A Disulfone-Based Approach to *ansa*-Titanocenes: Synthesis of (Ethylenebis(2-indenyl))titanium Dichloride

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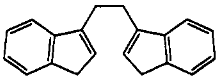
Summary: The synthesis of 1,2-bis(2-indenyl)ethane via a bis cycloalkylation–bis elimination sequence on 1,4-bis(phenylsulfonyl)butane is presented. The dilithio salt derived from the bis(indene) was treated with $TiCl_3$·3THF to afford (ethylenebis(2-indenyl))titanium dichloride, the parent complex for ethylene-bridged bis(2-indenyl) systems.

Introduction

The use of tethered bis(η^5-1-indenyl) and bis(η^5-tetrahydro-1-indenyl) ligands derived from 1,2-bis(1-indenyl)ethane (1)[1] has dominated the field of chiral *ansa*-metallocenes.[2] To date, the structurally isomeric 1,2-bis(2-indenyl)ethane (2a) has not been examined as a potential ligand system for *ansa*-metallocenes.[3] The C(1) alkylation of the dilithio derivative of 2a is a potentially useful entry to a variety of C(1)-substituted, C(2)-tethered bis(indenes) of the type 2b, precursors to chiral *ansa*-metallocenes 3b. As part of a program[4] focused on the synthesis and application of *ansa*-metallocenes, we report herein a practical synthesis of bis(indene) 2a and its subsequent complexation to afford the ethylene-bridged bis(2-indenyl)titanium dichloride 3a.



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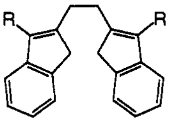
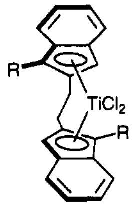


2a: R = H
2b: R = alkyl



3a: R = H
3b: R = alkyl

Results and Discussion

Ligand Syntheses. Geminal dianions stabilized by an adjacent phenylsulfonyl group have been shown to react with α,ω-dihalides to form carbocycles.[5] We investigated the use of disulfones as an extension of this methodology for the synthesis of bicyclic structures in a single step. Disulfone 4a (Scheme I) was prepared by the reaction of 1,4-dibromobutane with sodium benzenesulfinate.[6] Subsequent formation of a tetralithiated species, the $\alpha,\alpha,\alpha',\alpha'$-tetralithio disulfone [4b], was accomplished by the addition of 4 equiv of *n*-BuLi to a solution of 4a in THF at 0 °C. The double deprotonation of alkyl phenyl sulfones using *n*-BuLi is known to form two metalated species, an α,α-geminal dianion and/or an α-sulfonyl anion also metalated in the ortho position of the phenyl ring.[7] Fortunately, alkylation reactions using phenylsulfonyl dianions occur exclusively in the α position.[8,9] We deemed it prudent to first investigate the double carbocycle formation by using a simple α,ω-dihalide. On treatment of [4b] with an excess of *cis*-1,4-dichloro-2-butene, disulfone 5, the product of four successive α-carbon alkylations, was obtained in 35% yield. The balance of the material in this reaction constituted a complex mixture of mono-, di,- and trialkylated products including a variety of sulfone-eliminated byproducts formed as a consequence of the hyperbasicity of geminal sulfonyl dianions.

Interestingly, treatment of 4a with only 2 equiv of *n*-BuLi, forming the α,α'-dianion [4c], followed by cannulation into a solution of *cis*-1,4-dichloro-2-butene also yielded the tetraalkylated product, disulfone 5, in 39% yield. In this case, facile and possibly intramolecular proton transfer occurs between initially formed monoalkylated products and any unreacted α-sulfonyl anions to result in ring closures to give disulfone 5. A similar proton transfer process involving the bis alkylation of 1,4-disulfones has been observed by Lansbury and coworkers.[10] The elimination of the phenylsulfonyl groups

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[1] (a) Wild, F. R. W. P.; Zsolnai, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982,** *232,* 233. (b) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Ibid.* **1988,** *342,* 21. (c) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991,** *10,* 1501.

[2] Halterman, R. L. *Chem. Rev.* **1992,** *92,* 965.

[3] A single report has appeared regarding the synthesis of a (η^5-2-indenyl)-*ansa*-titanocene. In this example, a binaphthyl unit tethers the two indenyl rings at their respective C(2) positions: see ref 2.

[4] Sutton, S. C.; Nantz, M. H.; Parkin, S. R. *Organometallics* **1993,** *12,* 2248.

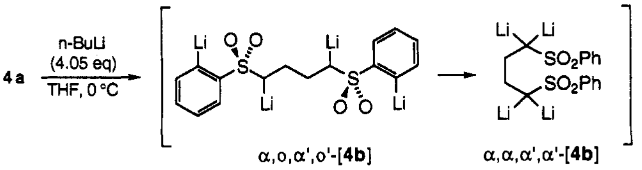
[5] (a) Gais, H.-J.; Ball, W. A.; Bund, J. *Tetrahedron Lett.* **1988,** *29,* 781. (b) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 610. (c) Eisch, J.; Dua, S.; Behrooz, M. *J. Org. Chem.* **1985,** *50,* 3674. (d) Eisch, J.; Behrooz, M.; Dua, S. *J. Organomet. Chem.* **1985,** *285,* 121. (e) Kaiser, E. M.; Solter, L. E.; Schwarz, R. A.; Beard, R. D.; Hauser, C. R. *J. Am. Chem. Soc.* **1971,** *93,* 4237.

[6] For a general preparation of alkyl phenyl sulfones, see: Crandall, J. K.; Pradat, C. *J. Org. Chem.* **1985,** *50,* 1327.

[7] Gais, H.-J.; Vollhardt, J. *Tetrahedron Lett.* **1988,** *29,* 1529.

[8] (a) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 277. (b) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Ibid.* **1985,** *24,* 610. (c) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Ibid.* **1985,** *24,* 696.

[9] An α,o-dilithiated phenylsulfonyl dianion has been shown to be the kinetically formed species on treatment of alkyl phenyl sulfones with 2 equiv of BuLi at low temperature. Subsequent proton transfer occurs on warming to give an α,α-dilithiated phenylsulfonyl dianion.[8b,c] When the tetraanion formed from 4a was quenched with either methyl iodide or deuterium oxide at 0 °C, ^1H NMR analysis of the products indicated 95% tetramethylation and 88% deuterium incorporation α to the sulfone groups, respectively. No detectable methylation or deuterium incorporation was observed on the phenyl rings, thereby suggesting these conditions are suitable for the formation of the tetraanionic species $\alpha,\alpha,\alpha',\alpha'$-[4b].



[10] Lansbury, P. T.; Spanguolo, C. J.; Zhi, B.; Grimm, E. L. *Tetrahedron Lett.* **1990,** *31,* 3965.

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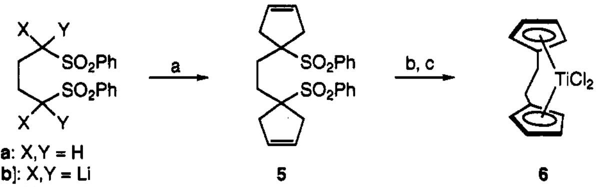
Scheme I[a]



4a: X,Y = H
[4b]: X,Y = Li
[4c]: X = H, Y = Li

5

6

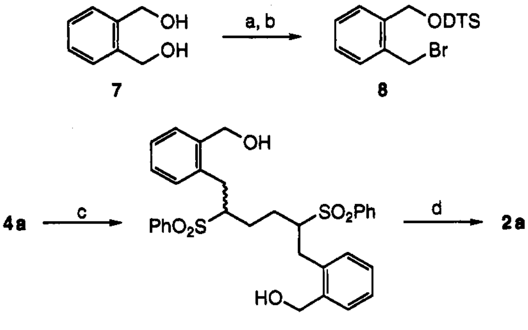
[a] Legend: (a) (i) *n*-BuLi (4.10 equiv), THF, 0 °C, (ii) *cis*-1,4-dichloro-2-butene (2.05 equiv), 0–25 °C, 35%; or (i) *n*-BuLi (2.0 equiv), THF, −30 °C, (ii) cannulation into *cis*-1,4-dichloro-2-butene (3.0 equiv), THF, −78 °C, 39%; (b) KO-*t*-Bu (excess), THF, 40 °C, 6 h, 85%; (c) (i) *n*-BuLi (2.0 equiv) THF, 0–25 °C, (ii) $TiCl_3{\cdot}3THF$ (1.0 equiv), −40 °C to reflux, (iii) 12 M HCl, −40 to +25 °C, air, 80%.

of **5** was effected by treatment with KO-*t*-Bu in THF at 40 °C. The resultant bis(cyclopentadiene) was isolated and subsequently complexed with $TiCl_3{\cdot}3THF$ to yield *ansa*-titanocene **6**.[11]

Having established a new route to *ansa*-titanocenes, we examined the application of the tetraanion chemistry in the synthesis of **2a**. Tetraanion **[4b]** was treated with *o*-bis(chloromethyl)benzene.[12a] Isolation of the bis cyclized disulfone intermediate was avoided; rather, direct treatment with lithium diisopropylamide resulted in the elimination of benzenesulfinate to give the bis(indene) **2a** as part of a complex product mixture. We were gratified to obtain pure **2a** by simple Soxhlet extraction of the crude reaction mixture using hexane. In this manner, bis(indene) **2a** was separated from the insoluble polymeric and sulfone-containing byproducts and was obtained in 12–15% yield on a multigram scale. It is probable that the formation of excessive amounts of polymeric materials during the formation of **2a** is due in part to competitive cross-alkylations of the benzylic chlorides. Attempts to improve the yield by changing the electrophile were unsuccessful. For example, the use of *o*-bis(bromomethyl)benzene[12a,b] and *o*-bis(mesyloxymethyl)benzene[12c] resulted in lower isolated yields of **2a**.

In an attempt to obtain **2a** by a route which precludes the cross-alkylation possibility, we pursued a stepwise approach in which only one benzylic site was available for alkylation (Scheme II). A dimethylthexylsilyl ether was used to protect one of the benzylic sites against alkylation. Diol **7**[12a] was monoprotected and subsequently converted to the benzylic bromide **8** using the Corey–Kim procedure[13] in 72% overall yield. The alkylation of **4a** using bromide **8** proceeded smoothly and was followed by desilylation to deliver a mixture of a diastereomeric diols **9** in 49% recrystallized yield. The Corey–Kim procedure was used again to transform the benzylic alcohol groups of **9** into the corresponding benzylic chlorides, and the subsequent ring closure was effected by treatment with excess lithium diethylamide to give **2a** in 84% yield. Although the overall yield of 41% for the stepwise preparation of **2a** from **4a**, as shown in Scheme II, exceeded the yield of **2a** obtained *via* the tetraanion route, the expediency of the tetraanion methodology and the commercial availability of the benzylic dichloride combine to make the tetraanion approach more practical.[14]

Scheme II[a]



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[a] Legend (DTS = dimethylthexylsilyl): (a) (i) *n*-BuLi (1.0 equiv), THF, −78 °C, (ii) DTS–Cl (0.9 equiv), 93%; (b) NBS, Me_2S, CH_2Cl_2, −20 °C, 73%; (c) (i) *n*-BuLi (2.0 equiv), THF, −78 °C, (ii) **8**, −78 to +25 °C, (iii) *n*-Bu_4NF, THF, 25 °C, 49%; (d) (i) NCS, Me_2S, CH_2Cl_2, −20 °C, (ii) Et_2NLi (8.0 equiv), THF, −78 to 0 °C, 84%.

(Ethylenebis(2-indenyl))titanium Dichloride. The conversion of bis(indene) **2a** into its corresponding *ansa*-titanocene was initially problematic. Attempts using the standard literature procedures[11,15] in which the dilithium salt of **2a** is treated with either $TiCl_3{\cdot}3THF$ or $TiCl_4{\cdot}2THF$[16] resulted in the recovery of **2a** on workup. (Ethylenebis(2-indenyl))titanium dichloride (**3a**) was eventually obtained by the inclusion of a vigorous oxidation procedure after metalation with $TiCl_3{\cdot}3THF$. Dry air was bubbled through the reaction mixture during workup for 1 h to result in the gradual precipitation of titanocene **3a**. Additional material was precipitated from the reaction solution by the addition of diethyl ether. Filtration of the precipitate followed by rinsing with diethyl ether gave complex **3a** in 54% yield. Single crystals of compound **3a** were grown *via* slow diffusion of ether into a dichloromethane solution at 25 °C, leading to small, dark-red stratified plates. X-ray diffraction analysis confirmed the structure of **3a**. Complete tabulation of all atomic coordinates and isotropic displacement parameters, bond distances and angles, and anisotropic displacement parameters and listings of observed and calculated structure factors for **3a** are reported elsewhere.[17]

Concluding Remarks. This work describes a general approach to ethylene-bridged *ansa*-titanocenes from a 1,4-disulfone using a bis cycloalkylation–bis elimination strategy. The two step formation of 1,2-bis(2-indenyl)ethane (**2a**) and its subsequent complexation is to our

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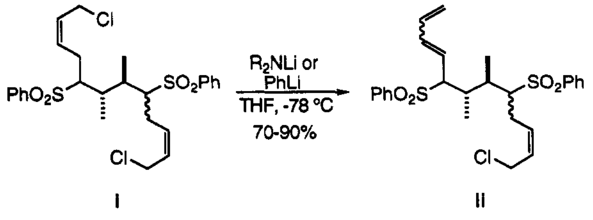
[11] Brintzinger, H. H.; von Seyerl, J.; Huttner, G.; Smith, B. A. *J. Organomet. Chem.* **1979**, *173*, 175.

[12] (a) Commercially available from the Aldrich Chemical Co. (b) Prepared from *o*-xylene, see: Shet, B.; Zapan, M. *J. Org. Chem.* **1986**, *51*, 929. (c) Prepared from diol **7** and methanesulfonyl chloride.

[13] Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, *23*, 4339.

[14] We have also found that a stepwise approach to tethered cyclopentadienes using β,β'-disubstituted disulfones fails in the bis cyclization step. For example, when the β,β'-dimethyl disulfone **i**, prepared in a manner similar to that of disulfone **9**, was treated with base, the elimination product **ii** was obtained as the major product.



i

ii

[15] Burger, P.; Hortmann, K.; Diebold, J.; Brintzinger, H. H. *J. Organomet. Chem.* **1991**, *417*, 9.

[16] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

[17] Parkin, S.; Hitchcock, S. R.; Nantz, M. H.; Hope, H. *Acta Crystallogr., Sect. C*, in press.

knowledge the first reported synthesis of an ethylene-bridged bis(2-indenyl)titanocene dichloride.

Experimental Section

All nuclear magnetic resonance spectra were recorded on a General Electric QE-300 spectrometer (^1H at 300 MHz and ^{13}C at 74 MHz). Infrared spectra were recorded by an IBM FTIR-32 operating system with a resolution of 2 cm^{-1}. Elemental analyses were performed by Midwest Microlabs and mass spectral analyses were conducted at the University of California, Davis, Facility for Advanced Instrumentation. Tetrahydrofuran was distilled from Na/K-benzophenone immediately prior to use. Diethyl ether was purified by distillation from sodium and benzophenone. Methylene chloride was distilled from calcium hydride. All chemical reagents were purchased and used without further purification. $TiCl_3 \cdot 3THF$ was prepared by the method of Manzer.[16]

Preparation of 1,4-Bis(phenylsulfonyl)butane (4a). A 500-mL round bottom flask fitted with a condenser was charged with sodium benzenesulfinate (40.0 g, 243 mmol), tetrabutylammonium bromide (9.66 g, 30.0 mmol), water (40 mL), benzene (30 mL), and acetone (30 mL). The resultant slurry was allowed to stir for 5 min at room temperature before the addition of 1,4-dibromobutane (12.0 mL, 100 mmol). The reaction temperature was elevated by submersing the reaction flask in an oil bath heated to 85 °C. After stirring at this temperature for 30 h, the reaction mixture was cooled to 25 °C and diluted with ethyl acetate (200 mL). The layers were separated, and the organic layer was washed twice with brine. The organic extract was dried over magnesium sulfate and filtered, and the solvent was removed by rotoevaporation. The crude product was obtained as a yellow solid and was recrystallized from methanol to yield 20.1 g (60%) of **4a** as white needles: mp = 125–126 °C; ^1H NMR ($CDCl_3$) δ 1.79–1.82 (m, 4H), 3.05 (br t, J = 6.6 Hz, 4H), 7.52 (t, J = 7.7 Hz, 4H), 7.62 (t, J = 7.3 Hz, 2H), 7.83 (d, J = 7.6 Hz, 4H); ^{13}C ($CDCl_3$) δ 21.5, 55.3, 127.8, 129.3, 133.7, 138.9; MS (EI) [*m/e* (relative intensity)] 197 ($M^+ - SO_2Ph$, 76), 143 (98), 77 (100).

Preparation of 1,2-Bis[(1-phenylsulfonyl)cyclopent-3-en-1-yl]ethane (5). A 250-mL round bottom flask was charged with 1,4-bis(phenylsulfonyl)butane (**4a**) (3.93 g, 11.6 mmol) and THF (50 mL). The solution was cooled to 0 °C and *n*-BuLi (19.0 mL of a 2.50 M solution in hexane, 47.5 mmol) was added dropwise. After 45 min, *cis*-1,4-dichloro-2-butene (2.50 mL, 23.8 mmol) was added and the reaction was allowed to warm to room temperature and stirred 12 h. The reaction mixture was recooled to 0 °C and quenched by the addition of $NaHCO_3$. The reaction mixture was diluted with EtOAc, and the organic layer separated and washed with brine (×2). The aqueous layer was extracted with CH_2Cl_2, and the combined organic extract was dried over $MgSO_4$ and filtered. To the filtrate was added SiO_2 (3 g), and the suspension was stirred for 30 min at room temperature. The solution was subsequently filtered, and the solvent was removed by rotary evaporation to give the crude product as a light yellow solid. Purification was accomplished by recrystallization from methanol to afford 1.79 g (35%) of **5**; mp = 182–183 °C; ^1H NMR ($CDCl_3$) δ 1.72 (s, 4H), 2.17 (d, J = 15 Hz, 4H), 3.2 (d, J = 15 Hz, 4H), 7.52 (t, J = 7.1 Hz, 4H), 7.65 (t, J = 7.8 Hz, 4H), 7.81 (d, J = 7.1 Hz, 2H); ^{13}C ($CDCl_3$) δ 30.52, 38.92, 70.37, 127.9, 128.7, 129.8, 133.6, 136.1; IR (KBr) 3071, 2928, 1701, 1442, 1284 cm^{-1}. Anal. Calcd for $C_{24}H_{26}S_2O_4$: C, 65.13; H, 5.92. Found: C, 65.24; H, 5.99.

Preparation of (Ethylenebis(cyclopentadienyl))titanium Dichloride (6). To a suspension of potassium hydride (0.50 g, 12.5 mmol) in THF (20 mL) at 0 °C was added *t*-BuOH (1.20 mL, 12.5 mmol). In a second flask, disulfone **5** (0.69 g, 1.56 mmol) was dissolved in THF (30 mL), and the mixture was cooled to 0 °C and then slowly cannulated into the KO-*t*-Bu solution. On complete addition, the reaction was warmed to 40 °C and stirred for 6 h. The reaction was then cooled to 0 °C and quenched by addition of aqueous NH_4Cl (5 mL). The reaction mixture was diluted with water and extracted with Et_2O, and the organic layer was separated and dried ($MgSO_4$). The Et_2O was removed by rotary evaporation at 0 °C, and the remaining THF was removed by short path distillation at reduced pressure. The residue was taken up in pentane and quickly filtered through a short column of silica gel using pentane as the eluent. The solvent was evaporated from the collected fractions using a nitrogen flow to give 0.21 g (85%) of 1,2-bis(cyclopentadienyl)ethane. This material was used immediately in the next transformation.

A solution of the bis(cyclopentadiene) (0.21 g, 1.33 mmol) in THF (20 mL) was degassed using nitrogen and subsequently cooled to 0 °C. To this solution was added dropwise *n*-BuLi (1.10 mL, 2.5 M solution in hexane, 2.77 mmol). The reaction solution was warmed to room temperature, stirred for 30 min, and then cooled to −40 °C. $TiCl_3 \cdot 3THF$ (0.49 g, 1.33 mmol) was added in one portion. The resultant dark-green mixture was warmed to room temperature followed by heating to reflux for 4 h, after which the reaction mixture was recooled to −40 °C and quenched by addition of 140 μL of 12 M HCl. The reaction mixture was allowed to come to room temperature and stirred 2 h open to the atmosphere. Dilution with CH_2Cl_2 (10 mL) was followed by filtration through a 1-in. pad of silica gel. The filtrate was concentrated by rotary evaporation to give 0.29 g (80%) of **6** as dark-red crystals. The spectral data for this compound matched the literature data.[11]

Preparation of 1,2-Bis(2-indenyl)ethane (2a). Method A (Tetraanion Route). To a solution of disulfone **4a** (16.9 g, 50.0 mmol) in THF (0.5 L) at 0 °C was added dropwise *n*-BuLi (82.0 mL, 2.5 M in hexane, 205 mmol). After stirring for 1 h at 0 °C, the reaction mixture was stirred vigorously while *rapidly* adding a solution of *o*-bis(chloromethyl)benzene (17.9 g, 102 mmol) in THF (0.5 L). On complete addition, the reaction mixture was warmed to room temperature and stirred for 2 h before cooling to −50 °C. A solution of lithium diisopropylamide (413 mmol), previously prepared by the addition of *n*-BuLi (165 mL, 2.5 M solution in hexane) to a solution of diisopropylamine (57.7 mL) in THF (250 mL) at 0 °C, was cannulated into the reaction mixture. Stirring was continued at −50 °C for 30 min after complete addition of the LDA solution and followed by gradual warming to 0 °C. The reaction was quenched at 0 °C by the addition of 5% HCl (200 mL) and extracted using EtOAc (250 mL × 2). The combined organic extract was washed with brine and dried ($MgSO_4$). The solvents were removed *in vacuo* to give a yellow crystalline solid which was placed in a Soxhlet thimble and extracted with hexanes over 18 h. Evaporation of the hexane extract afforded 2.0 g (15%) of bis(indene) **2a**: mp 164–165 °C; ^1H NMR ($CDCl_3$) δ 2.82 (s, 4H), 3.36 (s, 4H), 6.57 (s, 2H), 7.11 (t, J = 7.1 Hz, 2H), 7.19–7.28 (m, 4H), 7.38 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.7, 41.2, 120.1, 123.4, 123.8, 126.3, 126.7, 143, 145.5, 149.7; IR (CCl_4) 3062, 3022, 1613, 1463, 1394 cm^{-1}. Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.80; H, 6.99.

Preparation of 1-(((Dimethylthexylsilyl)oxy)methyl)-2-(bromomethyl)benzene (8). To a solution of *o*-bis(hydroxymethyl)benzene (8.57 g, 62.0 mmol) in THF (200 mL) at −78 °C was added *n*-BuLi (6.20 mL, 10.0 M in hexane, 62.0 mmol). The reaction mixture was warmed to room temperature and stirred for 1 h. The resulting white slurry was then recooled to −78 °C, and dimethylthexylsilyl chloride (11.0 mL, 55.9 mmol) was added. On complete addition, the reaction mixture was allowed to warm to 0 °C and stirred for 1 h. The reaction was quenched by the addition of water and extracted with Et_2O (3 × 100 mL). The combined organic extract was washed with brine and dried ($MgSO_4$). Rotary evaporation of the solvents afforded the crude product which was purified by column chromatography (SiO_2) using hexane:EtOAc (4:1, R_f = 0.26) as the eluent to give 16.1 g (93%) of 1-(((dimethylthexylsilyl)oxy)methyl)-2-(hydroxymethyl)benzene as an oil: ^1H NMR ($CDCl_3$) δ 0.19 (s, 6H), 0.87 (s, 3H), 0.88 (s, 3H), 0.90 (d, J = 4.1 Hz, 6H), 1.66 (m, 1H), 3.10 (br t, 1H), 4.70 (d, J = 6.0 Hz, 2H), 4.81 (s, 2H), 7.29–7.37 (m, 4H).

To a solution of *N*-bromosuccinimide (5.31 g, 29.8 mmol) in CH_2Cl_2 (124 mL) at 0 °C was added dimethyl sulfide (2.19 mL, 29.8 mmol) over a period of 5 min. The reaction mixture was allowed to stir 0.5 h before addition of a solution of 1-(((dimethylthexylsilyl)oxy)methyl)-2-(hydroxymethyl)benzene (6.97 g, 24.8 mmol) in CH_2Cl_2 (20 mL). The reaction was protected from light and allowed to warm to room temperature overnight. The reaction mixture was quenched by addition of 0 °C water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extract was dried ($MgSO_4$), and the solvents were removed by rotary evaporation. The residue was chromatographed (SiO_2) using hexane as the eluent ($R_f = 0.63$, hexane: EtOAc, 10:1) to give 6.20 g (73%) of **8** as an oil: ^1H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.9 (s, 6H), 0.91 (d, J = 6.0 Hz, 6H), 1.63–1.72 (m, 1H), 4.59 (s, 2H), 4.85 (s, 2H), 7.26 (m, 3H), 7.46 (d, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ −3.53, 18.3, 20.1, 25.0, 30.6, 30.7, 34.0, 62.0, 127, 128, 129, 130, 134, 140; IR (CCl_4) ν_{max} 3080, 3025, 1464, 1379, 1253, 1104, 1072 cm^{-1}. Anal. Calcd for $C_{16}H_{27}BrOSi$: C, 55.97; H, 7.93. Found: C, 56.26; H, 8.02.

Preparation of Disulfone 9. Disulfone **4a** (1.46 g, 4.31 mmol) was dissolved in THF (43 mL) and cooled to −78 °C. *n*-BuLi (3.53 mL of a 2.51 M hexane solution, 8.84 mmol) was added dropwise, and the reaction mixture was allowed to stir for 0.5 h. Bromide **8** (3.26 g, 9.52 mmol) was added in one portion, and the solution was allowed to stir at −78 °C for 5 min followed by warming to 25 °C over 30 min. The reaction was quenched with aqueous NH_4Cl (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extract was dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was filtered through a short column of SiO_2 using hexane:EtOAc (4:1) to yield 2.45 g of the bis alkylated sulfone as a mixture of diastereomers. This material was used directly in the next step without further purification or separation.

The bis alkylated sulfone (2.82 g, 3.26 mmol) was dissolved in THF (3.3 mL), and tetrakis(*n*-butyl)ammonium fluoride (13 mL, 1.0 M solution in THF, 13 mmol) was added dropwise. The solution was allowed to stir at room temperature for 15 min. The reaction mixture was quenched by addition of water (50 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product was recrystallized using EtOAc:hexane (85:15) to give 1.27 g (67%) of disulfone **9** (R_f = 0.05, EtOAc) as a white solid: mp 158–160 °C; ^1H NMR ($CDCl_3$) δ 1.77 (br s, 4H), 2.13 (t, J = 5.4 Hz, 2H), 2.55 (apparent t, J = 11 Hz, 2H), 3.24–3.34 (m, 4H), 4.41 (d, J = 5.1 Hz, 4H), 6.89 (d, J = 7.3 Hz, 2H), 7.18–7.29 (m, 4H), 7.36 (d, J = 7.6 Hz), 7.53 (t, J = 7.6 Hz, 4H), 7.66 (t, J = 7.1 Hz, 2H), 7.74 (d, J = 7.9 Hz, 4H); ^{13}C ($CDCl_3$) δ 25.6, 31.8, 62.8, 65.6, 127.4, 128.3, 128.9, 129.2, 129.7, 130.4, 133.8, 135.5, 137.3, 139; IR (CCl_4) 3468–3431 (broad), 1448, 1295, 1139, 1083, 1013 cm^{-1}. Anal. Calcd for $C_{32}H_{34}O_6S_2$: C, 66.41; H, 5.92; S, 11.08. Found: C, 66.42; H, 5.91; S, 11.06.

Preparation of 1,2-Bis(2-indenyl)ethane (2a). Method B (Stepwise Cycloalkylation Route). To a solution of *N*-chlorosuccinimide (0.29 g, 2.1 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added dropwise dimethyl sulfide (0.15 mL, 2.1 mmol). The resulting solution was allowed to stir for 0.5 h before addition of a solution of disulfone **9** (0.40 g, 0.70 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was protected from light and stirred overnight at room temperature. The reaction mixture was quenched at 0 °C by the addition of water. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined extract was dried ($MgSO_4$). The solvent was removed under reduced pressure give the crude dichloride as an oil which was dissolved in THF (6 mL). The resulting dichloride solution was added to a solution of lithium diethylamide, prepared previously from diethylamine (0.58 mL, 5.6 mmol) and *n*-BuLi (2.2 mL, 2.5 M in hexane, 5.6 mmol) in THF (3 mL) at − 78 °C, *via* cannula. The reaction solution was allowed to stir at −78 °C for 30 min, warmed, and subsequently quenced at 0 °C with aqueous 5% HCl (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined extract dried ($MgSO_4$). The solvent was removed by rotary evaporation, and the crude product was chromatographed (SiO_2) hexane:EtOAc (49:1) to give 0.15 g (84%) of **2a** which was spectrally identical to the material prepared *via* the tetraanion route.

Preparation of (Ethylenebis(2-indenyl))titanium Dichloride (3a). Nitrogen was bubbled through a solution of bis(indene) **2a** (0.30 g, 1.2 mmol) in THF (15 mL) for 5 min followed by cooling to 0 °C. *n*-BuLi (0.97 mL, 2.5 M solution in hexane, 2.4 mmol) was added slowly, and the reaction mixture was stirred for 1 h at 0 °C followed by warming to 25 °C. The reaction mixture was then cooled to −25 °C, and $TiCl_3 \cdot 3THF$ (0.53 g, 1.4 mmol) was added in one portion. After stirring 5 min, the reaction mixture was gradually warmed to room temperature and then refluxed for 4 h. The resultant dark-brown reaction mixture was cooled to −78 °C, 6.0 N HCl (1 mL) was added, and the reaction solution was warmed to 25 °C. Dry air was vigorously bubbled through the reaction solution to result in the formation of a red precipitate. After 1 h, Et_2O (15 mL) was added and the precipitate was collected and washed successively with water (20 mL) and Et_2O (25 mL) and subsequently dried under vacuum to yield 0.28 g (54%) of **3a** as a red solid: ^1H NMR ($CDCl_3$) δ 3.33 (s, 4H), 6.56 (s, 4H), 7.22 (dd, J = 3.1, 6.5 Hz, 4H), 7.47 (dd, J = 3.1, 6.4 Hz, 4H); ^{13}C ($CDCl_3$) δ 30.7, 110.0, 125.9, 127.8, 131.9, 139.7; IR (KBr) 3030, 1520, 1440, 820, 710 cm^{-1}. Anal. Calcd for $C_{20}H_{16}TiCl_2$: C, 64.03; H, 4.30. Found: C, 63.27; H, 4.30. HRMS calcd for $C_{20}H_{16}TiCl_2$ 374.0108, found 374.0095.

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