

# Synthesis of ansa-2,2'-bis[(4,7-dimethyl-inden-1-yl)methyl]-1,1'-binaphthyl and ansa-2,2'-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1'-binaphthyltitanium and -zirconium dichlorides<sup>1</sup>

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## Abstract

2,2'-Bis[(4,7-dimethyl-inden-1-yl)methyl]-1,1'-binaphthyl and [2,2'-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1'-binaphthyl]titanium and -zirconium dichlorides have been synthesized from 2,2'-bis(bromomethyl)-1,1'-binaphthylene. 2,2'-Bis(bromomethyl)-1,1'-binaphthylene was alkylated with the lithium salt of 4,7-dimethylindene to yield 2,2'-bis[1-(4,7-dimethyl-indenyl)methyl]-1,1'-binaphthylene (S)-(–)-**9**. The lithium salt of **9** was metalated with either titanium trichloride followed by oxidation or zirconium tetrachloride to give titanocene dichloride (S)-(+) **10** and zirconocene dichloride **11**. The known complexes ansa-[2,2'-bis[(1-indenyl)methyl]-1,1'-binaphthyl]titanium and -zirconium dichlorides were formed and hydrogenated to ansa-[2,2'-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1'-binaphthyl]titanium and -zirconium dichlorides **12** and **14** or to ansa-[2,2'-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl]titanium dichloride **13** whose solid state structure was determined by X-ray crystallography. Complex **13** adopts a C<sub>1</sub>-symmetrical conformation in the solid state, but is conformationally mobile in solution, exhibiting C<sub>2</sub>-symmetry in its room temperature NMR spectra.

**Keywords:** Zirconium; Titanium; Binaphthyl; ansa-Metallocene

## 1. Introduction

Group IV transition metal complexes have gained much attention recently for their application towards stereoselective catalysis such as asymmetric epoxidation [1], olefin isomerization [2], reduction of ketones [3] and imines [4], hydrogenation [5], and isotactic polymerization [6]. Owing to their importance, a number of bridged indenyl and tetrahydroindenyl metallocene dihalides have been prepared [7]. One of the most studied titanocene complexes is Brintzinger's complex **1**, introduced in 1982 [8]. Since that time several complexes containing chiral bridges (**2–6**) have been studied to

develop more direct routes to resolved complexes with modified steric demands [2,8–12].

We have previously reported the preparation of the enantiomerically enriched 1,1'-binaphthyl-2,2'-dimethyl-bridged titanocene complex **2a** and its results in the asymmetric catalytic epoxidation of unfunctionalized olefins [1]. In an effort to modify the steric environment around the catalytic site in complexes containing this chiral bridge, we have now prepared hydrogenated tetrahydroindenyl complexes **12–14** and substituted complexes **10** and **11**.

## 2. 2,2'-Bis-[(4,7-dimethylinden-1-yl)methyl]-1,1'-binaphthylene complexes

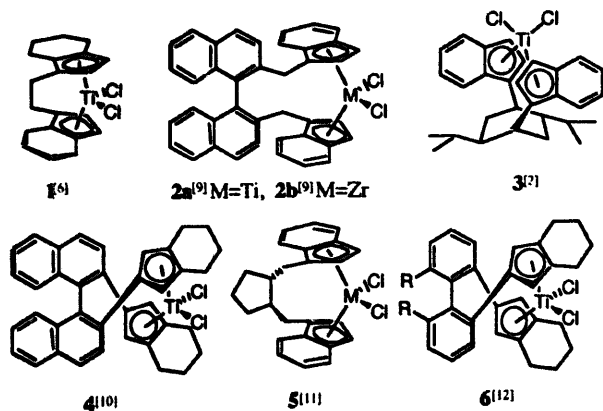
Alkyl substitutions have previously been introduced at the C4 and/or C7 positions of the indenyl moiety in bis(indenyl)metal complexes containing achiral bridges [13]. We have adopted this method for the preparation

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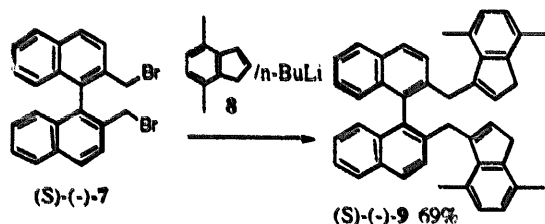
<sup>2</sup> Phillips Petroleum Foundation Fellow 1996.

<sup>3</sup> Patricia Roberts Harris Fellow 1992–1995.

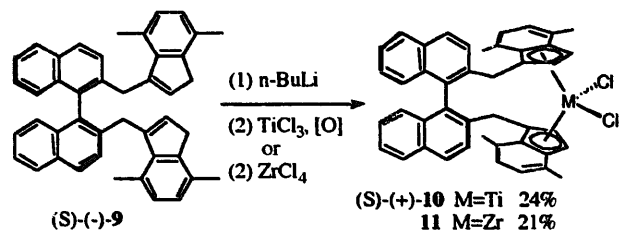


of substituted complexes with a chiral bridge. The synthesis of enantiomerically enriched bis(1-indenyl)-binaphthylene ligand (S)-(-)-9 follows a procedure outlined by our group [9,2b] beginning from 2,2'-bis(bromomethyl)-binaphthylene (7) as shown in Scheme 1. Resolved dibromide 7 can be prepared from 1-bromo-2-methylnaphthylene via Grignard cross-coupling followed by *N*-bromosuccinimide bromination [14], or perhaps more conveniently and reliably on a large scale from racemic 7 using a procedure published by Maigrot and Mazaleyrat [15] in three steps with at least 95% enantiomeric excess. Treating (S)-2,2'-bis(bromomethyl)-1,1'-binaphthylene with lithiated 4,7-dimethylindene (8) [13a] at  $-78^{\circ}\text{C}$  gave the desired bis(4,7-dimethylindene) (S)-(-)-9 in 69% yield as a white solid after chromatographic purification (Scheme 2). Attempts to alkylate *rac*-7 with lithiated 4,7-diisopropylindene were unsuccessful, leading to recovered dibromide 7. The failure of this more hindered indene to react is presumably due to unfavorable  $A_{1,3}$  steric interactions between the isopropyl groups and the binaphthyl alkylating reagent.

Metalation of (S)-(-)-9 with titanium trichloride [9] followed by oxidation [16], and *rac*-9 with zirconium tetrachloride [14] produced dark green solid titanocene dichloride (S)-(+)-10 and solid yellow zirconocene dichloride 11 in 24% and 21% yields respectively. As was the case for the metalation to the unsubstituted complex 2a, these dimethylindenyl complexes 10 and 11 were formed as conformationally mobile, diastereomerically pure,  $C_2$ -symmetrical complexes. No evi-



Scheme 1.

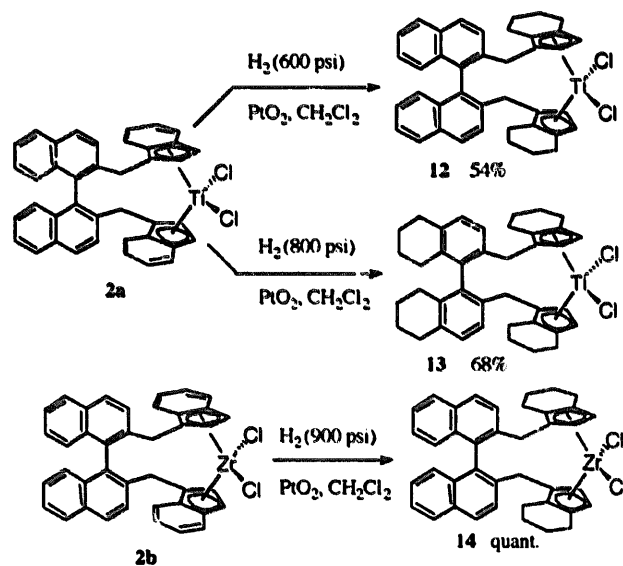


Scheme 2.

dence for the formation of the diastereomeric  $C_1$ -symmetrical (meso-like) ansa-metallocene complexes was observed in the NMR spectra of the crude reaction products. Evidence for the formation of the metal complexes included a characteristic spreading of the  $^1\text{H}$  NMR signals for methyl groups on the indenyl moiety from 2.25 ppm to 2.05 and 2.35 ppm for titanocene complex 10 and 2.23 and 2.10 ppm for zirconocene complex 11 respectively. The average  $C_2$ -symmetry of the complexes in solution was readily identifiable through the reduced number of NMR signals.

### 3. 2,2'-Bis-[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1'-binaphthylene and 1,1'-bitetralin complexes

Another method used for the steric and electronic modification of ansa-metallocenes containing achiral bridges has been the hydrogenation of the indenyl moiety to give tetrahydroindenyltitanium or -zirconium dichlorides starting from the indenyl metal complexes [8,17]. We have adopted this procedure for the preparation of ansa-tetrahydroindenyl complexes containing a chiral bridge [12a]. Thus, the known ansa-bis(indenyl) titanium dichloride 2a and ansa-bis(indenyl)zirconium dichloride 2b were prepared and treated with hydrogen



Scheme 3.

Table 1  
Crystal data and structure refinement for 13

Identification code	k146
Empirical formula	C <sub>41</sub> H <sub>46</sub> Cl <sub>4</sub> Ti
Formula weight	728.48
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.656(3) \text{ \AA}$ $\alpha = 89.66(3)^\circ$ $b = 12.083(5) \text{ \AA}$ $\beta = 96.65(3)^\circ$ $c = 16.901(6) \text{ \AA}$ $\gamma = 89.84(3)^\circ$
Volume $z (\text{\AA}^3)$	1755.8(11)
Density (calc.) ( $\text{Mg m}^{-3}$ )	1.378
Absorption coefficient ( $\text{mm}^{-1}$ )	0.578
$F(000)$	764
Crystal size ( $\text{mm}^3$ )	0.42 × 0.28 × 0.22
Theta range for data collection	1.69° to 22.46°
Limiting indices	$0 \leq h \leq 8, -12 \leq k \leq 12, -18 \leq l \leq 18$
Reflections collected	3734
Independent reflections	3734 [ $R(\text{int}) = 0.0000$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3717/0/415
Goodness-of-fit on $F^2$	1.037
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0516, wR_2 = 0.1339$
$R$ indices (all data)	$R_1 = 0.1736, wR_2 = 0.1784$
Largest diff. peak and hole ( $e \text{ \AA}^{-3}$ )	0.308 and $-0.401$

and PtO<sub>2</sub> in dichloromethane with stirring in a Parr reactor. Aliquots were periodically removed and examined by TLC or NMR spectroscopy to follow the course of the hydrogenations. Methylene chloride was found to be a suitable solvent due its good ability to dissolve the metallocene dichlorides; other solvents, including ethyl acetate, were notably inferior in this reaction. Treatment of 2a for 6 h at 600 psi hydrogen at room temperature

in the presence of PtO<sub>2</sub> gave tetrahydroindenyl titanocene dichloride 12 as a red solid in 54% yield after chromatography. Evidence for the formation of 1 included the appearance of methylene signals in the <sup>1</sup>H NMR spectrum at 2.85, 2.53, and 1.65 ppm, and a shift in the cyclopentadienyl signals from 6.12 and 5.12 ppm to 6.06 and 5.66 ppm. When the ansa-bis(indenyl)titanium dichloride 2a was subjected to 800

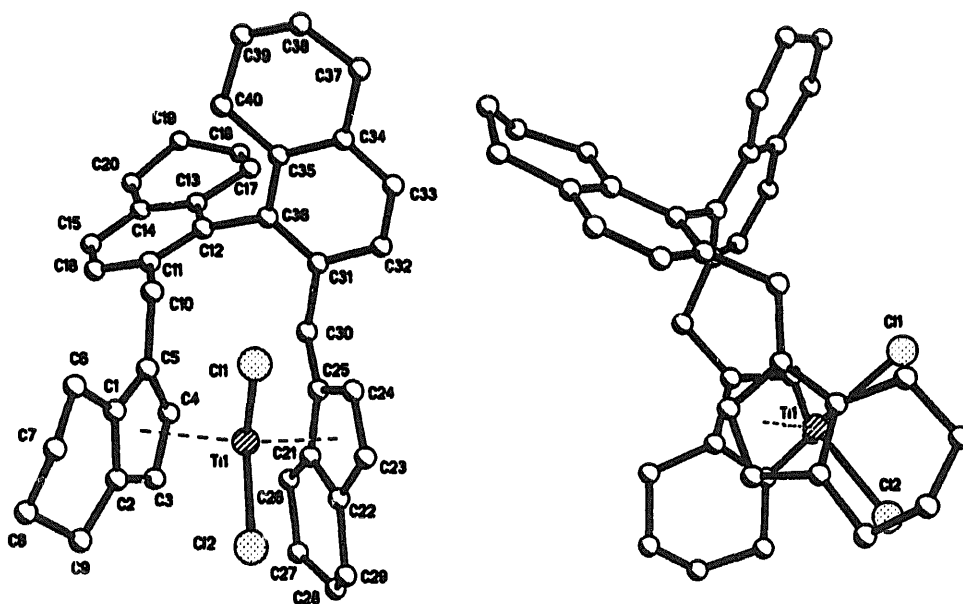


Fig. 1. ORTEP drawing of two views of the solid state structure of 13.

psi of hydrogen in the presence of PtO<sub>2</sub> at room temperature for 72 h, bitetralin **13** was formed in 68% yield as a solid red powder after purification by flash chromatography. Under these more forcing conditions, not only were the indenyl rings hydrogenated, but the binaphthalene system was also reduced to a bitetralin system. Samples taken during the course of the reaction showed that the hydrogenation of the indene rings proceeded fastest, but before the indenenes were completely reduced the naphthalene rings started to exhibit signifi-

cant reduction. Thus, intermediate samples contained an inseparable mixture of (indenyl)naphthyls, (tetrahydroindenyl)naphthyls and (tetrahydroindenyl)tetralins. When the samples were exhaustively hydrogenated, pure C<sub>2</sub>-symmetrical bitetralin **13** could be isolated and its structure was evidenced by a characteristic shift in the cyclopentadienyl <sup>1</sup>H NMR signals to 5.98 and 5.61 ppm, and the appearance of methylene signals at 2.65 ppm and 1.95 to 1.65 ppm. The molecule is completely fluxional on the NMR time scale at room temperature. The solid state structure was also obtained by X-ray crystallography and is discussed below.

The hydrogenation of ansa-2,2'-bis[(1-indenyl)methyl]-1,1'-binaphthylzirconium dichloride **2b** was carried out under 900 psi of hydrogen for 12 h to give ansa-[2,2'-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1'-binaphthyl]zirconium dichloride **12** in quantitative yield. A shift of the cyclopentadienyl signals and the appearance of the methylene signals at 2.86, 2.45, and 1.63 ppm was observed in the <sup>1</sup>H NMR spectrum of **12**. In contrast to the titanium complex above, even when the zirconium complex was reacted for longer times or under higher pressures of hydrogen, only traces of what seems to be the bitetralin complexes were observed in the NMR spectra.

Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **13**

Atom	x	y	z	$U_{eq}$
Ti(1)	-3809(2)	3289(1)	7986(1)	38(1)
Cl(1)	-5737(3)	2317(2)	7184(1)	61(1)
Cl(2)	-5548(2)	4695(2)	8247(1)	60(1)
C(1)	-4592(8)	1846(5)	8967(4)	36(2)
C(2)	-4271(9)	2811(5)	9403(4)	37(2)
C(3)	-2713(9)	3106(6)	9299(4)	42(2)
C(4)	-2098(9)	2273(5)	8857(4)	36(2)
C(5)	-3259(8)	1499(5)	8625(4)	34(2)
C(6)	-6106(9)	1250(6)	8952(4)	44(2)
C(7)	-7306(10)	1954(7)	9257(5)	59(2)
C(8)	-6720(10)	2548(8)	10002(5)	72(3)
C(9)	-5384(10)	3336(6)	9894(4)	53(2)
C(10)	-3113(8)	471(5)	8157(4)	38(2)
C(11)	-1523(8)	-53(5)	8245(4)	35(2)
C(12)	-668(8)	-160(5)	7606(4)	34(2)
C(13)	793(9)	-700(5)	7700(4)	34(2)
C(14)	1366(8)	-1134(5)	8439(4)	39(2)
C(15)	517(10)	-991(6)	9080(4)	45(2)
C(16)	-876(9)	-465(5)	8978(4)	40(2)
C(17)	1688(9)	-814(7)	6996(4)	53(2)
C(18)	3283(12)	-1285(11)	7188(6)	105(4)
C(19)	3506(12)	-2085(8)	7809(6)	84(3)
C(20)	2868(10)	-1779(6)	8570(4)	56(2)
C(21)	-1258(9)	4082(6)	7774(4)	40(2)
C(22)	-2396(9)	4886(6)	7575(5)	47(2)
C(23)	-3411(9)	4465(6)	6931(4)	46(2)
C(24)	-2889(9)	3454(7)	6738(4)	45(2)
C(25)	-1542(8)	3171(6)	7252(4)	38(2)
C(26)	157(10)	4291(6)	8343(4)	55(2)
C(27)	141(17)	5447(8)	8692(7)	124(5)
C(28)	-864(15)	6218(10)	8352(11)	155(7)
C(29)	-2380(12)	6004(6)	7950(6)	73(3)
C(30)	-414(8)	2236(5)	7160(4)	42(2)
C(31)	-1006(8)	1363(5)	6565(4)	36(2)
C(32)	-1350(9)	1668(6)	5769(4)	48(2)
C(33)	-2004(9)	909(7)	5225(4)	51(2)
C(34)	-2337(9)	-152(6)	5428(4)	43(2)
C(35)	-1949(8)	-495(5)	6215(4)	34(2)
C(36)	-1258(8)	265(6)	6788(4)	37(2)
C(37)	-3065(10)	-935(7)	4806(4)	64(2)
C(38)	-3480(18)	-1999(10)	5105(6)	145(6)
C(39)	-2810(16)	-2406(8)	5802(6)	115(4)
C(40)	-2274(9)	-1661(6)	6465(4)	46(2)
C(41)	2202(16)	4884(14)	6053(10)	183(7)
Cl(3)	3174(6)	5713(6)	5527(3)	266(4)
Cl(4)	412(6)	5248(6)	6162(3)	233(3)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

### 3.1. X-ray analysis of **13**

Crystals suitable for X-ray analysis were obtained from a methylene chloride/hexane solution of racemic bis(tetrahydroindenyl)bitetralin titanium complex **13**. Details of the crystal data and refinement are given in Table 1 and ORTEP plots of two views of the molecule are shown in Fig. 1. The carbon atoms C27, C28, C38, C39, and the two chlorine atoms display large thermal motion indicating substantial disorder; see Table 2 for the atomic coordinates. The presence of the bitetralin moiety is evidenced by the bond lengths C17–C18–C19–C20, C37–C38–C39–C40, as well as by the puckering of these rings; see Table 3 for a list of all bond lengths. As in the solid state structure of the ansa-bis(indenyl)titanium dichloride **2a**, ansa-bis(tetrahydroindenyl)titanium complex **13** is found in a C<sub>1</sub>-symmetrical conformation.

## 4. Summary

ansa-2,2'-Bis[(4,7-dimethylinden-1-yl)methyl]-1,1'-binaphthyl and ansa-[2,2'-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1'-binaphthyl]titanium and -zirconium dichlorides have been synthesized through alkylation of 4,7-dimethylindene with 2,2'-bis(bromomethyl)-1,1'-binaphthylene followed by metalation, or through the hydrogenation of ansa-2,2'-bis[(1-indenyl)methyl]-1,1'-binaphthyltitanium and -zirconium dichlorides. As in

Table 3  
Bond lengths (Å) for 13

Ti(1)–C(4)	2.309(6)
Ti(1)–C(3)	2.320(7)
Ti(1)–C(23)	2.330(7)
Ti(1)–Cl(2)	2.345(2)
Ti(1)–Cl(1)	2.347(2)
Ti(1)–C(24)	2.347(7)
Ti(1)–C(22)	2.429(7)
Ti(1)–C(5)	2.433(6)
Ti(1)–C(25)	2.444(7)
Ti(1)–C(21)	2.473(7)
Ti(1)–C(2)	2.537(6)
Ti(1)–C(1)	2.546(7)
C(1)–C(2)	1.395(9)
C(1)–C(5)	1.412(9)
C(1)–C(6)	1.494(9)
C(2)–C(3)	1.427(10)
C(2)–C(9)	1.486(10)
C(3)–C(4)	1.397(9)
C(4)–C(5)	1.399(9)
C(5)–C(10)	1.489(9)
C(6)–C(7)	1.480(10)
C(7)–C(8)	1.491(11)
C(8)–C(9)	1.526(11)
C(10)–C(11)	1.505(9)
C(11)–C(12)	1.384(9)
C(11)–C(16)	1.388(9)
C(12)–C(13)	1.413(9)
C(12)–C(36)	1.504(9)
C(13)–C(14)	1.389(9)
C(13)–C(17)	1.499(10)
C(14)–C(15)	1.390(10)
C(14)–C(20)	1.508(10)
C(15)–C(16)	1.354(10)
C(17)–C(18)	1.492(11)
C(18)–C(19)	1.418(12)
C(19)–C(20)	1.505(11)
C(21)–C(22)	1.393(10)
C(21)–C(25)	1.418(9)
C(21)–C(26)	1.491(10)
C(22)–C(23)	1.415(10)
C(22)–C(29)	1.496(11)
C(23)–C(24)	1.357(9)
C(24)–C(25)	1.412(9)
C(25)–C(30)	1.512(9)
C(26)–C(27)	1.519(12)
C(27)–C(28)	1.35(2)
C(28)–C(29)	1.431(14)
C(30)–C(31)	1.510(9)
C(31)–C(32)	1.391(9)
C(31)–C(36)	1.401(9)
C(32)–C(33)	1.377(10)
C(33)–C(34)	1.365(10)
C(34)–C(35)	1.395(9)
C(34)–C(37)	1.502(10)
C(35)–C(36)	1.421(9)
C(35)–C(40)	1.506(9)
C(37)–C(38)	1.440(12)
C(38)–C(39)	1.341(13)
C(39)–C(40)	1.476(10)
C(41)–Cl(3)	1.634(13)
C(41)–Cl(4)	1.641(13)

the case of bis(indenyl) titanium complex **2a**, the bis(tetrahydroindenyl)bitetralin titanium complex **13** adopts a  $C_1$ -symmetrical conformation in the solid state, but is conformationally mobile in solution, exhibiting  $C_2$ -symmetry in its room temperature NMR spectra.

## 5. Experimental

### 5.1. General

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Ether, THF, DME, hexanes, toluene, and benzene were distilled under  $N_2$  from sodium and benzophenone. All reactions involving air- or moisture-sensitive compounds were performed under argon or nitrogen atmospheres utilizing standard Schlenk line techniques and/or in a Vacuum Atmospheres dry box (under nitrogen). All metalations were conducted on Schlenk line, and run under argon. All glassware was oven dried prior to use. Routine solvent removal was performed on a Buchi RE-111 rotary evaporator at 20 mmHg. Solvent removal in vacuo was accomplished on a vacuum line at below 0.01 mmHg or on a Schlenk line at below 0.001 mmHg (oil diffusion).

All  $^1H$  NMR and  $^{13}C$  NMR spectra were obtained using a Varian XL-300 instrument. Data are reported as follows: chemical shifts ( $X$ -scale) in parts per million (ppm) relative to residual solvent peaks (multiplicity, coupling constants in hertz (rounded to 0.5 Hz), number of hydrogens). For  $^1H$  NMR spectra, the peaks due to residual  $CDCl_3$ ,  $C_6D_6$ , or  $DMSO-d_6$  are listed at 7.24, 7.15 or 2.49 ppm respectively, and for  $^{13}C$  spectra the central peak of the  $CDCl_3$ ,  $C_6D_6$ , and  $DMSO-d_6$  multiplets are assigned chemical shifts of 77.0, 128.0 and 39.5 ppm respectively. Unless otherwise noted, multiplicities and compound ratios are deduced from electronic integration. Infrared spectra were recorded on a Bio-Rad FTS-7 FT-IR with a Bio-Rad 3240-SPC computer. Only characteristic and/or strong signals are reported. Low-resolution mass spectra (reported as  $m/z$  (relative intensity at 70 eV)) were recorded on a Hewlett Packard 5985 instrument.

Preparative column chromatography was performed on flash silica gel (Merck reagent silica gel 60 Å, 230–400 mesh ASTM). Melting points were determined in Pyrex capillary tubes on a Mel-Temp apparatus and are uncorrected. Analytical thin layer chromatography was performed on 0.2 mm Kieselgel silica gel 60F-254.

4,7-Dimethylindene (**8**) was synthesized in one step from cyclopentadiene and acetonylacetone according to the literature [13a]. dl-2,2'-Bis(dibromomethyl)-1,1'-binaphthylene and S-(–)-2,2'-bis(dibromomethyl)-1,1'-binaphthylene (**7**) were prepared from 1-methylnaphthylene according to the literature [15].

### 5.2. *S*-(–)-2,2'-bis[(4,7-dimethylinden-1-yl)methyl]-1,1'-binaphthylene (*S*)-(–)-**9**)

To a solution of 4,7-dimethylindene (**8**) (1.77 g, 12.3 mmol) in THF (5 ml) was added *n*-butyllithium (2.70 M in hexanes, 4.55 ml, 12.3 mmol) dropwise at  $-78^{\circ}\text{C}$  to give a heterogenous reaction mixture. Upon warming the reaction mixture to room temperature the solid white precipitate dissolved, and the reaction became a clear red solution which was allowed to stir for an additional 30 min. The reaction solution was then cooled to  $0^{\circ}\text{C}$ , and a solution of (*S*)-(–)-**7** (1.35 g, 3.1 mmol) in THF (5 ml) was added dropwise. The resulting solution was then allowed to warm to room temperature and stir for an additional 3 h. The reaction was then quenched with a saturated solution of  $\text{NH}_4\text{Br}$  and separated. The aqueous layer was extracted with ethyl acetate, and the organic layers were combined. The organic layer was washed with brine followed by water, dried with  $\text{MgSO}_4$ , filtered and concentrated. The crude yellow solid was purified by column chromatography ( $\text{SiO}_2$ , petroleum ether), yielding (*S*)-(–)-**9** (1.21 g, 69%) as a white solid, m.p.  $129\text{--}130^{\circ}\text{C}$ ,  $[\alpha]_{589}^{23} - 22.2$  ( $c = 0.814$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94 (d,  $J = 8.0$  Hz, 2H), 7.92 (d,  $J = 8.5$  Hz, 2H), 7.55 (d,  $J = 8.5$  Hz, 2H), 7.46 (m, 2H), 7.26 (m, 2H), 7.18 (d,  $J = 8.0$  Hz, 2H), 6.90 (s, 4H), 5.89 (bs, 2H), 3.89 (s, 4H), 2.98 (dd,  $J = 25.0$  Hz, 2H), 2.68 (dd,  $J = 25.0$  Hz, 2H), 2.25 (s, 6H), 2.24 (s, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.8, 144.0, 142.5, 137.0, 134.8, 133.2, 132.5, 130.7, 130.3, 129.1, 128.3, 128.0, 127.9, 127.6, 126.3, 126.0, 125.7, 125.3, 36.1, 35.1, 19.8, 18.1. IR (thin film): 3046, 2967, 2934, 2865, 1498, 1454, 1379, 1117. (EI 70 eV,  $m/z$ , rel. int.): 566 (77%), 421 (3<sup>+</sup>), 408 (10), 279 (27), 265 (21), 145 (72), 40 (100).

### 5.3. *S*-(+)-[2,2'-bis[(4,7-dimethylinden-1-yl)methyl]-1,1'-binaphthyl]dichlorotitanium (*S*)-(+)-(**10**)

*n*-Butyllithium (2.70 M in hexanes, 0.16 ml, 0.43 mmol) was added dropwise to a solution of (*S*)-(–)-**9** (117 mg, 0.21 mmol) in THF (2 ml) at  $-78^{\circ}\text{C}$ . After the addition the reaction mixture was allowed to warm, and upon reaching room temperature it had become a dark red solution. The solution was then cooled to  $0^{\circ}\text{C}$ , and added slowly via syringe to a slurry of  $\text{TiCl}_3$  (48 mg, 0.31 mmol) in THF (1 ml) at  $-78^{\circ}\text{C}$ . Upon completion of the addition, the reaction mixture was allowed to warm to room temperature, and was heated to reflux for 6 h which resulted in a dark solution. The solution was then cooled to room temperature and concentrated in vacuo. The solid green residue was then dissolved in chloroform (5 ml) at  $0^{\circ}\text{C}$ , and air was slowly bubbled into the green solution for 2 h [18]. 2N HCl was then added, and the aqueous layer was sepa-

rated. The aqueous layer was extracted twice with dichloromethane, and the combined organic layers were washed with 2N HCl then water, dried with  $\text{MgSO}_4$ , filtered and concentrated. The solid green powder was then dissolved in dichloromethane followed by slow addition of pentane until a precipitate was seen. The solution was allowed to sit for 30 min at room temperature and filtered. The green solid was washed twice with pentane yielding (*S*)-(+)-(**10**) (34 mg, 24%) as a dark green powder, m.p.  $216\text{--}230^{\circ}\text{C}$  (dec.)  $[\alpha]_{589}^{23} + 2490$  ( $c = 0.026$ ,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J = 8.5$  Hz, 2H), 7.94 (d,  $J = 8.5$ , 2H), 7.55 (d,  $J = 8.5$  Hz, 2H), 7.47 (m, 2H), 7.27 (m, 2H), 7.04 (d,  $J = 8.5$  Hz, 2H), 6.97 (d,  $J = 7.0$  Hz, 2H), 6.89 (d,  $J = 7.0$  Hz, 2H), 6.37 (bs, 2H), 5.28 (bs, 2H), 4.53 (d,  $J = 16.5$  Hz, 2H), 4.38 (d,  $J = 16.5$  Hz, 2H), 2.35 (s, 6H), 2.05 (s, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.7, 135.3, 135.2, 135.1, 133.3, 132.6 (2C), 129.6, 129.5 (2C), 128.7, 128.3, 128.2, 127.0, 126.6, 125.9, 125.7, 121.3, 113.0, 35.1, 21.5, 18.3. IR (neat): 3054, 2961, 1506, 1457, 1426, 1332, 1263, 1026. (EI 12 eV,  $m/z$ , rel. int.): 682 (24%), 647 (56), 564 (93), 421 (100), 408 (25), 395 (30), 279 (11), 143 (65).

### 5.4. *dl*-[2,2'-Bis[(4,7-dimethylinden-1-yl)methyl]-1,1'-binaphthyl]dichlorozirconium (**11**)

To a solution of *dl*-2,2'-bis[1-(4,7-dimethylindenylmethyl)]-1,1'-binaphthylene **9** (685 mg, 1.21 mmol) in ether (5 ml) was added dropwise *n*-butyllithium (1.05 M in hexanes, 2.54 mmol, 2.69 M in hexanes) at  $-78^{\circ}\text{C}$ . After the addition the reaction mixture was allowed to slowly warm to room temperature and stir for 6 h, at which time a fine white precipitate could be seen.  $\text{ZrCl}_4$  (423 mg, 1.82 mmol) was added via a side arm to the heterogenous mixture, causing an rapid color change from white to bright yellow. The yellow heterogenous mixture was allowed to stir for an additional 12 h at room temperature, and then concentrated in vacuo to give a bright yellow solid. To the crude solid was added dichloromethane (5 ml), resulting in an orange heterogenous mixture which was then Schlenk filtered. The resulting orange solution was concentrated to 0.5 ml in vacuo followed by the slow addition of hexanes causing a light yellow precipitate to form. The heterogenous mixture was back filtered, and the yellow powder was rinsed with hexanes ( $2 \times 2$  ml) then concentrated in vacuo to give **11** (0.181 g, 21%), m.p.  $> 290^{\circ}\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (d,  $J = 8.5$  Hz, 2H), 7.95 (d,  $J = 8.5$  Hz, 2H), 7.63 (d,  $J = 8.5$  Hz, 2H), 7.47 (m, 2H), 7.28 (m, 2H), 7.10 (d,  $J = 8.5$  Hz, 2H), 6.81 (s, 4H), 6.49 (d,  $J = 3.5$  Hz, 2H), 5.23 (d,  $J = 3.5$  Hz, 2H), 4.47 (d,  $J = 16.0$  Hz, 2H), 4.34 (d,  $J = 16.0$  Hz, 2H), 2.23 (s, 6H), 2.10 (s, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  136.0, 135.1, 133.7, 133.4, 132.7, 132.6,

129.5, 129.0, 128.4, 128.2, 127.5, 126.7, 126.6, 125.9, 125.8, 125.3, 121.0, 119.3, 103.7, 34.0, 21.6, 18.4. IR (thin film): 3049, 2963, 2923, 1634, 1495, 1449, 1328, 1258, 1075, 1026. (EI 12 eV,  $m/z$ , rel. int.): 724 ( $M^+$ , 4%), 725 ( $M^+ + 1$ , 6), 726 ( $M^+ + 2$ , 4), 728 ( $M^+ + 4$ , 7), 564 (63), 421 (46), 408 (23), 279 (29), 171 (37), 145 (100).

#### 5.5. [2,2'-Bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-1,1'-binaphthyl]dichlorotitanium (12)

An autoclave was charged with ansa-[2,2'-bis[(1-indenyl)methyl]-1,1'-binaphthyl]dichlorotitanium (**2a**) (106 mg, 0.15 mmol),  $PtO_2$  (6.8 mg, 0.03 mmol), and dichloromethane (100 ml), and was brought to 600 psi of hydrogen gas with stirring. After 6 h at room temperature the solution was diluted with dichloromethane (100 ml) and filtered over a Celite bed. The bed was washed with dichloromethane (25 ml). The solution was dried with anhydrous magnesium sulfate and evaporated. The crude red solid was chromatographed ( $SiO_2$ , 5% ethyl acetate/petroleum ether) and gave **12** (51 mg, 54% yield) as a red solid, m.p. > 300°C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.93 (d,  $J = 8.5$  Hz, 2H), 7.89 (d,  $J = 8.2$  Hz, 2H), 7.44 (d,  $J = 8.5$  Hz, 2H), 7.44 (m, 2H), 6.82 (d,  $J = 8.7$  Hz, 2H), 6.06 (d,  $J = 3.0$  Hz, 2H), 5.66 (d,  $J = 2$  Hz, 2H), 2.85 (ddd,  $J = 17.0$ , 5.6, 6.0 Hz, 2H), 2.53 (m, 6H), 1.65 (m, 8H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  139.6, 135.2, 134.9, 133.5, 132.5, 131.9, 130.7, 128.4, 128.3, 128.0, 126.5, 126.4, 125.8, 120.8, 113.1, 33.1, 30.6, 29.7, 26.4, 23.4, 21.9. IR (thin film): 3048, 2927, 2857, 1490, 1454, 1427, 1262, 1095, 1025, 817, 760  $cm^{-1}$ . MS,  $m/z$  (FAB, rel. int.): 599 ( $M-Cl$ , 77%), 562 (28), 395 (26), 365 (28), 345 (38), 265 (100).

#### 5.6. ansa-[2,2'-Bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl]-titanium dichloride (13)

An autoclave was charged with ansa-[2,2'-bis[(1-indenyl)methyl]-1,1'-binaphthyl]dichlorotitanium (**2a**) (168 mg, 0.27 mmol),  $PtO_2$  (12.2 mg, 0.05 mmol) and dichloromethane (100 ml) and pressurized with 800 psi of hydrogen with stirring at room temperature for 72 h at which time, through monitoring by TLC, the reaction was deemed complete. The reaction mixture was diluted with dichloromethane (25 ml). The solution was dried over anhydrous magnesium sulfate and concentrated. The crude product was purified by flash chromatography ( $SiO_2$ , 5% ethyl acetate/petroleum ether), yielding **13** as a fine red powder (68% yield), m.p. > 300°C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.02 (d,  $J = 7.9$  Hz, 2H), 6.97 (d,  $J = 7.9$  Hz, 2H), 5.98 (d,  $J = 2.9$  Hz, 2H), 5.61 (d,  $J = 2.9$  Hz, 2H), 3.52 (d,  $J = 17.1$  Hz, 2H), 3.25 (d,

$J = 17.1$  Hz, 2H), 2.65 (m, 14H), 1.95 (m, 4H), 1.70 (m, 6H), 1.65 (m, 8H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  139.4, 139.0, 136.1, 135.2, 133.3, 132.1, 131.8, 128.4, 127.8, 121.0, 112.9, 31.9, 29.9, 27.8, 26.4, 23.5, 23.3, 22.8, 22.1, 21.8. IR (thin film): 2930, 2857, 1489, 1454, 1435, 1094, 1020  $cm^{-1}$ . MS,  $m/z$  (EI 70 eV, rel. int.): 642 ( $M^+$ , 77%), 606 (27), 570 (100), 432 (23), 303 (21), 273 (22).

#### 5.7. 2,2'-Bis-(4,5,6,7-tetrahydroindenylmethyl)-1,1'-binaphthylidichlorozirconium (14)

An autoclave was charged with ansa-[2,2'-bis[(1-indenyl)methyl]-1,1'-binaphthyl]dichlorozirconium (**2b**) (50 mg, 0.07 mmol),  $PtO_2$  (3.4 mg, 0.014 mmol) and dichloromethane (50 ml) and pressurized to 900 psi with hydrogen and stirred at room temperature for 12 h at which time, through monitoring aliquots by TLC, the reaction was found to be complete. The solution was diluted with dichloromethane (50 ml) and filtered through a Celite bed. The bed was washed with dichloromethane (10 ml). The solution was dried with anhydrous magnesium sulfate and evaporated. The crude product was dissolved in benzene and filtered, providing **14** as a pale yellow solid in quantitative yield, m.p. 239–243°C (dec.).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.94 (d,  $J = 8.5$  Hz, 2H), 7.89 (d,  $J = 7.9$  Hz, 2H), 7.50 (d,  $J = 8.5$  Hz, 2H), 7.41 (m, 2H), 6.83 (d,  $J = 8.6$  Hz, 2H), 5.94 (d,  $J = 3.2$  Hz, 2H), 5.62 (d,  $J = 3.2$  Hz, 2H), 3.72 (d,  $J = 3.2$  Hz, 2H), 3.55 (d,  $J = 3.2$  Hz, 2H), 2.86 (ddd,  $J = 15.5$ , 5.0, 5.0 Hz, 2H), 2.45 (m, 6H), 1.63 (m, 8H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  135.4, 134.8, 134.3, 133.6, 132.6, 128.5, 128.2, 128.1, 127.7, 126.5, 126.4, 126.2, 125.7, 116.7, 108.3, 32.2, 25.5, 23.2, 22.4, 22.3. IR (thin film): 3053, 2930, 2856, 1457, 1433, 1026, 908, 817, 732  $cm^{-1}$ . MS,  $m/z$  (12 eV DIP, rel. int.): 678.3 ( $M^+$ , 46%), 640.3 (100), 512.4 (27), 446 (32), 395 (41), 278 (53).

#### 5.8. X-ray analysis of ansa-[2,2'-bis[(4,5,6,7-tetrahydroinden-1-yl)methyl]-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl]titanium dichloride (13)

Single crystals suitable for X-ray diffraction were obtained from methylene chloride by slow diffusion with hexanes under static vacuum for 2 days. The data was collected on a Nonius CAD-4 diffractometer with Mo  $K\alpha$  radiation. The data was corrected for Lorentz and polarization effects; absorption correction was not applied since it was judged to be insignificant. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using all reflections (SHELXTL 5.03). Hydrogen atoms were added in the visualized positions. See Table 1 for full crystallographic data.

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