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Chiral complexes of titanium containing a linked amido-cyclopentadienyl ligand: synthesis, structure, and asymmetric imine hydrogenation catalysis

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Abstract

A series of mono- and disubstituted derivatives (−)-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)(X)Cl (X = CH_2SiMe_3, BH_4) and (−)-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)X_2 (X = OSO_2CF_3, O*i*Pr, Me, CH_2Ph) was prepared from (−)-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)Cl_2 without significant racemization at the stereogenic center. The monosubstituted complexes are formed as mixtures of diastereomers. One diastereomeric monoalkyl (S_{Ti}, S_C)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)(CH_2SiMe_3)Cl was characterized by X-ray single crystal structure analysis. When the (−)-(*S*)-NCHMePh group is attached to planar chiral ring moieties 3-^{t}BuC_5H_3, C_9H_6, and $C_9H_5(SiMe_3)$-3 and coordinated at the titanium center, diastereomeric mixtures are formed. A series of titanium complexes Ti(η^5:η^1-$C_5R_4SiMe_2NR'$)Cl_2 (R = H, Me; R′ = $CHMeC_{10}H_7$, $CHMeCMe_3$, $CHPhCMe_3$, $CHMeC_6H_{11}$, (1*S*)-pinanyl-3, (1*R*)-bornyl-2) containing an enantiomerically pure linked amido-cyclopentadienyl ligands were synthesized and characterized by ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry, and elemental analysis. The crystal structure of a three-legged piano-stool molecule was determined for (+)-(1*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2$pinanyl-3)Cl_2 by a single-crystal X-ray diffraction study. Upon activation with *n*-butyllithium a selection of these dichloro complexes catalyzed the hydrogenation of acetophenone *N*-benzylimine with good conversions for R = H, but with low enantioselectivities.

Keywords: Chiral complexes; Imine hydrogenation catalyst; Titanium complexes; Linked amido-cyclopentadienyl ligand

1. Introduction

For the application of high throughput and combinatorial methods in the development of homogeneous catalysts, consistently high yield, transparent protocols for the variation of substituent patterns within a lead structure based on a constant ligand array are required [1]. The ubiquitous metallocene fragment constitutes such a consistent ligand architecture. The linked amido-cyclopentadienyl ligand is also emerging as a ligand structure with the possibility of wide variations, at least for the Group 3 and 4 metals [2]. We have recently shown that titanium complexes containing a linked amido-cyclopentadienyl ligand with a chiral, enantiomerically pure amido substituent can function as hydrogenation catalysts for imines when activated with *n*-butyllithium [3]. In contrast to the highly efficient and enantioselective Brintzinger-type C_2-symmetric *ansa*-titanocenes employed in this reaction [4,5], the chiral amido substituent was deemed to be pivotal in increasing the stereoselectivity. Solution dynamic study of the prototypical complex (−)-(*S*)-Ti(η^5:η^1-$C_5H_4SiMe_2$-NCHMePh)Cl_2 revealed the preference for an asymmetric conformation despite the low activation barrier to the rotation about the bond between the amido-nitrogen and the stereogenic α-carbon atom [3]. We report here the variation of the ligand sphere first by introducing anionic ligands different from chloride in (−)-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)Cl_2 and the synthesis of some (*S*)-1-phenylethylamido derivatives with planar chiral ring ligands [6]. The synthesis of an

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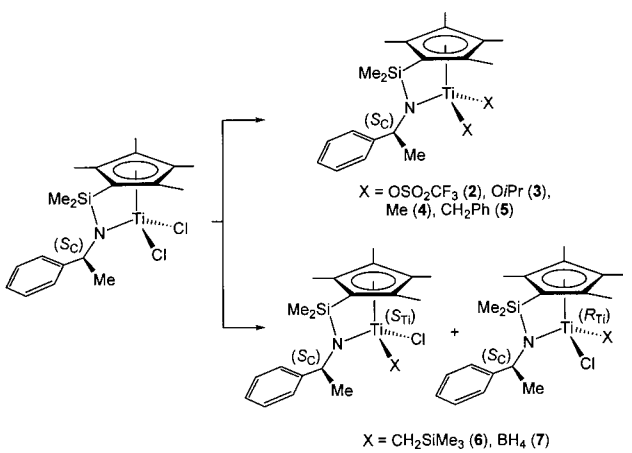
extensive series of dichloro titanium complexes with different chiral, optically active amido substituents were performed in order to expand the number of this type of precatalysts for the homogeneous imine hydrogenation.

2. Results and discussion

2.1. Derivatives of $(-)$-(S)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)Cl_2

As summarized in Scheme 1, a variety of derivatives of the type $(-)$-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)X_2 or $(-)$-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)Cl_2 can be prepared starting from the dichloro complex $(-)$-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)Cl_2 ((*S*)-**1**). Upon treatment with silver triflate, (*S*)-**1** gives orange prisms of $(-)$-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)$(OSO_2CF_3)_2$ ((*S*)-**2**) in good yields. Although alcoholysis of (*S*)-**1** to give $(-)$-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)$(OiPr)_2$ ((*S*)-**3**) is feasible, (*S*)-**3** can be also obtained as a yellow oil by the reaction of Li_2{(*S*)-$C_5Me_4SiMe_2$NCHMePh} with $TiCl_2(OiPr)_2$ [7]. Alkylation with methyl and benzyl magnesium chloride gives the dialkyl complexes $(-)$-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)X_2 (X = Me ((*S*)-**4**), CH_2Ph ((*S*)-**5**)). In all cases racemization at the stereogenic carbon of the 1-phenylethylamido moiety does not take place to a significant amount, as judged by the values of the optical rotation. The reaction of (*S*)-**1** with $Mg(CH_2SiMe_3)Cl$ in diethylether results in the formation of a 1:0.6 mixture of two diastereomers of the monoalkyl complex (S_C)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)$(CH_2SiMe_3)Cl$ ((S_C)-**6**) as yellow crystals. As depicted in Fig. 1, the majority of the resonances for the two diastereomers **A** and **B** are well-separated and by the use of NOE measurements, the major diastereomer **A** are unambiguously assigned as (S_{Ti}, S_C)-**6**. This diastereomer selectively crystallizes in low yield from hexane at -20°C and its absolute configuration is confirmed by an X-ray single crystal structure analysis as (S_{Ti}, S_C) (Table 1, Fig. 2). All metrical parameters are within the expected range of complexes containing a linked amido-cyclopentadienyl ligand. The angle at the methylene carbon of 123.9(3)° is slightly enlarged and may hint at an α-agostic bonding (Ti–H20a 2.64(5), Ti–H20b 2.44(5) Å), similar to the situation in the dibenzyl complex Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2Ph$)-$(CH_2Ph)_2$ [8]. We suspect that the major diastereomer **A** is thermodynamically somewhat favored due to the decreased steric strain between the phenyl and the trimethylsilymethyl group. As in configurationally stable 18-electron half-sandwich complexes with pianostool structure [9], no epimerization at the titanium center was observed by ^{1}H-NMR spectroscopy in solution at temperatures up to 80°C.

The reaction of (*S*)-**1** with (up to tenfold) excess of $LiBH_4$ in pentane gives yellow needles of (S_C)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)$(BH_4)Cl$ ((*S*)-**7**) as a 1:1 diastereomeric mixture. Here the fractional crystallization did not lead to separation of the two diastereomers, but a poor X-ray single crystal structure analysis (due to crystal decay) of the (S_{Ti}, S_C)-diastereomer confirmed the postulated configuration with a η^3-BH_4 group. The ^{1}H- and ^{13}C-NMR spectra show doubled signal patterns and the temperature-dependent resonances for the BH_4 ligand suggest a fluxional η^2- or η^3-coordination. In the ^{11}B-NMR spectrum two quintets with $J_{BH} = 88$ Hz are detected at -6.9 and -6.2 ppm.



Scheme 1.

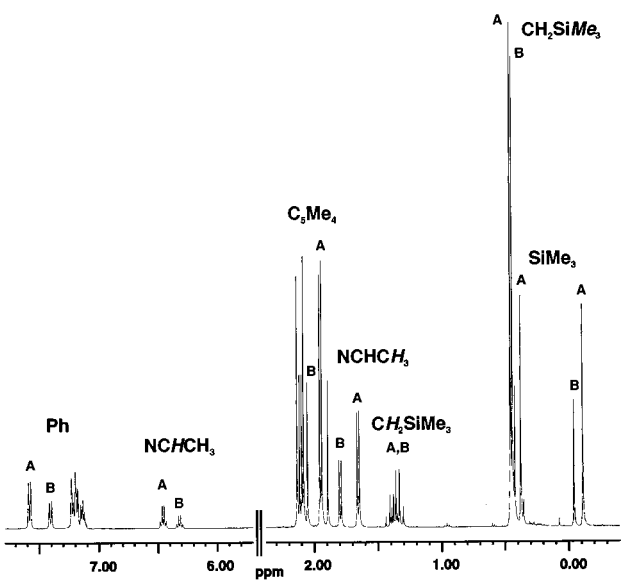


Fig. 1. ^{1}H-NMR spectrum (400 MHz, C_6D_6, 25°C) of the diastereomeric mixture of (S_{Ti}, S_C)- and (R_{Ti}, S_C)-Ti(η^5:η^1-$C_5Me_4SiMe_2$NCHMePh)$(CH_2SiMe_3)Cl$ ((S_C)-**6**). Resonances marked **A** are for the (S_{Ti}, S_C)- and those marked **B** are for the (R_{Ti}, S_C)-diastereomer.

Table 1
Crystallographic data for (S_{Ti}, S_C)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)(CH_2SiMe_3)Cl (**6**) and (+)-(1*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2$pinanyl-3)Cl_2 ((1*S*)-**20**)

Compound	**6**	(1*S*)-**20**
Formula	$C_{23}H_{38}ClNSi_2Ti$	$C_{22}H_{37}Cl_2NSiTi$
Formula weight	468.07	462.42
Crystal shape	Prism	Plate
Crystal color	Yellow	Yellow
Crystal size (mm)	$1.0\times0.3\times0.3$	$0.6\times0.7\times0.2$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)
Unit cell dimensions		
a (Å)	10.081(4)	8.534(2)
b (Å)	14.779(1)	7.6810(7)
c (Å)	17.732(2)	19.162(4)
α (°)		
β (°)		98.10(2)
γ (°)		
V (Å^3)	2642(1)	1243.5(4)
Z	4	2
ρ_{calc} (g cm^{-1})	1.177	1.235
Wavelength (Å)	0.7107 (Mo–K_α)	0.7107 (Mo–K_α)
$\mu_{lin.}$ (mm^{-1})	0.525	0.615
θ Scan range (°)	30	30
Reflections measured	7187	6877
Independent reflections observed	4326	5458
[$I>2\sigma(I)$]	[$R_{int}=0.0238$]	[$R_{int}=0.0170$]
Parameters refined	275	277
Final R indices R_1, wR_2 (observed data)	0.0548/0.1084	0.0403/0.1032
Final R indices R_1, wR_2 (all data)	0.1109/0.1412	0.0487/0.1140
Goodness-of-fit	1.171	1.127
Absolute structure parameter	−0.06(5)	0.02(3)
Residual density: max., min. $\Delta\rho$ (e Å^{-3})	0.421, −0.473	0.542, −0.499

2.2. Planar chiral derivatives with a linked 1-phenylethylamido ligand

In order to determine the diastereoselectivity during the formation of linked amido-cyclopentadienyl complexes, we introduced three planar chiral ligand moieties: 3-*tert*-butylcyclopentadienyl, 1-indenyl, and 3-trimethylsilyl-1-indenyl attached to the (*S*)-1-phenylethylamido group through the dimethylsilanediyl group (Scheme 2). The synthesis follows the established route of assembling the ligand precursor and coordinate them using $TiCl_3(THF)_3$ followed by oxidation by $PbCl_2$ [8,11]. In each of these cases the crude reaction mixtures reveal the formation of mixtures of diastereomers in the approximate ratio of 1:1. While in the case of the 3-*tert*-butylcyclopentadienyl derivative (S_C)-**8** separation of diastereomers is not possible, the indenyl derivatives (S_C)-**9** and (S_C)-**10** can be separated by fractional crystallization. The diastereomer (p-*R*, S_C)-**9** can be obtained from toluene–hexane which corresponds to the diastereomer independently synthesized by Waymouth et al. and fully characterized crystallographically [6a]. The conformation is such that the

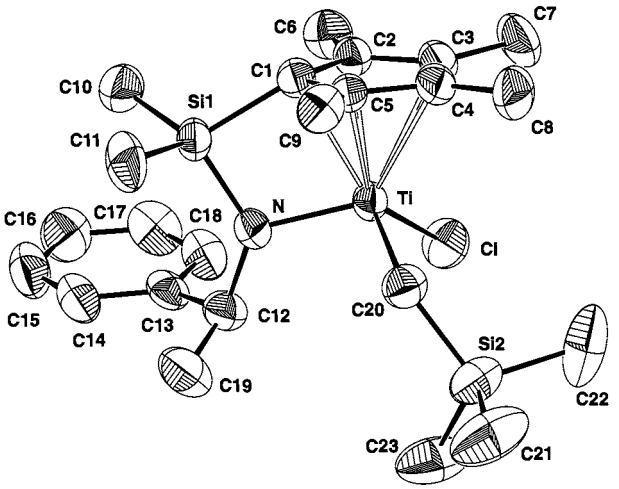
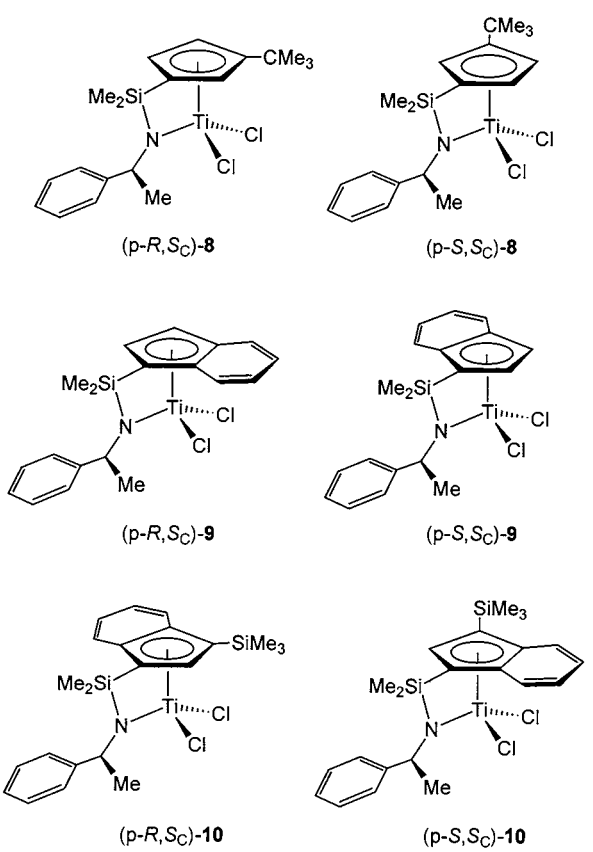
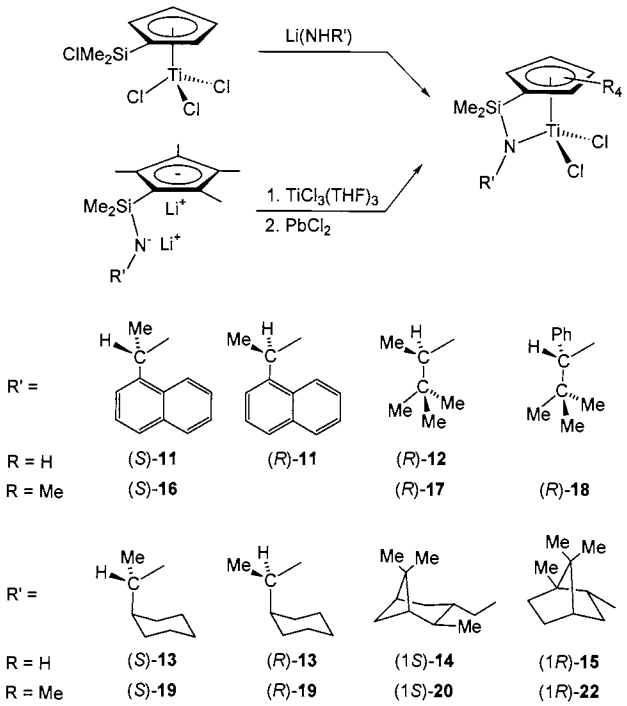


Fig. 2. ORTEP diagram of the molecular structure of (S_{Ti}, S_C)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)(CH_2SiMe_3)Cl ((S_{Ti}, S_C)-**6**); thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (°) of (S_{Ti}, S_C)-**6**: Ti–N 1.909(3), Ti–Cl 2.279(1), Ti–C20 2.106(5), Ti–Cp(centroid) 2.030(4), Ti–C1 2.283(4), Ti–C2 2.316(4), Ti–C3 2.399(4), Ti–C4 2.434(4), Ti–C5 2.374(4), Cl–Ti–C20 106.8(2), Cp(-centroid)–Ti–N 107.2(1), Ti–N–Si1 105.7(2), C12–N–Ti 123.3(3).



Scheme 2.



Scheme 3.

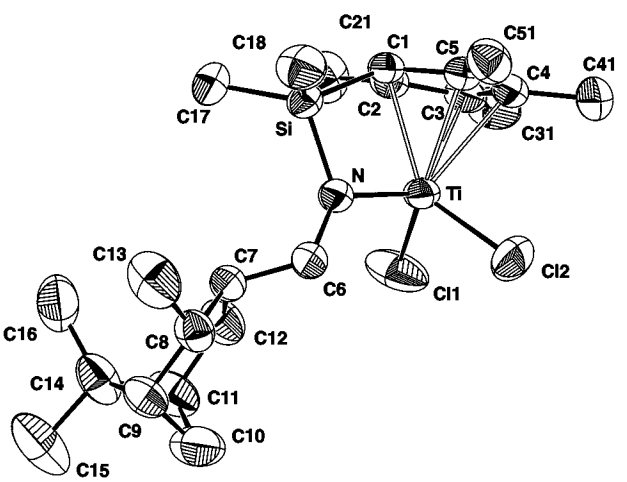


Fig. 3. ORTEP diagram of the molecular structure of (+)-(1*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2$-pinanyl)Cl_2 ((1*S*)-**20**); thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (°) of (1*S*)-**20**: Ti–N 1.901(2), Ti–Cl1 2.2675(9), Ti–Cl2 2.264(1), Ti–Cp(-centroid) 2.028(3), Ti–C1 2.289(2), Ti–C2 2.352(3), Ti–C3 2.424(3), Ti–C4 2.409(2), Ti–C5 2.322(2), Cl1–Ti–Cl2 102.74(5), Cp(centroid)–Ti–N 107.08(9), Ti–N–Si 106.3(1), C6–N–Ti 126.8(2).

annealed benzo group is disposed trans to the phenyl group of the amido substituent. When the related complex (S_C)-**10** containing the 3-trimethylsilyl substituted indenyl ligand is recrystallized from hexane, the (p-*R*, S_C) diastereomer with the 3-trimethylsilyl group *trans* to the phenyl group can be selectively isolated. The determination of the configuration was performed by NOE measurements.

2.3. Complexes with new chiral amido-substituents

Following established synthetic methods [8,11], two series of titanium dichloro complexes (S_C)-Ti(η^5:η^1-$C_5R_4SiMe_2NR'$)Cl_2 (R = H, Me) with various optically active amido substituents R′ are synthesized. While the complexes of the C_5H_4 series **11**–**15** are prepared by the reaction of the complex Ti(η^5:η^1-$C_5H_4SiMe_2Cl$)Cl_3 [10] with the corresponding lithium amide LiNHR' in the presence of triethylamine, the derivatives containing the C_5Me_4 ring ligand **16**–**22** requires the synthesis of the ligand precursors $(C_5Me_4H)SiMe_2NHR'$ which are doubly deprotonated with *n*-butyllithium and converted into the corresponding dichloro complex following the established procedure. The new compounds, isolated as yellow crystals, of this study are compiled in Scheme 3. They were completely characterized by elemental analysis, mass spectrometry, ^{1}H- and ^{13}C-NMR spectroscopy as well as by their optical rotation values. In agreement with the expected asymmetrical structure, the NMR spectra of all complexes confirm the lack of any symmetry element. In the ^{1}H-NMR spectra the most conspicuous parameter is the chemical shift for the protons α to the amido nitrogen NC*H* which invariably appear at unusually low field ($\delta > 5$ ppm). We have previously ascribed this effect to the anisotropy caused by the titanium-nitrogen double bond [2b,3,11].

The single crystal X-ray structure analysis of the 3-pinanylmethylamido derivative (1*S*)-**20** (Fig. 3) reveals a conformation similar to that found in linked amido-cyclopentadienyl titanium complexes of the general type Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2R''$)Cl_2, where R″ = Ph [8], H, CH_3 [12]. The typical conformation is characterized by the orientation of the methylene hydrogen atoms towards the titanium center which causes the bulky R″ group to be turned away from the metal. All other metrical parameters in the crystal structure of (1*S*)-**20** are within the expected range [2b] and merit no further discussion.

2.4. Imine hydrogenation

A selection of the complexes prepared above are activated with two equivalents of *n*-butyllithium and used for the enantioselective hydrogenation of acetophenone *N*-benzylimine using dihydrogen at a pressure of 150 bar. The conversions and the enantioselectivities under standardized conditions (substrate: Ti = 1000:1, toluene, 80°C, 12 h) [3,5] are summarized in Table 2. In general it can be concluded that the enantiomeric excesses achieved are not exceeding those of the prototypical 1-phenethylamido derivative (+)-(*S*)-Ti(η^5:η^1-$C_5H_4SiMe_2NCHMePh$)Cl_2 and no clear-cut structure–selectivity relationship can be recognized at this stage. However, the activities are normally higher for the precatalysts of the C_5H_4 series (*S*)-**11**,

Table 2
Results of the hydrogenation of acetophenone *N*-benzylimine using *n*-butyllithium-activated complexes $Ti(\eta^5:\eta^1\text{-}C_5R_4SiMe_2NR')Cl_2$ [a]

Precatalyst	% Conversion	% ee
R = H, R′ =		
(*S*)-CHMePh [3]	100	18
(*S*)-$CHMeC_{10}H_7$ ((*S*)-**11**)	90	15
(*R*)-$CHMeC_6H_{11}$ ((*R*)-**13**)	100	14
(+)-CH_2pinanyl (**14**)	40	8
(*R*)-bornyl ((1*R*)-**15**)	100	<5
R = Me, R′ =		
(*S*)-CHMePh [3]	10	<5
(*S*)-$CHMeC_{10}H_7$ ((*S*)-**16**)	30	<5
(*R*)-$CHMeC_6H_{11}$ ((*R*)-**19**)	100	24
(*R*)-bornyl ((1*R*)-**22**)	15	<5

[a] Activation: titanium complex 0.1 mmol, *n*-butyllithium 0.2 mmol in 20 ml of toluene at 25°C. Hydrogenation: imine 100 mmol, 150 bar of H_2 gas at 80°C for 12 h.

(*R*)-**13**, **14**, and (*S*)-**15** than those for the complexes with the C_5Me_4 ligand which show lower conversions as did the 1-phenylethylamido complex (*S*)-**1** previously studied [3]. In order to obtain more insight into the activation process, we treated (*S*)-**1** with one equivalent of *n*-butyllithium in hexane–THF at −78°C and isolated an extremely sensitive dark red solid product in low yield from the greenish reaction mixture. This compound appears to be the monosubstitution compound (*S*)-$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCHMePh)(^nBu)Cl$ according to the elemental analysis and ^{1}H-NMR spectrum. We obtained earlier evidence that the linked amido-cyclopentadienyl ligand framework stabilizes higher *n*-alkyl groups with β-hydrogen atoms at Group 4 metal centers [13]. However, in the presence of excess *n*-butyllithium and hydrogen as a reductant, we assume that such as compound is reduced to a trivalent titanium complex 'Ti($\eta^5:\eta^1$-$C_5Me_4SiMe_2NCHMePh$)H'. As expected, the reaction of (*S*)-**1** with $Li(BEt_3H)$ results in the formation of a green paramagnetic reaction mixture. The generation of half-sandwich complexes with trivalent titanium of the type $Ti(\eta^5\text{-}C_5R'_5)Cl_2$ is well-documented in the literature [14], as are trivalent titanocene derivatives including the hydride complex $Ti(\eta^5\text{-}C_5Me_4Ph)_2H$ [15].

In conclusion, we have shown that an extensive series of optically active titanium complexes containing a chiral linked amido-cyclopentadienyl ligand other than that derived from 1-phenylethylamido can be prepared and characterized. Although configurationally stable, their enantioselectivity as homogeneous hydrogenation catalysts improved only marginally. It appears that in comparison with the Brintzinger-type *ansa*-titanocenes, this class of complexes may not offer a reaction site capable of efficiently discriminating the enantiotopic sides of the imine substrate. We are investigating related systems containing chiral elements in the bridge [16].

3. Experimental

3.1. General considerations

All experiments were performed under argon using standard Schlenk or glovebox techniques. Diethyl ether, THF, pentane, and hexane were purified by distillation from sodium–benzophenone ketyl. Toluene was distilled over sodium sand. (−)-(*S*)-$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCHMePh)Cl_2$ ((*S*)-**1**) [3], $(C_5Me_4H)SiMe_2Cl$ [17], $C_9H_7SiMe_2Cl$ [18], $C_9H_6(SiMe_3)SiMe_2Cl$ [18], $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ [19], $TiCl_3(THF)_3$ [20], and $Mg(CH_2Ph)_2(THF)_2$ [19] were prepared according to literature procedures. All other reagents were commercially available and used as received. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz; ^{11}B, 128 MHz) in C_6D_6 at 298 K, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{11}B spectra were referenced externally to $BF_3(Et_2O)$. Optical rotations were measured on Perkin–Elmer Polarimeter 241 at $\lambda = 578$ and 546 nm and converted to the D-line of sodium. Mass spectra were recorded on a Finnigan 8230 spectrometer. Elemental analyses were performed by the microanalytical laboratory of this department. Although pure according to their NMR spectra, several titanium complexes showed low carbon contents. The best values were reported.

3.2. (−)-(S)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)-$(OSO_2CF_3)_2$ ((S)-2)

A solution of (−)-(*S*)-$Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCHMePh)Cl_2$ ((*S*)-**1**) (416 mg, 1.00 mmol) in 30 ml of CH_2Cl_2 was treated with silver triflate (514 mg, 2.00 mmol) at −78°C. After stirring the reaction mixture at room temperature (r.t.) for 16 h in the dark, the suspension was filtered and the solvent was removed in vacuo. Crystallization from 15 ml of diethyl ether at −20°C afforded 530 mg (82%) of orange–red prisms. $[\alpha]_D^{22} = -159.5$ ($c = 1.0$ in diethyl ether); $[\alpha]_D^{22} = -124.6$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ −0.22, 0.27 (s, 2 × 3 H, $SiCH_3$), 1.50 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.88, 1.94, 1.96, 1.97 (s, 4 × 3 H, C_5Me_4), 6.00 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 7.08 (m, 3 H, C_6H_5), 7.21 (m, 2 H, C_6H_5). ^{13}C-NMR: δ 1.8, 3.9 ($SiCH_3$), 12.0, 12.1, 15.4, 15.5 (C_5Me_4), 21.0 ($NCHCH_3$), 64.0 ($NCHCH_3$), 110.6 (ring C at Si), 115.0–124.5 (q, $^1J_{FC} = 318$ Hz, CF_3), 127.6, 128.4, 129.1 (C_6H_5), 142.5, 142.7, 145.6, 145.7 (C_5Me_4). EIMS: *m*/*z* (%): 643 (11, M^+), 628 (100, M^+–Me), 494 (100,

$M^+-SO_3CF_3$), 361 (32, $M^+-SO_3CF_3$, $-SO_2CF_3$), 178 (74, $C_5Me_4SiMe_2^+$). Anal. Calc. for $C_{21}H_{27}F_6NO_6S_2SiTi$ (643.5): C, 39.20; H, 4.23; N, 2.18. Found: C, 39.26; H, 4.27; N, 2.13%.

3.3. (−)-(S)-Ti(η⁵:η¹-C₅Me₄SiMe₂NCHMePh)(OiPr)₂ ((S)-3)

A solution of $Li_2\{(S)$-$C_5Me_4SiMe_2NCHMePh\}$ (1.80 mg, 5.78 mmol) in 80 ml of a mixture of toluene–THF (7:1) was added to a solution of $TiCl_2(OiPr)_2$ (1.37 g, 5.78 mmol) in 50 ml of toluene at −70°C. After stirring the reaction mixture for 16 h at r.t. all volatiles were removed in vacuo. The residue was extracted with 30 ml of hexane and the solvent removed. Distillation at 161°C/0.1 mbar afforded 1.86 g (69%) of a yellow oil. $[\alpha]_D^{22} = -110.0$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.26, 0.48 (s, 2×3 H, $SiCH_3$), 1.19, 1.20 (d, $^3J_{HH} = 6$ Hz, 2×3 H, $CH(CH_3)$), 1.24, 1.27 (d, $^3J_{HH} = 6$ Hz, 2×3 H, $OCH(CH_3)$), 1.30 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.98, 1.99, 2.20, 2.23 (s, 4×3 H, C_5Me_4), 4.57, 4.65 (sept, $^3J_{HH} = 6$ Hz, 2×1 H, $CH(CH_3)_2$), 5.13 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 7.17 (m, 1 H, C_6H_5), 7.26 (m, 2 H, C_6H_5), 7.48 (m, 2 H, C_6H_5). ^{13}C-NMR: δ 4.2, 6.3 ($SiCH_3$), 11.5, 11.6, 14.2, 14.3 (C_5Me_4), 24.5 ($NCHCH_3$), 26.8, 26.9, 27.0 ($OCHCH_3$), 61.0 ($NCHCH_3$), 74.9, 75.0 ($OCH(CH_3)_2$), 104.1 (ring C at Si), 126.6, 127.3, 126.7 (C_6H_5), 127.8, 127.9, 129.2, 129.3 (C_5Me_4), 148.8 (C-*ipso*). EIMS: m/z (%): 463 (23, M^+), 448 (100, M^+-Me), 407 (47, $M^+-OC_3H_7$), 345 (37, $M^+-2\ OC_3H_7$). Anal. Calc. for $C_{25}H_{41}NO_2SiTi$ (463.6): C, 64.77; H, 8.91; N, 3.02. Found: C, 63.78, H, 8.47; N, 4.08%.

3.4. (−)-(S)-Ti(η⁵:η¹-C₅Me₄SiMe₂NCHMePh)Me₂ ((S)-4)

A solution of (−)-(S)-Ti(η⁵:η¹-$C_5Me_4SiMe_2$-NCHMePh)Cl_2 ((S)-**1**) (670 mg, 1.61 mmol) in 50 ml of diethyl ether was treated with a suspension of methylmagnesium chloride (241 mg, 3.22 mmol) in 20 ml of diethyl ether at −50°C. Crystallization from pentane afforded 440 mg (73%) of pale yellow needles. $[\alpha]_D^{22} = -37.9$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.04, 0.22 (s, 2×3 H, $SiCH_3$), 0.57, 0.58 (s, 2×3 H, $TiCH_3$), 1.86 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.87, 1.92, 2.02, 2.03 (s, 4×3 H, C_5Me_4), 5.86 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 7.12 (m, 1 H, C_6H_5), 7.21 (m, 2 H, C_6H_5), 7.40 (d, $^3J_{HH} = 7$ Hz, 2 H, C_6H_5). ^{13}C-NMR: δ 3.2, 5.1 ($SiCH_3$), 11.9, 14.3, 15.0, 15.1 (C_5Me_4), 24.9 ($NCHCH_3$), 50.8, 50.9 (Ti–CH_3), 59.9 ($NCHCH_3$), 97.7 (ring C at Si), 127.1, 127.3, 128.6 (C_6H_5), 128.8, 134.2, 134.5 (C_5Me_4), 147.8 (C-*ipso*). EIMS: m/z (%): 375 (1, M^+), 360 (42, M^+-Me), 345 (100, M^+-2 Me), 105 (45, $C_8H_9^+$). Anal. Calc. for $C_{21}H_{33}NSiTi$ (375.5): C, 67.18; H, 8.86; N, 3.73. Found: C, 65.03; H, 9.87; N, 4.42%.

3.5. (S)-Ti(η⁵:η¹-C₅Me₄SiMe₂NCHMePh)(CH₂Ph)₂ ((S)-5)

A solution of (−)-(S)-Ti(η⁵:η¹-$C_5H_4SiMe_2$NCH-MePh)Cl_2 ((S)-**1**) (240 mg, 0.58 mmol) in of 50 ml diethyl ether was treated with benzylmagnesium chloride (1.27 ml of a 0.91 M solution in diethyl ether) at −50°C. After stirring for 16 h at r.t. all volatiles were removed in vacuo. Extracting the residue with 20 ml of hexane followed by concentrating the extracts and crystallization at −70°C afforded 180 mg (59%) of a red solid. ^{1}H-NMR: δ 0.21, 0.44 (s, 2×3 H, $SiCH_3$), 1.34 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.67, 1.74, 1.85, 1.91 (s, 4×3 H, C_5Me_4), 2.01, 2.40, 2.41, 2.50 (d, $^2J_{HH} = 10$ Hz, 4×1 H, CH_2Ph), 5.61 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 6.66 (d, $^3J_{HH} = 8$ Hz, 2 H, C_6H_5), 6.89 (m, 1 H, C_6H_5), 7.01 (m, 1 H, C_6H_5), 7.10 (m, 5H, C_6H_5), 7.19 (m, 2 H, C_6H_5), 7.26 (m, 4H, C_6H_5). ^{13}C-NMR: δ 5.0, 6.3 ($SiCH_3$), 11.3, 11.5, 14.5, 15.2 (C_5Me_4), 25.3 ($NCHCH_3$), 60.6 ($NCHCH_3$), 79.6, 84.3 ($TiCH_2$), 98.5 (ring C at Si), 122.2, 122.3, 126.6, 127.0, 127.3, 127.7, 128.5, 128.8 (C_6H_5), 130.2, 130.3, 134.9, 135.1 (C_5Me_4), 146.9, 149.3, 149.4 (C-*ipso*). EIMS: m/z (%): 436 (27, $M^+-C_7H_7$), 345 (84, $M^+-2\ C_7H_7$), 91 (100, $C_7H_7^+$).

3.6. (S_C)-Ti(η⁵:η¹-C₅Me₄SiMe₂NCHMePh)-(CH₂SiMe₃)Cl ((S_C)-6)

A solution of (−)-(S)-Ti(η⁵:η¹-$C_5Me_4SiMe_2$-NCHMePh)Cl_2 ((S)-**1**) (460 mg, 1.10 mmol) in 60 ml of diethyl ether was treated with trimethylsilylmethylmagnesium chloride (2.4 ml of a 1.0 M solution in diethyl ether) at −78°C. After stirring the reaction mixture for 4 h at r.t. the solvent was removed in vacuo. The residue was extracted with 30 ml of hexane. Concentrating the extract and crystallization at −20°C afforded 380 mg (74%) of a diastereomeric mixture of (S_{Ti}, S_C)- and (R_{Ti}, S_C)-**6** in a 1:0.6 ratio as yellow needles. (S_{Ti}, S_C)-**6**: ^{1}H-NMR: δ −0.14, 0.34 (s, 2×3 H, $SiCH_3$), 0.43 (s, 9 H, $CH_2Si(CH_3)_3$), 1.27(m, 2 H, $CH_2Si(CH_3)_3$), 1.62 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.91, 1.93, 2.05, 2.10 (s, 4×3 H, C_5Me_4), 6.43 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 7.08–7.19 (m, 3 H, C_6H_5), 7.37–7.39 (m, 1 H, C_6H_5), 7.56 (m, 1 H, C_6H_5). (R_{Ti}, S_C)-**6**: ^{1}H-NMR: δ −0.07, 0.39 (s, 2×3 H, $SiCH_3$), 0.41 (s, 9 H, $CH_2Si(CH_3)_3$), 1.38 (m, 2 H, $CH_2Si(CH_3)_3$), 1.76 (d, $^3J_{HH} = 7$ Hz, 3H, $NCHCH_3$), 1.86, 2.02, 2.07, 2.08 (s, 4×3 H, C_5Me_4), 6.29 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 7.08–7.19 (m, 3 H, C_6H_5), 7.37–7.39 (m, 1 H, C_6H_5), 7.54 (m, 1 H, C_6H_5). Both isomers: ^{13}C-NMR: δ 2.4, 2.5 ($CH_2Si(CH_3)_3$), 2.8, 3.4, 5.2 ($SiCH_3$), 12.4, 12.5, 12.6, 12.7, 15.4, 15.5 (C_5Me_4), 20.8, 22.5 ($NCHCH_3$), 60.3, 61.2 ($NCHCH_3$), 70.5, 70.8 ($CH_2Si(CH_3)_3$), 100.7 (ring C at Si), 127.3, 127.4, 127.8, 128.5, 128.7, 131.7, 131.8, 135.9, 136.8,

136.9, 143.5, 144.2, 144.3 (C_5Me_4 and C_6H_5). EIMS: m/z (%): 380 (100, $M^+-CH_2SiMe_3$), 261 (14, $M^+-CH_2SiMe_3$, $-NC_8H_9$). Anal. Calc. for $C_{23}H_{38}ClNSi_2Ti$ (468.1): C, 59.02; H, 8.18; N, 2.99. Found: C, 59.07; H, 8.28; N, 3.56%.

3.7. (S)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMePh$)(BH_4)Cl ((S)-7)

A solution of (−)-(*S*)-Ti(η^5:η^1-$C_5Me_4SiMe_2$-NCHMePh)Cl_2 ((*S*)-**1**) (624 mg, 1.50 mmol) in 25 ml of THF was treated at r.t. with lithium tetrahydoborate (327 mg, 15.0 mmol). After refluxing the reaction mixture for 15 min the solvent was removed in vacuo. The residue was extracted with 30 ml of hexane. Concentrating the extracts and crystallization at −20°C afforded 450 mg (76%) of a 1:1.2 diastereomeric mixture of (R_{Ti}, S_C)- and (S_{Ti}, S_C)-**7** as yellow needles. ^{1}H-NMR: δ −0.29, 0.41 (s, 2 × 3 H, $SiCH_3$), −0.17, 0.47 (s, 2 × 3 H, $SiCH_3$), 0.25–1.09 (br s, 2 × 4 H, BH_4), 1.45, 1.58 (d, $^3J_{HH}$ = 7 Hz, 3 H, NCHCH_3), 1.89, 1.96, 1.95, 1.99, 2.00, 2.02, 2.20, 2.27, (s, 8 × 3 H, C_5Me_4), 6.25 (q, $^3J_{HH}$ = 7 Hz, 1 H, NCHCH_3), 6.33 (q, $^3J_{HH}$ = 7 Hz, 1 H, NCHCH_3), 7.08–7.46 (m, 25 H, C_6H_5). ^{13}C-NMR: δ 2.1, 2.3, 5.0, 5.3 ($SiCH_3$), 12.7, 12.8, 12.9, 13.1, 16.0, 16.3, 16.4 (C_5Me_4), 19.3, 20.6 (NCHCH$_3$), 66.4, 67.8 (NCHCH$_3$), 104.8 (ring C at Si), 127.1, 128.6, 128.7, 134.3, 134.7, 137.8, 137.9, 140.5, 144.7 (C_5Me_4 and C_6H_5). ^{1}H-NMR (C_7D_8): δ −0.34, 0.36 (s, 2 × 3 H, $SiCH_3$), −0.20, 0.41 (s, 2 × 3 H, $SiCH_3$), 0.52 (br q, $^1J_{BH}$ = 88 H, 2 × 4 H, BH_4), 1.40 (d, $^3J_{HH}$ = 7 Hz, 3 H, NCHCH_3), 1.49 (d, $^3J_{HH}$ = 7 Hz, 3 H, NCHCH_3), 1.89, 1.93, 1.94, 1.95, 2.05, 2.07, 2.09, 2.17, (s, 8 × 3 H, C_5Me_4), 5.97(q, $^3J_{HH}$ = 7 Hz, 1 H, NCHCH_3), 6.09 (q, $^3J_{HH}$ = 7 Hz, 1 H, NCHCH_3), 6.94–7.34 (m, 2 × 5 H, C_6H_5), 7.37–7.39 (m, 2 H, C_6H_5), 7.54–7.56 (m, 2 H, C_6H_5).^{11}B-NMR: δ −4.9 (quint, $^1J_{BH}$ = 88 Hz, BH_4). EIMS: m/z (%): 381 (36, M^+-BH_3), 276 (75, M^+-BH_3, $-C_8H_9$). Anal. Calc. for $C_{19}H_{31}BClNSiTi$ (395.7): C, 57.67; H, 7.90; N, 3.54. Found: C, 57.54; H, 8.03; N, 3.62%.

3.8. (S_C)-Ti(η^5:η^1-3-^{t}Bu$C_5H_3SiMe_2NCHMePh$)Cl_2 ((S)-8)

Li[(*S*)-NHCHMePh] (1.91 g, 15.0 mmol) dissolved in 40 ml of a mixture of hexane–THF (3:1) was added dropwise at 0°C to (3-^{t}BuC_5H_4)$SiMe_2Cl$ (3.22 g, 15.0 mmol) in 40 ml of hexane. After being stirred for 2 h at r.t. the suspension was filtered. Removal of all volatiles in vacuo gave crude (*S*)-(3-^{t}BuC_5H_4)$SiMe_2$NHCH-MePh which was distilled at 90–100°C/5 × 10^{-3} mbar to give a yellow oil, yield 3.78 g (80%) of a mixture of isomers. Anal. Calc. for $C_{19}H_{29}NSi$ (299.5): C, 76.19; H, 9.76; N, 4.68. Found: C, 75.52; H, 9.72; N, 6.52%. A suspension of $TiCl_3(THF)_3$ (2.22 g, 6.00 mmol) in 50 ml of THF was treated with a solution of Li_2[(*S*)-(3-^{t}BuC_5H_3)$SiMe_2$NCHMePh] (1.87 g, 6.00 mmol), prepared from (*S*)-(3-^{t}BuC_5H_4)$SiMe_2$NHCHMePh and *n*-butyllithium in 70 ml of THF, at −78°C. After stirring the reaction mixture for 2 h, $PbCl_2$ (1.67 g, 6.00 mmol) was added and stirred overnight. All volatiles were removed in vacuo, the residue washed with 20 ml of diethyl ether and extracted with warm 1:1 mixture of hexane–toluene. Filtration and crystallization gave 420 mg (21%) of dark yellow solid as mixture of 1:1 diastereomers. ^{1}H-NMR: δ −0.31, 0.24 (s, 2 × 3 H, $SiCH_3$), −0.38, 0.26 (s, 2 × 3 H, $SiCH_3$), 1.30 (s, 9 H, $C(CH_3)_3$), 1.31 (s, 9 H, $C(CH_3)_3$), 1.45(d, $^3J_{HH}$ = 7 Hz, NCHCH_3), 1.59 (d, $^3J_{HH}$ = 7 Hz, NCHCH_3), 6.15 (m, 2 × 1 H, C_5H_3), 6.23 (m, 2 × 1 H, C_5H_3), 6.59 (q, $^3J_{HH}$ = 7 Hz, 1 H, NCHCH_3), 6.64 (q, $^3J_{HH}$ = 7 Hz, 1 H, NCHCH_3), 6.71 (m, 2 × 1 H, C_5H_3), 7.07–7.12 (overlap m, 2 × 3 H, C_6H_5), 7.38 (m, 2 × 3 H, C_6H_5). ^{13}C-NMR: δ −3.1, −2.6, −0.6, −0.4 ($SiCH_3$), 18.6, 19.8 (NCHCH$_3$), 30.6, 30.7 ($C(CH_3)_3$), 33.5, 33.6 ($C(CH_3)_3$), 64.9, 65.0 (NCHCH$_3$), 107.4, 107.7 (ring C at Si), 120.8, 120.9, 122.5, 122.8 (C_5H_3), 127.3, 127.5, 127.9, 128.1, 128.7, 128.8 (C_6H_5), 144.3, 144.5 (C-*ipso*), 155.2, 155.6 (C_5H_3^{t}Bu). EIMS: m/z (%): 415 (3, M^+), 400 (43, M^+–Me), 295 (10, M^+–Me, $-C_8H_9$), 105 (100, $C_8H_9^+$). Anal. Calc. for $C_{19}H_{27}Cl_2NSiTi$ (416.3): C, 54.82; H, 6.54; N, 3.36. Found: C, 54.84; H, 6.81; N, 3.25%.

3.9. (R_C)-Ti(η^5:η^1-3-^{t}Bu$C_5H_3SiMe_2NCHMePh$)Cl_2 ((R)-8)

(*R*)-(3-^{t}BuC_5H_4)$SiMe_2$NHCHMePh was synthesized from (3-^{t}BuC_5H_4)$SiMe_2Cl$ (3.28 g, 1.53 mmol) and Li[(*R*)-NHCHMePh] (1.94 g, 1.53 mmol) in a manner analogous to that described for the preparation of the (*S*)-enantiomer. Distillation at 96–110°C/8 × 10^{-3} mbar afforded 400 mg (87%) of yellow oil (mixture of isomers). Anal. Calc. for $C_{19}H_{29}NSi$ (299.5): C, 76.19; H, 9.76; N, 4.68. Found: C, 76.10; H, 9.82, N, 4.67%. Following a procedure analogous to that described for the preparation of the (*S*)-enantiomer, $TiCl_3(THF)_3$ (1.93 g, 5.20 mmol) was reacted with Li_2{(*R*)-(3-^{t}BuC_5H_3)$SiMe_2$NCHMePh} (1.62 g, 5.20 mmol) and $PbCl_2$ (1.45 g, 5.20 mmol) to give 630 mg (29%) of dark yellow solid. Anal. Calc. for $C_{19}H_{27}Cl_2NSiTi$ (416.3): C, 54.82; H, 6.54; N, 3.36. Found: C, 54.11; H, 7.41; N, 3.32%.

3.10. (S_C)-Ti(η^5:η^1-$C_9H_6SiMe_2NCHMePh$)Cl_2 ((S)-9)

Chlorodimethylsilylindene (2.09 g, 10.0 mmol) in 40 ml of hexane was treated at −78°C with a suspension of Li[(*S*)-NHCHMePh] (1.27 g, 10.0 mmol) in 40 ml of hexane. The mixture was stirred for 30 h at r.t. Filtration of the resulting suspension through kieselguhr and

removal of all volatives in vacuo gave (*S*)-$C_9H_7SiMe_2NHCHMePh$ which was distilled at 123°C/3×10^{-2} mbar to give a mixture of three isomers, yield 2.08 g (71%) of an orange oil. EIMS: *m*/*z* (%): 294 (64, M^+), 178 (100, $M^+-C_9H_7$). Anal. Calc. for $C_{19}H_{23}NSi$ (293.5): C, 77.76; H, 7.90; N, 4.77. Found: C, 77.14; H, 7.82; N, 4.62%. Following a procedure analogous to that described for the preparation of (*S*)-**8**, $TiCl_3(THF)_3$ (1.12 g, 3.01 mmol) was reacted with $Li_2[(S)$-$C_9H_6SiMe_2NCHMePh]$ (0.92 g, 3.01 mmol) and $PbCl_2$ (837 mg, 3.01 mmol) to give 680 mg (55%) of a mixture of isomers (5:1). (R_{Ti}, S_C)-**9**: ^{1}H-NMR (C_6D_6): δ −0.32, 0.47 (s, 3 H, $SiCH_3$), 1.46 (d, $^3J_{HH} = 7$ Hz, 3H, NCHCH_3), 6.24 (d, $^3J_{HH} = 3$ Hz, 1 H, C_9H_6), 6.35 (q, $^3J_{HH} = 7$ Hz, 1 H, NCHCH$_3$), 6.84 (d, $^3J_{HH} = 3$ Hz, 1 H, C_9H_6), 6.97–7.00 (m, 1 H, C_9H_6), 7.04–7.10 (m, 4 H, aromat. H), 7.32–7.38 (m, 3 H, aromat. H), 7.58 (d, $^3J_{HH} = 8$ Hz, 1 H, C_9H_6). ^{13}C-NMR: δ −2.2, 2.3 ($SiCH_3$), 18.9 (NCHCH$_3$), 64.0 (NCHCH$_3$), 97.4 (ring C at Si), 116.9 (C_9H_6), 127.1, 127.3, 127.4, 128.9, 129.1, 129.2 (aromat. CH), 134.6, 135.4, 144.2 (C-*ipso*). (S_{Ti}, S_C)-**9**: ^{1}H-NMR: δ −0.09, 0.25 (s, 3H, $SiCH_3$), 1.58 (d, $^3J_{HH} = 7$ Hz, 3 H, NCHCH_3), 6.29 (d, $^3J_{HH} = 3$ Hz, 1 H, C_9H_6), 6.35 (q, $^3J_{HH} = 7$ Hz, 1 H, NCHCH$_3$), 6.88 (d, $^3J_{HH} = 3$ Hz, 1 H, C_9H_6), 6.97–7.00 (m, 1 H, C_9H_6), 7.04–7.10 (m, 4 H, aromat. H), 7.32–7.38 (m, 3 H, aromat. H), 7.48 (d, $^3J_{HH} = 8$ Hz, 1 H, C_9H_6). EIMS: *m*/*z* (%): 395 (10, M^+–Me), 105 (100, $C_8H_9^+$). Anal. Calc. for $C_{19}H_{21}Cl_2NSiTi$ (410.3): C, 55.63; H, 5.16; N, 3.41. Found: C, 57.93; H, 6.72; N, 3.32%.

3.11. (p-*R*, S_C)-Ti{η^5:η^1-$C_9H_5(SiMe_3)$-$SiMe_2NCHMePh$}Cl_2 ((p-*R*, S_C)-**10**) and (p-*S*, S_C)-Ti{η^5:η^1-$C_9H_5(SiMe_3)SiMe_2NCHMePh$}$Cl_2$ ((p-*S*, S_C)-**10**)

(*S*)-$C_9H_6(SiMe_3)SiMe_2NHCHMePh$ was synthesized from $C_9H_6(SiMe_3)SiMe_2Cl$ (6.90 g, 24.6 mmol) and Li[(*S*)-NHCHMePh] in a manner analogous to that described for the preparation of (*S*)-$C_9H_7SiMe_2$-NHCHMePh. Distillation at 120–150°C/3×10^{-2} mbar afforded 6.77 g (75%) of a mixture of six isomers as an orange oil. EIMS: *m*/*z* (%): 365 (43, M^+), 350 (8, M^+-CH_3), 178 (100, $M^+-C_9H_5SiMe_3$). Anal. Calc. for $C_{22}H_{31}NSi_2$ (365.7): C, 72.30; H, 8.54; N, 3.83. Found: C, 69.27; H, 8.43; N, 3.89%. A suspension of $TiCl_3(THF)_3$ (834 mg, 2.25 mmol) in 15 ml of THF was treated at −78°C with $Li_2[(S)$-$C_9H_5(SiMe_3)SiMe_2$-NCHMePh] (0.85 g, 2.25 mmol in 30 ml of THF), obtained by deprotonation of (*S*)-$C_9H_6(SiMe_3)SiMe_2$-NHCHMePh with two equivalents of *n*-butyllithium. After stirring the reaction mixture for 1 h at r.t., $PbCl_2$ (626 mg, 2.25 mmol) was added and stirred for another 3 h. Removal of all volatiles and extracting the residue with 30 ml of hexane afforded red crystals as a 1:1-mixture, yield 73%. (p-*R*, S_C)-**10**: ^{1}H-NMR: δ −0.24, 0.54 (s, 2 × 3 H, $SiCH_3$), 0.51 (s, 9 H, $Si(CH_3)_3$), 1.46 (d, $^3J_{HH} = 7$ Hz, 3 H, NCHCH_3), 6.35 (q, $^3J_{HH} = 7$ Hz, 1 H, NCHCH$_3$), 6.67 (s, 1 H, C_9H_5), 7.05–7.20 (m, 5 H, aromat. H), 7.37–7.39 (m, 2 H, aromat. H), 7.73 (d, $^3J_{HH} = 9$ Hz, 1 H, aromat. H), 7.78 (d, $^3J_{HH} = 8$ Hz, 1 H, aromat. H). ^{13}C-NMR: δ −2.2, 2.7 ($SiCH_3$), −0.6 ($Si(CH_3)_3$), 19.2 (NCHCH$_3$), 64.2 (NCHCH$_3$), 100.8 (ring C at Si), 127.2, 127.5, 128.1, 128.8, 129.1, 134.9 (aromat. CH), 131.2 (CSiMe$_3$), 139.2, 139.5, 144.3 (C-*ipso*). (p-*S*, S_C)-**10**: ^{1}H-NMR: δ −0.02, 0.34 (s, 2 × 3H, $SiCH_3$), 0.52 (s, 9H, $Si(CH_3)_3$)), 1.52 (d, $^3J_{HH} = 7$ Hz, 3H, NCHCH_3), 6.35 (q, $^3J_{HH} = 7$ Hz, 1 H, NCHCH$_3$), 6.70 (s, 1 H, C_9H_5), 7.09–7.13 (m, 5H, aromat. H), 7.28–7.31 (m, 2 H, aromat. H), 7.70 (d, $^3J_{HH} = 7$ Hz, 1 H, aromat. H), 7.77 (d, $^3J_{HH} = 7$ Hz, 1 H, aromat. H). ^{13}C-NMR: δ −0.6 ($Si(CH_3)_3$), 0.3, 0.5 ($SiCH_3$), 18.4 (NCHCH$_3$), 63.6 (NCHCH$_3$), 100.2 (ring C at Si), 127.2, 127.3, 127.4, 127.6, 128.5, 128.6, 128.8, 134.8 (aromat. CH), 131.3 (CSiMe$_3$), 139.0, 139.6, 144.6 (C-*ipso*). EIMS: *m*/*z* (%): 481 (30, M^+), 466 (76, M^+–Me), 105 (100, $C_8H_9^+$). Anal. Calc. for $C_{22}H_{29}Cl_2NSi_2Ti$ (482.4): C, 54.77; H, 6.06; N, 2.90. Found: C, 54.68; H, 6.02; N, 2.93%.

3.12. (−)-(S)-Ti(η^5:η^1-$C_5H_4SiMe_2NCHMeC_{10}H_7$)$Cl_2$ ((*S*)-**11**)

To a solution of Li{(*S*)-NHCHMe$C_{10}H_7$} (500 mg, 2.82 mmol) in 40 ml of diethyl ether–THF mixture (5:1) was added triethylamine (0.39 ml, 2.82 mmol). This solution was added dropwise to a suspension of Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (880 mg, 2.82 mmol) in 40 ml of diethyl ether at −78°C. The reaction mixture was stirred for 30 min, allowed to warm to r.t. and stirred for 2 h. After filtration the solvent was removed in vacuo and the residue extracted with diethyl ether. The extracts were filtered and concentrated. Upon cooling to −20°C, 390 mg (34%) of yellow needles were isolated. $[\alpha]_D^{22} = -174.8$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ −1.00, 0.08 (s, 2 × 3 H, $SiCH_3$), 1.89 (d, $^3J_{HH} = 7$ Hz, 3 H, NCHCH_3), 5.92, 6.12 (m, 2 × 1 H, C_5H_4), 6.55–5.58 (m, 2 × 2 H, C_5H_4), 6.92 (q, $^3J_{HH} = 7$ Hz, 1 H, NCHCH$_3$), 7.17 (m, 1 H, $C_{10}H_7$), 7.29 (m, 2 H, $C_{10}H_7$), 7.53 (m, 1 H, $C_{10}H_7$), 7.57 (d, $^3J_{HH} = 8$ Hz, 1 H, $C_{10}H_7$), 7.63 (d, $^3J_{HH} = 8$ Hz, 1 H, $C_{10}H_7$), 8.68 (d, $^3J_{HH} = 9$ Hz, 1 H, $C_{10}H_7$). ^{13}C-NMR: δ −3.6, −1.1 ($SiCH_3$), 20.2 (NCHCH$_3$), 60.8 (NCHCH$_3$), 111.2 (ring C at Si), 124.6, 124.7, 125.3, 126.1 (C_5H_4), 123.3, 125.3, 126.0, 126.7, 128.7 ($C_{10}H_7$), 132.9, 134.5, 140.4 (*ipso* C). EIMS: *m*/*z* (%): 409 (3, M^+), 394 (10, M^+–Me), 156 (100, $C_{12}H_{12}^+$), 122 (13, $C_5H_4SiMe_2^+$). Anal. Calc. for $C_{19}H_{21}Cl_2NSiTi$ (410.3): C, 55.62; H, 5.16; N, 3.41. Found: C, 55.09; H, 6.30; N, 3.36%.

3.13. (+)-(R)-Ti(η^5:η^1-$C_5H_4SiMe_2NCHMeC_{10}H_7$)$Cl_2$ ((R)-**11**)

Following a procedure analogous to that described for the preparation of (*S*)-**11**, Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (963 mg, 3.09 mmol) was reacted with Li{(*R*)-$NHCHMeC_{10}H_7$} (547 mg, 3.09 mmol) in the presence of triethylamine (0.43 ml, 3.09 mmol) to give 340 mg (27%) of a yellow solid. $[\alpha]_D^{22} = +105.6$ ($c = 0.5$ in diethyl ether). Anal. Calc. for $C_{19}H_{21}Cl_2NSiTi$ (410.3): C, 55.62; H, 5.16; N, 3.41. Found C, 53.62; H, 5.95; N, 3.33%.

3.14. (+)-(R)-Ti(η^5:η^1-$C_5H_4SiMe_2NCHMe^tBu$)Cl_2 ((R)-**12**)

Following a procedure analogous to that described for the preparation of (*S*)-**11**, Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (3.12 g, 10.0 mmol) was reacted with lithium amide, obtained by deprotonation of (+)-(*R*)-pinacolyl amine (1.01 g, 10.0 mmol) with *n*-butyllithium (4 ml of a 2.5 M solution in hexane), in the presence of triethylamine (0.76 ml, 10.0 mmol) to give 580 mg (17%) of yellow needles. $[\alpha]_D^{22} = +34.4$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.20, 0.40 (s, 2×3 H, $SiCH_3$), 0.85 (s, 9 H, $C(CH_3)_3$), 1.02 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 5.72 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 5.97, 6.06, 6.58, 6.62 (m, 4×1 H, C_5H_4). ^{13}C-NMR: δ −0.8, 1.6 ($SiCH_3$), 15.9 ($NCHCH_3$), 27.5 ($C(CH_3)_3$), 37.7 ($C(CH_3)_3$), 69.7 ($NCHCH_3$), 106.9 (ring C at Si), 124.9, 125.1, 125.5, 125.6 (C_5H_4). EIMS: *m*/*z* (%): 282 (100, $M^+ - C_4H_9$), 240 (29, $M^+ - NC_6H_{12}$), 122 (6, $C_5H_4SiMe_2^+$). Anal. Calc. for $C_{13}H_{23}Cl_2NSiTi$ (340.2): C, 45.90; H, 6.81; N, 4.12. Found: C, 45.90; H, 6.84; N, 4.03%.

3.15. (+)-(S)-Ti(η^5:η^1-$C_5H_4SiMe_2NCHMeC_6H_{11}$)$Cl_2$ ((S)-**13**)

Following a procedure analogous to that described for the preparation of (*S*)-**11**, Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (1.55 g, 4.96 mmol) in 50 ml of hexane was reacted with lithium amide, obtained by deprotonation of (*S*)-1-cyclohexylethylamine (631 mg, 4.96 mmol) with *n*-butyllithium (2.0 ml of a 2.5 M solution in hexane), in the presence of triethylamine (0.69 ml, 4.96 mmol) to give 945 mg (52%) of yellow needles. $[\alpha]_D^{22} = +15.2$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.19, 0.28 (s, 2×3 H, $SiCH_3$), 0.77–1.28 (m, 6H, C_6H_{11}), 1.03 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.57–1.76 (m, 5 H, C_6H_{11}), 5.28 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 6.05, 6.09, 6.52, 6.60 (m, 4×1 H, C_5H_4). ^{13}C-NMR: δ −0.7, −0.6 ($SiCH_3$), 19.1 ($NCHCH_3$), 26.5, 26.6, 26.7, 30.3, 32.0, 48.1 (C_6H_{11}), 67.6 ($NCHCH_3$), 108.1 (ring C at Si), 124.0, 124.5, 125.5, 125.5 (C_5H_4). EIMS: *m*/*z* (%): 365 (2, M^+), 281 (100, $M^+ - C_6H_{11}$), 240 (37, $M^+ - NCHMeC_6H_{11}$), 122 (27, $C_5H_4SiMe_2^+$). Anal. Calc. for $C_{15}H_{25}Cl_2NSiTi$ (366.2): C, 49.19; H, 6.88; N, 3.82. Found: C, 49.12; H, 7.41; N, 3.70%.

3.16. (−)-(R)-Ti(η^5:η^1-$C_5H_4SiMe_2NCHMeC_6H_{11}$)$Cl_2$ ((R)-**13**)

Following a procedure analogous to that described for the preparation of (*S*)-**13**, Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (1.62 g, 5.19 mmol) in 50 ml of hexane was reacted with lithium amide, obtained by deprotonation of (*R*)-1-cyclohexylethylamine (660 mg, 5.19 mmol) with *n*-butyllithium (2.0 ml of a 2.5 M solution in hexane), in the presence of triethylamine (0.7 ml, 5.19 mmol) to give 910 mg (48%) of yellow crystals. $[\alpha]_D^{22} = -22.7$ ($c = 0.5$ in diethyl ether). Anal. Calc. for $C_{15}H_{25}Cl_2NSiTi$ (366.2): C, 49.19; H, 6.88; N, 3.82. Found: C, 49.05; H, 7.03; N, 3.83%.

3.17. (+)-(1S)-Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2$pinanyl-3)Cl_2 ((1S)-**14**)

Following a procedure analogous to that described for the preparation of (*S*)-**11**, Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (3.11 g, 10.0 mmol) in 50 ml of hexane was reacted with lithium amide, obtained by deprotonation of (1*S*)-3-aminomethylpinane (1.67 g, 9.98 mmol) with *n*-butyllithium (4.0 ml of a 2.5 M solution in hexane), in the presence of triethylamine (1.40 ml, 10.0 mmol) to give 2.60 g (64%) of a yellow solid. $[\alpha]_D^{22} = +11.7$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.18, 0.26 (s, 2×3 H, $SiCH_3$), 0.84 (d, $^3J_{HH} = 10$ Hz, 1 H, pinane 6-CH_{ax}), 0.99 (s, 3 H, CCH_3), 1.80 (d, $^3J_{HH} = 7$ Hz, 3 H, $CHCH_3$), 1.18 (s, 3 H, CCH_3), 1.62 (m, 1 H, $CHCH_3$), 1.71–1.77 (overlap m, 2 H, pinane 1-CH, 4-H_{eq}), 1.90 (m, 2 H, pinane 3-H, 5-H), 2.04 (m, 1 H, pinane 4-H_{ax}), 2.29 (m, 1 H, pinane 6-CH_{eq}), 4.22 (dd, $^2J_{HH} = 14$ Hz, $^3J_{HH} = 4$ Hz, 1 H, NCH_2), 4.48 (dd, $^2J_{HH} = 14$ Hz, $^3J_{HH} = 11$ Hz, 1 H, NCH_2), 6.13, 6.19, 6.51, 6.57 (m, 4×1 H, C_5H_4). ^{13}C-NMR: δ −3.4, −2.2 ($SiCH_3$), 21.9 (2-CCH_3), 23.0, 28.1 (7-CCH_3), 33.7 (CH_2-4), 34.3 (CH_2-6), 38.9 (C-7), 41.0 (CH-3), 41.8 (CH-2), 42.1 (CH-5), 48.1 (CH-1), 67.9 (NCH_2), 108.7 (ring C at Si), 124.0, 124.1, 125.6, 125.7 (C_5H_4). Complete assignments were achieved by ^{1}H/^{1}H and ^{1}H/^{13}C COSY. EIMS: *m*/*z* (%): 405 (34, M^+), 369 (100, $M^+ - Cl$), 315 (30, $M^+ - Cl$, $-C_4H_6$). Anal. Calc. for $C_{18}H_{29}Cl_2NSiTi$ (406.3): C, 53.21; H, 7.19; N, 3.45. Found: C, 52.72; H, 8.17; N, 3.35%.

3.18. (+)-(1R)-Ti(η^5:η^1-$C_5H_4SiMe_2$Nbornyl-2)Cl_2 ((1R)-**15**)

Following a procedure analogous to that described for the preparation of (*S*)-**11**, Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (855 mg, 2.74 mmol) in 50 ml of hexane was reacted with lithium amide, obtained by deprotonation of (+)-

(1*R*)-bornylamine (420 mg, 2.74 mmol) with *n*-butyllithium (1.1 ml of a 2.5 M solution in hexane), in the presence of triethylamine (0.38 ml, 2.74 mmol) to give 610 mg (57%) of orange–yellow needles. $[\alpha]_D^{22} = -124.6$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.30, 0.42 (s, 2×3 H, $SiCH_3$), 0.57 (dd, $^3J_{HH} = 14$ Hz, $^3J_{HH} = 5$ Hz, 1 H, bornyl), 0.77, 0.90 (s, 2×3 H, CCH_3), 1.01 (m, 1 H, bornyl), 1.14 (s, 3 H, CCH_3), 1.18 (t, $^3J_{HH} = 7$ Hz, 2 H, bornyl), 1.54–1.67 (2 overlap. m, 2×1 H, bornyl), 2.94 (m, 1 H, bornyl), 6.04 (m, 1 H, C_5H_4), 6.09 (m, 1 H, C_5H_4), 6.36 (m, 1 H, NCH), 6.56 (m, 2 H, C_5H_4). ^{13}C-NMR{DEPT} (C_6D_6): δ −1.2, 0.9 ($SiCH_3$), 14.2, 18.9, 20.2 (CH_3), 29.0, 29.7, 36.4 (CH_2), 44.4 (CH), 48.4, 52.6 (C-*ipso*), 68.8 (NCH), 106.7 (ring C at Si), 124.4, 125.2, 125.4, 125.8 (C_5H_4). Anal. Calc. for $C_{17}H_{27}Cl_2NSiTi$ (392.3): C, 52.01; H, 6.94; N, 3.57. Found: C, 51.91; H, 7.23; N, 4.20%.

3.19. (−)-(S)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMeC_{10}H_7$)$Cl_2$ ((S)-**16**)

3.19.1. (−)-(S)-(C_5Me_4H)$SiMe_2NHCHMeC_{10}H_7$

A solution of (C_5Me_4H)$SiMe_2Cl$ (651 mg, 3.03 mmol) in 50 ml of THF was treated with a solution of Li{(*S*)-$NHCHMeC_{10}H_7$} (537 mg, 3.03 mmol) in 30 ml THF at −78°C. The reaction mixture was allowed to warm to r.t. and stirred for 16 h. The solvent was removed in vacuo, hexane was added to the mixture and the suspension filtered. Removal of the solvent gave 1.01 g (96%) of a pale yellow oil. ^{1}H-NMR (C_6D_6, 200 MHz): δ 0.02, 0.03 (s, 2×3 H, $SiCH_3$), 0.85 (d, $^3J_{HH} = 9$ Hz, 1 H, NH), 1.40 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.84, 1.87, 1.98, 2.04 (s, 4×3H, C_5Me_4H), 2.84 (s, 1 H, C_5Me_4H), 4.82–4.87 (m, 1 H, $NCHCH_3$), 7.31–7.44 (m, 3H, $C_{10}H_7$), 7.59–7.65 (m, 2 H, $C_{10}H_7$), 7.72–7.76 (m, 1 H, $C_{10}H_7$), 8.08 (d, $^3J_{HH} = 8$ Hz, 1 H, $C_{10}H_7$). ^{13}C-NMR (C_6D_6, 200 MHz): δ −0.7 ($Si(CH_3)_2$), 11.2, 11.9, 15.2, 15.3 (C_5Me_4H), 28.4 ($NCHCH_3$), 48.3 ($NCHCH_3$), 57.4 (ring C at Si), 123.2, 123.7, 125.9, 126.3, 126.4, 128.8, 129.8 ($C_{10}H_7$), 133.5, 136.4 (C_5Me_4H), 131.5, 134.9, 146.0 (C-*ipso*).

Crude Li_2\{(*S*)-$C_5Me_4SiMe_2NCHMeC_{10}H_7$\} (910 mg, 2.52 mmol), obtained by double deprotonation of (−)-(*S*)-(C_5Me_4H)$SiMe_2NHCHMeC_{10}H_7$ with *n*-butyllithium in hexane, was dissolved in 40 ml of THF and added dropwise to a suspension of $TiCl_3(THF)_3$ (934 mg, 2.52 mmol) in 50 ml of THF at −78°C. The reaction mixture was allowed to warm to r.t. and after 2 h treated with $PbCl_2$ (700 mg, 2.52 mmol). After stirring for 16 h, the solvent was removed in vacuo and the residue was washed with diethyl ether (10 ml) and extracted with a warm mixture of toluene–hexane (2:1). Crystallization at −20°C afforded 320 mg (24%) of orange microcrystals. $[\alpha]_D^{22} = -28.2$ ($c = 0.5$ in CH_2Cl_2). ^{1}H-NMR: δ −0.79, 0.28 (s, 2×3 H, $SiCH_3$), 1.87 (s, 6 H, C_5Me_4), 1.94 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 2.05, 2.06 (s, 2×3 H, C_5Me_4), 6.77 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$), 7.20 (m, 1 H, $C_{10}H_7$), 7.29 (m, 2 H, $C_{10}H_7$), 7.51 (m, 1 H, $C_{10}H_7$), 7.50 (d, $^3J_{HH} = 8$ Hz, 1 H, $C_{10}H_7$), 7.65 (d, $^3J_{HH} = 8$ Hz, 1 H, $C_{10}H_7$), 8.75 (d, $^3J_{HH} = 9$ Hz, 1 H, $C_{10}H_7$). ^{13}C-NMR: δ 1.7, 4.2 ($SiCH_3$), 12.9, 13.0, 15.9, 16.1 (C_5Me_4), 20.9 ($NCHCH_3$), 59.0 ($NCHCH_3$), 105.1 (ring C at Si), 123.2, 125.4, 126.2, 126.3, 126.5, 128.5, 128.7 ($C_{10}H_7$), 136.8, 136.9, 141.1, 141.2 (C_5Me_4), 133.2, 134.6, 141.4 (C-*ipso*). EIMS: *m*/*z* (%): 465 (19, M^+), 450 (100, M^+–Me), 295 (27, M^+–$CHMeC_{10}H_7$, –Me), 156 (84, $C_{12}H_{12}^+$). Anal. Calc. for for $C_{23}H_{29}Cl_2NSiTi$ (466.4): C, 59.24; H, 6.27; N, 3.00. Found: C, 58.84; H, 6.21; N, 2.94%.

3.20. (R)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMe^tBu$)Cl_2 ((R)-**17**)

(*R*)-(C_5Me_4H)$SiMe_2NHCHMe^tBu$ was synthesized from (C_5Me_4H)$SiMe_2Cl$ (4.58 g, 21.3 mmol) and lithium amide, obtained by deprotonation of pinacolyl amine (2.16 g, 21.3 mmol) with *n*-butyllithium (8.5 ml of a 2.5 M solution in hexane), in a manner analogous to that described for the preparation of (*S*)-(C_5Me_4H)$SiMe_2NHCHMeC_{10}H_7$. Distillation at 92°C/5×10^{-3} mbar afforded 3.17 g (53%) of a pale yellow oil. $[\alpha]_D^{22} = +24.0$ ($c = 5.0$ in diethyl ether). ^{1}H-NMR: δ 0.11, 0.17 (s, 2×3 H, $SiCH_3$), 0.86 (s, 9 H, $C(CH_3)_3$), 0.92 (m, 1 H, NH), 0.96 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.88 (s, 6 H, C_5Me_4H), 2.04 (s, 6 H, C_5Me_4H), 2.42–2.50 (m, 1 H, $NCHCH_3$), 2.81 (s, 1 H, C_5Me_4H). ^{13}C-NMR: δ −1.0, −0.2 ($SiCH_3$), 11.4, 14.9 (C_5Me_4H), 20.9 ($NCHCH_3$), 26.5 ($C(CH_3)_3$), 35.3 ($C(CH_3)_3$), 56.0 ($NCHCH_3$), 56.8 (ring C at Si), 132.9, 135.6 (C_5Me_4H). EIMS: *m*/*z* (%): 279 (25, M^+), 263 (2, M^+–Me), 222 (13, M^+–C_4H_9), 178 (19, $C_5Me_4SiMe_2^+$), 158 (100, M^+–C_5Me_4H). Anal. Calc. for $C_{17}H_{33}NSi$ (279.5): C, 73.04; H, 11.90; N, 5.01. Found: C, 72.40; H, 11.80; N, 5.15%.

Following a procedure analogous to that described for the preparation of (*S*)-**16**, $TiCl_3(THF)_3$ (637 mg, 1.72 mmol) was reacted with $Li_2(C_5Me_4SiMe_2NCHMe^tBu)$ (500 mg, 1.72 mmol) and $PbCl_2$ (478 mg, 1.72 mmol) to give 190 mg (28%) of orange microcrystals. $[\alpha]_D^{22} = +66.2$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR ($CDCl_3$): δ 0.64, 0.81 (s, 2×3 H, $SiCH_3$), 0.91 (s, 9H, $C(CH_3)_3$), 1.02 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 2.07, 2.09, 2.21, 2.22 (s, 3H, C_5Me_4), 5.16 (q, $^3J_{HH} = 7$ Hz, 1 H, $NCHCH_3$). ^{13}C-NMR ($CDCl_3$): δ 4.8, 7.13 ($SiCH_3$), 13.0, 13.2, 15.9, 16.1 (C_5Me_4), 16.2 ($NCHCH_3$), 27.4 ($C(CH_3)_3$), 37.8 ($C(CH_3)_3$), 66.5 ($NCHCH_3$), 100.6 (ring C at Si), 136.9, 137.1, 140.5, 140.9 (C_5Me_4). Anal. Calc. for $C_{17}H_{31}Cl_2NSiTi$ (396.3): C, 51.52; H, 7.88; N, 3.53. Found: C, 50.99; H, 8.05; N, 2.31%.

3.21. (R)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCH^tBuPh$)Cl_2 ((R)-**18**)

(+)-(*R*)-(C_5Me_4H)$SiMe_2NHCH^tBuPh$ was synthesized from (C_5Me_4H)$SiMe_2Cl$ (651 mg, 3.03 mmol) and Li[(*R*)-$NHCH^tBuPh$], obtained by deprotonation of (+)-(*R*)-(1-phenyl)neopentylamine (1.63 g, 10.0 mmol) with *n*-butyllithium (4.0 ml of a 2.5 M solution in hexane), in a manner analogous to that described for the preparation of (*S*)-(C_5Me_4H)$SiMe_2NHCHMeC_{10}H_7$. Distillation at 108°C/5×10^{-3} mbar afforded 2.03 g (59%) of a pale yellow oil. $[\alpha]_D^{22} = +5.3$ ($c = 1.0$ in diethyl ether). ^{1}H-NMR: δ −0.06, 0.12 (s, 2×3H, $SiCH_3$), 0.88 (s, 9H, $C(CH_3)_3$), 1.07 (d, $^3J_{HH} = 8$ Hz, 1 H, NH), 1.88 (s, 3H, C_5Me_4H), 1.97, 2.02 (s, 3H, C_5Me_4H), 2.76 (s, 1 H, C_5Me_4H), 3.48 (d, $^3J_{HH} = 8$ Hz, 1 H, NCH), 7.09–7.19 (m, 5H, C_6H_5). ^{13}C-NMR: δ −1.0, −0.4 ($SiCH_3$), 11.2, 14.5, 14.6 (C_5Me_4H), 26.8 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 56.0 (NCH), 65.3 (ring C at Si), 126.2, 127.5, 128.5 (C_6H_5), 132.8, 135.3 (C_5Me_4H), 145.4 (C-*ipso*). EIMS: *m*/*z* (%): 341 (23, M^+), 284 (28, $M^+ - C_4H_9$), 222 (100, $M^+ - C_5Me_4H$). Anal. Calc. for $C_{22}H_{35}NSi$ (341.6): C, 77.35; H, 10.33; N, 4.10. Found: C, 76.41; H, 10.54; N, 4.37%.

Following a procedure analogous to that described for the preparation of (*S*)-**16**, $TiCl_3(THF)_3$ (1.87 g, 5.04 mmol) was reacted with Li_2{(*R*)-$C_5Me_4SiMe_2NCH^tBuPh$} (1.78 g, 5.04 mmol) and treated with $PbCl_2$ (1.40 mg, 5.04 mmol) to give 835 mg (36%) of dark yellow crystals. ^{1}H-NMR: δ 0.65, 0.70 (s, 2×3 H, $SiCH_3$), 1.09 (s, 9 H, $C(CH_3)_3$), 1.71, 1.95, 2.04, 2.07 (s, 4×3 H, C_5Me_4), 6.05 (s, 1 H, NCH), 7.07–7.38 (m, 5H, C_6H_5). ^{13}C-NMR: δ 6.2, 6.9 ($SiCH_3$), 12.9, 13.0, 16.0, 16.2 (C_5Me_4), 28.4 ($C(CH_3)_3$), 39.0 ($C(CH_3)_3$), 77.0 (NCH), 101.4 (ring C at Si), 127.1, 128.1, 130.5 (C_6H_5), 137.8, 137.9, 140.4, 140.6 (C_5Me_4), 141.2 (C-*ipso*). Anal. Calc. for $C_{22}H_{33}Cl_2NSiTi$ (458.4): C, 57.65; H, 7.25; N, 3.06. Found: C, 56.65; H, 7.26; N, 2.90%.

3.22. (+)-(S)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMeC_6H_{11}$)$Cl_2$ ((S)-**19**)

(+)-(*S*)-(C_5Me_4H)$SiMe_2NHCHMeC_6H_{11}$ was synthesized from (C_5Me_4H)$SiMe_2Cl$ (2.01 g, 9.34 mmol) and lithium amide, obtained by deprotonation of (*S*)-1-cyclohexylethylamine (1.19 g, 9.34 mmol) with *n*-butyllithium (8.5 ml of a 2.5 M solution in hexane), in a manner analogous to that described for the preparation of (*S*)-(C_5Me_4H)$SiMe_2NHCHMeC_{10}H_7$ and isolated as a waxy solid, yield 65%. ^{1}H-NMR ($CDCl_3$): δ −0.05, 0.01 (s, 2×3 H, $SiCH_3$), 0.18–0.23 (m, 1 H, NH), 0.82–1.21 (m, 7 H, C_6H_{11}), 0.94 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.56–2.03 (m, 4 H, C_6H_{11}), 1.81, 1.96 (s, 6 H, C_5Me_4H), 2.53–2.59 (m, 1 H, $NCHCH_3$), 2.80 (s, 1 H, C_5Me_4H). ^{13}C-NMR ($CDCl_3$): δ −1.4, −0.9 ($SiCH_3$), 11.2, 14.6 (C_5Me_4H), 22.6 ($NCHCH_3$), 26.6, 26.7, 26.8, 28.9, 29.0, 46.5 (C_6H_{11}), 51.7 ($NCHCH_3$), 56.9 (ring C at Si), 132.9, 135.3 (C_5Me_4H). EIMS: *m*/*z* (%): 305 (22, M^+), 184 (100, $M^+ - C_5Me_4H$), 179 (9, $C_5Me_4HSiMe_2^+$).

Following a procedure analogous to that described for the preparation of (*S*)-**16**, $TiCl_3(THF)_3$ (1.24 g, 3.34 mmol) was reacted with Li_2{(*S*)-$C_5Me_4SiMe_2NCHMeC_6H_{11}$} (1.06 g, 3.34 mmol) and $PbCl_2$ (929 mg, 3.34 mmol) to give 590 mg (42%) of yellow microcrystals. $[\alpha]_D^{22} = +2.1$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.50, 0.51 (s, 2×3 H, $SiCH_3$), 0.83–0.91 (m, 1 H, C_6H_{11}), 1.06–1.28 (m, 5 H, C_6H_{11}), 1.12 (d, $^3J_{HH} = 7$ Hz, 3 H, $NCHCH_3$), 1.58–1.90 (m, 5 H, C_6H_{11}), 2.02, 2.03, 2.05, 2.07 (s, 4×3 H, C_5Me_4), 5.02–5.09 (m, 1 H, $NCHCH_3$). ^{13}C-NMR: δ 4.5, 4.9 ($SiCH_3$), 12.8, 13.0, 15.9, 16.1 (C_5Me_4), 19.7 ($NCHCH_3$), 26.6, 26.7, 30.4, 32.0, 48.4 (C_6H_{11}), 64.9 ($NCHCH_3$), 101.8 (ring C at Si), 136.2, 140.1, 140.4 (C_5Me_4). EIMS: *m*/*z* (%): 338 (100, $M^+ - C_6H_{11}$), 295 (25, $M^+ - CHMeC_6H_{11}$, −Me). Anal. Calc. for $C_{19}H_{33}Cl_2NSiTi$ (422.4): C, 54.03; H, 7.88; N, 3.32%. Found: C, 53.20; H, 8.13; N, 3.64%.

3.23. (−)-(R)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCHMeC_6H_{11}$)$Cl_2$ ((R)-**19**)

(+)-(*R*)-(C_5Me_4H)$SiMe_2NHCHMeC_6H_{11}$ was synthesized in a manner analogous to that described for the preparation of the (*S*)-enantiomer. Distillation at 112°C/5×10^{-3} mbar afforded 3.96 g (54%) of a pale yellow oil. $[\alpha]_D^{22} = -14.6$ ($c = 2.5$ in diethyl ether). Anal. Calc. for $C_{19}H_{35}NSi$ (305.6): C, 74.68; H, 11.54; N, 4.58. Found: C, 72.38; H, 11.21; N, 5.26%.

Following a procedure analogous to that described for the preparation of (*S*)-**16**, $TiCl_3(THF)_3$ (1.67 g, 4.52 mmol) was reacted with Li_2{(*R*)-$C_5Me_4SiMe_2NCHMeC_6H_{11}$} (1.43 g, 4.53 mmol) and $PbCl_2$ (1.26 g, 4.52 mmol) to give 705 mg (37%) of an orange solid. $[\alpha]_D^{22} = -2.9$ ($c = 0.5$ in diethyl ether). Anal. Calc. for $C_{19}H_{33}Cl_2NSiTi$ (422.4): C, 54.03; H, 7.88; N, 3.32. Found: C, 53.98; H, 7.97; N, 3.57%.

3.24. (+)-(1S)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2$pinanyl-3)Cl_2 ((1S)-**20**)

(+)-(C_5Me_4H)$SiMe_2NHCH_2$pinanyl-3 was synthesized from (C_5Me_4H)$SiMe_2Cl$ (10.80 g, 50.3 mmol) and lithium amide, obtained by deprotonation of 3-aminomethylpinane (8.42 g, 50.3 mmol) with *n*-butyllithium (8.5 ml of a 2.5 M solution in hexane), in a manner analogous to that described for the preparation of (*S*)-(C_5Me_4H)$SiMe_2NHCHMeC_{10}H_7$. Distillation at 130–136°C/8×10^{-3} mbar afforded 13.10 g (75%) of a pale yellow oil. $[\alpha]_D^{22} = +23.2$ ($c = 2.0$ in diethyl ether). ^{1}H-NMR: δ 0.11, 0.12 (s, 2×3 H, $SiCH_3$), 0.42 (m, 1 H, NH), 0.80 (d, $^3J_{HH} = 10$ Hz, 1 H, pinane), 1.05 (s, 3 H, CCH_3), 1.11 (d, $^3J_{HH} = 7$ Hz, 3 H, $CHCH_3$), 1.25 (s,

3H, CCH_3), 1.50 (m, 1 H, pinane), 1.66 (m, 2 H, pinane), 1.80 (m, 2 H, pinane), 1.91 (s, 6 H, C_5Me_4H), 1.95 (m, 1 H, pinane), 2.06 (s, 6 H, C_5Me_4H), 2.10 (m, 1 H, pinane), 2.32 (m, 1 H, pinane), 2.57 (m, 1 H, NCH_2), 2.77 (m, 1 H, NCH_2), 2.89 (br s, 1 H, C_5Me_4H). ^{13}C-NMR{DEPT} (C_6D_6): δ −2.0 ($SiCH_3$), 11.4, 15.0 (C_5Me_4H), 22.4, 23.1, 28.2 (CH_3), 32.6, 33.9 (CH_2), 39.1 (C-*ipso*), 40.7, 40.9, 42.2, 48.4 (CH), 51.2 (NCH_2), 56.8 (ring C at Si), 132.8, 135.5 (C_5Me_4H). EIMS: m/z (%): 345 (32, M^+), 224 (40, $M^+-C_5Me_4H$), 88 (100, $C_7H_{14}^+$). Anal. Calc. for $C_{22}H_{39}NSi$ (345.6): C, 76.45; H, 11.37; N, 4.05. Found: C, 75.12; H, 11.18; N, 4.19%.

$(C_5Me_4H)SiMe_2NHCH_2$pinanyl-3 (3.65 g, 10.6 mmol) in 50 ml of hexane was treated with *n*-butyllithium (8.4 ml of a 2.5 M solution in hexane). After 2 h the viscous orange reaction mixture was dissolved in THF. This solution was reacted in a manner analogous to that described for the preparation of (*S*)-**16** with $TiCl_3(THF)_3$ (3.93 g, 10.6 mmol) and $PbCl_2$ (2.95 g, 10.6 mmol) to give 2.79 g (57%) of yellow needles. $[\alpha]_D^{22} = +31.9$ ($c = 0.5$ in diethyl ether). ^{1}H-NMR: δ 0.43, 0.52 (s, 2 × 3 H, $SiCH_3$), 0.87 (d, $^3J_{HH} = 10$ Hz, 1 H, pinane), 1.04 (s, 3 H, CCH_3), 1.10 (d, $^3J_{HH} = 7$ Hz, 3 H, $CHCH_3$), 1.19 (s, 3 H, CCH_3), 1.65 (m, 1 H, pinane), 1.74 (m, 1 H, pinane), 1.86–2.15 (m, 4 H, pinane), 2.01, 2.04, 2.07, 2.09 (s, 4 × 3 H, C_5Me_4), 2.29 (m, 1 H, pinane), 4.13 (dd, $^2J_{HH} = 13$ Hz, $^3J_{HH} = 3$ Hz, 1 H, NCH_2), 4.45 (dd, $^2J_{HH} = 13$ Hz, $^3J_{HH} = 11$ Hz, 1 H, NCH_2). ^{13}C-NMR: δ 1.8, 3.2 ($SiCH_3$), 12.7, 12.8, 15.9, 16.0 (C_5Me_4), 21.8, 23.0, 28.1 (CH_3), 33.6, 34.3 (CH_2), 38.9 (C-7), 41.5, 41.8, 48.1 (CH), 65.4 (NCH_2), 102.9 (ring C at Si), 135.9, 136.0, 140.5, 140.7 (C_5Me_4). EIMS: m/z (%): 461 (6, M^+), 426 (6, M^+-Cl), 324 (100, $M^+-C_{10}H_{19}$), 295 (63, $M^+-C_{11}H_{20}$, $-CH_3$), 178 (10, $C_5Me_4SiMe_2^+$). Anal. Calc. for $C_{22}H_{37}Cl_2NSiTi$ (462.4): C, 57.14; H, 8.07; N, 3.03. Found: C, 57.15, H, 8.16; N, 3.04%.

3.25. (1S)-Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2$pinanyl-3)-($OiPr$)$_2$ (**21**)

This compound was synthesized from $TiCl_2(OiPr)_2$ (917 mg, 3.87 mmol) and $Li_2(C_5Me_4SiMe_2NCH_2$-pinanyl-3) dissolved in 60 ml of a mixture of hexane–THF (5:1), obtained by deprotonation of (C_5Me_4H)-$SiMe_2NHCH_2$-pinane (1.34 g, 3.87 mmol) with *n*-butyllithium (3.1 ml of a 2.5 M solution in hexane), in a manner analogous to that described for the preparation of **3**. Crystallization from hexane at −78°C afforded 395 mg (20%) of a waxy yellow solid. ^{1}H-NMR: δ 0.64, 0.70 (s, 2 × 3H, $SiCH_3$), 0.99 (d, $^3J_{HH} = 10$ Hz, 1 H, pinane), 1.13 (s, 3 H, CCH_3), 1.20–1.27 (overlap., 18 H, $CHCH_3$, CCH_3, $CH(CH_3)_2$), 1.73 (m, 1 H, pinane), 1.80–1.95 (m, 4 H, pinane), 1.98, 1.99 (s, 2 × 3 H, C_5Me_4), 2.03 (m, 1 H, pinane), 2.21, 2.27 (s, 2 × 3 H, C_5Me_4), 2.39 (m, 1 H, pinane), 3.62 (dd, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 11$ Hz, 1 H, NCH_2), 3.75 (dd, $^2J_{HH} = 12$ Hz, $^3J_{HH} = 4$ Hz, 1 H, NCH_2), 4.61–4.68 (2 overlap. sep, 2 H, $CH(CH_3)_2$). ^{13}C-NMR: δ 3.2, 4.8 ($SiCH_3$), 11.5, 11.6, 14.3 (C_5Me_4), 22.4, 23.1 (CCH_3), 27.2 ($CH(CH_3)_2$) 28.1 ($CHCH_3$), 33.2, 33.9 (CH_2), 39.2 (C-7), 41.6, 42.1, 42.3, (CH), 63.7 (NCH_2), 74.6 ($OCH(CH_3)_2$), 103.4 (ring C at Si), 127.4, 129.6, 129.7 (C_5Me_4). EIMS: m/z (%): 509 (29, M^+), 450 (33, $M^+-OC_3H_7$), 372 (83, $M^+-C_{10}H_{17}$), 313 (100, $M^+-C_{10}H_{17}$, $-OC_3H_7$). Anal. Calc. for $C_{28}H_{51}NO_2SiTi$ (509.7): C, 65.98; H, 10.09; N, 2.75. Found: C, 64.75; H, 10.06; N, 3.41%.

3.26. (1R)-Ti(η^5:η^1-$C_5Me_4SiMe_2N$bornyl-2)Cl_2 (**22**)

$(C_5Me_4H)SiMe_2NH$-bornyl was synthesized from $(C_5Me_4H)SiMe_2Cl$ (539 mg, 2.51 mmol) and lithium (1*R*)-bornyl-2-amide (400 mg, 2.51 mmol) in a manner analogous to that described for the preparation of (*S*)-$(C_5Me_4H)SiMe_2NHCHMeC_{10}H_7$ to give 800 mg (96%) of a pale yellow oil. ^{1}H-NMR: δ 0.11, 0.17 (s, 2 × 3 H, $SiCH_3$), 0.41 (m, 1 H, NH), 0.66 (dd, $^3J_{HH} = 4$ Hz, $^3J_{HH} = 11$ Hz, 1 H, bornyl), 0.85 (s, 3 H, CCH_3), 0.88 (s, 2 × 3 H, CCH_3), 1.08–1.24 (m, 2 H, bornyl), 1.54–1.75 (m, 3 H, bornyl), 1.90, 2.05 (br s, 6H, C_5Me_4H), 2.25 (m, 1 H, bornyl), 2.81 (s, 1 H, C_5Me_4H), 3.01 (m, 1 H, NCH). ^{13}C-NMR: δ −1.2, 1.0 ($SiCH_3$), 11.1, 13.6, 14.0, 14.5, 14.6, 18.2, 20.2 (CH_3), 26.6, 28.6 (CH_2), 42.4 (CH), 45.1 (NCH), 47.3, 49.3 (C-*ipso*), 56.6 (ring C at Si), 132.5, 135.1 (C_5Me_4H). EIMS: m/z (%): 331 (66, M^+), 210 (100, $M^+-C_5Me_4H$), 179 (22, $C_5Me_4HSiMe_2^+$), 100 (43, $C_7H_{11}^+$), 58 (66, $SiMe_2^+$).

Following a procedure analogous to that described for the preparation of (*S*)-**16**, $TiCl_3(THF)_3$ (767 mg, 2.07 mmol) was reacted with $Li_2(C_5Me_4SiMe_2N$bornyl-2) (710 mg, 2.07 mmol) and $PbCl_2$ (575 mg, 2.07 mmol) to give 95 mg (10%) of a yellow powder. ^{1}H-NMR: δ 0.55, 0.66 (s, 2 × 3 H, $SiCH_3$), 0.69–0.77 (m, 3 H, bornyl), 0.80, 0.97, 1.11 (s, 3 × 3 H, CCH_3), 1.22–1.30 (m, 1 H, bornyl), 1.39–1.46 (m, 1 H, bornyl), 1.64–1.71 (m, 1 H, bornyl), 2.00, 2.02, 2.03, 2.05 (s, 4 × 3 H, C_5Me_4), 2.83 (m, 1 H, bornyl), 6.02 (m, 1 H, NCH). ^{13}C-NMR: δ 4.5, 6.8 ($SiCH_3$), 13.0, 14.5, 16.1, 16.2, 19.0, 20.3 (C_5Me_4, CH_3-bornyl), 29.2, 29.5, 36.9 (CH_2), 44.7 (CH), 48.5, 52.5 (C-*ipso*), 66.1 (NCH), 100.4 (ring C at Si), 136.5, 136.8, 140.2, 140.4 (C_5Me_4).

3.27. Hydrogenation

A solution of the titanium complex (0.1 mmol) in 20 ml of toluene was treated with a solution of *n*-butyllithium (0.2 mmol) at r.t. and stirred for 5 min. Acetophenone *N*-benzylimine (21 g, 100 mmol) in 10 ml of toluene was added and the mixture stirred in an autoclave for 12 h at 80°C under 150 bar of hydrogen gas.

After cooling to r.t., the vessel was vented and discharged. Removal of all volatiles and distillation of the residue in a kugelrohr apparatus afforded (+)-(1*R*)-*N*-benzyl-1-phenylethylamine. Enantiomeric excesses were determined by GC analysis of the product mixture after trifluoroacetylation. The results are compiled in Table 2.

*3.28. X-ray crystal structural analysis and determination of the structures of **6** and (1S)-**20***

Data sets were obtained with an ENRAF-Nonius CAD4 diffractometer in the ω-scan mode. The reflections were corrected for *Lp* effects using the program system MolEN [21] and for absorption using ψ-scans [22]. All structures were solved by Patterson and Fourier methods using the program SHELXS-86 [23a]. The refinements were carried out using the program SHELXL-93 based on F^2 [23b]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. For both compounds, the hydrogen atoms were refined in their positions or calculated into idealized positions, whereby rotating group refinements were applied for the hydrogen atoms of the methyl groups. Results are given in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142273 for **6**, and CCDC no. 142274 for (1*S*)-**20**. 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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