Chiral metallocenes: the synthesis and X-ray crystal structures of TiCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$R*) (R* = menthyl or neomenthyl) and related compounds

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Abstract: The syntheses of the chiral ansa-metallocene complexes TiCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$R*) (R* = menthyl (**4a**) or neomenthyl (**4b**)) are reported; initially **4a** was obtained as a 3:1 mixture of (R:S) diastereoisomers, which differ only in which face of the asymmetrically substituted cyclopentadienyl ring is bonded to the titanium (chiral descriptor shown). The major diastereomer **4a$_R$** was crystallized out optically pure from the initial reaction mixture, whereas the **4a$_S$** diastereoisomer was isolated after isomerizing a racemic mixture of **4a** to a 1:3 mixture of (R:S) diastereoisomers using UV irradiation. The corresponding neomenthyl complex **4b** was obtained as a 1.3:1 mixture of diastereoisomers that could not be separated. The optically pure **4a$_R$** was converted stereoselectively into the corresponding (R)-TiMe$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$R*) (R* = menthyl). Syntheses of the related indenyl ligand system C$_5$Me$_4$SiMe$_2$C$_9$H$_7$ (**3**) is reported but complexation to titanium proved to be problematic although ZrCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_9$H$_6$) (**6**) was isolated. The crystal structures of both **4a$_R$** and **4a$_S$** are reported and compared. Crystals of **4a$_R$** are orthorhombic, a = 27.857(11), b = 9.985(5), and c = 9.596(4) Å, Z = 4, space group $P2_12_12_1$ (D_2^4, No. 19), and those of **4a$_S$** are monoclinic, a = 8.5810(10), b = 38.679(4), and c = 8.5842(10) Å, β = 113.001(2)°, Z = 4, space group $P2_1$ (C_2^2, No. 4). The structures were solved by the Patterson method and **4a$_R$** was refined by blocked-cascade least-squares procedures to R = 0.0628 (R_ω = 0.0503) for 902 reflections with $|F|/\sigma(|F|) \geq 3.0$, whereas **4a$_S$** was refined by full-matrix least-squares procedures to R = 0.0646 (wR_2 = 0.1829) for 5734 reflections with $|F|/\sigma(|F|) \geq 4.0$. Both diastereomers of **4a** catalyze hydrosilylation of ketones, but as expected from a comparison of the two crystal structures, the **4a$_R$** isomer is the more stereoselective catalyst, i.e., hydrosilylation of acetophenone followed by hydrolysis gives 82% enantiomeric excess (ee) of (S)-PhCH(Me)OH with **4a$_R$** whereas only 16% ee of (R)-PhCH(Me)OH with **4a$_S$**.

Key words: titanium, metallocene, chiral, structure, catalyst.

Résumé : On a réalisé la synthèse des complexes ansa-métallocènes chiraux TiCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$R*) (R* = menthyle (**4a**); R* = néomenthyle (**4b**)). Originalement **4a** a été obtenu sous la forme d'un mélange 3:1 des diastéréomères (R) et (S) qui ne diffèrent que par quelle face du noyau cyclopentadiényle substitué de façon asymétrique est liée au titane (on explicite le descripteur chiral). Le diastéréomère principal, **4a$_R$** a été retiré optiquement pur par cristallisation du mélange réactionnel initial; le diastéréomère **4a$_S$** n'a été isolé qu'après avoir isomérisé un mélange racémique de **4a** en un mélange 1:3 des diastéréomères (R) et (S) par irradiation UV. Le complexe néomenthylique correspondant **4b** a été obtenu sous la forme d'un mélange 1:4:1 de diastéréomères qui n'a pas pu être séparé. Le produit **4a$_R$** a été optiquement pur a été transformé stéréosélectivement en (R)-TiMe$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$R*) (R* = menthyle) correspondant. On rapporte aussi la synthèse du système de ligand indényle apparenté C$_5$Me$_4$SiMe$_2$C$_9$H$_7$ (**3**), mais sa complexation avec le titane s'est avérée être problématique même si on a pu isoler le ZrCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_9$H$_6$) (**6**). On a déterminé les structures cristallines des composés **4a$_R$** et **4a$_S$** et on en a fait une comparaison. Les cristaux de **4a$_R$** sont orthorhombiques, groupe d'espace $P2_12_12_1$ (D$_2^4$, No. 19), avec a = 27,857(11), b = 9,985(5) et c = 9,596(4) Å et Z = 4 alors que ceux de **4a$_S$** sont monocliniques, groupe d'espace $P2_1$ (C_2^2, No. 4), avec a = 8,5810(10), b = 38,679(4) et c = 8,5842(10) Å, β = 113,001(2)° et Z = 4. Les structures ont été résolues par la méthode de Patterson et celle de **4a$_R$** a été affinée par des méthodes de moindres carrés à cascade bloquée jusqu'à des valeurs de R = 0,0628 (R_ω = 0,0503) pour 902 réflexions avec $|F|/\sigma|F| \geq 3,0$ alors que celle de **4a$_S$** a été affinée par la méthode des moindres carrés (matrice complète) jusqu'à des valeurs de R = 0,0646 (wR_2 = 0,1829) pour 5734 réflexions avec $|F|/\sigma|F| \geq 4,0$. Les deux diastéréomères de **4a** catalyzent l'hydrosilylation des cétones mais, comme on peut s'y attendre sur la base d'une comparaison des deux structures cristallines, l'isomères **4a$_R$** est plus stéréosélectif; par exemple l'hydrosilylation de l'acétophénone, suivie d'une hydrolyse, conduit à un mélange avec 82% d'ee du (S)-PhCH(Me)OH avec **4a$_R$** alors que l'on n'obtient que 16% d'ee de (R)-PhCH(Me)OH avec **4a$_S$**.

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Introduction

Chiral metallocenes have attracted considerable attention in the last decade (1) fueled by their spectacular successes in catalyzing stereoselectively a wide range of organic transformations (2), including the stereospecific polymerization of α-olefins (3). We were particularly impressed by the report of Marks and co-workers (4) that lanthanide complexes, containing a chiral ansa-bis(cyclopentadienyl)[2] ligand (**1**), cata-
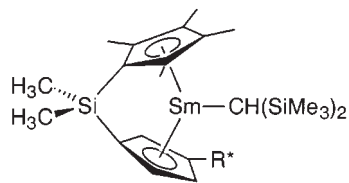
1 (R* = menthyl or neomenthyl)

lyzed the hydrogenation of nonfunctionalized alkenes in up to 96% enantiomeric excess (ee). To put this in context, the best result that we know of for the hydrogenation of a nonfunctionalized alkene using a rhodium(I)–chiral bis(phosphine) catalyst is 48% ee (5), and results of 0–20% ee are typical even with well-known phosphines such as Diop (6) and Binap (7). Organolanthanide complexes are, however, notoriously moisture-sensitive, and synthesizing and handling them requires special techniques. We, therefore, wondered if the chiral ansa-bis(cyclopentadienyl) ligand developed by Marks and co-workers (4), and related ligands, could be complexed to less moisture-sensitive transition metals and still give impressive results in enantioselective synthesis. We report herein our studies involving the syntheses of the corresponding titanium complexes. Our choice of titanium was influenced by the fact that two other research groups had reported impressive results for the hydrogenation of nonfunctionalized alkenes using titanocene systems, but with C_2-symmetric chiral ligands (8). We should also point out that, after the start of this work, hydrogenation of nonfunctionalized alkenes with ee's of up to 98% were reported using an iridium – chiral phosphanodihydrooxazole system (9) and also using a cationic zirconocene catalyst (10).

Results and discussion

Ligand syntheses

The ansa-cyclopentadiene ligands consisting of a 2,3,4,5-tetramethylcyclopentadienyl ring linked via a dimethylsilyl bridge to a menthyl- (**2a)** or neomenthyl- (**2b**) cyclopentadienyl moiety were synthesized by a modification of the procedure reported by Marks and co-workers (4) (Scheme 1). In our experience, the key to successful synthesis of these ligands is to use freshly prepared 1-(chlorodimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene; if this is not possible then this reagent should be distilled immediately before use.

The corresponding indenyl analogue (**3**) was synthesized using similar procedures (Scheme 1).

Metal complexes

Complexation of ligands **2a** and **2b** to titanium was carried out as shown in Scheme 1. The dilithium salt of the appropriate ligand precursor was formed via double deprotonation with two equiv of *n*-butyllithium in THF and was then reacted in situ with one equiv of $TiCl_3 \cdot 3THF$ in refluxing THF for 12 h. The resulting Ti(III) complex was then oxidized to the desired Ti(IV) complex by stirring with concentrated hydrochloric acid, open to the air, and worked up, followed by removal of solvent to give the crude products **4a** and **4b** as red solids. The ligands **2a** and **2b** are chiral by virtue of the menthyl or neomenthyl substituent, but in addition, the two faces of the asymmetrically substituted cyclopentadiene ring are different and, therefore, complexation to titanium introduces an element of planar chirality into the system. Hence, the titanium complexes **4a** and **4b** are obtained as a mixture of diastereoisomers. This is readily apparent from the ^{1}H NMR spectra; the asymmetry of the complex renders all four methyl groups on the tetramethyl-substituted cyclopentadienyl ring chemically inequivalent and the four methyl signals corresponding to each diastereoisomer are readily assigned from their relative intensity. Thus, the diastereoisomeric ratio can be easily measured via integration of a major and its corresponding minor peak. In this way the diastereoisomeric ratios were found to be 3.0:1 for **4a** and 1.3:1 for **4b**, i.e., 75 and 57% diastereoselectivities, respectively. In contrast, Marks and co-workers (4) found that both these ligands complexed to lanthanides with much higher diastereoselection (>80%) under similar reaction conditions. In both cases ligand complexation takes place to the metal in the +3 oxidation state, and we had expected that complexation to the smaller titanium atom would have led to an increase in the diastereoselection compared to that observed for the lanthanides. We can only presume that as a result of solvent coordination the lanthanides are more sterically congested and hence more stereo-differentiating.

In the case of the menthyl derivative **4a**, which was formed in a diastereomeric ratio of 3:1, cooling a hexane solution to –60°C resulted in the selective crystallization of the major isomer, presumed to be the kinetically favoured isomer. By X-ray crystallography (see below) we were able to show that this was the $\mathbf{4a_R}$ diastereomer where the *R* chiral descriptor refers to the planar chirality of the asymmetric cyclopentadienyl ring. There are several reports of photo-induced racemate–meso interconversions of group IV ansa-metallocene dichlorides, which it is generally agreed, proceed via photolytic homolytic cleavage of a Ti-(η^5-cyclopentadienyl) bond, rotation of the cyclopentadienyl radical about the linking-Cp bond, and recombination of the Ti(III) centre with the opposite face of the cyclopentadienyl

[2]Prefix ansa Latin for bent handle, attached at both ends.

Scheme 1.

2a R* = menthyl
2b R* = neomenthyl

i. *n*-BuLi
ii TiCl₃.3THF
iii HCl/air

MeMgBr

R- 5, R* = menthyl

4a R* = menthyl
4b R* = neomenthyl

major H H
3
minor

R = H

i. *n*-BuLi
ii. ZrCl₄(THF)₂

menthyl =

neomenthyl =

6

ligand (11). We were, therefore, interested to see the effect of photolysis upon these chiral titanium complexes. Photolyzing the mother liquor left from the recrystallization of the **4a_R** diastereomer, which now consisted of an approximately equal mixture of diastereomers, with UV radiation at –30°C slowly led to a change in this isomeric ratio with preferential formation of the most thermodynamically stable product, i.e., the **4a_S** diastereomer, which was initially the minor isomer. Thus, after irradiating for 1 week, the solution contained a 1:3 ratio of **4a_R**:**4a_S**, and upon cooling to –60°C the **4a_S** diastereomer selectively crystallized out.

Hence, both diastereomers could be obtained and the crystal structures of both were determined.

In contrast, the separation of the two diastereoisomers of the neomenthyl complex **4b** by recrystallization was not possible because of the high solubility of both diastereoisomers in hydrocarbon solvents. For example, no crystals were formed even after cooling a hot, saturated hexane solution of **4b** to –30°C for a number of days. Attempts to significantly increase the diastereomeric ratio by UV irradiation were also unsuccessful. Thus, the initial diastereomeric ratio of 1.3:1 changed to only 1:1.4 after UV irradiation for 1 week at

–30°C. Further irradiation had no effect upon this ratio. Crystallization from pentane was attempted, but no single diastereoisomer was isolated by this method.

The use of silanized silica as a stationary phase in liquid chromatography has proved successful for the purification of ansa-bis(η^5-cyclopentadienyl)dichlorotitanium complexes (12). Therefore, silica gel was modified via treatment with chlorotrimethylsilane (see *Experimental*), and the resulting silanized silica gel was used as a stationary phase for the attempted separation of the two diastereoisomers of **4b**. Unfortunately, no separation of the two diastereoisomers occurred, although there were no visible signs of decomposition either. Attempts to separate the diastereoisomers by converting the dichloride complex into a less soluble derivative by reaction with either 1,2-benzenedimethanol or (*R*)-(–)-acetylmandelic acid failed to yield stable characterizable products.

From the diastereoselectivity observed in the initial formation of the titanium complexes it is clear that the difference in free energy between the two menthyl diastereomers is greater than the difference in free energy between the two neomenthyl diastereomers. The initial diastereomeric ratio is determined by kinetic control but under UV irradiation the diastereomers are in equilibrium and the ratio is determined by their relative thermodynamic stabilities. Hence, it is possible to estimate the difference in free energy between the two diastereoisomers of the menthyl substituted complex (**4a$_R$** and **4a$_S$**) at –30°C as 2.2 kJ mol^{-1} and that of the neomenthyl diastereomers as 0.7 kJ mol^{-1}.

The NMR spectra of the titanium complexes **4a** and **4b** are worthy of comment; the three cyclopentadienyl protons are grouped together in a similar manner in both diastereoisomers of both catalysts with one proton exhibiting a greater degree of deshielding than the other two protons adjacent to the silicon bridge. This proton sits directly over one of the chloride ligands, and the magnetic anisotropy of the halogen atom has been ascribed as the origin of the low-field shift of such protons (13).

The optically pure dichloro-complex **4a$_R$** was reacted with methylmagnesium bromide to give the corresponding (*R*)-TiMe$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$R*) (R* = menthyl) (**5$_R$**). We were surprised and disappointed to find that this compound was rather unstable, like the corresponding Ti(C$_5$H$_5$)$_2$Me$_2$ (14), as compared to the more robust Ti{(C$_5$H$_4$)$_2$SiMe$_2$}Me$_2$ (15). Similarly, although synthesis of the related indenyl ligand system C$_5$HMe$_4$SiMe$_2$C$_9$H$_7$ (**3**) proved to be relatively straightforward, complexation of this ligand was not. The reaction of TiCl$_3$·3THF with the dilithium salt of **3** using similar reaction conditions as those successfully used for the syntheses of the titanium complexes **4a** and **4b** repeatedly failed to yield TiCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_9$H$_7$). Titanium indenyl complexes are notoriously difficult to synthesize or are unstable and, therefore, these are often prepared and reduced in situ to the corresponding more stable tetrahydroindenyl titanium complexes using hydrogen in the presence of a PtO$_2$ catalyst (12a, 16); unfortunately, even this strategy

Fig. 1. Molecular structure of TiCl$_2$\{η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$(menthyl)\}, (*R*)-diastereoisomer **4a$_R$**. Hydrogen atoms are omitted for clarity.
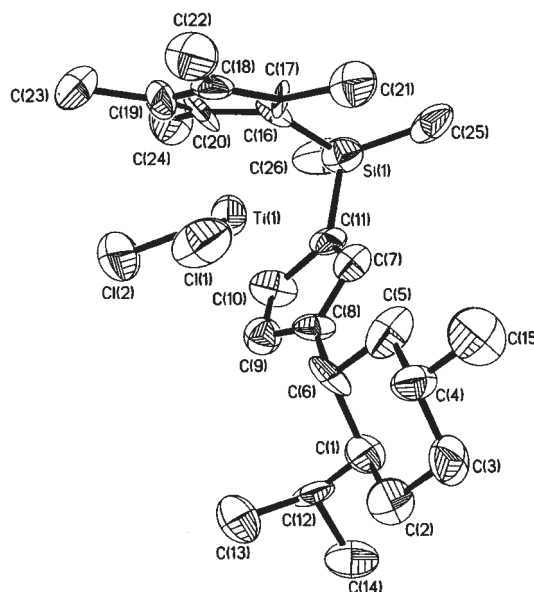
failed to yield a stable complex. More successful was the synthesis of the corresponding zirconium indenyl complex ZrCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_9$H$_6$) (**6**), although this too proved to be unstable in solution.

Comparison of the X-ray crystal structures of the diastereoisomers 4a$_R$ and 4a$_S$

Crystallographic data are presented in Table 1 and atomic cooordinates are listed in Table 2.[3] The crystal stucture of the menthyl complex with *R* planar chirality (**4a$_R$**) is shown in Fig. 1; the corresponding diastereoisomer with *S* planar chirality crystallized as two independent molecules per unit cell and these are shown as **4a$_S$** and **4a$_{S'}$** in Figs. 2*a* and *b*, respectively. As expected, the bond distances in all the diastereoisomers are essentially similar taking into account that the face of the menthyl-Cp is reversed on going from **4a$_R$** to **4a$_S$** and **4a$_{S'}$** (Table 3). In all the structures each cyclopentadienyl ring is asymmetrically pentahapto bonded to the titanium (Ti—C in the range 2.35–2.59 Å), with the greater asymmetry for the menthylated ring in which the menthylated carbon C(8) is always more distant from the titanium than any other ring carbon. All these Ti—C distances are within the range reported for similar titanium complexes (17). In each complex both five-membered rings are planar with the four methyl groups of the tetramethylcyclopentadienyl ring bent away from the titanium by up to 0.24 Å from the mean plane of the cyclopentadienyl ring. A consequence of the short bridging unit and the bulky menthyl substituent is that the angle between the planes of the two Cp rings (i.e., the bite angle) is relatively large at 58.0 and 59.2° for **4a$_R$** and **4a$_S$**, respectively, (Table 4) compared to

Table 1. Crystallographic data for diffraction studies of **4a$_R$** and **4a$_S$**.

	4a$_R$	**4a$_S$**
Crystal parameters		
Empirical formula	$C_{26}H_{40}Cl_2SiTi$	$C_{26}H_{40}Cl_2SiTi$
Formula weight	499.49	499.49
Color	Red	Red
Solvent	*n*-Pentane	*n*-Pentane
Crystal size (mm)	$0.80 \times 0.20 \times 0.05$	$0.07 \times 0.04 \times 0.03$
Habit	Elongated thin plates	Red plates
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (D_4^2, No. 19)	$P2_1$ (C_2^2, No. 4)
a (Å)	27.857(11)	8.5810(10)
b (Å)	9.985(5)	38.679(4)
c (Å)	9.596(4)	8.5842(10)
β (°)		113.001(2)
V (Å^3)	2669.1(18)	2622.6(5)
Z	4	4
D_{calcd} (Mg m^{-3})	1.243	1.265
μ (cm^{-1})	5.73	5.87
$F(000)$	1064	1064
Intensity data		
Diffractometer	Stoe Stadi-2 2-circle	Nicolet R3 4-circle
λ (Mo Kα radiation) (Å)	0.71073	0.71073
Monochromator	Graphite, incident beam	Graphite, incident beam
Reflections measured	$+h, +k, \pm l$	$+h, +k, \pm l$
2θ range (°)	6.5–50	2.11–23.32
Temperature (K)	293	150(2)
Scan type	ω	ω
Standard reflections	2 every 50 reflections	3 every 100 reflections
No. of reflections collected	2701	11784
No. of reflections used	902	5734
Acceptance criterion	$|F|/\sigma(|F|) > 3.0$	$|F|/\sigma(|F|) > 4.0$
Absorption coefficient (mm^{-1})	0.573	0.587
Transmissionn coefficient (min)	0.882	0.9601
Transmissn coefficient (max)	0.972	0.9826
Absorption correction	Gaussian integration	Semi-empirical
Structure solution		
Method	Patterson–Fourier	Patterson–Fourier
Programs	SHELXTL (25)	SHELXTL (25)
Scattering factors	Ref. 26	Ref. 26
Refinement method	Blocked-cascade least-squares	Full-matrix least-squares on F^2
R	0.0628	0.0646
wR_2		0.1829
R_ω	0.0503 (266 parameters)	
Weighting scheme	$\omega^{-1} = [\sigma^2(F) + 0.00021(F)^2]$	$\omega^{-1} = [\sigma^2(F_0^2) + (0.1148P)^2 + 0.3205P]$
Absolute structure parameter		0.00(5)
Largest diff. peak and hole (e Å^{-3})	+0.30 and −0.37	+0.494 and −0.536
H refinement	Riding mode	Riding mode

other ansa-dichlorotitanocenes; for example, [TiCl$_2$\{(η^5:η^5-C$_5$H$_4$)$_2$SiMe$_2$\}] has a bite angle of 56.2° (17a).

The Cl(1)-Ti-C(11) and Cl(1)-Ti-C(16) bond angles are 131(4) and 131.1(3)°, respectively, for **4a$_R$**, whereas the coresponding angles for **4a$_S$** are 124.1(2) and 123.11(19)°, showing the different relative orientations of the ligands about the titanium. However, the differences between the two diastereoisomers are best viewed by comparison of the space-filling models (Fig. 3). With the bulky C$_5$Me$_5$ ligand

occupying the top face of the complex it can be seen that the bottom face of **4a$_R$** is more sterically crowded because the *i*-Pr group of the menthyl substituent points across this face, whereas in **4a$_S$** the menthyl group is orientated such that the *i*-Pr group points away from this face. This steric crowding presumably accounts for the smaller Cl-Ti-Cl bond angle of 95.3(2)° found in **4a$_R$** compared to that of 97.75(8)° found in **4a$_S$**. If the structures of the diastereoisomers are similar in solution this would imply that the diastereoisomer **4a$_R$**

Table 2. Atomic coordinates (1 x 10^4) and equivalent isotropic displacement parameters (U_{eq}) (1 x 10^3) for the two diastereoisomers of [TiCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$(menthyl)].

Atom	x	y	z	U_{eq} (Å^2)
4a$_R$				
Ti(1)	3419(1)	3009(3)	4031(3)	53(1)*
Cl(1)	3908(2)	1180(4)	4427(5)	92(2)*
Cl(2)	2932(2)	1940(6)	2376(4)	113(2)*
Si(1)	3200(1)	6117(5)	4854(4)	55(2)*
C(1)	5008	3654(15)	1535(11)	54(6)*
C(2)	5498	3008(17)	1617(15)	66(7)*
C(3)	5746	3136(18)	3004(15)	64(7)*
C(4)	5455	2532(14)	4157(14)	53(7)*
C(5)	4955	3225(16)	4182(15)	70(7)*
C(6)	4689	3053(15)	2756(13)	48(5)*
C(7)	4054	4672(14)	3928(16)	42(6)*
C(8)	4207	3773(16)	2851(14)	44(6)*
C(9)	3814	3754(14)	1921(13)	52(4)
C(10)	3467	4674(14)	2303(13)	57(6)*
C(11)	3604	5277(14)	3590(13)	46(6)*
C(12)	4767	3519(12)	135(12)	53(6)*
C(13)	4680(5)	2087(14)	−352(12)	68(6)*
C(14)	5060(4)	4259(14)	−976(13)	67(7)*
C(15)	5701(4)	2694(15)	5549(12)	82(8)*
C(16)	3016(4)	4455(13)	5595(12)	39(5)*
C(17)	3327(4)	3600(15)	6376(14)	39(6)*
C(18)	3153(6)	2341(15)	6397(14)	48(6)*
C(19)	2739(5)	2308(14)	5508(15)	58(7)*
C(20)	2649(4)	3617(15)	5083(13)	62(6)*
C(21)	3740(5)	4040(13)	7288(14)	68(7)*
C(22)	3335(6)	1159(13)	7299(13)	84(7)*
C(23)	2415(5)	1045(15)	5306(16)	106(9)*
C(24)	2224(4)	4044(17)	4236(15)	88(8)*
C(25)	3512(4)	7278(13)	6011(15)	77(7)*
C(26)	2723(5)	7099(16)	4014(14)	89(7)*
4a$_S$				
Ti(1)	2610(1)	3540(1)	1003(1)	32(1)
Ti(1A)	1003(1)	398(1)	2610(1)	31(1)
Si(1)	−864(2)	3538(1)	−2404(2)	41(1)
Si(1A)	−2409(2)	401(1)	−866(2)	40(1)
Cl(1)	3090(3)	3568(1)	3851(2)	48(1)
Cl(1A)	3853(2)	370(1)	3082(2)	48(1)
Cl(2)	5432(2)	3511(1)	1308(2)	51(1)
Cl(2A)	1311(2)	426(1)	5433(2)	51(1)
C(1)	1476(13)	2413(3)	3246(13)	71(3)
C(2)	1848(14)	2306(5)	5067(16)	114(6)
C(3)	3785(16)	2274(5)	6124(16)	112(5)
C(4)	4743(15)	2594(3)	6109(12)	75(3)
C(5)	4280(10)	2720(3)	4279(11)	54(2)
C(6)	2408(11)	2769(2)	3333(11)	50(2)
C(7)	517(10)	3117(2)	656(9)	39(2)
C(8)	1992(9)	2924(2)	1585(9)	39(2)
C(9)	2964(10)	2912(2)	620(10)	42(2)
C(10)	2068(10)	3082(2)	−950(9)	41(2)
C(11)	482(9)	3196(2)	−998(9)	39(2)
C(12)	−399(12)	2399(3)	2089(14)	76(3)
C(13)	−1511(14)	2602(4)	2782(17)	101(5)
C(14)	−1011(17)	2023(5)	1700(20)	124(6)
C(15)	6647(13)	2538(3)	7040(13)	75(3)

Table 2 (*concluded*).

Atom	x	y	z	U_{eq} (Å^2)
C(16)	562(8)	3884(2)	−1089(8)	35(2)
C(17)	603(8)	3993(2)	540(8)	33(2)
C(18)	2167(9)	4167(2)	1437(9)	35(2)
C(19)	3139(9)	4156(2)	418(8)	35(2)
C(20)	2176(9)	3979(2)	−1085(8)	36(2)
C(21)	−766(9)	3967(2)	1194(9)	40(2)
C(22)	2652(10)	4362(2)	3067(9)	47(2)
C(23)	4776(9)	4333(3)	852(10)	52(2)
C(24)	2762(10)	3929(3)	−2523(8)	55(3)
C(25)	−967(12)	3492(3)	−4605(11)	68(3)
C(26)	−3064(9)	3541(3)	−2472(11)	55(2)
C(1A)	3246(14)	1527(3)	1498(12)	74(3)
C(2A)	5067(15)	1631(5)	1859(14)	111(6)
C(3A)	6121(16)	1665(5)	3752(15)	114(6)
C(4A)	6078(13)	1335(3)	4747(14)	76(3)
C(5A)	4279(10)	1215(2)	4297(9)	50(2)
C(6A)	3292(12)	1168(3)	2392(10)	55(2)
C(7A)	651(9)	822(2)	503(9)	37(2)
C(8A)	1600(10)	1014(2)	2000(9)	41(2)
C(9A)	610(10)	1023(2)	2980(10)	43(2)
C(10A)	−947(10)	854(2)	2066(9)	43(2)
C(11A)	−990(9)	741(2)	469(9)	40(2)
C(12A)	2086(15)	1538(3)	−379(11)	74(3)
C(13A)	2710(17)	1338(4)	−1521(13)	108(5)
C(14A)	1690(20)	1917(5)	−1034(16)	125(6)
C(15A)	7045(14)	1394(3)	6664(13)	80(3)
C(16A)	−1075(9)	52(2)	564(8)	37(2)
C(17A)	−1092(9)	−40(2)	2184(9)	40(2)
C(18A)	409(10)	−216(2)	3102(8)	36(2)
C(19A)	1424(9)	−230(2)	2159(9)	35(2)
C(20A)	534(9)	−61(2)	600(8)	33(2)
C(21A)	−2517(10)	13(3)	2773(10)	53(2)
C(22A)	824(11)	−391(3)	4798(10)	54(2)
C(23A)	3032(10)	−426(2)	2666(11)	50(2)
C(24A)	1214(10)	−30(2)	−774(9)	42(2)
C(25A)	−4631(10)	436(3)	−971(12)	67(3)
C(26A)	−2454(11)	396(3)	−3057(9)	56(2)

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

should be a more stereoselective catalyst. Preliminary results from hydrosilylation experiments (Table 5) are in keeping with this statement (18).

Experimental

All reactions of moisture sensitive reagents were performed under nitrogen. THF was heated under reflux over sodium benzophenone ketyl and distilled under nitrogen. Hexane, toluene, and diethyl ether were heated under reflux over sodium and freshly distilled under nitrogen prior to use.

Menthyltosylate [(1*R*, 2*S*, 5*R*)-(−)-2-isopropyl-5-methyl-cyclohexyl tosylate] and neomenthyltosylate [(1*S*, 2*S*, 5*R*)-(+)-2-isopropyl-5-methylcyclohexyl tosylate] were prepared by modifications of the literature procedures (19, 20) as we have previously described (21). (+)-Neomenthyl tosylate is thermally unstable, therefore, it is best stored at −10°C.

Table 3. Selected bond lengths (Å) with estimated standard deviations for the two diastereoisomers of [TiCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$(menthyl)].

	4a$_R$	4a$_S$	4a$_{S'}$
Ti(1)—Cl(1)	2.310(5)	2.3171(18)	2.3201(19)
Ti(1)—Cl(2)	2.346(5)	2.3349(19)	2.3352(17)
Ti(1)—C(7)	2.428(14)	2.359(8)	2.347(8)
Ti(1)—C(8)	2.585(14)	2.530(9)	2.535(9)
Ti(1)—C(9)	2.421(13)	2.484(8)	2.477(9)
Ti(1)—C(10)	2.352(13)	2.358(7)	2.370(8)
Ti(1)—C(11)	2.360(14)	2.366(7)	2.367(7)
Ti(1)—C(16)	2.366(12)	2.370(7)	2.367(7)
Ti(1)—C(17)	2.340(14)	2.381(7)	2.391(8)
Ti(1)—C(18)	2.479(14)	2.508(8)	2.500(8)
Ti(1)—C(19)	2.468(14)	2.516(8)	2.509(8)
Ti(1)—C(20)	2.448(13)	2.392(7)	2.398(7)
Si(1)—C(11)	1.855(14)	1.856(8)	1.852(9)
Si(1)—C(16)	1.877(14)	1.866(9)	1.882(8)
C(7)—C(8)	1.434(21)	1.416(11)	1.433(11)
C(7)—C(11)	1.431(19)	1.441(10)	1.432(11)
C(8)—C(9)	1.413(19)	1.387(11)	1.410(11)
C(9)—C(10)	1.383(19)	1.424(11)	1.418(11)
C(10)—C(11)	1.426(18)	1.417(11)	1.425(10)
C(16)—C(17)	1.430(18)	1.448(10)	1.441(10)
C(16)—C(20)	1.409(18)	1.432(10)	1.437(11)
C(17)—C(18)	1.347(22)	1.428(11)	1.397(11)
C(18)—C(19)	1.435(21)	1.426(10)	1.402(10)
C(19)—C(20)	1.393(20)	1.409(11)	1.416(11)

Table 4. Bond angles (°) with estimated standard deviations for the two diastereoisomers of [TiCl$_2$(η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$(menthyl)].

	4a$_R$	4a$_S$	4a$_{S'}$
Cl(1)-Ti(1)-C1(2)	95.3(2)	97.75(8)	97.86(8)
Cl(1)-Ti(1)-C(8)	78.7(4)	78.52(18)	78.26(19)
Cl(2)-Ti(1)-C(8)	109.2(3)	102.76(19)	102.77(17)
Cl(1)-Ti(1)-C(11)	131.3(4)	124.1(2)	123.7(2)
Cl(2)-Ti(1)-C(11)	116.2(4)	121.8(2)	122.3(2)
Cl(1)-Ti(1)-C(16)	131.1(3)	123.11(19)	122.64(19)
Cl(2)-Ti(1)-C(16)	115.6(3)	122.77(18)	122.89(18)
C(11)-Ti(1)-C(16)	68.4(4)	68.4(3)	68.5(3)
C(11)-Si(1)-C(16)	90.8(6)	91.3(3)	91.1(3)
C(6)-C(8)-C(7)	126.8(12)	125.2(7)	125.2(7)
C(6)-C(8)-C(9)	129.7(12)	127.6(7)	128.3(7)

Symmetry transformations used to generate equivalent atoms:

Fig. 2. Molecular structure of the two independent molecules of TiCl$_2$\{η^5:η^5-C$_5$Me$_4$SiMe$_2$C$_5$H$_3$(menthyl)\}, (S)-diastereoisomer **4a$_S$**. Hydrogen atoms are omitted for clarity.

Trichlorotris(tetrahydrofuran)titanium was synthesized by the procedure reported by Manzer (22).

Preparation of silanized silica gel

Dichloromethane (1500 cm^3) was added to silica gel (150 g) and the resulting slurry rapidly stirred by an overhead stirrer. Chlorotrimethylsilane (150 cm^3) was added and the slurry stirred for a further 1 h. The slurry was washed with saturated sodium hydrogencarbonate solution (100 cm^3) and then with water until the washings were neutral. The resulting silanized silica gel was washed with acetone and dried in an oven at 100°C overnight.
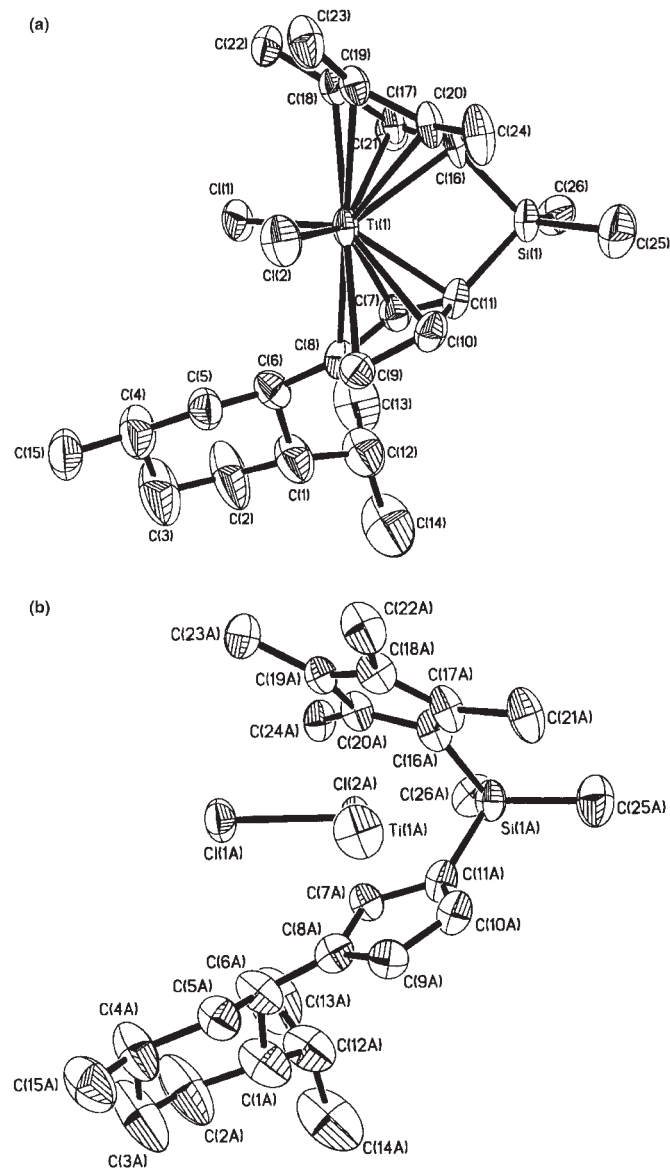
Menthylcyclopentadiene

This was prepared by the following modification of the literature procedure (23). NaH (9.6 g, 0.4 mol, i.e., 19.2 g 50% dispersion) was washed with hexane, and freshly distilled THF (150 cm^3) was added. Freshly cracked cyclopentadiene (26 g, 0.4 mol) in THF (50 cm^3) was added slowly over a 2 h period and the mixture stirred until the bubbling stopped and the NaH was consumed (approximately 30 min). The resulting pale red solution of sodium cyclopentadienide was added to a solution of (1S, 2S, 5R)-5-methyl-2-(2-propyl)-cyclohexyl tosylate (63.4 g, 0.2 mol) in THF (200 cm^3) at 0°C via cannula. This mixture was heated under reflux for 6 h producing a sodium tosylate precipitate. Then the mixture was cooled, filtered, and the solvent removed in vacuo. The brown viscous residue was redissolved in diethyl ether and washed with water (5 × 100 cm^3). After drying the organic layer over Na$_2$SO$_4$, the solvent was

Table 5. Catalytic hydrosilylations of ketones in toluene.

Substrate		Catalyst $4a_R$		Catalyst $4a_S$	
![ketone structure]	Temperature (°C)	Conversion (%)	ee (%)[a]	Conversion (%)	ee (%)[a]
X = H	25	100[b]	82 (S)	100[b]	16 (R)
X = F	65	100[c]	66 (S)	38[c]	12 (R)
X = OMe	65	100[c]	65 (S)	100[c]	23 (R)

[a]Absolute configurations of the product alcohols are shown in parentheses.
[b]After 24 h.
[c]After 1 h.

Fig. 3. The structures of the two diastereoisomers $4a_R$ and $4a_S$ compared.

$4a_R$ $4a_S$
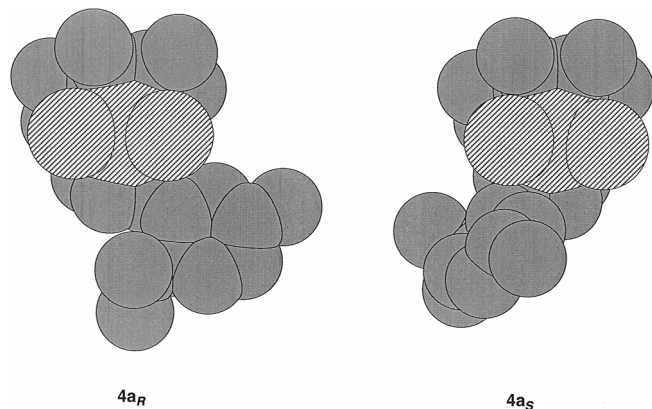
removed in vacuo to yield a brown oil which was distilled[4] to yield the product as a colourless liquid ($bp_{0.1}$ 70°C, 23.84 g, 58%). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 0.71 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH$_3$), 0.84 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH$_3$), 0.88 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH$_3$), 0.95–1.84 (m, 9H, CH$_2$'s and CH's), 2.31–2.48 (m, 1H, CH), 2.83–2.98 (m, 2H, allylic), 5.97–6.54 (m, 3H, vinylic). 95% pure by GC.

Preparation of neomenthylcyclopentadiene

An analagous procedure to that employed for the preparation of menthylcyclopentadiene but using menthyltosylate yielded the title product as a colourless liquid ($bp_{0.01}$ 70°C, 42%, 95% pure by GC). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 0.79–0.90 (m, 9H, CH$_3$), 0.90–1.86 (m, 9H, CH$_2$'s and CH's), 2.90–3.12 (m, 3H, CH and allylic), 6.08–6.58 (m, 3H, vinylic).

Preparation of 1,2,3,4-tetramethylcyclopentadiene

The synthesis was based on the method reported by Marks and co-workers (4). 2,3,4,5-Tetramethylcyclopent-2-enone (24) (18.8 g, 0.13 mol) in diethyl ether (50 cm^3) was added over 1 h to a suspension of lithium aluminium hydride (2.5 g, 0.07 mol) in diethyl ether (200 cm^3) and the mixture was stirred for 2 h. Aqueous hydrochloric acid (1.0 M, 300 cm^3) was added slowly and the mixture stirred for 16 h in air. The organic layer was separated and the aqueous layer washed with diethyl ether (3 × 100 cm^3). Both organic layers were

combined, washed with a saturated sodium carbonate solution (2 × 50 cm^3), and dried over Na$_2$SO$_4$. Removal of the solvent in vacuo gave a yellow liquid that was distilled to produce the title product as colourless liquid (30–35°C, 0.5 mm Hg, 6.59 g, 37%). (EI) GC–MS m/z (%): 122 (M$^+$, 60). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 1.80 (br s, 6H, 2CH$_3$), 1.95 (br s, 6H, 2CH$_3$), 2.75 (br s, 2H, C$_5$Me$_4$H$_2$).

Preparation of 1-(chlorodimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene

The literature procedure (4) was modified as follows. 1,2,3,4-Tetramethylcyclopentadiene (6 g, 0.05 mol) was dissolved in dry petroleum ether (bp 40–60°C) and a solution of n-butyllithium (2.5 M, 20 cm^3, 0.05 mol) was added at 0°C over 1 h. The mixture was stirred for 15 h at room temp to produce a milky white suspension which was thinned by the addition of THF (45 cm^3). A solution of dichlorodimethylsilane (9.7 g, 0.075 mol) in THF (30 cm^3) was added at 0°C over 1 h and the mixture stirred for 15 h. The yellow solution was filtered under nitrogen through Celite previously dried at 100°C under vacuum to remove the lithium chloride precipitate. The solvent was removed in vacuo to give the crude product as a yellow-brown oil which was distilled to give the title product as a yellow-green liquid; $bp_{0.1}$ 60–65°C (lit. $bp_{0.1}$ 56–60°C), 7.05 g (67%). EI-MS m/z (%): 214 (M$^+$, 60), 121 ([M – SiMe$_2$Cl]$^+$), 97, 106 ([M – SiMe$_2$Cl –Me]$^+$, 100). IR (neat) cm^{-1}: 2961s, 2916s, 2861s, 1445m, 1380m, 1258s, 1058br, 844s, 811br, 656m. ^{1}H NMR (250 MHz, CDCl$_3$) δ: 0.30 (s, 6H, 2Si-CH$_3$), 1.9 (s, 6H, 2CH$_3$), 2.06 (s, 6H, 2CH$_3$) 3.06 (br s, 1H, Cp-H).

Preparation of 1-(2,3,4,5)-tetramethylcyclopentadiene)-1′-(3′(-1R, 2S, 5R)-5-methyl-2-(2-propyl)-cyclohexylcyclopentadiene)dimethylsilane (2a)

The synthesis was based on the procedure reported by Marks and co-workers (4). A solution of lithium menthylcyclopentadienide was prepared by adding a solution of n-butyllithium (2.5 M, 5.6 cm^3, 0.014 mol) to a solution of (1R, 2S, 5R)-5-methyl-2-(2-propyl)-cyclohexylcyclopentadiene (2.81 g, 0.014 mol) in THF (50 cm^3) at 0°C and stirring the mixture for 30 min at room temp. The solution was then transferred via cannula at room temp to a solution of freshly distilled 1-(chlorodimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene (3.8 g, 0.018 mol) in THF (25 cm^3). The

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[4]The vacuum distillation must be performed at high vacuum since the product decomposes at higher temperatures and this is probably the main reason for the low yields. A two stage distillation and washing the condenser after the CpH–(CpH)$_2$ is distilled at 30°C is also recommended to ensure no CpH contaminates the product.

mixture was heated under reflux for 12 h, cooled to room temp, and filtered to remove the lithium chloride formed. Solvent was removed in vacuo to yield a brown residue which was redissolved in diethyl ether, washed with water (3×10 cm^3), dried over Na$_2$SO$_4$, and the solvent removed in vacuo to yield a yellow-brown oil. Excess 1-(chlorodimethylsilyl)-2,3,4,5-tetramethylcyclopentadiene was removed by distillation (heating to 80°C, 0.01 mm Hg) to yield the isomers of the desired menthyl product **2a** as a brown residue. Yield 3.55 g (67%). EI-MS m/z (%): 382 (M$^+$, 10), 261 ([M – TMCp]$^+$, 31), 204 ([M – TMCpSiMe$_2$]$^+$, 100). ^{1}H NMR (250 MHz, CDCl$_3$) δ:–0.35–0.10 (m, 6H, Si-CH$_3$), 0.62 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH$_3$), 0.75 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH$_3$), 0.80 (d, $^3J_{H,H}$ = 6 Hz, 3H, CH$_3$), 0.85–1.60 (m, 9H, CH$_2$'s), 1.60–1.75 (m, 6H, Cp-CH$_3$), 1.78 (s, 3H, Cp-CH$_3$), 1.90 (s, 3H, Cp-CH$_3$), 2.29 (m, 1H, menthyl CH), 2.61–3.21 (m, 2H, allylic), 5.8–6.60 (m, 3H, Cp-H). ^{13}C NMR (63 MHz, CDCl$_3$) δ: 151.9, 150.4, 145.5, 136.1, 133.5 (Cp tertiary), 143.0, 142.0, 133.9, 138.5, 131.1, 131.0, 130.4, 127.3, 126.8, 126.6 (Cp quaternary), 47.4, 46.6, 41.9, 33.0, 27.9, 27.7, 22.6, 21.6, 15.3, 14.7, 14.2, 11.3, 11.1 (CH$_3$'s and CH's), 43.7, 35.4, 24.5, (CH$_2$'s), 1.0, –4.0 (Si-CH$_3$).

Preparation of 1-(2,3,4,5-tetramethylcyclopentadienyl)-1′-(3′-(1S, 2S, 5R)-5-methyl-2-(2-propylcyclohexyl-cyclopentadienyl)dimethylsilane (2b)

An analogous procedure to that employed for the preparation of 1-(2,3,4,5-tetramethylcyclopentadienyl)-1′-[3′-menthylcyclopentadienyl]dimethylsilane but employing neomenthylcyclopentadiene yielded the desired neomenthyl product **2b** as a yellow oil (70%) found to be 91% pure by GC. (EI) GC–MS m/z (%): 382 (M$^+$, 12), 261 ([M – TMCp]$^+$, 78), 179 ([M – nmCp]$^+$, 100). ^{1}H NMR (250 MHz, CDCl$_3$) δ:–0.05–0.33 (m, 6H, Si-CH$_3$), 0.90–1.11 (m, 9H, neomenthyl CH$_3$), 1.07–1.85 (m, 9H, CH$_2$'s and CH's), 1.85–2.20 (m, 12H, Cp-CH$_3$'s), 3.00–3.40 (m, 3H, allylic, neomenthyl CH), 6.15 (br s, 1H, olefinic), 6.36–6.48 (m, 1H, olefinic), 6.61–6.72 (m, 1H, olefinic). ^{13}C NMR (63 MHz, CDCl$_3$) δ: 156.5, 147.7, 147.3, 142.6, 136.1, 135.2, 133.2, 132.4, 129.0, 119.7 (Cp's), 48.0, 47.9, 37.8, 37.7 (CH's), 42.4, 35.8, 26.1 (neomenthyl CH$_2$'s), 30.2, 26.5, 22.8, 21.4, 21.3, 14.7, 11.3 (CH$_3$'s), 1.1, –2.6 (SiMe$_2$).

Synthesis of (R/S)-dichloro[1-(η⁵-3′-(1R, 2S, 5R)-5-methyl-2-(2-propyl)cyclohexyl-cyclopentadienyl)-1′-(η⁵-2,3,4,5-tetramethylcyclopentadienyl)dimethylsilane]titanium (4a$_{R/S}$)

1-(2,3,4,5-Tetramethylcyclopentadiene)-1′-[3′-menthylcyclopentadiene]dimethylsilane (3.02 g, 7.9 mmol) was dissolved in THF (45 cm^3). A solution of n-butyllithium (2.5 M, 6.3 cm^3, 15.8 mmol) in hexanes was added at 0°C and the mixture stirred at room temp for 30 min. The solution was cooled to –78°C and TiCl$_3$·3THF (2.9 g, 7.9 mmol) was added rapidly against a stream of nitrogen and the mixture was allowed to warm to room temp before heating under reflux for 6 h. After cooling to room temp, chloroform (45 cm^3) and concentrated aqueous hydrochloric acid (1 M, 30 cm^3) were added and the mixture stirred at room temp in air for 30 min. The organic layer was separated, dried, and the solvent removed in vacuo to yield a red viscous oil which was shown by ^{1}H NMR to be a 3:1 mixture of R:S.

Isolation of (R)-dichloro[1-(η⁵-3′-(1R, 2S, 5R)-5-methyl-2-(2-propyl)cyclohexyl-cyclopentadienyl)-1′-(η⁵-2,3,4,5-tetramethylcyclopentadienyl)dimethylsilane]titanium (4a$_R$)

The above oil was dissolved in the minimum of boiling hexane and crystallized at –30°C, to yield the title product as red crystals. Yield 0.75g (19%), mp 162–164°C. [α]^{20} (c 0.032, DCM): –62.5° (589 nm), –103.1° (578 nm), and –256.3° (549 nm). EI-MS m/z (%): 498 (M$^+$, 10%), 463 ([M – Cl]$^+$, 100). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 0.66 (m, 3H, CH$_3$), 0.76 (m, 3H, CH$_3$), 0.79 (m, 3H, CH$_3$), 0.82 (m, 3H, CH$_3$), 0.83 (m, 3H, CH$_3$), 0.88–1.76 (m, 9H, CH's, CH$_2$'s), 1.84 (s, 3H, Cp-CH$_3$), 1.87 (s, 3H, Cp-CH$_3$), 2.00 (s, 3H, Cp-CH$_3$), 2.10 (s, 3H, Cp-CH$_3$), 2.69–2.81 (m, 1H, CH), 5.37 (t, $^4J_{H,H}$ = 3 Hz, 1H, Cp-H), 5.67 (t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 1H, Cp-H), 6.50 (t, $^3J_{H,H}$ $^4J_{H,H}$ = 3 Hz, 1H, Cp-H). ^{13}C NMR (63 MHz, CDCl$_3$) δ: 155.2, 145.7, 139.1, 137.4, 128.7, 103.4, 96.8 (Cp quarterary), 126.7, 122.6, 114.3 (C1, C3, C4), 48.6 (C12), 41.7, 41.2 (C6, C7), 35.2, 32.3 (C10, C8), 27.0 (C13), 24.8 (C11) 22.8, 21.8, 16.7, 16.3, 16.2, 13.8, 12.8 (TMCp CH$_3$'s and menthyl CH$_3$'s), 0.36, –1.5 (SiMe$_2$). Anal calcd. for C$_{26}$H$_{40}$Cl$_2$SiTi: C 62.5, H 8.1, Cl 14.2; found: C 62.4, H 8.1, Cl 14.1.

Isolation of (S)-dichloro[1-(η⁵-3′-(1R, 2S, 5R)-5-methyl-2-(2-propyl)cyclohexyl-cyclopentadienyl)-1′-(η⁵-2,3,4,5-tetramethylcyclopentadienyl)dimethylsilane]titanium (4a$_S$)

A 1:1 diastereomeric mixture (2 g) of (R)- and (S)-dichloro{1-[η⁵-3′-(menthylcyclopentadienyl)-1′-[η⁵-2,3,4,5-tetramethylcyclopentadienyl)dimethylsilane]}titanium was dissolved in toluene (200 cm^3), cooled to –30°C, and irradiated with UV light using a Hanovair medium pressure 125 W lamp. After 7 d the solvent was removed in vacuo and the mixture filtered through a silanized silica column, eluting with 4% diethyl ether in pet ether (40–60 ºC), resulting in a viscous red oil (1.1 g) which was shown by ^{1}H NMR spectroscopy to contain a S:R ratio of 3:1. The red oil was dissolved in boiling pentane and cooled to –30°C; the title compound crystallized as red-brown microcrystals which were collected by suction filtration (520 mg, 26%). FAB-MS m/z (%): 498 (M$^+$, 24), 463 ([M – Cl]$^+$, 100). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 0.70 (s, 3H, CH$_3$), 0.72 (m, 3H, CH$_3$), 0.81 (m, 3H, CH$_3$), 0.83 (m, 3H, CH$_3$), 0.86 (m, 3H, CH$_3$), 0.85–1.60 (m, 8H, CH's, CH$_2$'s), 1.69 (s, 3H, Cp-CH$_3$), 1.83 (s, 3H, Cp-CH$_3$), 2.05 (s, 3H, Cp-CH$_3$), 2.13 (s, 3H, Cp-CH$_3$), 2.25–2.88 (m, 1H, CH), 2.65–2.78 (m, 1H, CH), 5.05 (t, $^4J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 1H, Cp-H), 5.47 (t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 1H, Cp-H), 6.81 (t, $^3J_{H,H}$ = $^4J_{H,H}$ = 3 Hz, 1H, Cp-H). ^{13}C NMR (63 MHz, CDCl$_3$) δ: 148.3, 145.3, 141.6, 132.7, 127.8, 101.8, 96.5 (Cp quaternary), 134.9, 117.7, 115.0 (C1, C3, C4), 50.1 (C12), 41.8, 40.3 (C6, C7), 35.6 (C10), 32.7 (C8), 27.3 (C13), 24.9 (C11), 22.8, 21.7, 16.3, 15.7 (TMCp CH$_3$'s and menthyl CH$_3$'s), 0.0, 1.0 (SiMe$_2$). Anal. calcd. for C$_{26}$H$_{40}$Cl$_2$SiTi: C 62.5, H 8.1, Cl 14.2; found: C 62.8, H 8.3, Cl 14.3.

Preparation of (R/S)-dichloro[1-(η⁵-2,3,4,5-tetramethyl-cyclopentadienyl)-1′-(η⁵-3′-(1S, 2S, 5R)-5-methyl-2-(2-propyl)-cyclohexylcyclopentadienyl)dimethylsilane]titanium (4b$_{R/S}$)

1-(2,3,4,5-Tetramethylcyclopentadienyl)-1′-[3′-neomenthyl-cyclopentadienyl]dimethylsilane (3.07 g, 8 mmol) was dissolved in THF (45 cm^3). A solution of n-butyllithium (2.5 M,

6.4 cm^3, 16 mmol) in hexanes was added at 0°C via syringe and the mixture stirred at room temp for 30 min. The solution was cooled to –78 °C and TiCl$_3$·3THF (3.1 g, 8 mmol) was added rapidly against a stream of nitrogen; the mixture was maintained at –78°C for 5 h then allowed to warm to room temp and heated under reflux for a further 6 h. After cooling to room temp, chloroform (45 cm^3), together with concentrated aqueous hydrochloric acid (30 cm^3), was added and the mixture stirred at room temp in air for 30 min. The organic layer was separated, dried over Na$_2$SO$_4$, and the solvent removed in vacuo to yield a red, viscous oil. This was chromatographed on a silanized silica column eluting with hexane to remove organic residues and then a 4% diethyl ether – hexane mixture to elute a red band. Removal of solvent in vacuo yielded the title product (2.74 g, 68%), which was found to consist of a 1.3:1 mixture of (*R*) and (*S*) diastereoisomers, mp 122–130°C. [α]^{20} (*c* 0.026, CH$_2$Cl$_2$): +7.6° (589 nm), +30.8° (546 nm), and –61.5° (378 nm). FAB-MS *m/z* (%): 499 ([M + 1]$^+$, 20), 463 ([M – Cl]$^+$ 100). ^{1}H NMR (250 MHz, CDCl$_3$) δ: 0.05 (s, 6H, Si-CH$_3$), 0.79–0.96 (m, 9H, neomenthyl CH$_3$'s), 0.96–1.72 (m, 9H, neomenthyl CH's, CH$_2$'s), 1.77 (s, CH$_3$ (minor)), 1.79 (s, CH$_3$ (major)), 1.87 (s, CH$_3$ (major)), 1.93 (s, CH$_3$ (minor)), 2.09 (s, CH$_3$ (minor)), 2.12 (s, CH$_3$ (major)), 2.13 (s, CH$_3$ (major)), 2.18 (s, CH$_3$ (minor)), 3.50–3.60 (m, CH (minor)), 3.63–3.71 (m, CH (major)), 5.20–5.29 (m, 1H, Cp-H), 5.53–5.61 (m, 1H, Cp-H), 6.85–7.01 (m, 1H, Cp-H). ^{13}C NMR (63 MHz, CDCl$_3$) δ: 150.1, 146.4, 144.9, 144.0, 142.0, 141.6, 134.0, 132.0, 129.8, 128.9, 102.5, 102.1, 97.5, 97.1 (Cp quaternary), 137.0, 132.1, 119.1, 118.0, 116.5, 115.7 (Cp tertiary), 51.1, 49.6, 37.9, 37.2, 29.4, 29.1, 28.7, 28.0, 22.8, 22.6, 22.3, 21.9, 20.8, 16.3, 16.2, 16.0, 13.8, 13.7, 13.6, 13.3, 13.2, 1.0 (CH's, CH$_3$'s), 40.2, 38.8, 35.8, 35.7, 26.0, 25.0 (neomenthyl CH$_2$'s), 0.4, –0.3, –0.7, –1.0 (Si-CH$_3$'s). Anal. calcd. for C$_{26}$H$_{40}$Cl$_2$SiTi: C 62.5, H 8.1; found: C 61.2, H 8.2.

Synthesis of (*R*)-dimethyl[1-(η^5-3′-(–)-menthylcyclopentadienyl)-1′-(η^5-2,3,4,5-tetramethyl-cyclopentadienyl)dimethylsilane]titanium (5)

Methylmagnesium bromide (0.76 cm^3, 2.4 mmol, 3M in diethyl ether) was added to a red solution of **4a$_R$** in diethyl ether (15 cm^3) and the mixture stirred overnight in the dark. The diethyl ether was removed in vacuo from the resulting yellow solution and the product extracted by washing the residue with hexane (5 × 1 cm^3). The solvent was removed in vacuo. No further purification was attempted since previous attempts to crystallize the product or purify on a silanized silica column had failed. The product was stored under Ar$_{(g)}$ in a lightshielded flask at –30°C. FAB-MS *m/z*: 459 ([M + 1]$^+$), 429 ([M + 1 – 2CH$_3$]$^+$). ^{1}H NMR (250 MHz, C$_6$D$_6$) δ: –0.29 (s, 3H, Ti-CH$_3$), –0.19 (s, 3H, Ti-CH$_3$), 0.02 (s, 3H, Si-CH$_3$), 0.28, (s, 3H, Si-CH$_3$), 0.75 (d, *J* = 7 Hz, 3H, Me), 0.81 (d, *J* = 7 Hz, 3H, Me), 0.92 (d, *J* = 7 Hz, 3H, Me), 0.7–1.65 (m, 8H, menthyl-CH's, CH$_2$'s), 1.49 (s, 3H, TMCp CH$_3$), 1.59 (s, 3H, TMCp CH$_3$), 1.75 (s, 3H, TMCp CH$_3$), 2.11 (s, 3H, TMCp CH$_3$), 2.40 (m, 1H, menthyl CH), 2.70 (m, 1H, menthyl CH), 4.94 (t, $^4J_{H,H}$ = 2 Hz, $^4J_{H,H}$ = 2 Hz, 1H), 5.47 (t, $^3J_{H,H}$ = 2 Hz, $^4J_{H,H}$ = 2 Hz,1H), 6.93 (t, $^3J_{H,H}$ = 2 Hz, $^4J_{H,H}$ = 2 Hz, 1H). ^{13}C NMR (63 MHz, C$_6$D$_6$) δ: 143.3, 132.3, 129.9, 128.5, 122.7, 99.7, 94.3 (quarternary Cp),

122.3, 119.8, 111.3 (C1, C3, C4), 50.7, 47.5 (Ti-CH$_3$), 41.6, 35.6, 25.2 (neomenthyl CH$_2$'s), 47.9, 41.2, 33.0, 27.5, 23.0, 22.0, 16.3, 15.6, 15.4, 12.2, 12.1 (CH's, CH$_3$'s), 1.35, –1.9 (Si-CH$_3$).

Synthesis of 1-indenyl-1′-(2,3,4,5-tetramethylcyclopentadienyl)dimethylsilane (3)

Freshly distilled indene (48°C, 0.5 mm Hg, 4.3 cm^3, 37 mmol) was dissolved in THF (100 cm^3), cooled to 0°C, and then *n*-butyllithiium (2.5 M, 14.8 cm^3, 37 mmol) in hexanes was added over 30 min. The resulting orange-red solution was stirred at room temp for 2 h. 1-(Chlorodimethylsilyl)-2,3,4,5-tetramethyl-cyclopentadiene (10.0 g, 46 mmol) was dissolved in THF (75 cm^3) and the indenide solution transferred to this solution via cannula. The reaction mixture was heated to reflux for 18 h. The suspension was cooled to room temp and transferred via cannula through Celite, under nitrogen, to remove lithium chloride. The solvent was removed in vacuo from the filtrate yielding a red-brown oil which was redissolved in diethyl ether and washed with water (3 × 20 cm^3). The organic layer was dried over Na$_2$SO$_4$, filtered, and the solvent removed in vacuo to give an oil, which was heated to 80°C under 0.01 mm Hg to remove excess starting material and to leave the title product as an orange oil (7.29 g, 67.0%; 98% pure by GC). Attempts to separate isomers by recrystallization from pentane at –30°C were unsuccessful. Similarly, chromatography on alumina, eluting with pentane, failed to separate the isomers but did yield a yellow oil. (EI) GC–MS *m/z* (%): major, 294 (M$^+$, 33), 179 ([M – indenyl]$^+$, 44), 173 ([M – TMCp]$^+$, 100); minor, 294 (M$^+$, 52), 179 ([M – indenyl]$^+$, 49), 173 ([M – TMCp]$^+$, 100). ^{1}H NMR (250 MHz, CDCl$_3$) δ: –0.61, –0.21, –0.05 (s, 12H, 2SiCH$_3$ (major), 2SiCH$_3$ (minor)), 1.59 (s, 6H, 2Cp″CH$_3$ (major)), 1.71 (s, 6H, 2Cp″CH$_3$ (major)), 1.82 (s, 6H, 2Cp″CH$_3$ (minor)), 1.89 (s, 6H, 2Cp″CH$_3$ (minor)), 2.86 (br s, 2H, Cp″ipso-CH (major)), 3.05 (br s, 1H, Cp″ ipso-CH (minor)), 3.26 (d, *J* = 3 Hz, 2H, indenyl CH$_2$ (minor)), 3.45 (d, *J* = 3 Hz, 1H, indenyl SiCH (major)), 6.39 (dd, *J* = 11, 3 Hz, 2H, indenyl olefinic CH (major)), 6.49 (t, *J* = 3 Hz, 1H, indenyl olefinic CH (minor)), 6.69–6.75 (m, 2H, indenyl olefinic CH (major)), 6.95–7.15 (m, 6H, 2 × indenyl CH (major) and 2 × indenyl CH (minor)), 7.12–7.39 (m, 6H, 2 × indenyl CH (major) and 2 × indenyl CH (minor)). ^{13}C NMR (32.44 MHz, CDCl$_3$) δ: –5.9, -5.1, –3.7 (SiCH$_3$), 11.1, 11.3 (Cp″CH$_3$ (major)), 14.7, 14.8 (Cp″CH$_3$ (minor)), 40.8 (indenyl CH$_2$ (minor)), 44.4 (indenyl ipso-C (major)), 54.2 (Cp″ ipso-C (minor)), 54.6, (Cp″ ipso-C (major)), 120.8 (indenyl CH (major)), 122.2 (indenyl CH (minor)), 122.9 (indenyl CH (major)), 124.4 (indenyl CH (minor)), 123.7 (indenyl CH (major)), 126.0 (indenyl CH (minor)), 124.8 (indenyl CH (major)), 128.8 (indenyl CH (minor)), 129.1 (indenyl olefinic CH (major)), 135.7 (olefinic indenyl CH (major)), 144.3 (indenyl ipso-C (minor)), 144.4 (olefinic indenyl CH (minor)), 133.1, 135.1, 136.4, 136.5 (Cp″), 144.5, 144.9, 148.0 (indenyl).

Synthesis of dichloro[(η^5-1-indenyl)-1′-(η^5-2,3,4,5-tetramethylcyclopentadienyl)dimethyl silane]zirconium (6)

1-Indenyl-1′-(2,3,4,5-tetramethylcyclopentadienyl)dimethylsilane (1.01 g, 3.45 mmol) was dissolved in THF (10.0 cm^3) and the solution cooled to –78°C. *n*-Butyllithium (2.3 M,

3.00 cm^3, 6.89 mmol) in hexanes was slowly added and the reaction mixture stirred at –78°C for 10 min, then at room temp for a further 1 h, giving a dark red solution. Tetrachloro-bis(tetrahydrofuran)zirconium (1.30 g, 3.45 mmol), was dissolved in THF (25 cm^3), cooled to 0°C, and transferred via cannula onto the dianion solution at 0°C. The reaction mixture was stirred at room temp for 20 h giving a yellow suspension in an orange solution. The reaction was heated to 40°C for 72 h causing the mixture to become increasingly yellow. The mixture was filtered and washed with toluene yielding a bright yellow solid (1.41 g, 90.0% crude). Solutions were prepared immediately prior to running NMR spectra since the solid was unstable in solution. FAB-MS m/z (%): 455 (M$^+$, 5), 419 ([M – Cl]$^+$, 14), 247 (24), 173 (80). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.95, 1.15 (s, 6H, 2SiCH$_3$), 1.89, 1.93, 1.45, 1.47 (s, 12H, 4Cp″CH$_3$), 5.98, 7.24 (d, J = 3 Hz, 2H, indenyl), 7.06, 7.33, 7.50, 7.70 (m, 4H, indenyl).

Catalytic studies

Hydrosilylations were carried out by adding n-BuLi in toluene (1 cm^3, 0.08 M) to the titanium complex (20 mg, 0.04 mmol) at room temp. After stirring the mixture rapidly for 5 min., phenylsilane (108 μL, 0.88 mmol) was added followed 5 min later by the ketone (0.8 mmol). The mixture was then placed in a thermostatic bath and the reaction monitored by GC. The product alcohols were obtained by adding acetone and 0.1 M HCl to the mixture; after bubbling had ceased, excess HCl was neutralized with a saturated solution of NaHCO$_3$ and the product extracted into diethyl ether and run through a short plug of anhydrous MgSO$_4$. Enantiomeric excess was determined using chiral GC using a β-Dex support.

Acknowledgments

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