JOC*Article*

Synthesis of [Ethylene-1-(η^5-4,5,6,7-tetrahydro-1-indenyl)-2-(η^5-4′,5′,6′,7′-tetrahydro-2′-indenyl)]titanium Dichloride, the Elusive Isomer of the Brintzinger-Type *ansa*-Titanocenes

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We present a short synthesis of 1-(2-indenyl)-2-(3-indenyl)ethane (**5**) and a method for its conversion to the *ansa*-metallocene [ethylene(η^5-inden-1-yl)(η^5-inden-2-yl)]titanium dichloride (**13**). The synthetic strategy applied to prepare bisindene **5** relies on the efficient alkylation of 2-(phenylsulfonyl)-indane followed by HMPA-assisted E1cB-elimination of phenylsulfinate. This tandem sequence circumvents the predisposition of indene to undergo C(1)-alkylation and enables access to C(2)-substituted indenes. The key step in the synthesis of the title *ansa*-titanocene (**4**) features a previously unreported equilibration step to generate the bis(indenide anion) of **5**. Complexation with $TiCl_4$·$(THF)_2$ followed by hydrogenation of the product metallocene furnishes *ansa*-titanocene **4**.

Introduction

The use of titanocene- and zirconocene-based catalysts in the polymerization of α-olefins is considerably important for the production of commercial polymers, and much effort continues to be devoted toward preparing new metallocene catalysts to obtain greater control over polymer properties.[1] Enantioenriched group 4 metallocenes also have utility as catalysts for a variety of stereoselective organic transformations.[2] A major focus of research in these areas has been the study of alkyl- and silyl-bridged (aka *ansa*) bis(cyclopentadienyl) and, in particular, ethylene-bridged bis(indenyl) systems.[3] The syntheses of such bridged systems often involve difficult or low-yielding steps that deliver the *ansa*-metallocenes as mixtures of *rac*- and *meso*-diastereomers. These problems are evident in the synthesis of the prototypical *ansa*-titanocene dichlorides **1** and **2** (Figure 1), first disclosed by Brintzinger in 1982.[4] Refinements[5] to the synthetic and optical resolution protocols have led to the widespread availability of nonracemic **1** and its prominent use in catalysis.[6]

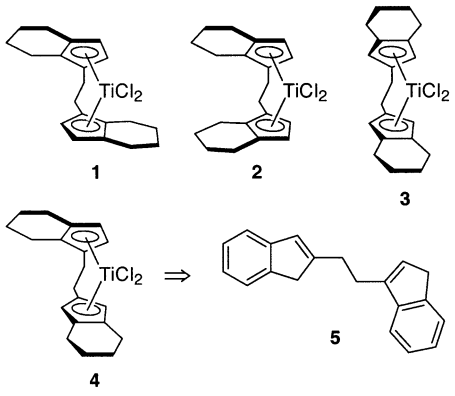

FIGURE 1.

Our interests in this field led us to develop synthetic routes to the isomeric bis(2-indenyl) complex **3** (Figure 1) and chiral 1-alkyl analogues thereof.[7] These syntheses, however, also were complicated by the formation of *rac*-

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(1) (a) *Organometallic Complexes and Olefin Polymerization*; Blom, R., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer: Berlin, Germany, 2001. (b) Halterman, R. L. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: New York, 1998; pp 455−544. (c) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (d) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(2) (a) Yun, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 767. (b) Troutman, M. V.; Appella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4916. (c) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 7026. (d) *Catalytic Enantioselective Alkylation of Alkenes by Chiral Metallocenes*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998. (e) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1263. (f) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807. (g) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562. (h) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *Tetrahedron Lett.* **1992**, *43*, 6423. (i) Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 2321.

(3) Shapiro, P. J. *Coord. Chem. Rev.* **2002**, *231*, 67.

(4) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

(5) (a) Schäfer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *328*, 87. (b) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21. (c) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* **1989**, *54*, 4154. (d) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501.

(6) The corresponding enantioenriched titanocene difluoride, and the titanocene and zirconocene binaphthyl-2,2′-diolates are available commercially.

(7) (a) Nantz, M. H.; Hitchcock, S. R.; Sutton, S. C.; Smith, M. D. *Organometallics* **1993**, *12*, 5012. (b) Hitchcock, S. R.; Situ, J. J.; Covel, J. A.; Olmstead, M. M.; Nantz, M. H. *Organometallics* **1995**, *14*, 3732.

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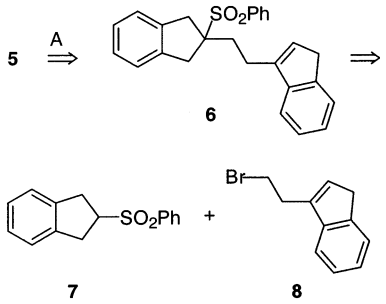


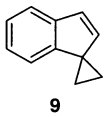
FIGURE 2.

and *meso*-isomers at the stage of titanium complexation. Interestingly, the only Brintzinger-type ethylene-bridged bis(indene) capable of forming a chiral complex yet incapable of forming a diastereomeric mixture on metalation has not been reported. Specifically, *ansa*-titanocene **4** would be formed on titanium complexation of 1-(2-indenyl)-2-(3-indenyl)ethane (**5**) and subsequent hydrogenation of the arene rings. We present herein the results of our efforts to synthesize **5** and on its metalation to arrive at the novel titanocene dichloride **4**.

Results and Discussion

We envisioned that synthesis of **5** would follow the retrosynthetic plan A outlined in Figure 2. The strategy requires a phenyl sulfone-mediated alkylation by 3-(2′-bromoethyl)indene (**8**)[8] followed by elimination of phenylsulfinate (**6** → **5**) to deliver the 2-indenyl ring. We have previously demonstrated use of the phenylsulfonyl group in the synthesis of 2-substituted indenes.[9,10]

We prepared 2-(phenylsulfonyl)Indane (**7**) from 2-indanyl phenyl sulfide[11] using a modified literature procedure.[12] Unfortunately, our attempts to alkylate the derived α-sulfonyl anion of **7** using bromide **8** failed to deliver any of the desired coupling product **6**, rather indene **9**[13] was the major product in this reaction (75%,



unoptimized). This result is not entirely unexpected since others have noted the propensity of 1-substituted indenes appropriately fitted with leaving groups to undergo spirocyclization.[14]

We next examined a complementary approach to prepare bisindene **5** wherein we transferred the electrophilic side chain to the ring bearing the phenyl sulfone group. As indicated by retrosynthetic analysis path B (Figure 3), alkylation of indene by halide **10** avoids the possibility of a spirocyclization event.

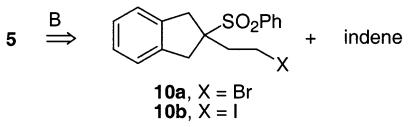
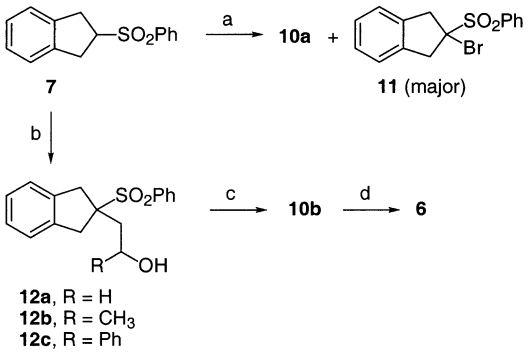


FIGURE 3.

SCHEME 1[a]



[a] Reagents and conditions: (a) (i) *n*-BuLi, THF; (ii) 1,2-dibromoethane. (b) (i) *n*-BuLi (1.05 equiv), THF, −78 °C to room temperature; (ii) epoxide, −78 °C to room temperature, 15 h. (c) **12a**, I_2, PPh_3, imidazole, Et_2O, CH_3CN, 80%. (d) Lithium indenide (2 equiv), THF, HMPA, −78 °C to room temperature, 4 h, 81%.

Metalation of sulfone **7** with *n*-BuLi followed by addition of excess 1,2-dibromoethane afforded a mixture of products containing only a trace quantity of desired product **10a**. The major product was identified as α-bromo sulfone **11** (Scheme 1), presumably the consequence of a direct attack on bromine.[15] Adjusting our approach once more, we pursued attachment of the electrophilic side chain using a two-step sequence involving epoxide ring-opening followed by alcohol-to-iodide conversion. In contrast to analogous epoxide cleavage reactions, treatment of α-lithiated **7** with ethylene oxide in THF proceeded without the need for Lewis acid assistance to give adduct **12a** in 70% yield.[16,17] The derived α-sulfonyl anion of **7** proved to be an excellent nucleophile for epoxide cleavage reactions as evidenced by the regioselective reactions with the epoxides of 1-propene and styrene, giving good yields of adducts **12b** and **12c**, respectively. The significance of these reactions lies in the potential for using this approach to furnish the *ansa*-bridge with

(8) Sugie, A.; Shimomura, H.; Katsube, J.; Yamamoto, H. *Tetrahedron Lett*. **1977**, *18*, 2759.

(9) (a) Palandoken, H.; McMillen, W. T.; Nantz, M. H. *Org. Prep. Proc. Intl*. **1996**, *28* 702. (b) Palandoken, H.; Wyatt, J. K.; Hitchcock, S. R.; Olmstead, M. M.; Nantz, M. H. *J. Organomet. Chem*. **1999**, *579*, 338.

(10) Several strategies have been reported for substitution of indene at the 2-position; for examples, see: (a) Greifenstein, L. G.; Lambert, J. B.; Nienhuis, R. J.; Fried, H. E.; Pagani, G. A. *J. Org. Chem*. **1981**, *46*, 5125. (b) Adamczyk, M.; Watt, D. S.; Netzel, D. A. *J. Org. Chem*. **1984**, *49*, 4226. (c) Kaminsky, W.; Rabe, O.; Schauwienold, A. M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem*. **1995**, *497*, 181. (d) Halterman, R. L.; Zhu, C. *Tetrahedron Lett*. **1999**, *40*, 7445.

(11) McCullough, K. J. *Tetrahedron Lett*. **1982**, *23*, 2223.

(12) Trost, B. M.; Curran, D. P. *Tetrahedron Lett*. **1981**, *22*, 1287.

(13) Kauffman, T.; Berghus, K.; Rensing, A. *Chem. Ber*. **1985**, *118*, 3737.

(14) (a) Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11* 1869. (b) Lee, I. M.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115. (c) Halterman, R. L.; Schumann, H.; Dübner, F. *J. Organomet. Chem*. **2000**, *604*, 12.

(15) In similar fashion, 1,2-dibromoethane is reported to brominate an ester enolate anion, see: Greene, A. E.; Muller, J. C.; Ourisson, G. *J. Org. Chem*. **1974**, *39*, 186.

(16) Achmatowicz, B.; Marczak, S.; Wicha, J. *J. Chem. Soc., Chem. Commun*. **1987**, 1226.

(17) An exothermic reaction occurred when $BF_3{\cdot}Et_2O$ was added to **i**. The THF cleavage product **ii** was isolated on aqueous workup. For an analogous reaction with THF, see: Christoffers, J.; Dötz, K. H. *Organometallics* **1994**, *13*, 4189.

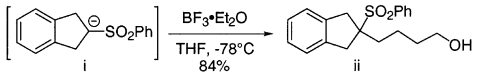
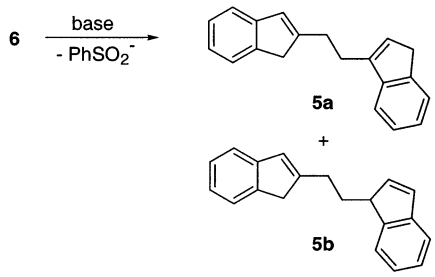


TABLE 1. Base-Mediated Conversion of Sulfone 6 → 5

entry	base (equiv)	conditions	yield (%)[a]
1	KO*t*-Bu (4.05)	THF, 10 °C → rt, 2 h	6
2	KDA (3.05)	THF, −78 °C → 0 °C, 1 h	46
3	*n*-BuLi (5.0)	THF, −78 °C → 0 °C, 1.5 h	50
4	*n*-BuLi (4.1)	9:1 THF:HMPA, −78 °C, 2 h	86

[a] Chromatographed.

SCHEME 2

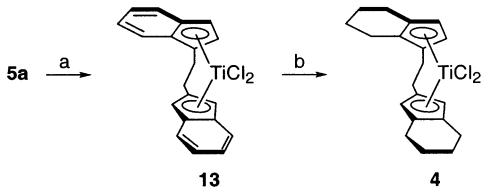


a stereogenic center, a structural feature that modulates metallocene formation[18] and reactivity.[3] Alcohol **12a** was converted uneventfully into iodide **10b** by using Corey's method.[19] Treatment of **10b** with lithium indenide in THF resulted in a low yield of the displacement product **6**. However, we were gratified to observe that addition of HMPA to the anion solution led to smooth alkylation on addition of **10b**, giving adduct **6** in good yield.

Treatment of homoallylic- or homobenzylic-positioned phenylsulfonyl groups with KO*t*-Bu in THF generally is sufficient to effect elimination of phenylsulfinate.[18b,20] However, the base-mediated elimination of tertiary cyclopentyl phenyl sulfones is particularly capricious.[21] Indeed, treatment of sulfone **6** with KO*t*-Bu (Table 1, entry 1) failed to adequately effect the desired elimination. Treatment with KDA (entry 2) provided a modest yield of the elimination product as a mixture (ca. 1:1) of double bond isomers **5a** and **5b** and led us to pursue the use of *n*-BuLi. The optimal *n*-BuLi condition for phenylsulfinate elimination (entry 4) gave **5a** as the exclusive regioisomer (Scheme 2). In summary, bisindene **5** was prepared in four steps from sulfone **7** in 39% overall yield without the assistance of column chromatography: the product of each transformation was obtained by simple recrystallization of the reaction mixture.

With the bisindene system available, we turned our attention to methods for titanocene formation. We and others previously used the reagent $TiCl_3$·3THF[22] with great success to obtain ethylene-bridged *ansa*-titanocenes.[7,23] However, attempted complexation of **5a** with this reagent under a variety of conditions led only to intractable material, and in some cases to recovery of

SCHEME 3[a]



[a] Reagents and conditions: (a) (i) *n*-BuLi (1.95 equiv), THF, −78 °C to room temperature, 12 h; (ii) $TiCl_4$·THF_2 (1.0). (b) H_2, cat. PtO_2, THF, rt, 57%.

starting bisindene. To our dismay, attempts to metalate **5a** with other protocols for titanocene formation, which included reactions with $TiCl_3$ (direct and inverse addition)[24] and $TiCl_3$/NaH,[25] also failed to furnish the corresponding *ansa*-titanocene.

In concurrent attempts to synthesize the *ansa*-zirconocene, application of the zirconation conditions developed by Jordan[26] with periodic analysis by ^{1}H NMR (**5a** + $Zr(NMe_2)_4$, toluene-d_8, 100 °C) indicated possible metallocene formation; however, continued reaction resulted in disappearance of the characteristic signals.[27] This result led us to examine metalation of **5a** using a Ti(IV) source. Unfortunately treatment of the dianion of **5a** with either $TiCl_4$·2THF[22] or $TiCl_4$[4] followed by either a standard workup or a nonaqueous, nonoxidative workup failed to deliver a Ti complex. To our surprise the desired titanocene complex **13** was obtained only when bisindene **5a** was treated with 1.95 equiv of base—instead of the more traditional approach using ≥2 equiv—followed by an equilibration protocol that involved stirring at room temperature. One possible explanation to account for the uniform, aforementioned problems in metalation is that the 2-alkyl indene ring of **5a** undergoes loss of a proton from the α-bridging methylene instead of from its benzylic position under kinetic deprotonation conditions to give rise to a dianion incapable of metallocene formation. ^{1}H NMR analysis of the crude product supports assignment of structure **13** as the principal product of the complexation reaction (Scheme 3). The four distinct C_5-indenyl signals are in agreement with the C_1-symmetric *ansa*-metallocene structure (Table 2). Attempts to purify complex **13** to obtain crystals suitable for X-ray analysis were unsuccessful and led to decomposition giving rise to unidentifiable material. The sensitive nature of complex **13** led us to examine whether it is compatible with the aqueous acid, oxidative workup procedures of our earlier Ti(III) complexation attempts. Exposure of **13** to 6 N HCl and air resulted in significant decomposition.

Catalytic hydrogenation of crude **13** with Adams catalyst under ambient conditions afforded a more robust metallocene. Purification of the resultant bis(tetrahy-

(18) (a) Hollis, T. K.; Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 2812. (b) Sutton, S. C.; Nantz, M. H.; Parkin, S. R. *Organometallics* **1993**, *12*, 2248. (c) Chen, Z.; Halterman, R. L. *Organometallics* **1994**, *13*, 3932. (d) Shapiro, P. J.; Kane, K. M.; Vij, A.; Stelck, D.; Matare, G. J.; Hubbard, R. L.; Caron, B. *Organometallics* **1999**, *18*, 3468.

(19) Singh, A. K.; Bakshi, R. K.; Corey, E. J. *J. Am. Chem. Soc.* **1987**, *109*, 6187.

(20) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

(21) Radisson, X.; Kwiatkowski, P. L.; Fuchs, P. L. *Synth. Commun.* **1987**, *17*, 39.

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

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

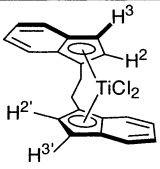
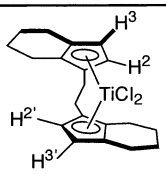
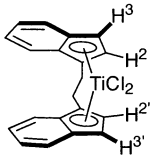
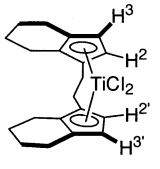
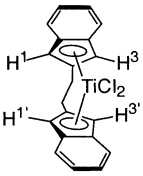
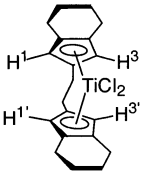
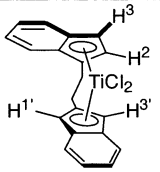
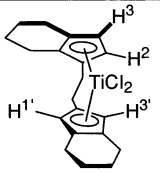
(24) (a) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883. (b) Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276.

(25) Chen, Z. C.; Eriks, K.; Halterman, R. L. *Organometallics* **1991**, *10*, 3449.

(26) (a) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. (b) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024.

(27) Emerging resonances at δ 5.84 (d, J = 2.4 Hz, 1H), 5.94 (d, J = 2.6 Hz), 6.11 (d, J = 2.9 Hz), and 6.45 (d, J = 2.9 Hz, 1H) within 3 h suggest zirconocene formation.

TABLE 2. Select ^{1}H NMR Data[a]

Titanocene	ppm, δ ($CDCl_3$)		Ref	Titanocene	ppm, δ ($CDCl_3$)		Ref.
	H^2, $H^{2'}$ 6.74	H^3, $H^{3'}$ 6.07	4	 **1**	H^2, $H^{2'}$ 6.58	H^3, $H^{3'}$ 5.55	4
	H^2, $H^{2'}$ 6.92	H^3, $H^{3'}$ 6.48	5a	 **2**	H^2, $H^{2'}$ 6.44	H^3, $H^{3'}$ 6.29	4
	H^1, $H^{1'}$, H^3, $H^{3'}$ 6.56		7a	 **3**	H^1, $H^{1'}$, H^3, $H^{3'}$ 5.51		7b
	H^2, 6.97 $H^{1'}$, 6.19	H^3, 6.48 $H^{3'}$, 6.50	*p*	 **4**	H^2, 6.57 $H^{1'}$, 5.30	H^3, 5.89 $H^{3'}$, 5.67	*p*

[a] *p* = present work.

droindenyl) titanocene dichloride was accomplished by using a combination of filtration (Celite) and chromatography (BioBeads SX-1). Spectral analysis of the product confirms the structural assignment as the elusive Brintzinger isomer, *ansa*-titanocene **4**.

Attempts to recrystallize complex **4** from various combinations of pentane, hexane, cyclohexane, isooctane, dichloromethane, diethyl ether, benzene, and toluene were unsuccessful. Recrystallization with the solvent mixture 20:1 isooctane:toluene did result in microcrystals of **4**; however, under close inspection these were deemed unsuitable for X-ray diffraction studies.

In conclusion, we have described an efficient synthesis of 1-(2-indenyl)-2-(3-indenyl)ethane using a (phenyl)-sulfone alkylation−elimination tandem sequence to couple differentially substituted indene rings. In the course of attempting to metalate this novel bisindene, we found that a thermodynamic equilibration of the derived dianion is crucial prior to metallocene formation. This observation may be of practical use for the complexation of C(2)-substituted bisindene systems. Indeed, we used this approach to prepare the last isomer of the Brintzinger family of *ansa*-titanocenes, ethylene-1-(η^5-4,5,6,7-tetrahydro-1-indenyl)-2-(η^5-4′,5′,6′,7′-tetrahydro-2′-indenyl)]titanium dichloride.

Experimental Section

Preparation of 2-Bromo-2-(phenylsulfonyl)indane (11). To a solution of sulfone **7** (3.0 g, 11.6 mmol) in THF (47 mL) at −78 °C was added dropwise *n*-BuLi (4.8 mL of a 2.5 M solution in hexane, 11.9 mmol). The reaction mixture was stirred 0.5 h at 0 °C and 0.5 h at room temperature, and then recooled to 0 °C whereupon a solution of dibromoethane (21.8 g, 11.6 mmol) in THF (12 mL) at 0 °C was added dropwise via cannula. The reaction was slowly warmed to room temperature and stirred 5 h, and then quenched by addition of saturated aq NH_4Cl. The reaction mixture was extracted with three portions of $CHCl_3$ and the combined organic extract was washed successively with H_2O and brine and then dried ($MgSO_4$). The solvents were removed by rotary evaporation. Recrystallization of the residue from 95% EtOH yielded 2.9 g (75%) of **11** as brown needles; mp 133−134 °C; ^{1}H NMR δ 3.42 (d, J = 17.0 Hz, 2H), 4.23 (d, J = 17.0 Hz, 2H), 7.20−7.27 (m, 4H), 7.59−7.76 (m, 3H), 8.09−8.13 (m, 2H); ^{13}C NMR δ 45.9, 81.5, 124.7, 127.7, 128.9, 131.0, 134.5, 134.9, 137.6; IR (KBr) 3070, 2969, 1583, 1446, 1322, 1228, 1178, 1149 cm^{-1}. Anal. Calcd for $C_{15}H_{13}BrO_2S$: C, 53.42; H, 3.89. Found: C, 53.50; H, 3.96.

Column chromatography (hexane:EtOAc, 6:1) on a small quantity of the crude residue afforded a minor amount of **10a** suitable for characterization; mp 107−110 °C; ^{1}H NMR 2.42−2.48 (m, 2H), 2.95 (d, J = 16.4 Hz, 2H), 3.23−3.29 (m, 2H), 3.82 (d, J = 16.4 Hz, 2H), 7.09−7.15 (m, 4H), 7.51−7.65 (m, 3H), 7.89 (d, J = 8.21 Hz, 2H); ^{13}C NMR δ 27.3, 39.3, 40.0, 72.7, 124.5, 127.7, 129.4, 130.2, 134.3, 136.3, 139.1; IR (KBr) 3062, 2940, 1446, 1294, 1147 cm^{-1}. Anal. Calcd for $C_{17}H_{17}BrO_2S$: C, 55.90; H, 4.48. Found: C, 55.71; H, 4.48.

Preparation of 2-(2-Hydroxyethyl)-2-(phenylsulfonyl)indane (12a). To a solution of sulfone **7** (40.0 g, 155 mmol) in THF (516 mL) at −78 °C was added dropwise *n*-BuLi (70.1

mL of a 2.32 M solution in hexane, 163 mmol). The reaction mixture was stirred 2 h at −78 °C and 0.5 h at 0 °C, and then recooled to −78 °C whereupon a solution of ethylene oxide (7.16 g, 163 mmol) in THF (325 mL) at −78 °C was added dropwise via cannula. The reaction was slowly warmed to room temperature, stirred 15 h, and then quenched by addition of saturated aqueous NH_4Cl. The reaction mixture was extracted with three portions of EtOAc and the combined organic extract was washed successively with H_2O and brine and then dried ($MgSO_4$). The solvents were removed by rotary evaporation. Recrystallization of the residue from 95% EtOH yielded 32.6 g (70%) of **12a** as white crystals; mp 163−166 °C; ^{1}H NMR δ 1.93 (s, 1H), 2.16 (t, J = 6.2 Hz, 2H), 3.03 (d, J = 17.0 Hz, 2H), 3.64 (t, J = 6.5 Hz, 2H), 3.81 (d, J = 16.4 Hz, 2H), 7.07−7.10 (m, 4H), 7.50−7.60 (m, 3H), 7.88−7.91 (m, 2H); ^{13}C NMR δ 38.4, 39.6, 58.8, 71.6, 124.1, 127.2, 128.9, 130.0, 133.8, 136.0, 139.2; IR (KBr) 3516, 3060, 2949, 1446, 1294, 1141 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.49; H, 6.05.

Preparation of 2-(2-Hydroxypropyl)-2-(phenylsulfonyl)indane (12b). Epoxide adduct **12b** was prepared analogously to **12a** from **7** (3.0 g, 11.6 mmol) with propylene oxide (0.73 g, 12.5 mmol): yield 76% (2.78 g) as a white solid; mp 174.5−175.5 °C; ^{1}H NMR δ 1.15 (d, J = 5.9 Hz, 3H), 1.97−2.12 (m, 2H), 2.33 (d, J = 4.1 Hz, 1H), 3.12 (d, J = 17.0 Hz, 1H), 3.20 (d, J = 17.0 Hz, 1H), 3.74 (d, J = 17.0 Hz, 1H), 3.83 (d, J = 17.0 Hz, 1H), 4.05−4.12 (m, 1H), 7.01−7.08 (m, 4H), 7.46 (m, 2H), 7.57 (m, 1H), 7.88 (m, 2H); ^{13}C NMR δ 24.9, 39.9, 40.4, 44.5, 64.4, 72.4, 124.1, 124.2, 127.1, 127.2, 128.8, 130.1, 133.7, 136.2, 139.4, 139.6; IR (KBr) 3542, 3052, 2969, 1448, 1267, 1137 cm^{-1}. Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.24. Found: C, 67.96; H, 6.24.

Preparation of 2-(2-Phenyl-2-hydroxyethyl)-2-(phenylsulfonyl)indane (12c). Epoxide adduct **12c** was prepared analogously to **12a** from **7** (1.65 g, 6.4 mmol) with styrene oxide (0.85 g, 7.0 mmol): yield 64% (1.56 g, recrystallized from EtOH), as a white solid; mp 144.4−146.3 °C; ^{1}H NMR δ 2.34 (d, J = 5.8 Hz, 2H), 2.53 (d, J = 3.5 Hz, 1H), 3.21 (d, J = 11.7 Hz, 1H), 3.27 (d, J = 11.1 Hz, 1H), 3.76 (d, J = 17.0 Hz, 1H), 3.87 (d, J = 17.0 Hz, 1H), 5.00 (m, 1H), 6.99−7.09 (m, 4H), 7.20−7.31 (m, 5H), 7.43 (m, 2H), 7.54 (dt, J = 7.6, 1.2 Hz, 1H), 7.85 (m, 2H); ^{13}C NMR δ 40.1, 40.2, 44.9, 70.9, 72.5, 124.1, 124.2, 125.6, 127.0, 127.1, 127.6, 128.5, 128.8, 130.1, 133.7, 136.2, 139.5, 139.6, 144.5; IR (KBr) 3511, 3027, 2942, 1448, 1282, 1135. Anal. Calcd for $C_{23}H_{22}O_3S$: C, 72.99; H, 5.86. Found: C, 72.21; H, 5.74.

Preparation of 2-(2-Iodoethyl)-2-(phenylsulfonyl)indane (10b). To a solution of hydroxysulfone **12** (27.0 g, 89.3 mmol) in a 1:1 mixture of Et_2O:CH_3CN (446 mL) at room temperature was added Ph_3P (70.3 g, 268 mmol) and imidazole (18.2 g, 268 mmol). The solution was cooled to 0 °C and I_2 (68.0 g, 268 mmol) was added in one portion. The dark brown reaction mixture was immediately warmed to room temperature and stirred 3 h before quenching by addition of aq NH_4Cl. The reaction mixture was extracted with two portions of EtOAc and the combined organic extract was washed successively with H_2O and brine and then dried ($MgSO_4$). The solvents were removed by rotary evaporation. The crude product was washed in a fritted glass funnel with cold absolute ethanol and the retentate was collected. The ethanol filtrate was evaporated and the solid residue was again washed in a funnel with cold ethanol. The two retentate crops were combined and recrystallized from ethanol to obtain 29.4 g (80%) of **10b** as fine white needles; mp 140−143 °C; ^{1}H NMR δ 2.49 (m, 2H), 2.94 (d, J = 17.0 Hz, 2H), 3.02 (m, 2H), 3.81 (d, J = 16.4 Hz, 2H), 7.07−7.105 (m, 4H), 7.52−7.67 (m, 3H), 7.87−7.90 (m, 2H); ^{13}C NMR δ −2.24, 38.8, 41.2, 73.5, 124.2, 127.4, 129.1, 129.9, 134.0, 136.0, 139.0; IR (KBr) 3053, 2902, 1448, 1288, 1135 cm^{-1}. Anal. Calcd for $C_{17}H_{17}IO_2S$: C, 49.52; H, 4.16. Found: C, 49.51; H, 4.15.

Preparation of 2-(2-Inden-3-ylethyl)-2-(phenylsulfonyl)indane (6). To a solution of indene (11.7 g, 100.5 mmol) in THF (200 mL) at −78 °C was added dropwise *n*-BuLi (43.1 mL of a 2.32 M solution in hexane, 100.1 mmol). The yellow slurry was stirred 10 min, warmed to room temperature, and stirred 45 min, and then cooled to −40 °C before addition of HMPA (44.6 mL). The reaction solution was then added dropwise via cannula to a stirred solution of iodo-sulfone **10b** (20.0 g, 49.0 mmol) in THF (245 mL) at −78 °C. The amber reaction mixture turned deep red as it was allowed to warm to room temperature over 4 h. The reaction was quenched by addition of aq NH_4Cl and then extracted with two portions of EtOAc. The combined organic extract was washed with H_2O and brine, and then dried ($MgSO_4$). The solvents were removed by rotary evaporation. The crude residue was dissolved in a minimum amount of CH_2Cl_2 and crystallization was induced by addition of EtOH, yielding 15.8 g (81%) of **6** as a white powder; mp 137−139 °C; ^{1}H NMR δ 2.20 (m, 2H), 2.43 (m, 2H), 3.01 (d, J = 17.0 Hz, 2H), 3.19 (s, 2H), 3.84 (d, J = 17.0 Hz, 2H), 7.05−7.17 (m, 7H), 7.33−7.52 (m, 4H), 7.83−7.85 (m, 2H); ^{13}C NMR δ 22.7, 34.2, 37.7, 39.3, 72.2, 118.7, 123.7, 124.1, 124.7, 126.0, 127.2, 127.9, 128.8, 130.0, 133.6, 136.5, 139.7, 143.2, 144.2, 144.7; IR (KBr) 3066, 2931, 1446, 1297, 1143 cm^{-1}. Anal. Calcd for $C_{26}H_{24}O_2S$: C, 77.97; H, 6.04. Found: C, 77.85; H, 6.09.

Preparation of 1-(2-Indenyl)-2-(3-indenyl)ethane (5a). To a solution of sulfone **6** (13.5 g, 33.7 mmol) in THF (170 mL) at −78 °C was added HMPA (17 mL) followed by dropwise addition of *n*-BuLi (58.8 mL of a 2.32 M solution in hexane, 136.5 mmol). The deep red solution was stirred 2 h before quenching by addition of 10% HCl. The reaction mixture was extracted with two portions of Et_2O and the combined organic extract was washed with H_2O and brine, and then dried ($MgSO_4$). The solvents were removed by rotary evaporation. The crude product was recrystallized from EtOH−acetone yielding 7.5 g (86%) of **5a**; mp 85−87 °C; ^{1}H NMR δ 2.88 (s, 4H), 3.32 (s, 2H), 3.36 (s, 2H), 6.24 (s, 1H), 6.58 (s, 1H), 7.10−7.47 (m, 8H); ^{13}C NMR δ 27.1, 29.6, 37.8, 41.1, 118.8, 120.0, 123.4, 123.7, 123.8, 124.6, 126.0, 126.2, 126.4, 128.0, 143.0, 143.7, 144.4, 145.3, 145.5, 150.1; IR (KBr) 3062, 3016, 2898, 1610, 1461, 1392 cm^{-1}. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.97; H, 7.01.

Preparation of [Ethylene-1-(η^5-inden-1-yl)-2-(η^5-inden-2′-yl)]titanium Dichloride (13). To a solution of bisindene **5a** (797 mg, 3.08 mmol) in THF (20 mL) at −78 °C was added *n*-BuLi (2.6 mL of a 2.32 M solution in hexane, 5.95 mmol). The reaction mixture was stirred 15 min to result in a pink slurry that was then warmed to room temperature. The resultant deep red solution was stirred 12 h. In a separate flask, $TiCl_4$·2THF (1.03 g, 3.10 mmol) was dissolved in THF (55 mL). The bisindene dianion and $TiCl_4$ solutions were simultaneously added dropwise over 30 min via cannula to a third flask containing 15 mL of THF cooled to −40 °C. The reaction mixture was warmed to room temperature and stirred an additional 1.5 h. The reaction solvent was removed by distillation in vacuo. The dark red residue was redissolved in CH_2Cl_2 and filtered through a pad of Celite. The filtrate was condensed in vacuo and the solids washed with Et_2O to afford 778 mg (67%) of the crude titanocene, which was used in the next reaction without further purification; ^{1}H NMR δ 3.46 (m, 2H), 3.85 (m, 2H), 6.19 (d, J = 2.3 Hz, 1H), 6.48 (d, J = 3.5 Hz, 1H), 6.50 (d, J = 2.3 Hz, 1H), 6.97 (d, J = 3.5 Hz, 1H), 7.24−7.69 (m, 8H); ^{13}C NMR δ 28.2, 31.5, 107.1, 113.2, 115.7, 121.5, 122.7, 123.5, 125.7, 125.9, 126.4, 127.8, 127.9, 128.4, 128.8, 129.4, 129.8, 131.8, 133.2, 140.2.

Preparation of [Ethylene-1-(η^5-4,5,6,7-tetrahydroinden-1-yl)-2-(η^5-4,5,6,7-tetrahydro-inden-2′-yl)]titanium Dichloride (4). A mixture of titanocene **13** (600 mg, 1.60 mmol) and PtO_2 (73 mg, 0.32 mmol) in THF (8.0 mL) was stirred under hydrogen at room temperature and ambient pressure for 36 h. The reaction mixture was filtered through a pad of Celite and the filtrate was condensed in vacuo. The deep red residue was dissolved in toluene and passed through a short column of BioBeads SX-2 (∼4 g), eluting with toluene.

After ca. three column volumes, a deep red solution eluted and was collected. Removal of solvent afforded 358 mg (57%) of *ansa*-titanocene **4**; ^{1}H NMR δ 1.48−1.66 (m, 4H), 1.76−1.93 (m, 3H), 2.00 (m, 1H), 2.26 (m, 1H), 2.42−2.58 (m, 3H), 2.67 (m, 1H), 2.96−3.25 (m, 7H), 5.30 (d, J = 2.5 Hz, 1H), 5.67 (d, J = 2.3 Hz, 1H), 5.89 (d, J = 2.9 Hz, 1H), 6.57 (d, J = 2.7 Hz, 1H); ^{13}C NMR δ 21.7, 21.8, 21.9 (2), 24.2, 24.7, 24.8, 25.2, 28.1, 30.8, 110.9, 111.9, 114.3, 125.3, 129.0, 133.9, 136.8, 137.6, 137.8, 139.0; IR (KBr) 3077, 2932, 2861, 1445, 1429 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{24}ClTi$ [M − Cl]$^+$ 347.1046, found 347.1037.

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Supporting Information Available: NMR spectra for obtained compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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