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Stereoselectivity in the synthesis of tetramethylethano-bridged 3,3′-di-tert-butyltitanocene dichloride

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Abstract

Racemic and meso *ansa*-(2,3-dimethyl-2,3-butano)-3,3′-bis(1,1′-dimethylethyl)cyclopenta-1,3-dien-5-yl)titanium dichloride (**5** and **4**) were prepared in a 1:4 to 1:2 ratio by the addition of $TiCl_3 \cdot 3THF$ to 2,3-bis[3-(1,1-dimethylethyl)-1,3-cyclopentadien-5-yl]-2,3-dimethylbutanedilithium (**3**) in THF with subsequent oxidation by HCl in a 44% yield. A 30% yield of the 1:1 racemic:meso ratio resulted when **3** was treated with titanocene dichloride in THF followed by carbon tetrachloride oxidation. In the attempts to synthesize the desired *anti* isomer, **3** was treated with *in-situ* generated racemic dichloro-1,1′-bi-2-naphtholatetitanium(IV) to give *ansa*-(2,3-dimethyl-2,3-butano)-*anti*-3,3′-bis(1,1-dimethylethyl)cyclopenta-1,3-dien-5-yl)titanium 1,1′-bi-2-naphtholate (**6**) in a 10–15% yield. **6** crystallized in a monoclinic space group $P2_1/c$ with $a = 10.084(2)$ Å, $b = 29.312(7)$ Å, $c = 12.190(2)$ Å, $\beta = 99.37(2)°$, $V = 3555(2)$ Å^3, and $Z = 4$. Refinement of 425 least squares variables converged to $R = 0.044$ and $R_w = 0.046$ for 4153 observed reflections with $I > 2\sigma(I)$. The molecule contains an approximate C_2 axis of symmetry with the t-butyl groups *anti* to each other. The C(Cp)–C(t-butyl) bonds are displaced from the plane defined by the cyclopentadienyls by about 10°.

Introduction

The stereochemistry of asymmetric hydrogenation [1] and isotactic Ziegler–Natta polymerization [2,3] is controlled using asymmetric titanocene and zirconocene dichloride precatalysts, respectively. Brintzinger and co-workers have reported the synthesis of bridged titanocene dichlorides, **4** (meso), where the t-butyl groups have a *syn* geometry with respect to each other, and **5** (racemic), where the t-butyl groups are *anti* to each other [4]. These complexes were prepared by reaction of the tetramethyl ethano-bridged di-t-butyl (TMEDT) cyclopentadienyl magnesium chloride with $TiCl_3 \cdot 3THF$ and resulted in a 2.5:1 selectivity favoring the desired racemic (*anti*) isomer over the meso (*syn*) isomer. The goal of our work was to devise an alternate synthesis to produce **5** exclusively. Our independent attempts to synthesize **5** using the analogous lithium reagent, **3**, with $TiCl_3 \cdot 3THF$, $TiCl_4$, and titanocene dichloride instead resulted in a 1:4 to a 1:1 racemic:meso mixture in a combined yield of 20% to 44% (Table 1). Collins and co-workers reported similar racemic:meso selectivities of 1:1.3 to 1:2.0 for the synthesis of the unmethylated

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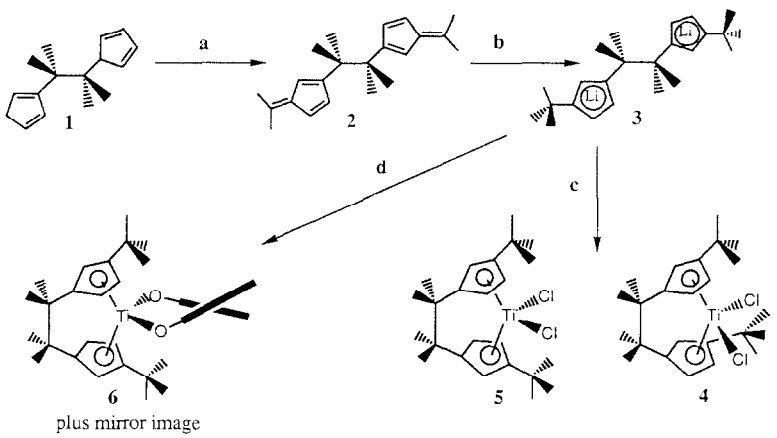
Table 1

Selectivity for the reaction of **3** with various Ti sources

Ti source	Temp. (°C)	Yield	rac : meso
$TiCl_4$	−78	20%	1 : 4
$TiCl_3 \cdot 3THF$	−78	44%	1 : 4
	24	36%	1 : 2
$TiCp_2Cl_2$	24	30%	1 : 1



Scheme 1. Synthetic route to compounds **2–6**. (a) Excess acetone, pyrrolidine, methanol, 25 °C. (b) Excess MeLi, ether. (c) $TiCl_3(THF)_3$, THF, then 6 *M* HCl. (d) $TiCl_2$ (1,1′-bi-2-naphtholate), THF.

ethano-bridged substituted titanocene dichlorides when the lithium biscyclopentadienide is used [5]. It is surprising that the magnesium and lithium biscyclopentadienides should prefer opposite isomers, but the relative energy difference between a 2.5 : 1 and 1 : 2 racemic : meso ratio is small.

Although many different titanium sources were used in attempts to favor the racemic isomer, only the use of a directing ligand on the titanium to control the stereoselection of titanium complexation of **3** was successful in producing the racemic isomer exclusively (Scheme 1). Others have used 1,1′-bi-2-naphtholate to concomitantly separate and resolve racemic bridged titanocene derivatives [6], but this method of directing the approach of the incoming substituted bridged biscyclopentadienide is novel.

Results

Synthesis of difulvene 2 and dilithio salt 3

The proton shift isomers of 2,3-bis-cyclopenta-1,4-diene-2,3-dimethylbutane were treated with pyrrolidine and excess acetone at room temperature in methanol to give difulvene **2** in a yield of 82%. Difulvene **2** is highly crystalline; the X-ray structure has been reported elsewhere [7]. Reaction of **2** with excess methyllithium in ether followed by washing of the dilithio salt with fresh ether gave **3**, which was dissolved in THF. This solution was then treated with various titanium sources as outlined below.

Synthesis of meso and racemic TMEDT–Ti–Cl_2

a. Via $TiCl_3 \cdot 3THF$ and $TiCl_4$. **3** was treated with $TiCl_3 \cdot 3THF$ or $TiCl_4$ in THF at $-78°C$ (pathway c of Scheme 1). After refluxing for 18–24 hours and standard work up, solvent removal gave titanocene dichloride isomers **5** and **4** in a 1 : 4 ratio as determined by ^1H NMR analysis. When $TiCl_3 \cdot 3THF$ was added at room temperature, the ratio of **5** to **4** increased to 1 : 2 in a similar yield (Table 1). Recrystallization of the 1 : 4 mixture in refluxing toluene yielded the pure meso isomer in two forms: red hexagonal plates (solvate), which lost solvent readily, and orange rectangular plates. Single-crystal X-ray analysis of the red and orange plates confirmed a *syn* geometry for the major isomer, **4**, which was reported in detail elsewhere [8].

b. Via titanocene dichloride. **3** was added to titanocene dichloride in THF at room temperature and was refluxed for 19 hours [9,10]. After oxidizing with CCl_4 and purification by flash chromatography with silica gel, the product ratio of **5** and **4** was 1 : 1 in a combined 30% yield.

The meso isomer, **4**, is photochemically inert unlike titanocene dichloride [11] and resists conversion to the racemic isomer, **5**, contrary to other examples of titanocene dichlorides of this type [12]. Therefore, an alternate synthesis was devised using a C_2 symmetric directing ligand at the titanium center to guide the incoming lithium TMEDT biscyclopentadienyl anion t-butyl groups in the anti geometry.

Synthesis of racemic TMEDT–Ti binaphtholate

Treatment of **3** with the freshly generated 1 : 1 adduct of racemic 1,1′-bi-2-naphtholate [13] and $TiCl_4$ gave the *anti* titanocene 1,1′-bi-2-naphtholate derivative, **6**, in a 15% yield as shown in pathway d of Scheme 1. Flash chromatography with silica gel, eluting with hexane–dichloromethane gradient, followed by recrystallization of **6** from refluxing toluene gave red rectangular plates. Figure 1 is a perspective drawing of **6**, the 1,1′-bi-2-naphtholate titanocene isomer. The 1 : 1 adduct of 1,1′-bi-2-naphtholate and $TiCl_4$ quickly oligomerizes so it must be treated with **3** promptly or the yield of any titanocene product is diminished. The yield of **6** was reduced to 8% and to 5% with longer reaction times at -78 C for the $TiCl_4$ and 1,1′-bi-2-naphtholate reaction. Also, the isolated adduct of 1,1′-bi-2-naphtholate and $TiCl_4$ gave no significant yield of **6** when reacted with **3**.

Compound **6** is not formed by reaction of unreacted $TiCl_4$ with **3** followed by a derivatization of only the *anti* titanocene isomer and a selective destruction of the meso isomer. The isolated 1 : 4 ratio of **5** and **4** when treated with 1,1′-bi-2-naphtholate under similar reaction conditions did not give an appreciable yield of the racemic titanocene product **6**, but the predominant product is a meso TMEDT–Ti binaphtholate chloride derivative (see Scheme 2). This compound is not formed in the synthesis of **6**.

Synthesis of racemic TMEDT–Ti–Cl_2

Treatment of **6** with excess HCl gas in hexane, solvent removal, and silica gel flash column chromatography with hexane/ether, as with the mixture of **4** and **5**, gave exclusively the racemic titanocene dichloride derivative, **5**, which matches the ^1H NMR assigned to the minor isomer produced by pathway c. The crystal structure of **5**, could not be solved with satisfactory resolution because of the presence of two independent molecules that are not related by symmetry and

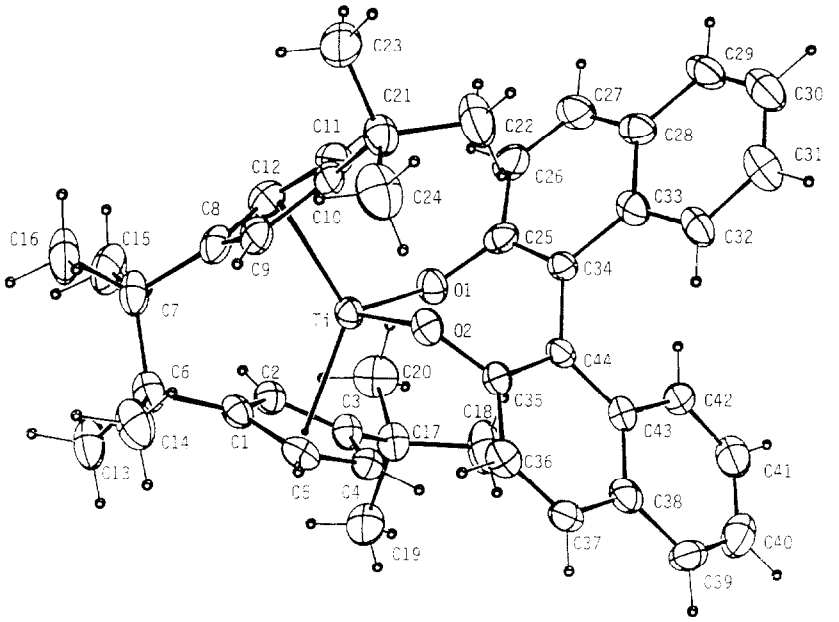
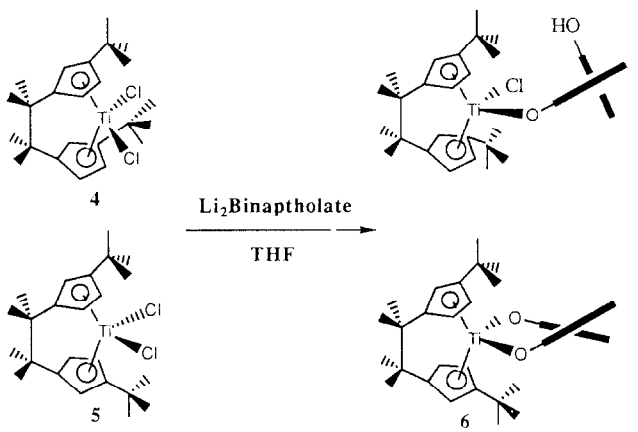


Fig. 1. Perspective drawing of **6**.



Scheme 2. Reaction of a 4:1 mixture of **4** to **5** with Li_2binaphtholate.

unresolved disorder in the tetramethylethano bridge, although the crystallographic data strongly suggest the expected anti conformation [14].

Discussion

Titanocene alkoxide and aryloxide complexes are common, and are typically synthesized via the action of an alkoxide or aryloxide on titanocene dichloride [6]. Our synthesis differs in that the bridged cyclopentadienyls react with a titanium

dichloride–binaphtholate adduct, thus replacing the chlorides with η^5-cyclopentadienyl ligands. The binaphtholate rings create a C_2 symmetric "groove" that directs the t-butyl groups on the cyclopentadienyls to a conformation of minimum steric interaction. Other diols were attempted as *anti*-directors at the titanium center in addition to 1,1′-bi-2-binaphthol. We investigated the use of vicinal diols that could form five-membered rings with titanium; however, 1,2-catechol, 2,3-dimethyl-2,3-butanediol, and hydrobenzoin titanium alkoxide-dichloride derivatives prepared according to the 1,1′-bi-2-binaphtholate titanium dichloride method failed to react with **3**.

Titanocene derivatives **4**, **5**, and **6** are inert toward silica gel. Other titanocene dichlorides and even bridged titanocene dichlorides are sensitive to purification on silica gel chromatography, requiring at least silanized silica gel and sometimes low temperatures [6,12]. An initial wash with hexane left **4** and **5** at the origin and eluted the hydrocarbon impurities. Hexane slowly eluted **6**. Hexane/dichloromethane gradient moved **4**, **5**, and **6** quickly, but eluted binaphthol very slowly. A hexane/ether gradient moved them equally as fast. These properties allow for easy purification and are important when precatalyst separation/recovery are considered.

The ^{1}H NMR spectra of **4**, **5**, and especially **6** have interesting features. The peak positions of the bridge methyl protons on **4** and **5** shift upfield by almost 0.5 ppm when the NMR solvent was changed from $CDCl_3$ (1.34 and 1.46 ppm for **4**; 1.37 and 1.43 ppm for **5**) to benzene-d_6 (0.92 and 0.99 ppm for **4**; 0.93 and 0.99 ppm for **5**) the solvent used by Brintzinger and co-workers. The ^{1}H NMR spectrum of **6** in $CDCl_3$ showed a relatively small shift in the bridge methyl protons (1.30, 1.41, 1.57, 1.81 ppm) from the values observed for **4** and **5**; however, the t-butyl group protons shift upfield (at 0.63 ppm) by almost 0.8 ppm from the t-butyl resonances of **4** and **5**. This upfield t-butyl shift due to shielding by the aromatic ring has precedent [6].

Inspection of the X-ray crystal structure of **6** shows that the desired *anti*-geometry is probably controlled by the steric interactions between t-butyl groups and the binaphtholate rings. The t-butyl groups in **6** are displaced outwards from the plane defined by their respective cyclopentadienyls (10.2° and 9.2°). The crystal structure of the meso titanocene dichloride showed a similar t-butyl group outward displacement of about 11° from the cyclopentadienyl plane. This is not much different than the t-butyl displacement observed in the unbridged dichlorobis(η^5-t-butyl cyclopentadienyl titanocene(IV)) (10.5°) [15] and the methyl displacement in the permethylated titanocene dichloride (~ 8°) [16]. However, steric interactions between binaphtholate and *syn* oriented t-butyls would have been prohibitive.

Bond lengths and selected bond angles are included in Table 2. Other structural features of note for **6** include O1–Ti–O2 bond angle of 94.09(6)°, which is similar to the Cl–Ti–Cl bond found in titanocene dichlorides, and the unequal Ti–O bond lengths: Ti–O1 = 1.908(2) Å and Ti–O2 = 1.923(2) Å. The centroid–Ti bond lengths are Ci1–Ti = 2.118 Å and Ti–Ci2 = 2.112 Å and the centroid–Ti–centroid bond angle is 128.5° which are similar to those found in **4** at 2.092 Å, 2.014 Å, and 128.8°, respectively. The torsion angle about the central C–C bond of the binaphtholate ligand is −60.8(4)°.

The solvate form of **6** crystallizes from 25 : 75 toluene : hexane as orange plates with composition $\mathbf{6} \cdot 1/2C_6H_{14}$. We have also determined the structure of this solvate by X-ray crystallography. The molecular structure of **6** in the solvate crystal is nearly identical to that in the unsolvated crystal, including the unequal Ti–O

Table 2

Bond distances (Å) and selected angles (°) of compound **6** (unsolvated)

Ti–O1	1.908(1)	C1–C6	1.515(3)
Ti–O2	1.923(1)	C2–C3	1.394(3)
Ti–C1	2.377(2)	C3–C4	1.403(3)
Ti–C2	2.433(2)	C3–C17	1.520(3)
Ti–C4	2.447(2)	C4–C5	1.407(3)
Ti–C5	2.351(2)	C6–C7	1.569(3)
Ti–C8	2.404(2)	C6–C13	1.548(3)
Ti–C9	2.448(2)	C6–C14	1.548(4)
Ti–C11	2.423(2)	C7–C8	1.526(3)
Ti–C12	2.337(2)	C7–C15	1.535(4)
O1–C25	1.348(2)	C7–C16	1.549(3)
O2–C35	1.356(2)	C8–C9	1.410(3)
C1–C2	1.427(3)	C8–C12	1.405(3)
C1–C5	1.408(3)	C9–C10	1.416(3)
C10–C11	1.400(3)	C28–C33	1.418(3)
C10–C21	1.518(3)	C29–C30	1.360(4)
C11–C12	1.419(3)	C30–C31	1.395(4)
C17–C18	1.532(3)	C31–C32	1.367(3)
C17–C19	1.538(3)	C32–C33	1.419(3)
C17–C20	1.524(3)	C33–C34	1.436(3)
C21–C22	1.531(3)	C34–C44	1.489(3)
C21–C23	1.536(3)	C35–C36	1.416(3)
C21–C24	1.526(3)	C35–C44	1.388(3)
C25–C26	1.419(3)	C36–C37	1.353(3)
C25–C34	1.386(3)	C37–C38	1.404(3)
C26–C27	1.356(3)	C38–C39	1.414(3)
C27–C28	1.406(3)	C38–C43	1.424(3)
C28–C29	1.416(3)	C39–C40	1.357(4)
C40–C41	1.394(4)	C42–C43	1.415(4)
C41–C42	1.360(3)	C43–C44	1.432(3)
O1–Ti–O2	94.09(6)	C1–C6–C13	107.2(2)
C6–C7–C8	108.5(2)	C1–C6–C14	108.8(2)
C6–C7–C15	112.7(2)	C7–C6–C13	112.9(2)
C6–C7–C16	113.0(2)	C7–C6–C14	112.8(2)
C8–C7–C15	109.3(2)	C25–C34–C44	121.9(2)
C8–C7–C16	107.4(2)	C33–C34–C44	119.7(2)
C15–C7–C16	105.992)	C34–C44–C35	121.4(2)
C1–C6–C7	109.3(2)	C34–C44–C43	120.5(2)

bond distances (1.904(3) and 1.926(3) Å). Unresolved disorder in the solvent led to lower precision for this structure, therefore it will not be discussed in detail.

Conclusion

Reaction of **3** with $TiCl_3 \cdot 3THF$ favored the meso titanocene dichloride derivative, **4**, with a temperature dependent selectivity of 4 : 1 to 2 : 1 over the racemic isomer, **5**. Reaction of 3 with the 1 : 1 adduct of 1,1′-bi-2-naphtholate and $TiCl_4$ gave the racemic titanocene derivative, **6**, with C_2 molecular symmetry. Compound **6** reacted with HCl to give the racemic titanocene dichloride derivative, **5**. The

crystal structure of **6** shows significant steric interactions of the 3,3′ substituents with the ancillary Ti ligands.

Experimental section

All reactions were carried out under argon atmosphere using Schlenk techniques. All reagents were used as received unless otherwise indicated. THF was distilled from potassium under argon. Ether was distilled from liquid Na/K under argon. Titanium tetrachloride was degassed and distilled prior to use. NMR spectra were recorded on the IBM AF100, Bruker AC/WP200, and Bruker AM400 multiprobe spectrometers. Infrared spectra were recorded on a Beckman IR4230. Elemental analysis were performed by Oneida Research Services Inc, Whitesboro, NY. High resolution mass spectrometry was performed by Midwest Center for Mass Spectrometry, Lincoln, NE.

Preparation of difulvene 2,3-bis[3-(1-methylethylidene)cyclopenta-1,4-diene]-2,3-dimethylbutane (2)

A suspension containing the proton shift isomers of 2,3-bis[3-cyclopenta-1,4-diene]-2,3-dimethylbutane [17] (1.9 g, 8.9 mmol) in 8.0 mL of reagent grade methanol was treated with reagent grade acetone (3.2 mL, 44 mmol) and pyrrolidine (2.5 mL, 30 mmol) at room temperature, the suspension immediately disappeared, forming a deep-red solution [18]. A yellow precipitate formed after 30 minutes and 3 hours later, **2** was isolated by vacuum filtration as a yellow powder (1.69 g, 65% yield) after washing with copious amounts of distilled water. An additional 0.45 g (17% yield) was recovered from the filtrate for an 82% overall yield. Further purification of **2** was accomplished by recrystallization from ethyl acetate; yellow crystals: m.p. 144°C; IR ($CDCl_3$) 3100, 2995, 2980, 2955, 2900, 2860, 1640, 1435, 1370, 1349, 1300, 1230, 1130 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$) δ 1.19 (s, 12 H), 2.15 (s, 12H), 6.15 (m, 2H), 6.38 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$) 22.69, 24.66, 41.31, 116.57, 118.77, 133.66, 141.83, 146.28, 153.42 ppm; MS, *m/z* (relative intensity) 294 (M^+, 1.9), 147 (100), 119 (17.6), 105 (30.2), 91 (14.6), 77 (18.1). Anal. Found: C, 89.67; H, 10.32. $C_{22}H_{30}$ calc.: C, 89.73; H, 10.27%.

Preparation of 2,3-bis[3-(1,1-dimethylethyl)cyclopenta-1,3-diene-5-yl]-2,3-dimethylbutanedilithium (3)

Difulvene **2** (2.38 g; 8.09 mmol) was treated with excess 1.4 *M* methyllithium (18.0 ml; 24.3 mmol) in 30 ml ether to give 2,3-bis[3-(1,1-dimethylethyl)-1,3-cyclopentadien-5-yl]-2,3-dimethylbutanedilithium, **3**, as an insoluble gel (not isolated), which was washed with ether (3 × 20 ml).

Preparation of racemic and meso ansa*-(2,3-dimethyl-2,3-butano)-3,3′-bis(1,1′-dimethylethyl)cyclopenta-1,3-diene-5-yl)titanium dichloride (4 and 5) by reaction of 3 with $TiCl_3 \cdot 3THF$*

3, as prepared above, was diluted with 250 ml of THF and treated with $TiCl_3 \cdot 3THF$ (3.0 g; 8.09 mmol) at −78°C. The reaction mixture was warmed to room temperature and then refluxed for 18–24 hours. After work up with 6 *M* hydrochloric acid (5.0 ml) for 4–5 hours and solvent removal under reduced pressure, the residue was redissolved in chloroform, separating it from the insolu-

bles. The deep red solution was dried with anhydrous magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica gel (60–200 mesh) by eluting first with hexane, then with 50/50 (v/v) hexane/ether. Solvent removal gave a red powder (1.58 g; 44% yield). Compound **4**, the meso isomer, m.p. 193–194°C, IR ($CDCl_3$) 3120, 2990, 2960, 2920, 2900, 2865, 1500, 1460, 1380, 1370, 1360, 1250, 1175 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.34 (s, 6H), 1.36 (s, 18H), 1.46 (s, 6H), 6.05 (t, 2H), 6.48 (t, 2H), 6.61 (t, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 27.40, 28.89, 30.84, 34.30, 45.70, 111.23, 114.98, 127.62, 142.09, 147.20 ppm; MS, *m/z* (relative intensity) 442 (M^+, 6.7), 282 (53.0), 280 (76.3), 246 (33.0), 244 (100), 228 (30.0); Anal. Found: C, 64.89; H, 8.23. $C_{24}H_{36}Cl_2Ti$ calc.: C, 65.02; H, 8.18%.

Preparation of racemic and meso ansa-*(2,3-dimethyl-3,4-butano)*-anti-*3,3′-bis(1,1′-dimethylethyl)cyclopenta-1,3-diene-5-yl)titanium dichloride (**4** and **5**) by reaction of **3** with titanocene dichloride*

A solution of **3** (4.04 mmol in 60 ml THF) was slowly added over 10 minutes to a solution of titanocene dichloride (1.00 g, 4.04 mmol in 65 ml THF) at room temperature and stirred for 45 minutes. After refluxing for 19 hours, the dark colored solution was cooled to 0°C and was treated with dry degassed CCl_4 (8.5 ml; 35 mmol) and left stirring at 0°C for 1 hour and for another 2 hours at room temperature. The solvent was removed under reduced pressure and the red residue purified by flash chromatography as previously described for **4** and **5**. A microcrystalline red solid (0.53 g; 30% yield) was recovered which was a 1 : 1 mixture of **5** and **4** as determined by ^1H NMR.

Preparation of ansa-*(2,3-dimethyl-2,3-butano)*-anti-*3,3′-bis(1,1-dimethylethyl)cyclopenta-1,3-dien-5-yl)titanium 1,1′-bi-2-naphtholate (**6**)*

1,1′-Bi-2-naphthol (2.32 g; 8.09 mmol) was deprotonated with 1.4 *M* methyllithium (11.6 ml; 16.2 mmol) in 75 ml of THF at −78°C. A of solution of $TiCl_4$ (1.53 g; 8.09 mmol) in 75 ml of THF was prepared at −78°C. The dilithio binaphtholate solution was added slowly to the $TiCl_4$ solution forming the $TiCl_2$(1,1′-bi-2-naphtholate) adduct [13]. After stirring 2 hours at −78°C (stirring for longer time periods decreases the yield), the red suspension was added to a THF solution of **3** (8.09 mmol in 75 ml) at −78°C and then refluxed for 18 hours. Column chromatography on silica gel (60–200 mesh) by eluting first with hexane, then with 50/50 (v/v) hexane/methylene chloride and solvent removal gave red microcrystals of the racemic titanocene 1,1′-bi-2-naphtholate derivative (0.80 g; 15% yield), m.p. 268–269°C; IR ($CDCl_3$) 3079, 3060, 3045, 2990, 2970, 2960, 2935, 2920, 2910, 2900, 2860, 1611, 1590, 1500, 1460, 1421, 1380, 1272, 1228, 1195, 1138, 1069 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.63 (s, 18H), 1.32 (s, 6H), 1.76 (s, 6H), 5.25 (t, 2H), 5.73 (t, 2H), 6.13 (t, 2H), 6.9–7.3 (m, 8H), 7.77 (t, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 26.54, 28.99, 29.78, 33.31, 44.73, 105.52, 108.60, 112.70, 117.39, 121.22, 121.78, 125.04, 126.99, 127.44, 128.57, 135.04, 143.48, 155.91, 165.54 ppm; MS, *m/z* (relative intensity) 656 (M^+, 25.6), 494 (100), 476 (23.8), 437 (55.3), 333 (66.3), 314 (18.2), 252 (19.1), 147 (18.8). Anal. Found: C, 80.74; H, 7.38. $C_{44}H_{48}O_2Ti$ calc.: C, 80.47; H, 7.36%.

Preparation of racemic ansa-*(2,3-dimethyl-2,3-butano)*-anti-*3,3′-bis(1,1′-dimethylethyl)cyclopenta-1,3-diene-5-yl)titanium dichloride (5)*

The pure racemic titanocene dichloride derivative was prepared quantitatively by treatment of **6** with HCl in hexane to produce **5**, which was purified by flash chromatography. Eluting with a hexane/dichloromethane gradient to separate the product from binaphthol and recrystallization from refluxing toluene yielded pure *ansa*-(2,3-dimethyl-2,3-butano)-*anti*-3,3′-bis(1,1′-dimethylethyl)cyclopenta-1,3-diene-5-yl)titanium dichloride (red rectangular plates, m.p. 248°C), IR ($CDCl_3$) 3160, 2960, 2925, 2900, 2880, 1800, 1500, 1462, 1385, 1372, 1264, 1251, cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (s, 18H), 1.37 (s, 6H), 1.43 (s, 6H), 6.21 (t, 2H), 6.34 (t, 2H), 6.5 m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 27.94, 28.38, 30.60, 34.51, 45.68, 111.47, 115.79, 123.15, 143.02, 151.27 ppm. MS, *m/z* (relative intensity) 442 (M^+, 5.4), 407 (16.38) 282 (64.2), 280 (94.8), 246 (33.2), 244 (100), 147 (35.6); HRMS *m/z* $C_{24}H_{38}Ti^{35}Cl_2$ calc. 442.1655, found 442.1688; and $C_{24}H_{38}Ti^{35}Cl^{37}Cl$ calc. 444.1643, found 444.1648.

Reaction of 1 : 4 mixture of 5 and 4 with dilithiobinaphtholate

A solution of dilithio-1,1′-bi-2-naphtholate (1.62 mmol in 20 ml THF) was added to a solution of a 1 : 4 mixture of **5** and **4** (0.720 g; 1.62 mmol in 20 ml THF) at −78°C. The solution was then refluxed for 19 hours. After solvent removal, the residue was purified by flash chromatography on silica. The hexane fraction contained pure **6** (0.06 g; 28% of the total **5** to be derivatized) according to ^1H NMR. The dichloromethane/hexane fraction contained traces of **4** and **5**. The major portion of this fraction appeared to be a binaphtholate–chloride derivative of **4**, see Scheme 2, characterized by ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (s, 9H), 1.27 (s, 9H), 1.30 (s, 3H) 1.41 (s, 3H), 1.57 (s, 3H), 1.81 (s, 3H), 4.04 (m, 1H), 5.62 (m, 1H), 5.66 (m, 1H), 5.97 (m, 1H), 6.28 (m, 1H), 6.70 (m, 1H), 6.81 (m, 1H), 6.93–6.96 (m, 2H), 7.08–7.18 (m, 4H), 7.63–7.70 (m, 2H), 7.75–7.81 (m, 2H), LRMS, *m/z* (no M^+) 656, 494, 437, 333, 287, 147, 107. HRMS *m/z* $C_{44}H_{48}O_2^{47}Ti$ calc.: 655.3179, found 655.3185.

This binaphtholate derivative was not present in the synthesis of **6**. A second purification of this fraction by flash chromatography and treatment with HCl gas yielded pure **4** according to ^1H NMR and melting point.

Photolysis of 4

Recrystallized **4** was photolyzed in quartz NMR tubes with UV radiation (450 W high pressure Hg lamp). The samples were photolyzed in 4 different solvents: $CDCl_3$, THF-d_8, acetonitrile-d_3–$CDCl_3$ (6 : 1), and MeOH-d_4–$CDCl_3$ (4 : 1). The reaction progress was followed by ^1H NMR by monitoring the changes in the characteristic cyclopentadienyl proton resonances. After 6 hours of photolysis, no changes in the ^1H NMR spectra were observed. In a separate experiment, **4** was photolyzed in $CDCl_3$ and in benzene-d_6 for 24 hours at 300 nm with no change in the ^1H NMR spectra of the cyclopentadienyl protons.

Crystal structure data for 6: ansa-*(2,3-dimethyl-2,3-butano)*-anti-*3,3′-bis(1,1-dimethylethyl)cyclopenta-1,3-dien-5-yl)titanium 1,1′-bi-2-naphtholate*

A summary of the key crystal data and parameters for the data collection for **6** (solvated and unsolvated forms) are given in Table 3. X-ray quality crystals of **6**

Table 3

Crystal data and collection parameters for **6**

	Solvated	Unsolvated
Formula	$TiC_{44}H_{48}O_2 \cdot 1/2C_6H_{14}$	$TiC_{44}H_{48}O_2$
M_r, g mol^{-1}	699.9	656.8
System	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	10.187(9)	10.084(2)
b, Å	12.421(3)	29.312(7)
c, Å	16.752(3)	12.190(2)
α, deg	82.54(2)	–
β, deg	76.62(4)	99.37(2)
γ, deg	69.19(4)	–
V, Å^3	1925(2)	3555(2)
Z	2	4
D_c, g/cm^{-3}	1.207	1.227
Cryst. size, mm	$0.1 \times 0.22 \times 0.30$	$0.28 \times 0.35 \times 0.40$
Radiation (graphite monochromated)	Mo-K_α ($\lambda = 0.71073$ Å)	Mo-K_α ($\lambda = 0.71073$ Å)
μ, cm^{-1}	2.5	2.7
Temp, K	296	295
Scan type	ω–2θ	ω–2θ
Collection range, deg	$2\theta = 2$–45	$2\theta = 2$–50
No. of unique data	5005	6237
No. of obsd data	3256 for $I > 1\sigma(I)$	4153 for $I > 2\sigma(I)$
p	0.02	0.02
No. of variables	452	425
R	0.071	0.044
R_w	0.059	0.046
Goodness of fit	1.595	1.623

were obtained as red plates (unsolvated) from refluxing toluene and orange plates (solvate) from a refluxing 25 : 75 hexane : toluene mixture. Intensity data were obtained from a red crystal mounted in random orientation on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined by a least-squares fit to setting angles of 25 reflections having $22 > 2\theta > 20°$. The θ values were derived from measurements at $\pm 2\theta$. One quadrant of data having $2 < 2\theta < 50°$, $0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 34$, $-14 \leqslant l \leqslant 14$ was measured using graphite-monochromated Mo-K_α radiation. The ω–2θ scans were made at speeds ranging from 0.91 to 4.0° min^{-1} to measure all significant data with approximately equal precision. Three standard reflections measured every 10,000 s of exposure time, exhibited only random fluctuations in intensity during data collection. Data reduction included corrections for background, Lorentz, and polarization. Absorption corrections were based on ψ scans, with minimum relative transmission coefficient 96.5%.

The space group was determined by systematic absences. The structure was solved by direct methods and refined by full-matrix least-squares based upon F, with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Determination Package* [19], scattering factors of Cromer and Waber [20], anomalous coefficients of Cromer [21], and 4153 data having $I > 2\sigma(I)$. Non-H atoms were refined anisotropically; the H atoms were located by difference maps and are not

refined. The largest shift was less than 0.01σ in the final cycle, maximum residual density 0.21, minimum -0.30 e $Å^{-3}$. A secondary extinction coefficient refined to a value of $1.71(11) \times 10^{-7}$. Atomic coordinates, bond angles, hydrogen atom coordinates, and anisotropic parameters of the unsolvated crystal are available as supplementary material *.

Analogous structure refinement of $\mathbf{6} \cdot 1/2C_6H_{14}$ was performed. Atomic coordinates for $\mathbf{6} \cdot 1/2C_6H_{14}$ are available as supplementary material *. The hydrogens were not refined and the hexane H's ignored. The largest shift was less than 0.01σ in the final cycle, maximum residual density 0.34, minimum -0.29 e $Å^{-3}$. A secondary extinction coefficient refined to a value of $3.2(3) \times 10^{-7}$.

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* Detailed structural data are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW (UK), on quoting the full journal citation.