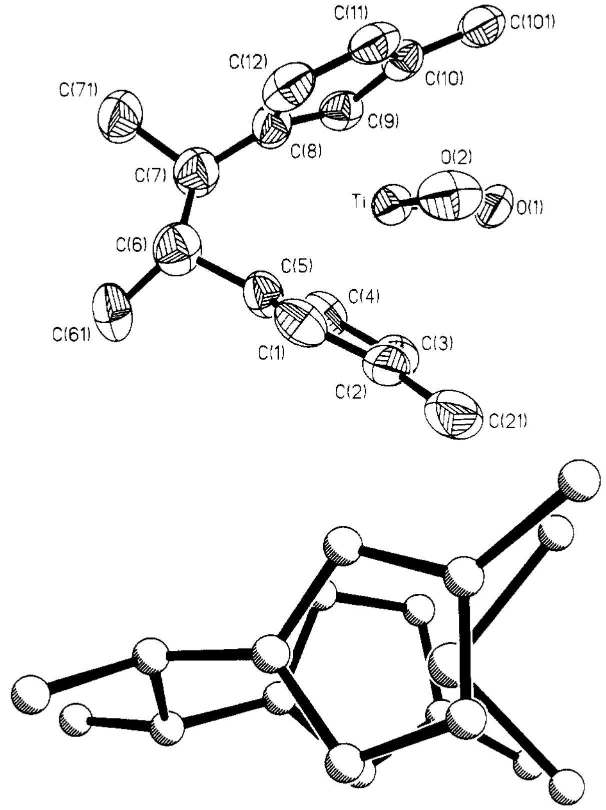


Figure 3. Molecular structure of compound **14b** with 50% probability ellipsoids depicted: (a, top) side view; (b, bottom) projection perpendicular to the $TiCl_2$ plane. The naphthalene portion of the 2-naphtholate ligands and the H atoms were removed for clarity.

was repeatedly washed with concentrated H_2SO_4, water, and $NaHCO_3$ followed by drying over $MgSO_4$ and distillation from $LiAlH_4$. Bromoform was washed with water and saturated $CaCl_2$ followed by drying over $CaCl_2$ and fractional distillation. The compound $TiCl_3$·3THF was prepared by the method of Manzer.[21] BioBeads SX-1 was purchased from BioRad Laboratories. Infrared spectra were determined on a IBM FTIR-32 instrument with an IBM 9000 data system. NMR spectra were determined with a General Electric QE-300 spectrometer (^1H at 300 MHz and ^{13}C at 75 MHz); chemical shifts are referenced with respect to residual undeuterated solvent (δ 7.26 for $CHCl_3$). Melting points were determined on an Electrothermal digital melting-point apparatus Model IA8100-A and are uncorrected. Elemental analyses were performed by Midwest Microlab of Indianapolis, IN.

Preparation of *meso*-2,3-Dimethylbutane-1,4-diol (*meso*-5). A 500-mL round bottom flask was charged with 2,3-dimethyl-2-carboxybutanedioic acid[16] (156 g, 821 mmol) and immersed in an oil bath heated at 130 °C. After an initial melting period, the slow evolution of carbon dioxide was observed. Heating was continued for 0.5 h followed by cooling to 25 °C. The resulting tan solid was dissolved in 6 N NaOH (280 mL). The aqueous phase was washed with ether until the rinses were colorless, cooled to 0 °C, and acidified to pH 1 with concentrated HCl. The resulting tan precipitate was collected, washed with cold 2-propanol (2 × 75 mL) and dried, giving 41 g of pure *meso*-2,3-dimethylsuccinic acid which was identical to the commercially available material. The yield was 68% based on a 1:1 ratio of *meso* to DL diastereomers which was determined by ^1H NMR of the reaction mixture. Extraction of the acidified aqueous phase as in ref 16 gave 79 g of a 4.6:1 mixture of DL:*meso* diacids. Conversion of this diacid mixture to the cyclic anhydrides[16] followed by crystallization from absolute ethanol afforded DL-2,3-dimethylsuccinic anhydride (35.7 g, 63%, >20:1, DL:*meso*). To a solution of *meso*-2,3-dimethyl succinic acid (8.9 g, 61 mmol) in THF (300 mL) at 0 °C was added BH_3·DMS (27 mL of a 10 M solution, 270 mmol) over 20 min. The reaction was allowed to warm to 25 °C and stirring was continued for 4 h. The reaction was quenched by the dropwise addition of methanol (130 mL) at 0 °C followed by stirring at 25 °C for 12 h. Removal of the solvents under reduced pressure gave a yellow oil which was treated with 25 mL of methanol. The methanol–trimethylborate mixture was removed under reduced pressure, and this process was repeated twice. Vacuum distillation gave 6.52 g (91%) of *meso*-**5** as a colorless oil, bp 83 °C (0.15 Torr). ^1H NMR ($CDCl_3$): δ 0.97 (d, J = 7.0 Hz, 6H), 1.74–1.94 (m, 2H), 3.44–3.68 (m, 4H), 3.38 (br s, 2 H). ^{13}C NMR ($CDCl_3$): δ 13.3, 38.4, 64.9. IR (CCl_4): 3265 (br), 1468, 1022 cm^{-1}.

Preparation of DL-2,3-Dimethylbutane-1,4-diol (DL-5). A solution of DL-2,3-dimethylsuccinic anhydride[16] (2.26 g, 17.6 mmol) in THF (20 mL) was slowly added to a suspension of $LiAlH_4$ (1.00 g, 26.4 mmol) in THF (20 mL) at 0 °C. Upon completion of the addition, the reaction mixture was allowed to warm to 25 °C and stirring was continued for 4 h. The excess

Table IX. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 14b

	x/a	y/b	z/c	U(eq)[a]
Ti	2558(1)	1418(1)	3856(1)	38(1)
O(1)	1720(4)	1049(2)	4518(4)	53(2)
O(2)	3024(5)	2094(2)	4599(4)	59(2)
C(1)	3383(7)	478(3)	3827(5)	47(3)
C(2)	3904(6)	634(3)	4779(5)	45(3)
C(21)	3803(7)	346(4)	5613(6)	60(4)
C(3)	4584(7)	1132(3)	4815(6)	53(3)
C(4)	4481(7)	1263(3)	3886(7)	57(4)
C(5)	3752(7)	835(3)	3276(5)	51(4)
C(6)	3431(8)	791(4)	2253(6)	63(4)
C(61)	4460(9)	591(4)	1988(7)	75(5)
C(7)	2871(8)	1347(4)	1779(6)	62(4)
C(71)	2282(9)	1345(4)	710(6)	69(4)
C(8)	2014(7)	1547(3)	2209(5)	48(3)
C(9)	1991(8)	2094(3)	2589(5)	54(3)
C(10)	1063(7)	2129(4)	2918(5)	52(3)
C(101)	736(9)	2656(4)	3328(6)	73(4)
C(11)	536(7)	1595(4)	2776(5)	52(3)
C(12)	1120(7)	1226(3)	2350(5)	47(3)
C(201)	760(7)	1166(4)	4743(5)	53(3)
C(202)	−63(7)	719(4)	4641(6)	60(4)
C(203)	−1000(8)	796(4)	4904(7)	67(4)
C(204)	−1153(7)	1311(3)	5282(6)	54(3)
C(205)	−2174(8)	1397(5)	5547(6)	68(4)
C(206)	−2325(9)	1919(5)	5879(6)	76(5)
C(207)	−1509(8)	2372(5)	5962(6)	76(5)
C(208)	−573(8)	2313(4)	5715(6)	68(4)
C(209)	−391(6)	1768(4)	5371(5)	52(3)
C(210)	623(7)	1689(4)	5108(5)	57(4)
C(211)	3840(12)	2283(5)	5408(7)	41(6)
C(212)	3956(11)	2045(5)	6294(8)	48(6)
C(213)	4858(11)	2260(6)	7137(7)	63(7)
C(214)	5663(12)	2702(6)	7090(8)	59(8)
C(215)	6609(12)	2905(6)	7941(9)	61(8)
C(216)	7384(16)	3344(8)	7851(9)	58(7)
C(217)	7229(14)	3592(8)	6964(10)	85(10)
C(218)	6305(11)	3381(6)	6130(8)	64(7)
C(219)	5529(12)	2936(6)	6196(7)	56(7)
C(220)	4593(10)	2740(5)	5343(8)	45(6)
C(311)	3961(21)	2382(11)	5164(10)	53(7)
C(312)	4521(15)	2807(7)	4802(11)	50(5)
C(313)	5511(15)	3123(7)	5428(9)	63(5)
C(314)	5914(19)	3037(10)	6420(9)	51(6)
C(315)	6926(24)	3360(13)	7031(13)	78(9)
C(316)	7326(38)	3278(20)	8024(13)	108(15)
C(317)	6824(20)	2835(10)	8409(12)	70(8)
C(318)	5796(17)	2527(9)	7793(10)	77(6)
C(319)	5331(22)	2619(12)	6788(9)	62(8)
C(320)	4342(15)	2286(8)	6150(11)	50(5)

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

Table X. Selected Bond Lengths (Å) for 14b[a]

Ti–O(1)	1.903(6)	Ti–O(2)	1.895(5)
Ti–C(1)	2.404(8)	Ti–C(2)	2.490(7)
Ti–C(3)	2.425(7)	Ti–C(4)	2.349(10)
Ti–C(5)	2.396(10)	Ti–C(8)	2.385(8)
Ti–C(9)	2.390(8)	Ti–C(10)	2.466(8)
Ti–C(11)	2.415(7)	Ti–C(12)	2.350(6)
C(1)–C(2)	1.404(10)	C(1)–C(5)	1.380(13)
C(2)–C(21)	1.495(13)	C(2)–C(3)	1.408(11)
C(3)–C(4)	1.423(14)	C(4)–C(5)	1.418(11)
C(5)–C(6)	1.477(12)	C(6)–C(61)	1.530(16)
C(6)–C(7)	1.507(12)	C(7)–C(71)	1.523(12)
C(7)–C(8)	1.508(15)	C(8)–C(9)	1.402(11)
C(8)–C(12)	1.402(12)	C(9)–C(10)	1.407(14)
C(10)–C(101)	1.497(13)	C(10)–C(11)	1.371(12)
C(11)–C(12)	1.425(13)	Cent–Ti	2.085(5)
Cent′–Ti	2.096(5)		

[a] Cent and Cent′ are the two centroids of the cyclopentadienyl rings.

$LiAlH_4$ was quenched by the dropwise addition of water (20 mL) at 0 °C, and the aqueous suspension was extracted with ethyl acetate (4 × 30 mL). The combined organic extract was washed with brine and dried ($MgSO_4$). Removal of the solvents gave

Table XI. Selected Bond Angles (deg) for 14b[a]

O(1)–Ti–O(2)	98.2(3)	C(6)–C(7)–C(71)	117.3(8)
C(2)–C(1)–C(5)	111.6(7)	C(6)–C(7)–C(8)	108.0(8)
C(1)–C(2)–C(21)	129.1(7)	C(71)–C(7)–C(8)	111.2(7)
C(1)–C(2)–C(3)	105.9(7)	C(7)–C(8)–C(9)	126.3(8)
C(21)–C(2)–C(3)	125.0(7)	C(7)–C(8)–C(12)	127.8(7)
C(2)–C(3)–C(4)	108.2(7)	C(9)–C(8)–C(12)	105.8(8)
C(3)–C(4)–C(5)	108.1(8)	C(8)–C(9)–C(10)	110.6(8)
C(1)–C(5)–C(4)	106.1(7)	C(9)–C(10)–C(101)	125.4(8)
C(1)–C(5)–C(6)	127.1(7)	C(9)–C(10)–C(11)	106.4(8)
C(4)–C(5)–C(6)	126.7(9)	C(101)–C(10)–C(11)	128.2(9)
C(5)–C(6)–C(61)	113.6(7)	C(10)–C(11)–C(12)	109.2(8)
C(5)–C(6)–C(7)	110.1(8)	C(8)–C(12)–C(11)	108.0(7)
C(61)–C(6)–C(7)	113.0(9)	Cent–Ti–Cent′	128.5(4)

[a] Cent and Cent′ are the two centroids of the cyclopentadienyl rings.

2.02 g (97%) of DL-**5** as a colorless oil. ^1H NMR ($CDCl_3$): δ 0.90 (d, J = 6.7 Hz, 6H), 1.60–1.75 (m, 2H), 2.55 (br s, 2H), 3.51 (dd, J = 11, 6 Hz, 2H), 3.63 (dd, J = 11, 4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 13.7, 37.8, 65.9. IR (CCl_4): 3265 (br), 1468, 1022 cm^{-1}.

Preparation of *meso*-2,3-Dimethyl-1,4-butanediol Bis(methanesulfonate) (*meso*-6). To a solution of *meso*-**5** (12.0 g, 102 mmol) in CH_2Cl_2 (500 mL) at −78 °C was added triethylamine (35.0 mL, 254 mmol) followed by the dropwise addition of methanesulfonyl chloride (18.0 mL, 234 mmol). The reaction mixture was stirred at −78 °C for 1 h and quenched by the addition of 5% HCl (100 mL). After warming to 25 °C, water (100 mL) and CH_2Cl_2 (100 mL) were added and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extract was washed successively with saturated $NaHCO_3$ and brine and then dried ($MgSO_4$). Removal of the CH_2Cl_2 gave 25 g (90%) of *meso*-**6** as a white solid, mp 73–74 °C. ^1H NMR ($CDCl_3$): δ 1.00 (d, J = 6.7 Hz, 6H), 1.90–2.10 (m, 2H), 2.98 (s, 6H), 4.08 (dd, J = 9.8, 5.8 Hz, 2H), 4.15 (dd, J = 9.8, 5.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 13.6, 34.7, 37.1, 71.9. IR ($CHCl_3$): 1354, 1221, 936 cm^{-1}. Anal. Calcd for $C_8H_{18}O_6S_2$: C, 35.02; H, 6.61; S, 23.37. Found: C, 35.14; H, 6.63; S, 23.46.

Preparation of DL-2,3-Dimethyl-1,4-butanediol Bis(methanesulfonate) (DL-6). DL-**5** (6.0 g, 51 mmol) was treated in a manner similar to that of *meso*-**5** to yield 11.0 g (80%) of a white solid, mp 98–100 °C. ^1H NMR ($CDCl_3$): δ 0.90 (d, J = 6.4 Hz, 6H), 2.03–2.11 (m, 2H), 2.97 (s, 6H), 4.07 (apparent d, J = 5.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 11.5, 33.4, 37.2, 72.0. IR ($CHCl_3$): 1354, 1221, 936 cm^{-1}. Anal. Calcd for $C_8H_{18}O_6S_2$: C, 35.02; H, 6.61; S, 23.37. Found: C, 35.12; H, 6.58; S, 23.20.

Preparation of *meso*-2,3-Dimethyl-1,4-di(thiophenyl)butane (*meso*-7). A 1-L, three-neck flask equipped with an overhead stirrer was flushed with argon and charged with KH (8.00 g, 200 mmol). DMF (400 mL) was added, and the suspension was cooled to 0 °C. Thiophenol (20.0 mL, 195 mmol) was added dropwise, and the reaction was allowed to warm to 25 °C. *meso*-**6** (25 g, 91 mmol) was added as a solution in DMF (100 mL). The yellow solution became very gelatinous, and vigorous stirring was continued for 5 h. The reaction was quenched by the addition of water (300 mL) at 0 °C, and the aqueous phase was extracted with Et_2O (3 × 200 mL). The combined extracts were washed successively with 1 N NaOH, water, and brine and dried ($MgSO_4$). Removal of the ether gave 26.8 g (97%) of a tan solid. A small portion of this material was recrystallized from methanol to give *meso*-**7** as a white solid, mp 40–42 °C. ^1H NMR ($CDCl_3$): δ 1.05 (d, J = 6.6 Hz, 6H), 1.82–1.88 (m, 2H), 2.72 (dd, J = 12, 8.6 Hz, 2H), 3.04 (dd, J = 12, 4.4 Hz, 2H), 7.12–7.20 (m, 2H), 7.23–7.34 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 16.4, 36.9, 38.0, 125.8, 128.8, 129.1, 137.0. IR (neat): 3078, 3063, 1686, 1586, 1482 cm^{-1}. FABMS: 302 (M^+, 15), 193 (M^+ − SPh, 100), 123 (M^+ − CH_2SPh, 54). Anal. Calcd for $C_{18}H_{22}S_2$: C, 71.47; H, 7.33; S, 21.20. Found: C, 71.50; H, 7.44; S, 21.29.

Preparation of DL-2,3-Dimethyl-1,4-di(thiophenyl)butane (DL-7). DL-**6** (10.4 g, 37.8 mmol) was treated in a manner similar to that of *meso*-**6** to yield 11.4 g (100%) of a tan solid. Recrystallization of a portion of this material from methanol gave DL-**7** as a white solid, mp 65–67 °C. ^1H NMR ($CDCl_3$): δ 0.95 (d, J = 6.7 Hz, 6H), 1.94–2.06 (m, 2H), 2.79 (dd, J = 13, 7.5

Hz, 2H), 2.91 (dd, J = 13, 6.1 Hz, 2H), 7.14–7.20 (m, 2H), 7.23–7.34 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 13.8, 35.6, 39.4, 125.8, 128.8, 129.2, 136.8. IR (neat): 3078, 3063, 1686, 1586, 1440 cm^{-1}. FABMS: 302 (M^+, 15), 193 (M^+ – SPh, 100), 123 (M^+ – CH_2SPh, 78). Anal. Calcd for $C_{18}H_{22}S_2$: C, 71.47; H, 7.33; S, 21.20. Found: C, 71.67; H, 7.46; S, 21.13.

Preparation of *meso*-2,3-Dimethyl-1,4-di(phenylsulfonyl)butane (*meso*-8). *meso*-7 (26.8 g, 88.6 mmol) was treated with 60% mCPBA (110 g, 380 mmol) in CH_2Cl_2 (600 mL) at 0 °C. The reaction was allowed to proceed at 0 °C for 0.5 h and then was warmed to 25 °C and stirred for 4 h. The excess mCPBA was quenched by the addition of dimethyl sulfide (13.0 mL, 177 mmol) at 0 °C. After stirring for 0.5 h at 25 °C, saturated $NaHCO_3$ (300 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extract was washed with brine and dried ($MgSO_4$). Removal of the solvent followed by recrystallization from methanol gave 26 g (80%) of *meso*-8 as a white solid, mp 148–149 °C. ^{1}H NMR ($CDCl_3$): δ 1.03 (d, J = 6.6 Hz, 6H), 2.19–2.27 (m, 2H), 2.83 (dd, J = 14, 8.0 Hz, 2H), 2.96 (dd, J = 14, 3.1 Hz, 2H), 7.57 (t, J = 7.8 Hz, 4H), 7.64–7.67 (m, 2H), 7.89 (d, J = 7.2 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 16.8, 33.1, 59.6, 127.9, 129.4, 133.8, 139.6. IR (KBr): 3095, 3068, 1287, 1254, 1145 cm^{-1}. FABMS: 367 (M^+ + H, 100), 84 (M^+ – $2SO_2Ph$, 32). Anal. Calcd for $C_{18}H_{22}O_4S_2$: C, 58.99; H, 6.05; S, 17.50. Found: C, 59.00; H, 6.13; S, 17.66.

Preparation of DL-2,3-Dimethyl-1,4-di(phenylsulfonyl)butane (DL-8). DL-7 (11.4 g, 37.8 mmol) was treated in a manner similar to that of *meso*-7 to yield 9.3 g (67%) of DL-8 as a white solid, mp 146–147 °C. ^{1}H NMR ($CDCl_3$): δ 0.95 (d, J = 6.6 Hz, 6H), 2.20–2.33 (m, 2H), 2.87 (dd, J = 14, 7.6 Hz, 2H), 3.05 (dd, J = 14, 3.9 Hz, 2H), 7.55 (t, J = 8.1 Hz, 4H), 7.62–7.67 (m, 2H), 7.87 (d, J = 7.4 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 15.0, 32.4, 60.3, 127.8, 129.3, 133.7, 139.5. IR (KBr): 3095, 3068, 1287, 1254, 1145 cm^{-1}. FABMS: 367 (M^+ + H, 100), 84 (M^+ – $2SO_2Ph$, 30). Anal. Calcd for $C_{18}H_{22}O_4S_2$: C, 58.99; H, 6.05; S, 17.50. Found: C, 59.01; H, 6.03; S, 17.39.

Preparation of (5*R*,6*S*)-2,5,6,9-Tetramethyl-(3*E*,7*E*)-1,3,7,9-decatetraene (*meso*-9). Finely powdered *meso*-8 (0.72 g, 2.0 mmol) was dissolved in THF (10 mL). Cooling the solution to –78 °C resulted in precipitation of the disulfone which redissolved on addition of nBuLi (1.7 mL of a 2.5 M solution in hexanes, 4.3 mmol). The resulting solution was allowed to warm to –30 °C over 0.5 h and then cooled to –78 °C and added via a transfer needle over 0.5 h to a solution of 3-bromo-2-methyl-1-propene (0.86 g, 6.4 mmol) in THF (5 mL) at 25 °C. The cannula used to transfer the bis(α-sulfonyl) anion was kept cold by rubbing dry ice on the outer surface. Stirring was continued for 3 h at 25 °C, and the reaction was quenched at 0 °C with saturated NH_4Cl (2 mL). Extraction with ethyl acetate (3 × 30 mL) followed by drying ($MgSO_4$) and removal of the solvents gave 0.86 g of a yellow oil. The ^{1}H NMR of the crude product indicated the presence of three diastereomeric disulfones as well as a small amount of material containing a 1,3-diene moiety. The crude material was dissolved in THF (10 mL) and added to a solution of KOtBu (0.67 g, 6.0 mmol) in THF (10 mL) at –10 °C. The reaction was allowed to warm to 0 °C over 2 h and quenched with saturated NH_4Cl (5 mL) and water (15 mL). The aqueous phase was extracted with Et_2O (3 × 15 mL), and the combined organic extract was washed with brine, dried ($MgSO_4$), and concentrated. Analysis of the crude extract by GC and ^{1}H NMR indicated the formation of a single isomer. Purification by silica gel chromatography (hexane) gave 0.36 g (94%) of *meso*-9 as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 1.04 (d, J = 6.6 Hz, 6H), 1.90 (s, 6H), 2.10–2.22 (m, 2H), 4.88 (s, 4H), 5.53 (dd, J = 15.7, 7.8 Hz, 2H), 6.11 (d, J = 15.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 18.4, 18.7, 42.8, 114.4, 132.2, 134.8, 142.1. IR (neat): 3081, 1690, 1612, 1454, 1360 cm^{-1}. MS (CI): 191 (M^+ + H, 100). Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.45; H, 11.67.

Preparation of (5*RS*,6*RS*)-2,5,6,9-Tetramethyl-(3*E*,7*E*)-1,3,7,9-decatetraene (DL-9). DL-8 (3.67 g, 10.0 mmol) was treated in a manner similar to that of *meso*-8. Analysis of the crude extract by GC and ^{1}H NMR indicated the formation of a major isomer (3*E*,7*E*) and a minor isomer (3*E*,7*Z*) in a 20:1 ratio. DL-9 (1.59 g, 84%) was obtained as a colorless oil after purification. ^{1}H NMR ($CDCl_3$): δ 1.00 (d, J = 6.6 Hz, 6H), 1.83 (s, 6H), 2.20–2.30 (m, 2H), 4.88 (s, 4H), 5.56 (dd, J = 15.7, 7.6 Hz, 2H), 6.11 (d, J = 15.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 17.4, 18.7, 42.2, 114.4, 132.2, 134.1, 142.2. IR (neat): 3081, 1692, 1612, 1454, 1365 cm^{-1}. FABMS: 191 (M^+ + H, 27). Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.27; H, 11.60.

Preparation of *meso*-10. A solution of *meso*-9 (1.85 g, 9.72 mmol) in pentane (10 mL) was added to a suspension of KOtBu (3.0 g, 27 mmol) in pentane (15 mL) at 0 °C. Freshly distilled bromoform (2.0 mL, 23 mmol) was added over 1 h as a solution in pentane (25 mL). The reaction was allowed to stir for an additional hour at 0 °C and was quenched with saturated NH_4Cl (5 mL) and water (10 mL). The aqueous phase was extracted with hexane (2 × 10 mL), and the combined organic extract was dried ($MgSO_4$) and concentrated at 25 °C. Removal of the *tert*-butanol was accomplished by quickly passing the crude extract through a 3-in. pad of silica gel with hexane as the eluent. Removal of the hexane at 25 °C gave 5.1 g (98%) of *meso*-10 as a nearly colorless oil. ^{1}H NMR ($CDCl_3$): [mixture of three diastereomers] δ 0.90–0.99 (m, 6H), 1.48 (br s, 6H), 1.59 (d, J = 7.5 Hz, 2H), 1.77 (d, J = 7.5 Hz, 2H), 2.06–2.14 (m, 2H), 5.46–5.49 (m, 4H). FABMS: 533 (M^+, with Br_4 isotope ratio). The bis(dibromocyclopropane)s (*meso*-10 and DL-10) decompose if left at 25 °C for more than 12 h but are stable for several days at –20 °C.

Preparation of DL-10. DL-9 (1.1 g, 5.8 mmol) was treated in a manner similar to that of *meso*-9 to yield 3.1 g (100%) of DL-10. ^{1}H NMR ($CDCl_3$): δ 0.97–1.01 (m, 6H), 1.48, 1.49, 1.50 (3s, 6H), 1.58, 1.61 (2d, J = 3.1 Hz, 2H), 1.73–1.79 (m, 2H), 2.14–2.22 (m, 2H), 5.54–5.51 (m, 4H). FABMS: 533 (M^+, with Br_4 isotope ratio).

Preparation of (2*R*,3*S*)-2,3-Bis(3-methyl-2,5-cyclopentadienyl)butane (*meso*-11). To *meso*-10 (5.1 g, 9.7 mmol) in Et_2O (20 mL) was added MeLi (28 mL of a 1.4 M solution in Et_2O, 39 mmol) dropwise at –78 °C. The reaction was allowed to stir for 1 h and was quenched with saturated NH_4Cl (5 mL) allowing the solution to slowly warm to 0 °C. The aqueous phase was extracted with Et_2O (2 × 10 mL), and the combined organic extract was washed with brine, dried ($MgSO_4$), and concentrated at 10 °C. The resulting yellow oil was dissolved in hexane (15 mL) in a double-tube recrystallization apparatus, and a white solid precipitated upon cooling to –78 °C. The solid was isolated and washed with cold hexane (5 mL), yielding 1.0 g (48%) of *meso*-11. ^{1}H NMR ($CDCl_3$): δ 0.98 (d, J = 6.5 Hz, 6H), 2.05 (d, J = 1.4 Hz, 6H), 2.44–2.51 (m, 2H), 2.83 (s, 4H), 5.77 (apparent t, J = 1.3 Hz, 2H), 6.06 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 16.4, 19.1, 39.8, 44.1, 123, 128, 145, 152. IR (CCl_4): 3051, 1624, 1451, 1379 cm^{-1}. FABMS: 215 (M^+ + H).

Preparation of (2*RS*,3*RS*)-2,3-Bis(3-methyl-2,5-cyclopentadienyl)butane (DL-11). Treatment of DL-10 with MeLi at –78 °C as described above gave 1.1 g of a yellow oil which was dissolved in 7 mL of hexane in a double-tube recrystallization apparatus. Cooling the resulting solution to –130 °C (pentane–$N_{2(l)}$) resulted in the precipitation of a solid which was collected and washed with cold hexane (2 mL). The solid melted upon warming to 25 °C, giving 0.27 g (22%) of DL-11 as a colorless oil. Attempts to purify the portion of DL-11 remaining in the filtrate via neutral alumina and silica gel chromatography were unsuccessful due to incomplete separation of the allene side products. Significant decomposition of DL-11 on silica TLC was also noted. Unlike *meso*-11, which was stable at –20 °C for up to 30 days, the solid formed upon cooling DL-11 to –20 °C was stable for less than 3 days. ^{1}H NMR ($CDCl_3$): δ 0.98 (d, J = 6.87 Hz, 6H), 2.04 (d, J = 1.4 Hz, 6H), 2.70–2.74 (m, 2H), 2.83 (s, 4H), 5.77 (apparent t, J = 1.3 Hz, 2H), 6.09 (m, 2H).

Preparation of Titanocene Dichlorides 12a–c. A solution of *meso*-11 (0.23 g, 1.1 mmol) in THF (20 mL) was purged with dry nitrogen and cooled to 0 °C. nBuLi (0.86 mL of a 2.5 M solution in hexanes, 2.2 mmol) was added over 10 min. The solution was warmed to 25 °C and stirred for 0.5 h. $TiCl_3 \cdot 3THF$ (0.40 g, 1.1 mmol) was added in one portion at –40 °C. The mixture was warmed to 25 °C and heated at reflux for 4 h. The dark brown solution was cooled to −40 °C, and concentrated HCl (100 μL) was added. After warming the solution to 25 °C and stirring open to the ambient atmosphere for 1 h, the solution became dark red. The mixture was passed through a 1-in. pad of silica gel (230–400 mesh), washing with CH_2Cl_2. Concentration of the eluent and precipitation of the resulting gum from CH_2Cl_2–hexane followed by removal of the solvents gave 0.35 g (98%) of **12a**:**12b**:**12c** (2.6:1.0:1.0) as a red solid. IR (CCl_4): 3020, 2924, 2874, 1458, 1343, 1078, 1048 cm^{-1}. FABMS: 330 (M^+, with appropriate isotope distribution), 295 (M^+ − Cl, 100). A portion of this material was treated as follows to selectively crystallize compound **12a**. The mixture (100 mg) was partially dissolved in toluene (0.25 mL) at 25 °C. Hexane (0.25 mL) was added and the precipitate was collected, yielding a red powder (**12a**:**12b**:**12c** = 20:2.4:1.0). Recrystallization via slow evaporation from benzene–isooctane gave well-formed highly crystalline prisms of compound **12a**: ^{1}H NMR ($CDCl_3$): δ 1.33 (d, J = 7.2 Hz, 3H), 1.38 (d, J = 7.0 Hz, 3H), 2.27 (s, 3H), 2.37 (s, 3H), 3.57 (dq, J = 10, 7.2 Hz, 1H), 3.71 (dq, J = 10, 7.2 Hz, 1H), 5.82 (pt, J = 2.1, 1.6 Hz, 1H), 5.88 (pt, J = 2.4, 1.6 Hz, 1H), 6.02 (pt, J = 2.8, 2.4 Hz, 1H), 6.27 (pt, J = 2.8, 2.1 Hz, 1H), 6.44 (pt, J = 2.8, 1.6 Hz, 1H), 6.57 (pt, J = 2.8, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 15.4, 16.0, 16.6, 16.8, 40.6, 40.8, 112.6, 114.1, 114.9, 117.5, 125.6, 129.9, 133.1, 138.9, 139.9, 141.7. Anal. Calcd for $C_{16}H_{20}Cl_2Ti$: C, 58.03; H, 6.09. Found: C, 58.07; H, 6.15.

Compound 12b. ^{1}H NMR ($CDCl_3$): δ 1.30 (d, J = 6.2 Hz, 6H), 2.44 (s, 6H), 3.57 (m, 2H), 5.76 (pt, J = 1, 1 Hz, 2H), 6.48 (pt, J = 2.9, 2 Hz), 6.50 (pt, J = 2.9, 1 Hz, 2H).

Compound 12c. ^{1}H NMR ($CDCl_3$): δ 1.43 (d, J = 6.5 Hz, 6H), 2.35 (s, 6H), 3.67 (m, 2H), 5.73 (pt, J = 2.4, 1.6 Hz, 2H), 6.21 (pt, 2.8, 2.4 Hz, 2H), 6.36 (pt, J = 2.8, 1.6 Hz, 2H).

Preparation of Titanocene Dichlorides 13a–c. DL-11 (0.25 g, 1.2 mmol) was treated in a manner similar to that of *meso*-11 to yield a red oil which was purified by flashing through a short column of BioBeads SX-1 with toluene as the eluent. The eluate was concentrated *in vacuo* to provide 0.32 g (83%) of **13a**, **13b**, and **13c** (4.6:2.8:1.0). IR (CCl_4): 3020, 2965, 2872, 1451, 1378, 1095, 1047 cm^{-1}. FABMS: 330 (M^+, with appropriate isotope distribution), 295 (M^+ − Cl, 100). Anal. Calcd for $C_{16}H_{20}Cl_2Ti$: C, 58.03; H, 6.09. Found: C, 58.30; H, 6.49.

Compound 13a. ^{1}H NMR ($CDCl_3$): δ 1.32 (d, J = 6.7 Hz, 6H), 2.37 (s, 3H), 2.40 (s, 3H), 2.85–2.96 (m, 1H), 3.17–3.27 (m, 1H), 5.60 (pt, J = 2.5, 2.1 Hz, 1H), 5.64 (pt, J = 2.5, 2.1 Hz, 1H), 5.91 (pt, J = 2.9, 2.5 Hz, 1H), 6.24 (pt, J = 2.9, 2.5 Hz, 1H), 6.54 (pt, J = 2.5, 2.1 Hz, 1H), 6.64 (pt, J = 2.9, 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 15.9, 17.0, 21.5, 22.2, 43.9, 44.7, 109.3, 110.9, 115.8, 119.1, 126.2, 131.9, 132.9, 139.6, 140.1, 141.5.

Compound 13b. ^{1}H NMR ($CDCl_3$): δ 1.33 (d, J = 5.6 Hz, 6H), 2.34 (s, 6H), 3.08–3.12 (m, 2H), 5.42 (pt, J = 2.1, 1.8 Hz, 2H), 6.02 (pt, J = 2.9, 2.1 Hz, 2H), 6.35 (pt, J = 2.9, 1.8 Hz, 2H).

Compound 13c. ^{1}H NMR ($CDCl_3$): δ 1.32 (d, J = 6.7 Hz, 6H), 2.31 (s, 6H), 3.02–3.08 (m, 2H), 5.64 (pt, J = 2.4, 1.8 Hz, 2H), 5.85 (pt, J = 2.6, 2.4 Hz, 2H), 6.43 (pt, J = 2.6, 1.8 Hz, 2H).

Preparation of Titanocene Dinaphtholates 14a–c. The mixture of **13a**, **13b**, and **13c** (4.6:2.8:1.0) was dissolved in dry Et_2O and cooled to −78 °C under an atmosphere of argon. The resulting precipitate was collected and the filtrate was concentrated to give a mixture enriched in **13b** and **13c** (**13a**:**13b**:**13c** = 2.5:2.5:1). To molten sodium metal (83 mg, 3.6 mmol) at 70 °C in toluene (10 mL) was added the above mixture of titanocene dichlorides (0.10 g, 0.30 mmol) and 2-naphthol (90 mg, 0.63 mmol) as a solution in toluene (5 mL). The mixture was heated at 70 °C for 10 h, cooled, and diluted with petroleum ether. The resulting mixture was filtered through dry Celite, washing with dry Et_2O. The solvents were removed *in vacuo* and in the three diastereomeric complexes were separated by flash chromatography on silica gel using hexane–CH_2Cl_2 (70:30) as the eluent. After removing the solvents, 22 mg of **14a** (R_f = 0.22, 70:30, hexane–CH_2Cl_2), 26 mg of **14b** (R_f = 0.31, 70:30, hexane–CH_2Cl_2) and 5 mg of **14c** (R_f = 0.34, 70:30, hexane–CH_2Cl_2) were obtained (32%). Crystallization of the resulting solids via slow evaporation of concentrated CH_2Cl_2–cyclohexane solutions gave red needles of **14a** and red blocks of **14b**.

Compound 14a. ^{1}H NMR ($CDCl_3$): δ 1.40 (d, J = 6.3 Hz, 3H), 1.41 (d, J = 6.3 Hz, 3H), 1.82 (s, 3H), 1.86 (s, 3H), 3.15–3.31 (m, 2H), 5.87–5.91 (m, 3H), 5.95 (pt, J = 2.7 Hz, 1H), 6.01 (d, J = 2.4 Hz, 2H), 6.95–7.13 (m, 4H), 7.20–7.24 (m, 2H), 7.37 (overlapping t, J = 7.7 Hz, 2H), 7.65–7.76 (m, 6H). IR (CCl_4): 3056, 2928, 2853, 1659, 1593, 1462, 1269, 1260 cm^{-1}. FABMS: 546 (M^+, with appropriate isotope distribution), 403 (M^+ − 2-naphthol, 100), 260 (M^+ − 2 × (2-naphthol), 40). Anal. Calcd for $C_{36}H_{34}O_2Ti$: C, 79.11; H, 6.27. Found: C, 79.23; H, 6.31.

Compound 14b. ^{1}H NMR ($CDCl_3$): δ 1.39 (d, J = 6.0, 6H), 1.96 (s, 6H), 3.21–3.27 (m, 2H), 5.71–5.76 (m, 4H), 5.97 (pt, J = 2.5 Hz, 2H), 6.97–7.02 (m, 4H), 7.25 (t, J = 6.9 Hz, 2H), 7.38 (t, J = 8.1 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.7, 22.1, 43.8, 102.7, 111.1, 114.4, 121.7, 122.2, 123.1, 125.8, 126.3, 127.6, 127.9, 128.7, 133.5, 135.2, 140.7, 168.5.

Compound 14c. ^{1}H NMR ($CDCl_3$): δ 1.36 (d, J = 6.2 Hz, 6H), 2.03 (s, 6H), 3.16–3.20 (m, 2H), 5.59 (pt, J = 2.7 Hz, 2H), 5.67 (pt, J = 2.4 Hz, 2H), 5.80 (pt, J = 2.4 Hz, 2H), 6.93–7.04 (m, 4H), 7.25 (t, J = 6.9 Hz, 2H), 7.37 (t, J = 7.0 Hz, 2H), 7.64 (d, J = 9.8 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H).

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Supplementary Material Available: Listings of crystal data, data collection, and solution and refinement details of the X-ray diffraction studies, bond distances and angles, anisotropic displacement parameters, atomic coordinates, and isotropic displacement coefficients for complexes **12a**, **14a**, and **14b** (30 pages). Ordering information is given on any current masthead page.

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