Reductive dehydroxy coupling of 2-(hydroxymethyl)indenes to prepare ethano-bridged bis(2-indenyl) *ansa*-titanocenes

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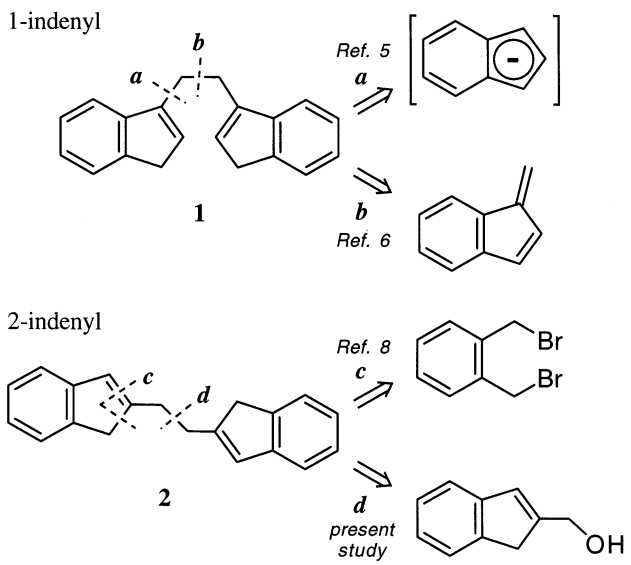
Abstract

New examples of *ansa*-titanocenes derived from 1,2-bis(2-indenyl)ethane have been prepared. The titanium-mediated reductive coupling of 2-(hydroxymethyl)indenes provided a convenient method for substrate dimerization. Alkyl substitution of the indene ring at C(3) improved the regioselectivity of the reductive coupling to provide the ethylene bis(2-indenyl)*ansa*-ligands in 29–62% yield.

1. Introduction

Chiral *ansa*-titanocenes have shown promise as homogeneous catalysts for various organic transformations including alkene epoxidation and hydrogenation [1]. The field has primarily featured *ansa*-titanocenes based on 1,2-bis(1-indenyl)ethane (**1**, Scheme 1, [2]). We have examined the reactivity of *ansa*-titanocenes derived from structurally isomeric 1,2-bis(2-indenyl)ethane (**2**) and observed that these systems also are capable of catalytic reactivity [3]. However, the synthesis of chiral bis(2-indenyl) *ansa*-titanocenes poses a greater synthetic challenge due to the intrinsic inactivity of the indenyl C(2) position [4]. Examination of the approaches used to synthesize ethano-bridged indenyl *ansa*-ligands illustrates the difference in ease of preparation (Scheme 1). Two straightforward strategies, depicted by the key retrosynthetic considerations *a* and *b*, have been used to prepare 1,2-bis(1-indenyl)ethane and its derivatives. The direct alkylation of an indenyl anion with a 1,2-dihaloethane [5] (route *a*) and the metal-mediated coupling reaction of benzofulvene [6,7] (route *b*)



Scheme 1. General approaches to ethano-bridged bis(indenyl) systems.

Table 1
Results of Ti-mediated coupling reactions (Eq. (1))

Alcohol	R^1	R^2	Yield %[a] (**4**+**5**)	Ratio[b] **4**:**5**
3a	H	H	36	1:1
3b	CH_3	H	36	1:1
3c	H	*i*-Bu	35	6:1
3d	H	*i*-Pr	33	8.3:1
3e	H	Bn	44	Only **4e**
3f	H	$SiMe_3$[c]	25	Only **4f**
3g	H	Ph	82	3.2:1

[a] Isolated.
[b] Determined by ^{1}H-NMR.
[c] R^2 on C(1), see structure, Scheme 2.

have provided convenient access to bis(1-indenyl) *ansa*-ligands. These methods, however, cannot be employed with ease to obtain the 1,2-bis(2-indenyl)ethane framework due to the inactivity of the C(2) position.

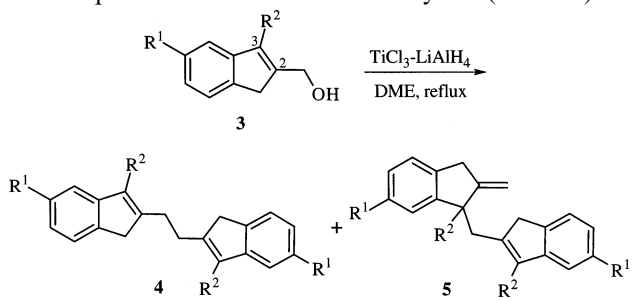
To date, ethano-bridged 2-indenyl *ansa*-ligands have been prepared by tetraalkylation of 1,4-bis(phenylsulfonyl)butane using *o*-bis(halomethyl)benzenes (route *c*) [8]. Although expedient, the tetraalkylation approach delivers **2** in optimized yields of only 12–15%. To improve the availability of bis(2-indenyl) *ansa*-ligands, we have examined a new synthesis based on retrosynthetic consideration *d*. We report herein on the reductive dehydroxy coupling of 2-(hydroxymethyl)indenes as a method for synthesis of ethano-bridged bis(2-indenyl) ligands.

2. Results and discussion

We became interested in 2-(hydroxymethyl)indene (**3a**) as a potentially useful precursor of 2-indenyl *ansa*-ligands due to the inherent symmetry of ethano-bridged *ansa*-metallocenes. Disconnection of the bridging carbons suggests a dimerization strategy. The low-valent titanium-mediated reductive coupling of allylic alcohols is known to be an effective means of alkyl dimerization [9]. Thus, we pursued the synthesis and reductive coupling of 2-indenyllic alcohols.

2.1. Ligand syntheses

Initially, we examined the reductive coupling reactions of 2-(hydroxymethyl)indene (**3a**) [10] and a methyl-substituted derivative, **3b**. Treatment of alcohol **3a** with low-valent titanium [9a] in 1,2-dimethoxyethane afforded a 1:1 mixture of the desired coupling product **4a** and the regioisomeric α-coupling product **5a** in 36% combined yield (Eq. (1), Table 1). The isolation of **5a** was not unexpected since the formation of allylic radicals has been postulated to occur on thermal fragmentation of intermediate titanium (II) dialkoxide species [9a]. Diradical coupling of the incipient allylic radicals at either the terminal methylene carbon or indenyl methine carbon accounts for the formation of **4a** and **5a**, respectively. Treatment of **3b** under similar reaction conditions gave identical results, affording a 1:1 mixture of products **4b** and **5b** in 36% yield (Table 1).

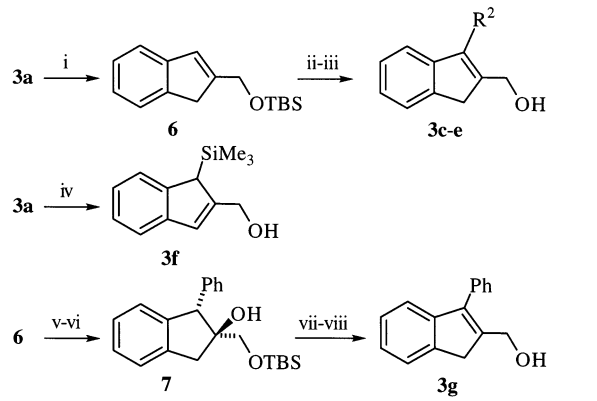


(1)

Substitution at C(3) was examined to minimize formation of the α-coupling products **5**, a strategy that alters only the order of alkylation previously reported for synthesis of C(3)-substituted bis(2-indenyl) *ansa*-ligands [3]. Silyl protection of the hydroxymethyl group of **3a** was followed by treatment with *n*-BuLi and addition of alkyl bromide to effect the alkylation (Scheme 2). Subsequent silyl group removal by treatment with tetrabutylammonium fluoride gave substituted indenes **3c**–**e** [11] in 30–74% overall yield.

Silylation of C(1) was accomplished by treatment of **3a** with two equivalents of *n*-BuLi followed by quenching with excess TMS-Cl. Aqueous work-up and silica gel column chromatography was sufficient for *O*-silyl group removal and gave indene **3f** in 97% yield.

Introduction of a phenyl group onto C(3) was accomplished by regioselective opening of an indenyl C(2)–C(3) epoxide at the benzylic position. This approach was initiated by treatment of **6** with mCPBA in-



Scheme 2. Indene substitution, [i] *tert*-butyldimethylsilyl chloride, Et_3N, CH_2Cl_2, cat. DMAP; [ii] (a) *n*-BuLi, THF, −78°C, (b) R^2Br, 55°C, 12 h; [iii] TBAF, THF; [iv] (a) *n*-BuLi (two equivalents), THF, −78°C, (b) trimethylsilyl chloride; [v] mCPBA, CH_2Cl_2, pH 7 phosphate buffer, 0°C, 8 h; [vi] PhMgBr, CuI, THF, −65 to −20°C, 1 h; [vii] $SOCl_2$, pyridine, 0°C to r.t., 3 h; [viii] DMSO, H_2O, 90°C, 3 h.

Table 2
Substituent effect on complexation diastereoselectivity (Eq. (2))

Bisindene	R^1	R^2	Ratio[a] **8**:**9**
4b	CH_3	H	1:1
4c	H	*i*-Bu	4:1
4d	H	*i*-Pr	2:1
4e	H	Bn	3.6:1[b]
4f	H	$SiMe_3$	–[c]
4g	H	Ph	4.3:1

[a] Determined by ^{1}H-NMR integration.
[b] Complexation ratio from Ref. [3].
[c] No metallocene formation, Ref. [16].

CH_2Cl_2. We observed that the epoxidation was effective only when a pH 7 phosphate buffer was used to prevent decomposition of the acid-sensitive benzylic epoxide [12]. Subsequent exposure of the epoxide to PhMgBr in the presence of catalytic CuI gave alcohol **7**. Elimination of the 3° alcohol was effected by reaction with thionyl chloride in pyridine. The crude elimination product was then heated in aqueous DMSO [13] to remove the silyl protection group. In this manner, indenyl alcohol **3g** was isolated in 31% yield from **3a**.

With the C(3)-substituted 2-(hydroxymethyl)indenes prepared, we examined their titanium-mediated reductive dehydroxy coupling using the conditions that were optimal for the coupling of **3a**. The reactions of the C(3)-substituted substrates afforded 1,2-bis(2-indenyl)ethane derivatives **4** with greater regioselectivity than the coupling of unsubstituted indenes (Table 1). The formation of less amounts of the α-coupled products **5** is consistent with the expectation that C(3)-substitution might deter reaction at the more hindered center. Substitution of C(3) with phenyl (e.g. **3g**) greatly improved the overall yield of the coupling reaction presumably due to greater stabilization of the radical intermediates. However, the regioselectivity of the coupling reaction in this case was somewhat diminished relative to the other C(3)-substituted examples.

2.2. Ligand complexation

Preparation of the corresponding *ansa*-titanocene complexes **8** and **9** from bis-indenes **4** was accomplished using a literature procedure [3]. Treatment of the corresponding dianions of **4** with $TiCl_3{\cdot}(thf)_3$ [14] was followed by oxidative work-up and immediate catalytic hydrogenation of the crude reaction mixture. Mixtures of racemic and *meso* bis(tetrahydroindenyl) *ansa*-titanocenes were obtained in varying ratios (Table 2). Previous complexation studies suggested a relationship between the size of the substituent proximal to the ethylene bridge and the diastereomeric (racemic:*meso*) ratio [3,15]. The observation that a sterically more demanding α-substituent slightly favors formation of the racemic isomer is supported by the new examples. Assignments of configuration were based on X-ray crystallographic analyses of recrystallized products obtained from **4b**–**d** (Figs. 1–3).

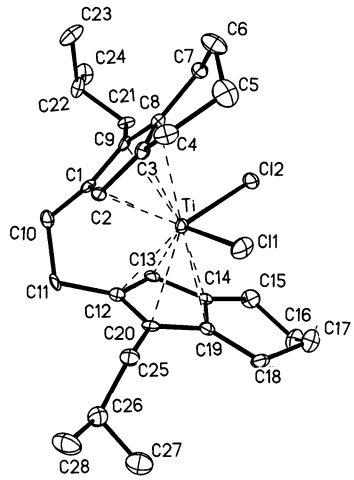
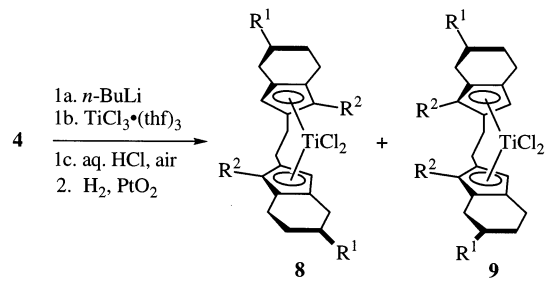


Fig. 1. Molecular structure of compound **8c** with 50% probability ellipsoids depicted and the H atoms removed for clarity.



(2)

The determination of diastereoselectivity in the complexation of **4e** was made by spectral comparison of the crude hydrogenation mixture to a reference sample of

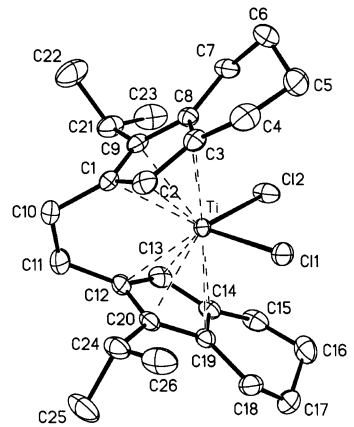


Fig. 2. Molecular structure of compound **8d** with 50% probability ellipsoids depicted and the H atoms removed for clarity.

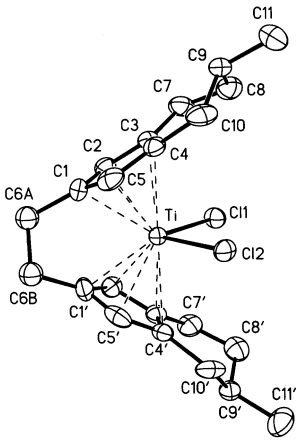


Fig. 3. Molecular structure of compound **9b** with 20% probability ellipsoids depicted and the H atoms removed for clarity.

the racemic benzyl-substituted (2-tetrahydroindenyl) *ansa*-titanocene [17].

The largest diastereoselectivity on titanium complexation was observed with phenyl-substituted bis-indene **4g**, affording a 4.3:1 preference for the racemic isomer **8g** (Table 2, [18]). Attempts to isolate **8g** by recrystallization from the hydrogenation reaction mixture were unsuccessful. The stereochemical assignment for **8g** is based on the ^{1}H-NMR spectrum observed for the crude complexation mixture prior to hydrogenation. Collins [15] has previously noted that the *meso* isomers of α-substituted ethylene-bridged *ansa*-titanocenes exhibit a compact 4H multiplet corresponding to the ethylene bridge. The racemic isomers exhibit a distinctly separate pair of 2H multiplets for the ethylene bridge [19]. The major *ansa*-titanocene that is formed on complexation of **4g** exhibits a pair of 2H multiplets at δ 3.12 and 2.44, thus suggesting the assignment of **8g** as the major isomer.

2.3. X-ray structures of ansa-titanocenes **8c-d** and **9b**

Crystal data for the three structures are given in Table 3 and selected bond lengths and angles are given in Tables 4–6. All structures were solved by direct methods (SHELXS [20]) and refined by full-matrix least squares based on F^2 (SHELXL-97 [21]); empirical absorption corrections (XABS2 [22]) were performed. For **9b**, there was disorder in the ethylene portion of the ligand. Two positions were used to model this carbon (the other is generated by a mirror plane). A chirality test on **8c** was performed and the flack parameter was refined to the value 0.078 (11), indicating the correct sense of chirality as depicted.

Table 3
Crystal data for **8c**, **8d**, and **9b**

	8c	**8d**	**9b**
Empirical formula	$C_{28}H_{40}Cl_2Ti$	$C_{26}H_{36}Cl_2Ti$	$C_{22}H_{28}Cl_2Ti$
Formula weight	495.40	467.35	411.24
Color and habit	Red needle	Red plate	Red parallelepiped
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/n$	*Pnma*
Unit cell dimensions			
a (Å)	8.6851(9)	8.377(2)	13.724(2)
b (Å)	10.875(2)	19.751(4)	19.891(4)
c (Å)	26.808(2)	13.839(3)	7.4166(9)
β (°)		93.79(2)	
V (Å^3)	2532.1(5)	2284.7(9)	2024.6(5)
Temperature (K)	130(2)	130(2)	293(2)
Z	4	4	4
Crystal size (mm)	$0.07\times0.11\times0.37$	$0.12\times0.50\times0.60$	$0.16\times0.20\times0.24$
$D_{calc.}$ (g cm^{-3})	1.300	1.359	1.349
Radiation (Å)	Cu–K$_\alpha$ ($\lambda = 1.54178$	Mo–K$_\alpha$ ($\lambda = 0.71069$)	Mo–K$_\alpha$ ($\lambda = 0.71069$)
μ(Mo–K$_\alpha$) (mm^{-1})	4.885	0.619	0.689
Range of trans. factors	0.59–0.76	0.73–0.94	0.86–0.91
Diffractometer	Syntex P21	Siemens R3m/V	Siemens R3m/V
Index ranges	$-2\le h\le10,\ -2\le k\le11,\ -4\le l\le29$	$-10\le h\le10,\ 0\le h\le25,\ 0\le h\le17$	$0\le h\le17,\ 0\le h\le25, 0\le h\le9$
Θ range (°)	3.30–57.08	1.80–27.50	2.05–27.49
Reflections collected	3751	5757	2385
Independent reflections	2916 [$R_{int} = 0.025$]	5250 [$R_{int} = 0.022$]	2385
Number of data refined	2916	5249	2385
Number of parameters refined	284	266	117
wR_2[a] (all data)	0.0874	0.1009	0.2285
$R1$[b] [$I>2\sigma(I)$]	0.0386	0.0412	0.0705

[a] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[(wF_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$.
[b] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

Table 4
Selected bond lengths and angles for titanocene **8c**[a]

Bond lengths (Å)			
Ti(1)–Cl(1)	2.0303	Ti(1)–C(12)	2.372
Ti(1)–Cl(2)	2.3475	Ti(1)–C(20)	2.427
Ti(1)–C(1)	2.372	Ti(1)–C(19)	2.515
Ti(1)–C(2)	2.342	C(12)–C(20)	1.410
Ti(1)–C(3)	2.487	C(19)–C(20)	1.440
C(1)–C(2)	1.430	C(18)–C(19)	1.502
C(2)–C(3)	1.432	C(17)–C(18)	1.519
C(3)–C(4)	1.494	C(16)–C(17)	1.527
C(4)–C(5)	1.536	CentA–Ti	2.115
C(5)–C(6)	1.503	CentB–Ti	2.111
Bond angles (°)			
Cl(1)–Ti(1)–Cl(2)	96.70	C(6)–C(5)–C(4)	112.2
C(9)–C(1)–C(2)	107.1	C(8)–C(9)–C(21)	125.4
C(1)–C(9)–C(8)	108.4	C(1)–C(10)–C(11)	108.9
C(8)–C(3)–C(4)	123.9	CentA-Ti-CentB	129.7

[a] CentA and CentB are the two centroids of the η5-coordinated cyclopentadienyl rings.

In summary, we have improved the access to derivatives of 1,2-bis(2-indenyl)ethane. Our approach relies on a titanium-mediated reductive dehydroxy coupling of C(3)-substituted 2-(hydroxymethyl)indenes as the key step. Application of this methodology has provided new chiral, α-substituted *ansa*-titanocenes that may find use in catalytic applications.

3. Experimental

Reactions were carried out under argon atmosphere using standard Schlenk techniques. THF and Et_2O were distilled from Na-benzophenone ketyl immediately prior to use. 1,2-Dimethoxyethane was distilled from $LiAlH_4$. DMF was distilled from $MgSO_4$. All reaction and work-up solvents were removed by rotary evaporation unless otherwise indicated. All column chromatography was performed using silica gel purchased from EM Separations Technology (230–400 mesh). NMR spectra were recorded on a General Electric QE-300 spectrometer. IR spectra were recorded as $CHCl_3$ solutions on a Mattson FTIR 3000 spectrometer. Melting points are uncorrected. Mass spectral analyses were performed by the University of Minnesota Mass Spectrometry Service Laboratory.

Table 5
Selected bond lengths and angles for titanocene **8d**[a]

Bond lengths (Å)			
Ti(1)–Cl(1)	2.3307	Ti(1)–C(12)	2.382
Ti(1)–Cl(2)	2.3426	Ti(1)–C(20)	2.431
Ti(1)–C(1)	2.385	Ti(1)–C(19)	2.525
Ti(1)–C(2)	2.342	C(12)–C(20)	1.428
Ti(1)–C(3)	2.468	C(19)–C(20)	1.430
C(1)–C(2)	1.401	C(18)–C(19)	1.505
C(2)–C(3)	1.415	C(17)–C(18)	1.538
C(3)–C(4)	1.491	C(16)–C(17)	1.514
C(4)–C(5)	1.509	CentA–Ti	2.116
C(5)–C(6)	1.515	CentB–Ti	2.111
Bond angles (°)			
Cl(1)–Ti(1)–Cl(2)	92.48	C(6)–C(5)–C(4)	111.1
C(9)–C(1)–C(2)	108.3	C(8)–C(9)–C(21)	127.9
C(1)–C(9)–C(8)	107.0	C(1)–C(10)–C(11)	111.3
C(8)–C(3)–C(4)	123.6	CentA–Ti–CentB	129.2

[a] CentA and CentB are the two centroids of the η5–coordinated cyclopentadienyl rings.

Table 6
Selected bond lengths and angles for titanocene **9b**[a]

Bond *lengths* (Å)			
Ti(1)–Cl(1)	2.334	Ti(1)–C(1′)	2.350
Ti(1)–Cl(2)	2.341	Ti(1)–C(5′)	2.361
Ti(1)–C(1)	2.350	Ti(1)–C(4′)	2.482
Ti(1)–C(5)	2.361	C(9)–C(10)	1.553
Ti(1)–C(4)	2.482	C(8)–C(9)	1.468
C(1)–C(5)	1.417	C(1)–C(6A)	1.576
C(4)–C(5)	1.402	CentA–Ti	2.092
C(4)–C(10)	1.550	CentB–Ti	2.092
Bond angles (°)			
Cl(1)–Ti(1)–Cl(2)	94.96	C(8)–C(9)–C(10)	110.7
C(5)–C(1)–C(2)	105.1	C(4)–C(10)–C(9)	109.4
C(3)–C(4)–C(5)	107.0	C(1)–C(6A)–C(6B)	104.1
C(4)–C(5)–C(1)	109.3	CentA–Ti–CentB	129.9

[a] CentA and CentB are the two centroids of the η5-coordinated cyclopentadienyl rings.

3.1. 2-(Hydroxymethyl)-5-methylindene (**3b**)

To a stirred solution of methyl phenylsulfonylacetate (12.5 g, 58.4 mmol) in DMF (90 ml) at 0°C, was added in one portion LiH (1.40 g, 175.2 mmol). After stirring for 2 h, 3,4-bis(chloromethyl)toluene (11.7 g, 61.9 mmol) was added and the reaction mixture was allowed to warm to room temperature (r.t.). The reaction was recooled to 0°C after 48 h, quenched by careful addition of saturated aqueous NH_4Cl, and then diluted with CH_2Cl_2 (200 ml) and H_2O (150 ml). The layers were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extract was washed with water, saturated brine, and dried (Na_2SO_4). The solvents were removed by rotary evaporation to afford the crude product. Recrystallization of the residue from methanol gave 15.5 g (80%) of 2-carbomethoxy-2-phenylsulfonyl-5-methylindan as a white solid, m.p. 113–114°C; IR ($CHCl_3$): 3029, 1735, 1320, 1258, 1146 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.29 (s, 3H), 3.64 (d, $J = 17.4$ Hz, 2H), 3.67 (s, 3H), 3.80 (d, $J = 16.8$ Hz, 2H), 7.02 (m, 3H), 7.54 (app. t, $J = 7.8$ Hz, 2H), 7.65 (app. t, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 7.5$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): δ 21.1, 38.0, 38.2, 53.4, 79.1, 123.8, 124.7, 128.1, 128.7, 129.7, 134.1, 135.3, 137.0, 138.5, 168.5. HRMS (EI) Calc. for $C_{18}H_{18}O_4S$: 330.0926. Found: 330.0927.

To a stirred solution of 2-carbomethoxy–2-phenylsulfonyl-5-methylindan (10.6 g, 32.2 mmol) in THF (110 ml) at −50°C was added a solution of KO*t*-Bu (90 ml, 1.45 M in THF, 130.5 mmol). On complete addition, the reaction mixture was stirred for 10 min and then quenched by addition of saturated aqueous NH_4Cl (200 ml). The quenched reaction was diluted with EtOAc and the layers were separated. The aqueous layer was extracted with EtOAc. The combined organic extract was washed with H_2O, saturated brine, and dried (Na_2SO_4). Removal of the solvents afforded the crude product as a 2:1 mixture of methyl and *tert*-butyl esters. ^{1}H-NMR ($CDCl_3$): δ 1.56 (s, 9H), 2.41 (s, 6H), 3.59 (br s, 2H), 3.64 (br s, 2H), 3.84 (s, 3H), 7.21–7.31 (m, 8H).

The crude mixture was dissolved in Et_2O (160 ml) and cooled to −78°C. To the solution diisobutylaluminum hydride was added dropwise (100 ml of a 1.0 M solution in hexane, 100 mmol). The reaction was allowed to warm to r.t. and stirred for 12 h. The reaction was quenched by slowly pouring the reaction mixture into an Erlenmeyer flask containing a vigorously stirred solution of 3 M NaOH (200 ml). The layers were separated and the aqueous phase was extracted with additional portions of Et_2O. The combined organic extract was washed with 10% HCl, saturated brine and dried ($MgSO_4$). Removal of the solvents by rotary evaporation afforded 5.03 g (97%) of **3b** as an inseparable mixture of isomers, m.p. 60–61°C; IR ($CHCl_3$): 3331, 2912, 2859, 1031 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.38 (br s, 3H), 3.39 (br s, 2H), 4.57 (br s, 2H), 6.71 (br s, 1H), 7.15–7.25 (m, 3H); ^{13}C-NMR ($CDCl_3$): δ 21.3, 38.4, 38.7, 61.7, 120.4, 121.5, 123.31, 124.6, 125.3, 127.0, 127.4, 134.1, 135.9, 140.3, 141.9, 143.7, 144.8, 147.6, 148.9; HRMS (EI) Calc. for $C_{11}H_{12}O$: 160.0888. Found: 160.0881.

3.2. 2-(*tert*-Butyldimethylsilyloxymethyl)indene (**6**)

To a solution of 2-(hydroxymethyl)indene (10.0 g, 68.4 mmol) in CH_2Cl_2 (250 ml) at r.t., Et_3N (14.3 ml, 103 mmol), DMAP (1.0 g, 6.8 mmol) and *tert*-butyldimethylsilyl chloride (11.3 g, 75.2 mmol) were added sequentially. After stirring for 2 h, the reaction mixture was cooled to 0°C and quenched by addition of saturated aqueous NH_4Cl. The layers were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extract was washed with water, saturated brine, and dried (Na_2SO_4). The solvents were removed and the residue was passed through a short column of silica, eluting with 3:1 hexane:ethyl acetate, to afford 16.9 g (95%) of **6** as a yellow solid; m.p. 35–36°C; IR ($CHCl_3$): 3059, 2955, 1471, 1097, 836 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.14 (s, 6H), 0.98 (s, 9H), 3.37 (s, 2H), 4.61 (s, 2H), 6.71 (s, 1H), 7.15–7.43 (m, 4H); ^{13}C-NMR ($CDCl_3$): δ −5.3, 18.4, 25.9, 38.7, 62.2, 120.6, 123.6, 124.1, 126.2, 126.6, 143.2, 144.9, 149.3; HRMS (EI) Calc. for $C_{16}H_{24}OSi$: 260.1596. Found: 260.1597.

3.3. 2-(*tert*-Butyldimethylsilyloxymethyl)-1-phenylindan-2-ol (**7**)

To a solution of 2-(*tert*-butyldimethylsilyloxymethyl)indene (107 mg, 0.411 mmol) in CH_2Cl_2 (6.9 ml), a phosphate buffer (6.9 ml, pH 7, 0.05 M in both KH_2PO_4 and Na_2HPO_4) was added. To the biphasic mixture at 0°C was added 'acid free' *m*-CPBA [23] (78 mg, 0.452 mmol) in one portion. After 8 h the reaction mixture was poured into a 1:1 mixture of saturated aqueous $NaHCO_3$ (20 ml) and saturated aqueous $Na_2S_2O_3$ (20 ml) and extracted with CH_2Cl_2 three times. The combined organic extract was dried over Na_2SO_4, and the solvents were removed under reduced pressure to afford the crude epoxide. ^{1}H-NMR ($CDCl_3$): δ 0.11 (s, 3H), 0.12 (s, 3H), 0.93 (s, 9H), 3.08 (d, $J = 17.7$ Hz, 1H), 3.16 (d, $J = 17.9$ Hz, 1H), 4.01 (d, $J = 11.7$ Hz, 1H), 4.11 (d, $J = 11.7$ Hz, 1H), 4.17 (d, $J = 0.74$ Hz, 1H), 7.15–7.26 (m, 3H), 7.46 (d, $J = 7.2$ Hz, 1H).

To a suspension of CuI in THF (3 ml) at −40°C, PhMgBr (411 ml, 3.0 M solution in Et_2O, 1.23 mmol) was added. After stirring for 15 min the reaction was cooled to −65°C and a solution of the crude epoxide in THF (1 ml) was added dropwise via cannula. The reaction was warmed to −20°C over 50 min in which time the reaction was quenched with a saturated aqueous solution of NH_4Cl and diluted with Et_2O. The organic layer was washed with water, saturated brine, and dried over Na_2SO_4. The solvents were removed and the residue was purified by chromatography, eluting with 2% ethyl acetate/hexane on SiO_2, to afford 119 mg (82%) of alcohol **7** as a colorless oil. IR (neat) 3563, 3466, 3064, 3027, 1602, 1558, 1494, 1089, 1079 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.01 (s, 3H), 0.04 (s, 3H), 0.97 (s, 9H), 3.07 (d, $J = 16.2$ Hz, 1H), 3.24, (s, 1H), 3.26 (d, $J = 16.4$ Hz, 1H), 3.32 (d, $J = 9.7$ Hz, 1H), 3.40 (d, $J = 9.7$ Hz, 1H), 4.54 (s, 1H), 7.13–7.39 (m, 9H); ^{13}C-NMR ($CDCl_3$): δ −5.7, −5.6, 18.1, 25.8, 42.8, 61.2, 66.9, 84.2, 124.7, 125.5, 126.6, 126.8, 127.0, 128.1, 129.0, 139.8, 140.9, 144.5; HRMS (EI) Calc. for $C_{22}H_{30}O_2Si$: 354.2015. Found: 354.2016.

3.4. 2-(Hydroxymethyl)-3-(2-methylpropyl)indene (**3c**)

To a solution of silyl ether **6** (4.0 g, 15.4 mmol) in THF (75 ml) at −78°C, *n*-BuLi (5.0 ml of a 2.5 M solution in hexanes, 17.5 mmol) was added dropwise. After stirring for 1 h, 1-bromo-2-methylpropane (2.5 ml, 23.1 mmol) and tetrabutylammonium iodide (1.14 g, 3.08 mmol) were added and the reaction mixture was

warmed gradually to r.t. and followed by stirring at 55°C for 12 h. The solution was then cooled to 0°C and quenched by addition of saturated aqueous NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic extract was washed with water, saturated brine, and dried (Na_2SO_4). The solvents were removed and the residue was dissolved in THF (100 ml) and then treated at r.t. with *tert*-butylammonium fluoride (46.2 ml of a 1 M solution in THF, 46.2 mmol). After stirring for 30 min, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic extract was washed with water, saturated brine, and dried (Na_2SO_4). The solvents were removed and the crude product was purified by chromatography, eluting with 5:1 hexane:ethyl acetate, to afford 1.49 g (48%) of alcohol **3c** as a yellow oil. IR ($CHCl_3$): 3363, 3019, 2945, 1460 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.93 (d, $J = 6$ Hz, 6H), 1.90–1.97 (m, 1H), 2.42 (d, $J = 6$ Hz, 2H), 3.46 (s, 2H), 4.51 (s, 2H), 7.14–7.32 (m, 3H), 7.41 (d, $J = 7.2$ Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 22.8, 28.0, 34.6, 38.9, 59.0, 119.6, 123.6, 124.6, 126.0, 139.2, 141.1, 143.0, 146.0; HRMS (EI) Calc. for $C_{14}H_{18}O$: 202.1358. Found: 202.1347.

3.5. 2-(Hydroxymethyl)-3-(1-methylethyl)indene (3d)

The preparation of 2-(hydroxymethyl)-3-(1-methylethyl)indene (**3d**) was accomplished according to the procedure described for the preparation **3c**: 2.0 g of **6** (7.68 mmol), and 0.96 ml of 2-iodopropane (9.6 mmol) were reacted to afford **3d** as a yellow oil (0.38 g, 26%). IR ($CHCl_3$): 3370, 2930, 1461 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.22 (d, $J = 6$ Hz, 6H), 3.01–3.10 (m, 1H), 3.26 (s, 2H), 4.38 (s, 2H), 7.03 (t, $J = 7.2$ Hz, 1H), 7.14 (t, $J = 6.6$ Hz, 1H), 7.27 (d, $J = 7.2$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 21.3, 26.6, 39.2, 58.6, 120.9, 123.7, 124.2, 125.6, 138.9, 143.5, 144.4, 145.0; HRMS (EI) Calc. for $C_{13}H_{16}O$: 188.1201. Found: 188.1197.

3.6. 3-Benzyl-2-(hydroxymethyl)indene (3e)

The preparation of 3-benzyl-2-(hydroxymethyl)indene (**3e**) was accomplished according to the procedure described for the preparation of **3c**: 0.86 g of **6** (3.31 mmol), and 0.59 ml of benzylbromide (4.97 mmol) were reacted to afford **3e** as a yellow solid (0.58 g, 74%). m.p. 87–88°C; IR ($CHCl_3$): 3339, 3061, 2915, 1601, 1494 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 3.57 (s, 2H), 3.98 (s, 2H), 4.63 (s, 2H), 7.17–7.44 (m, 8H), 7.45 (app. d, $J = 6.9$ Hz, 1H); ^{13}C-NMR ($CDCl_3$): δ 31.1, 39.1, 58.7, 119.8, 123.5, 124.7, 126.0, 126.1, 128.2, 128.4, 137.8, 139.3, 141.9, 142.9, 145.5; HRMS (EI) Calc. for $C_{17}H_{16}O$: 236.1201. Found: 236.1209.

3.7. 1-Trimethylsilyl-2-(hydroxymethyl)indene (3f)

To a solution of 2-(hydroxymethyl)indene (0.25 g, 1.71 mmol) in THF (5 ml) at 0°C, *n*-BuLi (1.40 ml of a 2.5 M solution in hexanes, 3.51 mmol) was added dropwise. After stirring at 0°C for 0.5 h and at r.t. for 0.5 h, the reaction mixture was recooled to 0°C and chlorotrimethylsilane (0.50 ml, 3.68 mmol) was added. The reaction mixture was gradually warmed to r.t. and stirred for 12 h. The solution was then cooled to 0°C and quenched by addition of saturated aqueous $NaHCO_3$. The layers were separated and the aqueous phase was extracted with EtOAc. The combined organic extract was washed with water, saturated brine, and dried ($MgSO_4$). The solvents were removed and the crude product was purified by chromatography, eluting with 5:1 hexane:ethyl acetate, to afford 0.36 g (97%) of alcohol **3f** as a yellow oil. IR ($CHCl_3$): 3335, 2952, 1457, 838 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ -0.07 (s, 9H), 3.50 (s, 1H), 4.48 (dd, $J = 15.3$, 1.0 Hz, 1 H), 4.58 (dd, $J = 15.3$, 1.0 Hz, 1 H), 6.74 (d, $J = 1.0$ Hz, 1 H), 7.06–7.17 (m, 2 H), 7.30–7.33 (app. d, $J = 8.7$ Hz, 2 H); ^{13}C-NMR ($CDCl_3$): δ -2.1, 46.3, 62.2, 120.8, 123.1, 123.2, 125.1, 125.7, 144.0, 145.6, 151.0; HRMS (EI) Calc. for $C_{13}H_{18}OSi$: 218.1127. Found: 218.1127.

3.8. 2-(Hydroxymethyl)-3-phenylindene (3g)

To a solution of 2-(*tert*-butyldimethylsilyloxymethyl)-1-phenylindan-2-ol (1.0 g, 2.8 mmol) in pyridine (28 ml) at 0°C, $SOCl_2$ (327 ml, 4.48 mmol) was added dropwise via syringe. The reaction was stirred 2 h at 0°C and then 30 min at r.t. The reaction was quenched by addition of saturated aqueous NH_4Cl and then diluted with Et_2O. The Et_2O layer was washed three times with saturated aqueous $CuSO_4$ and followed by washing with water. The combined aqueous layers were extracted with Et_2O. The combined Et_2O layers were washed with saturated brine and dried over Na_2SO_4. Removal of the solvents under reduced pressure afforded the crude silyloxy indene [^{1}H-NMR ($CDCl_3$): δ 0.07 (s, 6H), 0.94 (s, 9H), 3.68 (s, 2H), 4.64 (s, 2H), 7.13–7.55 (m, 9H)], which was dissolved in a 5:1 mixture of DMSO:water (16.8 ml) and heated to 90°C. After 3 h the reaction was poured into water and extracted with Et_2O. The combined organic layers were washed with water, saturated brine, and dried (Na_2SO_4). The solvents were removed and the residue was purified by chromatography, eluting with 20% ethyl acetate/hexane on aluminum oxide (activated, basic, Brockmann 1), to afford 243 mg (39%) of alcohol **3g** as a beige solid, m.p. 100–101°C; IR (powder): 3362, 3280, 2952, 1492, 1460, 1444 cm − 1; ^{1}H-NMR ($CDCl_3$): δ 1.46 (t, $J = 5.72$ Hz, 1H), 3.68 (s, 2H), 4.58 (d, $J = 6.35$ Hz, 2H), 7.20–7.53 (m, 9H); ^{13}C-NMR ($CDCl_3$): δ 39.5, 59.5, 120.5, 123.8, 125.1, 126.3, 127.6,

128.5, 129.1, 134.7, 141.3, 142.4, 143.0, 145.6; HRMS (EI) Calc. for $C_{16}H_{14}O$: 222.1045. Found: 222.1045.

3.9. 1,2-Bis(2-indenyl)ethane (**4a**)

To a stirred solution of $TiCl_3$ (1.6 g, 10.3 mmol) in 1,2-dimethoxyethane at 0°C, $LiAlH_4$ (0.13 g, 3.42 mmol) was added in one portion. After stirring for 15 min, a solution of **3a** (0.5 g, 3.42 mmol) in 1,2-dimethoxyethane was cannulated into the resultant black reaction mixture. After gradual warming to r.t., the reaction mixture was refluxed for 16 h. The solution was then cooled to 0°C and quenched by addition of 1 M HCl. The layers were separated and the aqueous phase was extracted with EtOAc. The combined organic extract was washed with water, saturated brine, and dried (Na_2SO_4). The solvents were removed and the crude product was purified by chromatography, eluting with hexane to afford 0.079 g (18%) of **4a** and 0.078 g (18%) of **5a**. [Note: purification problems were encountered when polar solvents such as CH_2Cl_2 were used during chromatography. For best results, a solution of the crude product is added to a small amount of silica and the suspension is evaporated to dryness. The dry impregnated silica is then added to the top of a silica gel chromatography column and eluted with hexane].

Compound **5a**: m.p. 55–56°C; IR ($CHCl_3$): 3068, 1653, 1609, 1478 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.84 (app. d, $J = 6.6$ Hz, 2H), 3.17 (br s, 2H), 3.57 (br s, 2H), 3.95 (m, 1H), 5.00 (d, $J = 1.8$ Hz, 1H), 5.05 (d, $J = 1.8$ Hz, 1H), 6.41 (s, 1H), 6.99–7.28 (m, 8H); ^{13}C-NMR ($CDCl_3$): δ 37.9, 38.6, 41.7, 49.1, 108.2, 120.1, 123.4, 123.7, 124.3, 124.4, 126.2, 126.4, 126.8, 128.7, 141.4, 143.3, 145.4, 145.6, 147.7, 152.3; HRMS (EI) Calc. for $C_{20}H_{18}$: 258.1408. Found: 258.1402.

3.10. 1,2-Bis[(5-methyl)-2-indenyl)]ethane (**4b**)

The preparation of **4b** was accomplished according to the procedure described for preparation of **4a**: 1.0 g of **3b** (6.24 mmol) was treated with $TiCl_3$ to afford **4b** as a mixture with **5b**.

Compound **4b**: white solid (0.16 g, 18%); m.p. 130–131°C; IR ($CHCl_3$): 2923, 2900, 1603, 878 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.48 (s, 6H), 2.96 (s, 4H), 3.39 (s, 4H), 6.61 (s, 2H), 6.96–7.34 (m, 6H); ^{13}C-NMR ($CDCl_3$): δ 21.4, 30.7, 40.7, 40.9, 104.9, 119.6, 120.8, 123.1, 124.4, 126.3, 126.5, 126.9; HRMS (EI) Calc. for $C_{22}H_{22}$: 286.1721. Found: 286.1726.

Compound **5b**: yellow oil (0.17 g, 18%); IR ($CHCl_3$): 3007, 2918, 1616, 805 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.20 (br s, 3H), 2.25 (br s, 3H), 2.78 (br s, 2H), 3.08 (br s, 2H), 3.50 (br s, 2H), 3.86 (br s, 1H), 4.94 (br s, 1H), 5.01 (br s, 1H), 6.34 (br s, 1H), 6.84–7.19 (m, 6H); ^{13}C-NMR ($CDCl_3$): δ 21.5, 37.6, 37.8, 38.0, 38.1, 38.3, 38.5, 40.9, 41.0, 41.1, 41.2, 48.5, 48.8, 48.9, 107.6,107.7, 107.9, 119.4, 119.5, 119.6, 120.4, 120.4, 120.5, 120.7, 122.7, 122.9, 123.0, 123.2, 123.3, 123.4, 123.5, 123.6, 123.7, 123.9, 124.0, 124.2, 124.3,, 124.5, 124.7, 124.9, 125.0, 125.2,125.3, 125.4; HRMS (EI) Calc. for $C_{22}H_{22}$: 286.1721. Found: 286.1730.

3.11. 1,2-Bis[(3-(2-methylpropyl)-2-indenyl)]ethane (**4c**)

The preparation of **4c** was accomplished according to the procedure described for the preparation of **4a**: 1.20 g of **3c** (5.93 mmol) was treated with $TiCl_3$ to afford a mixture of **4c** and **5c**.

Compound **4c**: white solid (0.33 g, 30%); m.p. 70–73°C; IR ($CHCl_3$): 2951, 1364, 787 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.95 (d, $J = 9$ Hz, 12H), 1.95–2.02 (m, 2H), 2.41 (d, $J = 9$ Hz, 4H), 2.69 (s, 4H), 3.37 (s, 4H), 7.10–7.16 (m, 6H), 7.40 (app. d, $J = 7.2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): δ 23.0, 23.1, 28.1, 29.2, 34.7, 40.1, 118.8, 123.2, 123.6, 126.0, 136.8, 142.5, 142.8, 146.8; HRMS (EI) Calc. for $C_{28}H_{34}$: 370.2660. Found: 370.2660.

Compound **5c**: yellow solid (0.058 g, 5%); m.p. 112–113°C; IR ($CHCl_3$): 3042, 1654, 1465, 882 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.49 (d, $J = 6.6$ Hz, 3H), 0.77 (d, $J = 6.6$ Hz, 3H), 0.85 (d, $J = 6.6$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 3H), 1.42 (m, 1 H), 1.86 (m, 3H), 2.27 (d, $J = 7.2$ Hz, 2H), 2.47 (d, $J = 22.8$ Hz, 1H), 2.70 (d, $J = 22.8$ Hz, 1H), 2.82 (d, $J = 14.4$ Hz, 1H), 2.95 (d, $J = 14.4$ Hz, 1H), 3.46 (d, $J = 21.3$ Hz, 1H), 3.60 (d, $J = 21.3$ Hz, 1H), 5.08 (m, 1H), 5.18 (m, 1H), 6.95–7.19 (m, 8H); ^{13}C-NMR ($CDCl_3$): δ 22.8, 23.2, 24.4, 25.1, 25.3, 28.0, 34.9, 39.2, 41.7, 43.8, 52.2, 56.3, 107.8, 118.8, 122.8, 123.4, 124.2, 124.3, 125.5, 126.4, 126.9, 138.8, 140.4, 141.1, 143.3, 146.3, 148.2, 154.9; HRMS (EI) Calc. for $C_{28}H_{34}$: 370.2660. Found: 370.2661.

3.12. 1,2-Bis[(3-(1-methylethyl)-2-indenyl)]ethane (**4d**)

The preparation of **4d** was accomplished according to the procedure described for the preparation of **4a**: 0.16 g of **3d** (0.82 mmol) was treated with $TiCl_3$ to afford **4d** as a mixture with **5d**.

Compound **4d**: white solid (0.041 g, 29%); m.p. 94–95°C; IR ($CHCl_3$): 2962, 1559, 1457, 766 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.31 (d, $J = 6.9$ Hz, 12H), 2.68 (s, 4H), 3.13 (m, 2H), 3.30 (s, 4H), 7.10 (m, 2H), 7.22 (m, 2H), 7.38 (app. d, $J = 7.5$ Hz, 2H), 7.45 (app. d, $J = 7.5$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): δ 21.1, 26.8, 29.5, 40.7, 120.3, 123.4, 123.5, 125.7, 140.5, 142.7, 143.2, 145.1; HRMS (EI) Calc. for $C_{26}H_{30}$: 342.2347. Found: 342.2345.

Compound **5d**: yellow oil (0.006 g, 4%); IR ($CHCl_3$): 3067, 2961, 1459, 885 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.78 (d, $J = 6.6$ Hz, 3H), 0.81 (d, $J = 6.6$ Hz, 3H), 1.18 (d, $J = 6.9$ Hz, 3H), 1.24 (d, $J = 6.9$ Hz, 3H), 1.92 (m, 1H),

2.38 (d, $J = 22.5$ Hz, 1H), 2.51 (d, $J = 22.5$ Hz, 1H), 3.00 (s, 2H), 3.12 (m, 1H), 3.45 (d, $J = 21.0$ Hz, 1H), 3.57 (d, $J = 21.0$ Hz, 1H), 5.02 (br s, 1H), 5.17 (br s, 1H), 6.87–7.36 (m, 8H); ^{13}C-NMR ($CDCl_3$): δ 17.7, 18.0, 20.8, 21.0, 26.8, 37.6, 40.1, 41.0, 41.7, 58.9, 108.4, 120.5, 123.0, 123.1, 123.5, 124.0, 124.4, 125.1, 126.3, 126.8, 141.4, 143.8, 144.0, 144.3, 147.5, 153.8; HRMS (EI) Calc. for $C_{26}H_{30}$: 342.2347. Found: 342.2347.

*3.13. 1,2-Bis[(3-phenyl)-2-indenyl]ethane (**4g**)*

To a stirred solution of $TiCl_3$ (256 mg, 1.66 mmol) in 1,2-dimethoxyethane (12 ml) at 0°C, $LiAlH_4$ (21 mg, 0.553 mmol) was added in one portion. After stirring for 15 min, a solution of 2-(hydroxymethyl)indene (123 mg, 0.553 mmol) in 1,2-dimethoxyethane (2 ml) was cannulated into the resultant black reaction mixture. Upon gradual warming to r.t. the reaction mixture was refluxed for 48 h. The solution was then cooled to 0°C and quenched by addition of 1 M HCl. The layers were separated and the aqueous phase was extracted with EtOAc. The combined organic extract was washed with water, saturated brine, and dried over Na_2SO_4. The solvents were removed and the crude product was recrystallized from hot hexanes to give 0.156g (46%) of bis-indene **4g** as a yellow solid. The mother liquor was concentrated and the residue (0.122g, 36%) was determined by ^{1}H-NMR to contain a 4:5 mixture of **4g**:**5g**.

Compound **4g**: m.p. 169–171°C; IR (powder) 3018, 2951, 2901, 1612, 1603, 1491, 1459 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 2.75 (s, 4H), 3.29 (s, 4H), 7.10–7.38 (m, 18H); ^{13}C-NMR ($CDCl_3$): δ 29.3, 40.5, 119.6, 123.4, 124.2, 126.2, 127.0, 128.4, 129.1, 135.5, 140.0, 142.5, 143.7, 146.4; HRMS (EI) Calc. for $C_{32}H_{26}$: 410.2035. Found: 410.2033.

Compound **5g**: ^{1}H-NMR ($CDCl_3$): δ 2.70 (d, $J = 23.0$ Hz, 1H), 2.88 (d, $J = 23.2$ Hz, 1H), 3.40 (d, $J = 14.3$ Hz, 1H), 3.44 (d, $J = 20.3$ Hz, 1H), 3.50 (d, $J = 14.0$ Hz, 1H), 3.57 (d, $J = 20.3$ Hz, 1H), 4.73 (app. t, $J = 2.3$ Hz, 1H), 5.01 (app. t, $J = 2.0$ Hz, 1H), 6.81–7.37 (m, 18H).

*3.14. rac- and meso-Ethylene bis[η^5-4,5,6,7-1-tetrahydro(5-methyl)-2-indenyl] titanium dichloride (**8b**, **9b**)*

To a degassed solution of 1,2-bis[(5-methyl)-2-indenyl]ethane (**4b**) (0.067 g, 0.23 mmol) in THF (3 ml) at −70°C, *n*-BuLi (0.19 ml of a 2.5 M solution in hexanes, 0.47 mmol) was added dropwise. After stirring for 1 h, $TiCl_3{\cdot}(thf)_3$ (0.088 g, 0.24 mmol) was added. The resultant dark red reaction mixture was then allowed to reach r.t. followed by refluxing for 4 h. After gradual cooling to r.t. and to −40°C, HCl (6 M, 1.5 ml, 9.2 mmol) was added. Dry air was gently bubbled through the reaction mixture while warming to r.t. for 1 h. The reaction mixture was extracted with CH_2Cl_2 and the organic layer was dried (Na_2SO_4). The solvents were removed and the crude product was dissolved in THF (2 ml). PtO_2 (0.001 g, 0.005 mmol) was added and the reaction mixture was placed under H_2 atmosphere. After stirring for 48 h, the reaction mixture was filtered through Celite and the removal of solvents gave 0.004 g (36%) of a mixture of racemic (**8b**) and meso (**9b**) *ansa*-titanocenes. The diastereomeric ratio was not readily determined by spectroscopic techniques because of the inherent similarities between the two stereoisomers. The crude product was characterized by its ^{1}H-NMR spectrum: ^{1}H-NMR ($CDCl_3$): δ 1.05 (d, $J = 6.3$ Hz, 6H), 1.60–1.74 (m, 4H), 2.46–2.62 (m, 4H), 2.83–3.04 (m, 4H), 3.11 (s, 4H), 5.48 (s, 1H), 5.49 (s, 1H), 5.54 (s, 1H), 5.55 (s, 1H). Recrystallization from CH_2Cl_2/hexane (1:2) gave *meso ansa*-titanocene **9b** as a red solid. IR ($CHCl_3$): 2956, 2923, 1514, 1447, 1419, 1376 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.05 ($CHCH_3$, d, $J = 6.3$ Hz, 6H), 1,60–1.74 (m, 6H), 2.46–2.62 (m, 4H), 2.83–3.04 (m, 4H), 3.11 (s, 4H), 5.48 (Cp–H, s, 1H), 5.49 (Cp–H, s, 1H), 5.54 (Cp–H, s, 1H), 5.55 (Cp–H, s, 1H); ^{13}C-NMR ($CDCl_3$): δ 22.2, 26.0, 29.6, 30.1, 31.0, 33.1, 111.1, 113.5, 137.4, 137.5, 137.8.

*3.15. rac-Ethylene bis[η^5-4,5,6,7-1-(2-methylpropyl)-tetrahydro-2-indenyl] titanium dichloride (**8c**)*

The preparation of **8c** was accomplished according to the procedure for ethylene bis[tetrahydro-(5-methyl)-2-indenyl] titanium dichloride: 0.22 g of **4c** (0.60 mmol) was treated with $TiCl_3{\cdot}(thf)_3$ to afford a crude mixture of **8c** and **9c** (0.26 g, 88%) with a 4:1 ratio as determined by ^{1}H-NMR. Recrystallization from CH_2Cl_2/hexane (1:2) gave pure racemic *ansa*-titanocene **8c** as a bright red solid, m.p. 271–272°C; IR ($CHCl_3$): 2949, 1558, 1506, 1456 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.86 ($CH(CH_3)_2$, m, 12H), 1.58–1.76 (m, 4H), 1.81–1.92 (m, 4H), 2.19 (m, 2H), 2.44 (m, 4H), 2.87 (d, $J = 8.4$ Hz, 2H), 3.07 (m, 4H), 3.26 (d, $J = 9$ Hz, 2H), 3.87 (t, $J = 5.7$ Hz, 4H), 5.14 (Cp–H, s, 2H); ^{13}C-NMR ($CDCl_3$): δ 21.9, 22.3, 22.4, 22.9, 24.1, 25.5, 28.0, 30.1, 36.7, 107.1, 131.3, 133.5, 134.9, 139.2; HRMS (FAB) Calc. for $C_{28}H_{40}TiCl_2$: 494.1986. Found: 494.2011.

*3.16. rac-Ethylene bis[η^5-4,5,6,7-1-(1-methylethyl)-tetrahydro-2-indenyl] titanium dichloride (**8d**)*

The preparation of **8d** was accomplished according to the procedure for ethylene bis[tetrahydro-(5-methyl)-2-indenyl] titanium dichloride: 0.022 g of **4d** (0.06 mmol) was treated with $TiCl_3{\cdot}(thf)_3$ to afford a crude mixture of **8d** and **9d** (0.021 g, 76%) with a 2:1 ratio as determined by ^{1}H-NMR. Recrystallization from CH_2Cl_2/hexane gave pure racemic *ansa*-titanocene **8d** as a red solid, IR ($CHCl_3$): 2955, 1457, 817 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 0.98 ($CH(CH_3)_2$, d, $J = 7.2$ Hz, 6H), 1.09

($CH(CH_3)_2$, d, $J = 6.9$ Hz, 6H), 1.43–1.62 (m, 4H), 1.78–1.86 (m, 4H), 2.29–2.50 (m, 4H), 2.88 (d, $J = 9.6$ Hz, 2H), 2.94–3.05 (m, 6H), 3.37 (d, $J = 9.6$ Hz, 2H), 5.24 (Cp–H, s, 2H); ^{13}C-NMR ($CDCl_3$): δ 21.8, 22.2, 24.4, 26.0, 28.1, 28.9, 38.7, 109.8, 126.3, 132.8, 134.7, 138.0; HRMS (FAB) Calc. for $C_{26}H_{36}TiCl_2$: 466.1673. Found: 466.1678.

*3.17. rac-Ethylene bis(η^5-4,5,6,7-1-benzyl-tetrahydro-2-indenyl) titanium dichloride (**8e**)*

The preparation of **8e** was accomplished according to the procedure for ethylene bis[tetrahydro-(5-methyl)-2-indenyl] titanium dichloride: 0.25 g of **4e** (1.07 mmol) was treated with $TiCl_3 \cdot (thf)_3$ to afford a crude mixture of **8e** and **9e** (0.039 g, 74%) with a 3.6:1 ratio as determined by ^{1}H-NMR. Recrystallization from CH_2Cl_2/hexane gave pure racemic *ansa*-titanocene **8e** as a red solid, m.p. 325°C (dec.); IR ($CHCl_3$): 3088, 2937, 1600, 1507, 1492 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.56 (m, 4H), 1.68–1.80 (m, 2H), 1.84–1.94 (m, 2H), 2.45 (m, 2H), 2.78 (m, 2H), 3.05–3.20 (m, 6H), 3.35 (m, 2H), 3.49 ($PhCH_2Cp$, d $J = 16$ Hz, 2H), 3.63 (PhCH2Cp, d, $J = 16$ Hz, 2H), 5.33 (Cp–H, s, 2H), 7.01 (d, $J = 7.4$ Hz, 4H), 7.16–7.29 (m, 6H); ^{13}C-NMR ($CDCl_3$): δ 21.8, 22.1, 23.9, 25.5, 27.9, 33.0, 107.4, 126.2, 128.0, 128.5, 129.1, 134.1, 135.7, 139.6, 139.8; HRMS (FAB) Calc. for $C_{34}H_{36}TiCl_2$ [$M^+ - Cl$]: 527.1985. Found: 527.1950.

4. Supplementary material

Further details of the crystal structure investigations are available on request from the Cambridge Crystallographic Data Centre, where the CCDC numbers are as follows: **8c** CCDC 104502; **8d** CCDC 104503; **9b** CCDC 104504. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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