Optically Active Titanium Complexes Containing Linked Amido-Cyclopentadienyl Ligands: Their Use as Asymmetric Hydrogenation Catalysts

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Optically active titanium complexes of the formula $Ti(\eta^5:\eta^1-C_5R_4SiMe_2NCHMePh)Cl_2$ (R = H, Me), containing the cyclopentadienyl ligand linked to a chiral 1-phenylethylamido moiety, were synthesized and characterized in both enantiomerically pure forms. A single-crystal X-ray structural analysis of (*S*)-(−)$Ti(\eta^5:\eta^1-C_5H_4SiMe_2NCHMePh)Cl_2$ shows a conformation in which the phenyl group is turned away from the metal center. NOE measurements suggest that a related structure is retained in solution. Upon activation with *n*-butyllithium, these complexes show hydrogenation activity toward imines with slight enantioselectivity.

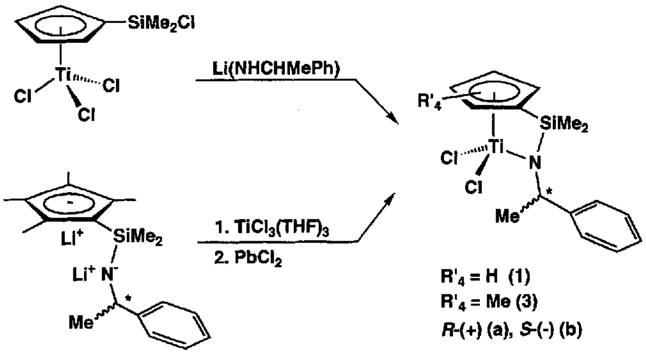
Introduction

Linked amido-cyclopentadienyl ligands[1–3] have recently attracted considerable attention as a novel ancillary ligand system for the generation of olefin polymerization catalysts with remarkable activity for copolymerization of ethylene with α-olefins[4]. In contrast to Brintzinger-type *ansa*-metallocenes[5], these half-sandwich complexes have so far not found much application other than as catalysts precursors for α-olefin copolymerization[6]. For example, chiral *ansa*-titanocenes with the ethylenebis(tetrahydroindenyl) ligand have recently been reported as enantioselective hydrogenation catalysts for trisubstituted alkenes[7a] and imines[7b,c]. We show here that optically active variants of titanium complexes with the bridged amido-cyclopentadienyl ligand can be easily prepared and are active as homogeneous hydrogenation catalysts for imines.

Results and Discussion

Following previously established methods[2,3,8], we have synthesized enantiomerically pure titanium complexes of the formula $Ti(\eta^5:\eta^1-C_5R_4SiMe_2NCHMePh)Cl_2$ for R = H and Me by introducing the appropriate enantiomers of 1-phenylethylamine (Scheme 1). For R = H, treatment of $Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3$ with one equivalent of optically pure (*R*)-(+)- or (*S*)-(−)-Li(NHCHMePh) in the presence of one equivalent of triethylamine gave good yields of yellow crystals of (*R*)-(+)- and (*S*)-(−)-enantiomers of $Ti(\eta^5:\eta^1-C_5H_4SiMe_2NCHMePh)Cl_2$ **1a,b**. The corresponding specific rotation values are $[\alpha]^{22}_{D} = +344.1°$ and $-344.3°$. ^1H- and ^{13}C-NMR spectroscopic as well as mass spectrometric and analytical data confirm the expected structure with a bidentate amido-cyclopentadienyl ligand. In the ^1H-NMR spectrum the diastereotopic $SiMe_2$ protons give two sharp resonances at $\delta = -0.45$ and $+0.13$, and four partially overlapping multiplates for the C_5H_4 protons, as well as five aromatic signals for the phenyl group, are detected. The methyl group at the stereogenic carbon atom is recorded as a doublet at $\delta = 1.53$. The methine proton is partially obscured by two C_5H_4 signals around $\delta = 6.5$, but the presence of a quartet in this region was established by decoupling experiments.

Scheme 1



NOE measurements of **1** revealed a conformation in solution that suggests a fairly unexpected arrangement of the phenyl group. The observation of a larger NOE between the methyl group of the stereogenic center and one of the two inequivalent methyl groups of the silylene link suggests hindered rotation about the amido-nitrogen−carbon bond, with the preferential conformation of the larger amido substituent pointing away from the metal center (Figure 1). A single-crystal X-ray structural analysis of the (*S*)-(−)-enantiomer **1b** also revealed a structure in which the phenyl group is arranged in a coplanar fashion to the C_5H_4 ring, turned away from the metal center (Figure 2). All other structural features are as expected for a titanium(IV) complex with the linked amido-cyclopentadienyl ligand, in particular the short titanium−nitrogen bond length of 188.8(4) pm and the planar geometry at the nitrogen

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atom (sum of the angles: 359.8°). A similar structure was found in $Ti(\eta^5:\eta^1-C_5H_4SiMe_2NCH_2CH_2OMe)Cl_2$[3h] and in $Ti(\eta^5:\eta^1-C_5H_4SiMe_2C_6H_3F_2-2,5)Cl_2$[9]. The absolute *S* configuration of the stereogenic carbon atom was also confirmed crystallographically. The geometry of the amido-substituent is such that the distance between the hydrogen atom on the stereogenic carbon and the titanium atom is 284 pm. This value is clearly beyond the value for a β-agostic interaction. However, given the similar conformation in solution, a weak interaction may be assumed, as was previously found in $Ti(\eta^5-C_5H_5)Cl_2(NiPr_2)$[10].

Figure 1. Results of selected NOE measurements for (*S*)-(−)-$Ti(\eta^5:\eta^1-C_5H_4SiMe_2NCHMeC_6H_5)Cl_2$ (**1b**) in C_6D_6 at 25°C

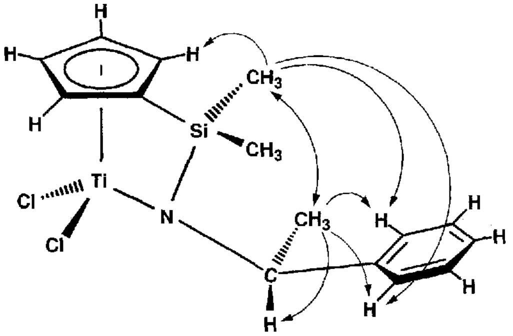
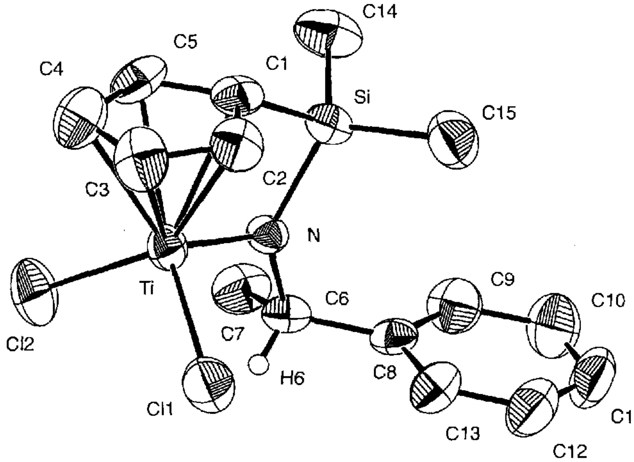


Figure 2. ORTEP diagram of the molecular structure of (*S*)-(−)-$Ti(\eta^5:\eta^1-C_5H_4SiMe_2NCHMeC_6H_5)Cl_2$ (**1b**); thermal ellipsoids are drawn at the 50-% probability level; hydrogen atoms are omitted for the sake of clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Ti−N 188.8(4), Ti−C1 229.4(5), Ti−C2 232.4(5), Ti−C3 238.7(6), Ti−C4 238.2(6), Ti−C5 230.6(6), Ti−Cl1 227.4(2), Ti−Cl2 225.5(2); N−C6−C7 110.4(5), Cl1−Ti−Cl2 104.5(4), Ti−N−Si 108.0(2), C6−N−Ti 120.5(3), Si−N−C6 131.3(4).

Derivatives of $Ti(\eta^5-C_5H_4SiMe_2NCHMePh)Cl_2$ (**1**) containing the C_5Me_4 ring **3** were prepared, in both enantiomeric forms, by following the protocol established for titanium complexes containing the ligand of the type $(C_5Me_4)SiMe_2NHR'$[2,3]. The optically active ligand precursors $(C_5Me_4H)SiMe_2NHCHMePh$ (**2**) were obtained as distillable oils in good yields by reacting $(C_5Me_4H)SiMe_2Cl$ with one equiv. of Li(NHCHMePh). ^1H- and ^{13}C-NMR spectroscopic as well as mass spectrometric and analytical data unequivocally confirm the structure of $Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCHMePh)Cl_2$. The specific optical rotation values are $[\alpha]_D^{22} = +235.7°$ and $-236.6°$ for the (*R*)- and (*S*)-enantiomers **3a** and **3b**, respectively.

Preliminary experiments demonstrated that racemic **1** efficiently catalyzes the hydrogenation of imines such as acetophenone *N*-benzylimine upon activation with two equiv. of *n*-butyllithium. The unexpectedly good catalytic efficiency is comparable to that observed with titanocene derivatives[11]. When optically pure **1a** was used, an enantiomeric excess of 12% was observed for *N*-benzyl-1-phenylethylamine, which formed in excellent yield.

In conclusion, we have demonstrated that enantiomerically pure titanium complexes with chirally modified linked amido-cyclopentadienyl ligands can be synthesized and that they are active in asymmetric homogeneous hydrogenation of imines[7b,c]. The simple access to this class of compounds, as compared to that to optically active *ansa*-metallocenes, bodes well for their future application in other types of asymmetric catalysis[13].

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Experimental

All manipulations were performed under argon using standard Schlenk techniques. Solvents were purified, dried, and distilled under argon. – ^1H and ^{13}C NMR: Bruker AC 200 or Bruker AM 400. – MS: Finnigan 8230. – Elemental analyses: Microanalytical Laboratory of this department. – The following reagents were synthesized using literature procedures: $Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3$[8], $C_5Me_4H(SiMe_2Cl)$[2c], and $TiCl_3(THF)_3$[11].

(R)-(+)-Dichloro[η⁵:η¹-(cyclopentadienyldimethylsilyl)(1-phenylethyl)amido]titanium (**1a**): (*R*)-(+)-1-Phenylethylamine (6.06 g, 50.0 mmol) dissolved in 150 ml of hexane was treated with *n*-butyllithium (20.0 ml of a 2.5 M solution in hexane) at room temp. and the mixture stirred for 16 h. The suspension was filtred and the white solid was washed several times with hexane to give 5.70 g (90%) of crude lithium [(*R*)-(+)-(1-phenylethyl)amide].

To a solution of $Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3$ (4.68 g, 15.0 mmol) and triethylamine (2.09 ml, 15.0 mmol) in 150 ml of diethyl ether was added dropwise a solution of crude lithium (1-phenylethyl)amide (1.91 g, 15.0 mmol) in 90 ml of a diethyl ether/THF mixture (5:1) at −78°C. The suspension was stirred for 30 min. and then was allowed to warm to room temp. and stirred for another 2 h. The mixture was filtered and the solvent was removed in vacuo. The residue was extracted with a diethyl ether/hexane mixture (200 ml) and the solvent evaporated. Crystallization from diethyl ether at −20°C afforded 4.02 g (74%) of **1a** as yellow prisms. – $[\alpha]_D^{22} = +344.1$ (*c* = 1.0 in diethyl ether). – ^1H NMR (C_6D_6): $\delta = -0.45$, 0.13 (s, 3H, $SiCH_3$), 1.53 (d, $^3J = 7$ Hz, 3H, $NCHCH_3$), 6.04, 6.09 (m, 1H, C_5H_4), 6.52–6.55 (overlap. m, 3H, C_5H_4, $NCHCH_3$), 7.04–7.07 (m, 3H, C_6H_5), 7.30–7.33 (m, 2H, C_6H_5). – ^{13}C NMR (C_6D_6): $\delta = -3.1$, −0.7 ($SiCH_3$), 19.1 ($NCHCH_3$), 64.6 ($NCHCH_3$), 109.5 (ring C at Si), 124.1, 124.4, 126.0, 126.1 (C_5H_4), 127.3 (2 × C-*ortho*), 128.1 (C-*para*), 128.8 (2 × C-*meta*), 144.1 (C-*ipso*). – EI MS: *m/z* (%) = 359 (8) [M^+], 344 (99) [$M^+ - Me$], 241 (35) [$M^+ - TiCl_2$], 122 (19) [$C_5H_4SiMe_2^+$], 106 (100) [$C_8H_{10}^+$]. – $C_{15}H_{19}Cl_2NSiTi$ (360.2): calcd. C 50.00, H 5.32, N 3.89; found C 49.87, H 5.31, N 3.79.

(S)-(−)-Dichloro[η⁵:η¹-(cyclopentadienyldimethylsilyl)(1-phenylethyl)amido]titanium (**1b**): Compound **1b** was synthesized from $Ti(\eta^5-C_5H_4SiMe_2Cl)Cl_3$ and lithium [(*S*)-(−)-(1-phenylethyl)amide] in a manner analogous to that described for the preparation of **1a** and isolated as yellow crystals in 72% yield. – $[\alpha]_D^{22} = -344.3$ (*c* = 1.0 in diethyl ether). – $C_{15}H_{19}Cl_2NSiTi$ (360.2): calcd. C 50.00, H 5.32, N 3.89; found C 49.91, H 5.38, N 3.84.

X-ray Crystal Structure Analysis of **1b**: Yellow prisms of **1b** were obtained by slow cooling in diethyl ether. Cell dimensions and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer: $C_{15}H_{19}Cl_2NSiTi$, $M = 360.2$, $a = 791.5(3)$, $b = 1348.1(3)$, $c = 1635.0(5)$ pm, $Z = 4$, $d_{calcd.} = 1.37$ Mgm^{-3}, orthorhombic, $P2_12_12_1$ (Nr. 19), Mo-K_α ($\lambda = 71.073$ pm), graphite monochromator, 0.10 × 0.20 × 0.50 mm, $T = 293$ K, $3.00° < \Theta < 29.00°$, $F(000) = 744$. Number of reflections measured 8252, 5062 independent reflections [R(int) = 0.03] of which 2328 were assigned observed [$I > 2\sigma(I)$], absorption coefficient 8.50 cm^{-1}. The structure was solved by direct methods (MULTAN) and difference Fourier synthesis, and refined using MolEN. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms except H6 were calculated at their idealized positions. The refinement (184 parameters) converged with $R = 0.048$, $R_w = 0.040$, $w = 1/\sigma^2(F_o)$ for the observed F_o data, goodness of fit 0.99. The residual electron density was $0.59 \cdot 10^{30}$ em^{-3}[12].

(R)-(+)-Dimethyl[(1-phenylethyl)amino](tetramethylcyclopentadienyl)silane (**2a**): Chlorodimethyl(tetramethylcyclopentadienyl)silane (4.47 g, 20.8 mmol) in 100 ml of THF was treated with a solution of lithium [(*R*)-(+)-(1-phenylethyl)amine] (2.67 g, 21.0 mmol) in 50 ml of THF at −78 °C. After being stirred for 2 h, the reaction mixture was allowed to warm to room temp. and stirred for 16 h. The solvent was removed in vacuo, hexane (50 ml) was added to the mixture and the suspension was filtered. Removal of solvent and distillation at 116 °C/$8 \cdot 10^{-3}$ mbar gave **2a** as a pale yellow oil, yield 4.87 g (78%). – $[\alpha]_D^{22} = +32.27$ ($c = 1.40$ in diethyl ether). – ^1H NMR (C_6D_6): $\delta = -0.04, -0.03$ (s, 3H, $SiCH_3$), 0.64 (d, $^3J = 9$ Hz, 1H, NH), 1.23 (d, $^3J = 7$ Hz, 3H, $NCHCH_3$), 1.82 (s, 6H, C_5CH_3), 1.92, 1.98 (s, 3H, C_5CH_3), 2.77 (s, 1H, C_5Me_4H), 3.90–4.01 (m, 1H, $NCHCH_3$), 7.13 (m, 1H, C_6H_5), 7.35–7.38 (m, 4H, C_6H_5). – ^{13}C NMR (C_6D_6): $\delta = -1.10, -0.78$ ($SiCH_3$), 11.4, 14.3, 14.7, 14.8 (C_5CH_3), 28.2 ($NCHCH_3$), 51.9 ($NCHCH_3$), 56.6 (ring C at Si), 126.0, 126.5 (C_6H_5), 132.8, 135.6 (C_5Me_4H), 149.6 (C-*ipso*). – EI MS: *m*/*z* (%) = 299 (20) [M^+], 179 (20) [$C_{11}H_{19}Si^+$], 178 (100) [$C_{10}H_{16}NSi^+$], 106 (90) [$C_8H_{10}^+$]. – $C_{19}H_{29}NSi$ (299.5): calcd. C 76.19, H 9.76, N 4.68; found C 75.41, H 9.77, N 4.65.

(R)-(+)-Dichloro[η^5:η^1-(dimethyltetramethylcyclopentadienylsilyl)(1-phenylethyl)amido]titanium (**3a**): Crude $Li_2[(R)\text{-}(+)\text{-}(C_5Me_4SiMe_2)N(CHMeC_6H_5)]$ (1.39 g, 4.46 mmol), obtained by double deprotonation of **2a** with *n*-butyllithium in hexane, was dissolved in 50 ml of THF and added dropwise to a suspension $TiCl_3(THF)_3$ (1.65 g, 4.45 mmol) in 50 ml of THF at −78 °C. The reaction mixture was allowed to warm to room temp. and after 2 h treated with $PbCl_2$ (1.24 g, 4.46 mmol). After stirring for 2 d, the solvent was removed in vacuo, the residue washed with 20 ml diethyl ether and extracted with a warm mixture of toluene/hexane (2:1) (90 ml). Crystallization at −20 °C afforded 1.39 g (75%) of **3a** as yellow-orange needles. – $[\alpha]_D^{22} = +235.7$ ($c = 0.5$ in diethyl ether). – ^1H NMR (C_6D_6): $\delta = -0.17, 0.36$ (s, 3H, $SiCH_3$), 1.63 (d, $^3J = 7$ Hz, 3H, $NCHCH_3$), 1.97, 2.03, 2.04, 2.05 (s, 3H, C_5CH_3), 6.34 (q, $^3J = 7$ Hz, 1H, $NCHCH_3$), 7.04–7.13 (m, 3H, C_6H_5), 7.40–7.42 (m, 2H, C_6H_5). – ^{13}C NMR (C_6D_6): $\delta = 2.3$, 4.7 ($SiCH_3$), 12.8, 12.9, 16.0, 16.1 (C_5CH_3), 20.0 ($NCHCH_3$), 62.5 ($NCHCH_3$), 103.6 (ring C at Si), 127.4, 127.9, 128.7 (C_6H_5), 136.3 (2 × C_5CH_3), 140.7, 140.9 (C_5CH_3), 145.1 (C-*ipso*). – EI-MS: *m*/*z* (%) = 415 (12) [M^+], 400 (100) [$M^+ - Me$], 295 (29) [$M^+ - CHMePh, - Me$], 105 (86) [$C_8H_9^+$]. – $C_{19}H_{27}Cl_2NSiTi$ (416.3): calcd. C 54.82, H 6.54, N 3.36; found C 54.91, H 6.62, N 3.27.

(S)-(−)-Dichloro[η^5:η^1-dimethyltetramethylcyclopentadienylsilyl)(1-phenylethyl)amido]titanium (**3b**): Compound **3b** was synthesized from **2b** {$[\alpha]_D^{22} = -32.81$ ($c = 1.55$ in diethyl ether)} and $TiCl_3(THF)_3$ in a manner analogous to that described for the preparation of **3a** and isolated as yellow crystals in 68% yield. – $[\alpha]_D^{22} = -236.6$ ($c = 0.5$ in diethyl ether). – $C_{19}H_{27}Cl_2NSiTi$ (416.3): calcd. C 54.82, H 6.54, N 3.36; found C 54.81, H 6.49, N 3.33.

Hydrogenation: A solution of **1a** (36 mg, 0.1 mmol) in 20 ml of toluene was treated with a solution of *n*-butyllithium (0.2 mmol) at room temp. and stirred for 5 min. Acetophenone *N*-benzylimine (21 g, 100 mmol) was added and the mixture stirred in an autoclave for 12 h at 80 °C under 150 bar of hydrogen gas. Removal of all volatiles and distillation of the residue in a kugelrohr apparatus afforded 92% of (1*R*)-benzyl(1-phenylethyl)amine. An enantiomeric excess of 12% was determined by GC analysis of the product mixture after trifluoroacetylation.

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[13] Note added in proof (October, 14, 1996): Prof. P. Royo has kindly informed us of his independent synthesis of *rac*-**1**: S. Circuelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, *Organometallics*, in press.

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