New Titanatranes: Characterization and Styrene Polymerization Behavior

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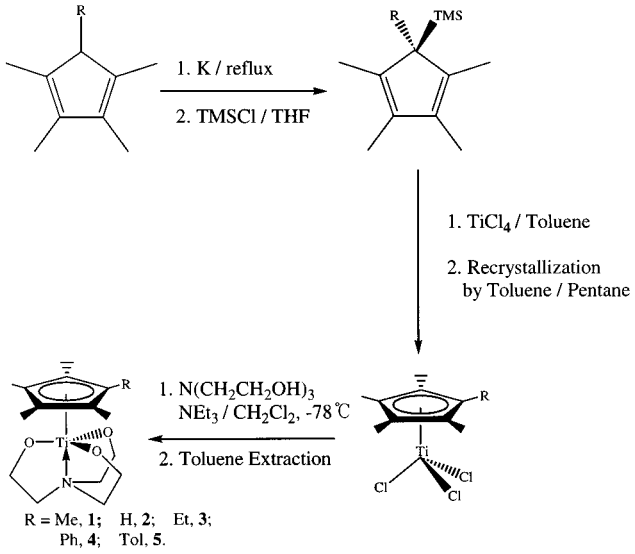
New titanatranes containing cyclopentadienyl ligands were prepared by the reactions of various kinds of trialkanolamines with $(C_5Me_4R)TiCl_3$ (Cp′ = C_5Me_4R) in the presence of triethylamine. The X-ray analyses reveal that they exist in the monomeric form in the solid state and the Ti atom adopts essentially an η^5 bonding posture with the Cp′ ring and a tetradentate bonding mode with the trialkanolatoamine ligand via a transannular interaction from the bridgehead N atom to Ti. All compounds show very high catalytic activity for the syndiospecific polymerization of styrene in the presence of modified methylaluminoxane (MMAO) cocatalyst.

Introduction

The chemistry of atranes, a class of compounds containing the triethanolatoamine ligand, has been intensively studied, and examples are now known across the periodic table.[1] However, most studies have focused on the use of main-group elements in the formation of atrane.[2] Only few reports on titanatranes have thus appeared.[3−9] In particular, Verkade et al. synthesized new several types of titanatranes via the displacement of the NR_2 group.[6] Moreover, Nugent et al. demonstrated that other type of titanatranes derived from enantiopure homochiral tri-2-propanolamine or its higher homologues could be synthesized and is efficient for the ring opening of meso epoxides under certain conditions with high selectivity (up to 93% ee).[7,8] However, we were somewhat surprised that, prior to our studies, no titanatrane has been applied in the field of homogeneous catalysis for olefin polymerization. In this regard, we have recently demonstrated that (pentamethylcyclopentadienyl)titanatrane/MMAO is the more active and syndiospecific catalyst system for the polymerization of styrene and functionalized styrenes than Cp*$TiCl_3$/MMAO over a wide range of polymerization conditions.[9] We have further extended the series of titanatranes to include various cyclopentadienyl ancillary ligands (see Scheme 1). We have also explored the coordination chemistry of new enantiopure homochiral trialkanolamines with titanium metal as summarized in Scheme

Scheme 1. Synthetic Routes to Compounds 1−5



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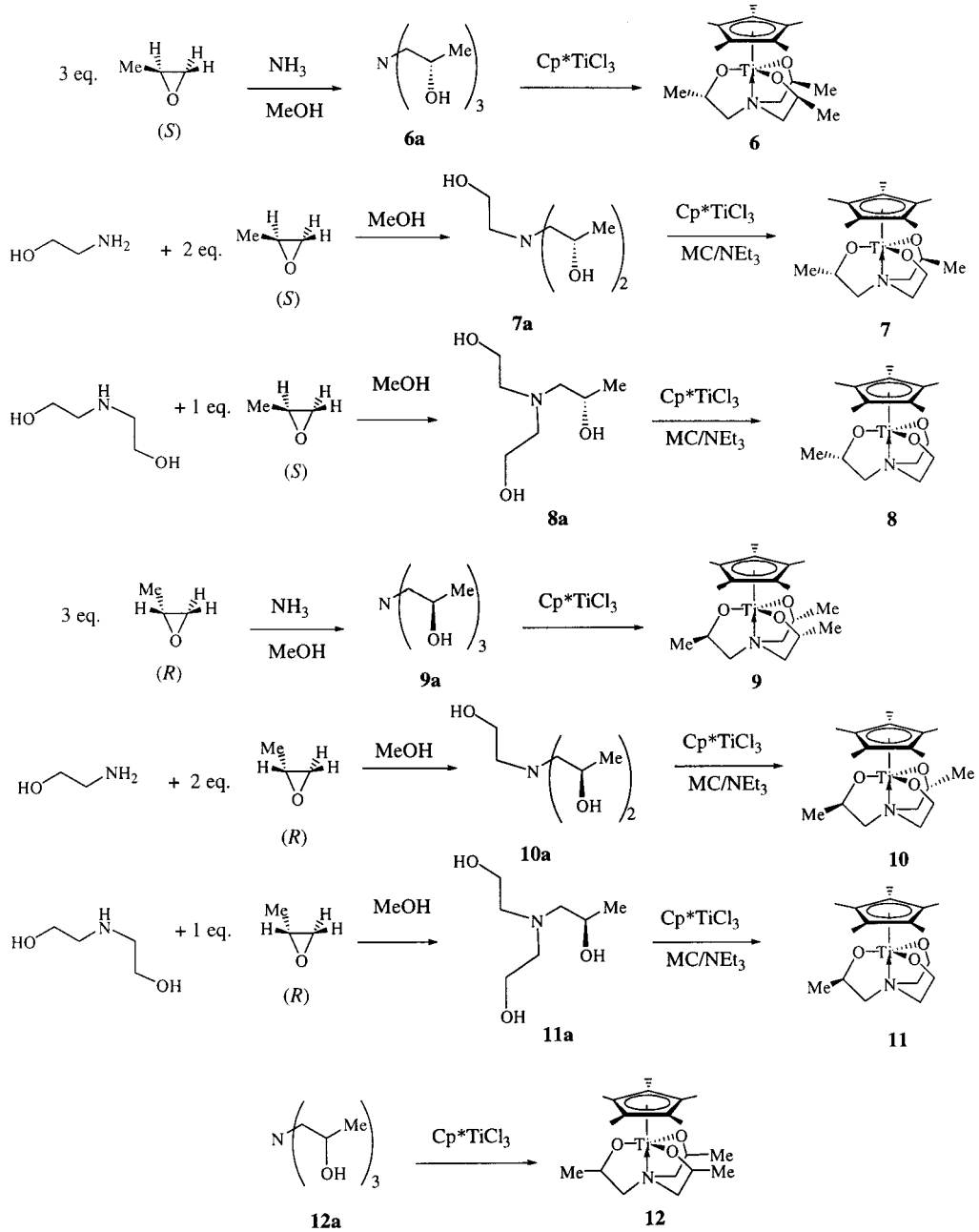
Scheme 2. Synthetic Routes to Ligands 6a−11a and Compounds 6−12



2. We expect that the synthesis, structures, and styrene polymerization behavior, reported herein, will facilitate the development of additional useful catalysts for olefin polymerization on the basis of these readily available ligands.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere using standard Schlenk and glovebox techniques.[10] Argon was deoxygenated with activated Cu catalyst (regenerated by heating to 300 °C under H_2 gas) and dried with Drierite. All solvents were dried by distilling from sodium−potassium alloy/benzophenone ketyl (toluene, tetrahydrofuran (THF), diethyl ether) or CaH_2 (methylene chloride) under a nitrogen atmosphere and stored over activated molecular sieves (3A).[11] $CDCl_3$ was dried over activated molecular sieves (4A) and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

Measurements. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM 300 or a Bruker Spectrospin 400 spectrometer at room temperature. The chemical shifts are referenced to the residual peaks of $CDCl_3$ (7.24 ppm for ^1H NMR and 77.0 ppm for $^{13}C\{^1H\}$ NMR). EI and HR mass spectra were obtained on a VG Auto spectrometer. Elemental analyses were performed by the Korea Basic Science Center, Seoul, Korea. The thermal properties of syndiotactic polystyrene (sPS) were investigated on a Thermal Analyst 200 DSC system under a nitrogen atmosphere at a heating rate of 20 °C/min. Molecular weights of sPS were determined at 140 °C in 1,2,4-trichlorobenzene on a PL 220+220R GPC calibrated with standard polystyrenes.

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Syntheses. Modified methylaluminoxane (MMAO; 3A type) was supplied by Akzo Co. Cp′$TiCl_3$[12] and Cp*Ti(TEA) (**1**)[9] were synthesized by the literature procedures. All other chemicals were purchased from Aldrich.

Syntheses of (η^5-C_5Me_4R)Ti(TEA) (R = H, 2; R = Et, 3; R = Ph, 4; R = Tol, 5). These compounds were prepared in a similar manner, as outlined in Scheme 1, and thus only one representative preparation is described. A reddish solution of (η^5-C_5Me_4H)$TiCl_3$ (1.4 g, 5.0 mmol) in 40 mL of CH_2Cl_2 was added dropwise to a stirred solution of triethanolamine (0.75 g, 5.0 mmol) and triethylamine (2.1 mL, 15 mmol) in 40 mL of CH_2Cl_2 at −78 °C. After the completion of the addition, the reaction mixture was warmed to room temperature and stirred for 12 h. The residue, obtained by removing the solvent under vacuum, was redissolved in toluene, and the resulting mixture was filtered through a Celite bed. The removal of solvent from the yellow filtrate gave the desired product **2** in 80% yield (1.3 g). **2**: ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm) δ 5.51 (s, 1H, C_5HMe_4), 4.27 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 2.91 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 1.98 (s, 6H, CH_3), 1.82 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, ppm) δ 124.80, 123.73, 114.19, 70.73, 58.05, 13.13, 10.86; EI-MS (intensity) *m*/*z* 315 (100%, M^+), 285 (94%, $M^+ - CH_2O$), 255 (98%, $M^+ - 2CH_2O$), 227 (83%, $M^+ - 2CH_2CH_2O$), 212 (77%, $M^+ - N(CH_2CH_2O)_2$), 194 (96%, M^+ − Cp′), 168 (85%, Cp′Ti^+), 134 (88%, $M^+ - N(CH_2CH_2O)_3$), 121 (69%, $M^+ - TiN(CH_2CH_2O)_3$). Anal. Calcd for $C_{15}H_{25}NO_3Ti$: C, 57.15; H, 7.99; N, 4.44. Found: C, 57.22; H, 7.92; N, 4.38.

3: yield 83%; ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm) δ 4.23 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 2.86 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 2.30 (q, 2H, CH_2Me), 1.88 (s, 6H, C_5Me_4Et), 1.85 (s, 6H, C_5Me_4Et), 1.00 (t, 6H, CH_2Me); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, ppm) δ 127.2, 122.3, 122.1, 70.65, 56.11, 19.40, 14.37, 11.00, 10.95; EI-MS (intensity) *m*/*z* 343 (98%, M^+), 313 (89%, $M^+ - CH_2O$), 283 (95%, $M^+ - 2CH_2O$), 255 (66%, $M^+ - 2CH_2CH_2O$), 240 (67%, $M^+ - N(CH_2CH_2O)_2$), 194 (100%, M^+ − Cp′), 149 (48%, $M^+ - TiN(CH_2CH_2O)_3$). Anal. Calcd for $C_{17}H_{29}NO_3Ti$: C, 59.48; H, 8.51; N, 4.08. Found: C, 59.44; H, 8.47; N, 4.12.

4: yield 81%; ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm) δ 7.28 (m, 5H, Ph), 4.26 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 2.92 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 1.96 (s, 6H, C_5Me_4Ph), 1.93 (s, 6H, C_5Me_4Ph); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, ppm) δ 137.17, 130.73, 127.27, 125.38, 124.84, 124.17, 122.15, 70.94, 56.16, 12.21, 11.11; EI-MS (intensity): *m*/*z* 391 (100%, M^+), 361 (89%, $M^+ - CH_2O$), 331 (80%, $M^+ - 2CH_2O$), 303 (77%, $M^+ - 2CH_2CH_2O$), 288 (78%, $M^+ - N(CH_2CH_2O)_2$), 244 (78%, M^+ - $N(CH_2CH_2O)_3$), 194 (96%, M^+ − Cp′). Anal. Calcd for $C_{21}H_{29}NO_3Ti$: C, 64.45; H, 7.47; N, 3.58. Found: C, 64.80; H, 7.36; N, 3.64.

5: yield 82%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 7.20 (d, 2H, Ph), 7.15 (d, 2H, Ph), 4.29 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 2.94 (t, 6H, $^3J_{HH}$ = 5.6 Hz, NCH_2CH_2O), 2.37 (s, 3H, $PhCH_3$), 1.98 (s, 6H, C_5Me_4Tol), 1.96 (s, 6H, C_5Me_4Tol); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 134.7, 134.1, 130.5, 128.1, 124.9, 124.1, 122.0, 70.90, 56.11, 21.21, 12.20, 11.10; EI-MS (intensity) *m*/*z* 405 (100%, M^+), 375 (84%, $M^+ - CH_2O$), 345 (85%, $M^+ - 2CH_2O$), 317 (73%, $M^+ - 2CH_2CH_2O$), 302 (77%, $M^+ - N(CH_2CH_2O)_2$), 258 (77%, $M^+ - N(CH_2CH_2O)_3$), 211 (35%, $M^+ - TiN(CH_2CH_2O)_3$), 194 (96%, M^+ − Cp′). Anal. Calcd for $C_{22}H_{31}NO_3Ti$: C, 65.19; H, 7.71; N, 3.46. Found: C, 65.44; H, 7.36; N, 3.40.

Syntheses of Homochiral Trialkanolamine Ligands (TAA) 6a−11a. Ligand **6a** was prepared according to the reported synthetic route,[7] and similar synthetic routes were employed in preparing **7a**−**11a** (see Scheme 2).

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6a: yield 96%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 5.10 (br s, 3H, $-OH$), 3.86 (m, 3H, OCH), 2.34 (dd, 3H, *J* = 10, 13 Hz, NCH_2 anti to OCH proton), 2.19 (dd, 3H, *J* = 1.6, 13 Hz, NCH_2 gauche to OCH proton), 1.08 (d, 9H, *J* = 6.3 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 63.66 (OCH), 63.24(NCH_2), 20.18($CHCH_3$).

7a: yield 94%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 4.10 (br s, 3H, $-OH$), 3.86 (m, 2H, OCH), 3.70 (m, 1H), 3.49 (m, 1H), 2.68 (m, 1H), 2.29 (m, 5H), 1.09 (d, 6H, *J* = 6.3 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 64.10 (OCH), 63.00 (OCH_2), 59.41 ($OCHCH_2$), 57.39 (OCH_2CH_2), 20.15 ($CHCH_3$).

8a: yield 96%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 5.01 (br s, 3H, $-OH$), 3.84 (m, 1H, OCH), 3.64 (m, 2H), 3.45 (m, 2H), 2.70 (m, 2H), 2.33 (m, 4H), 1.07 (d, 3H, *J* = 6.2 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 64.33 (OCH), 63.36 (OCH_2), 59.44 ($OCHCH_2$), 57.43 (OCH_2CH_2), 19.98 ($CHCH_3$).

9a: yield 94%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 5.18 (br s, 3H, $-OH$), 3.85 (m, 3H, OCH), 2.32 (dd, 3H, *J* = 10, 13 Hz, NCH_2 anti to OCH proton), 2.16 (dd, 3H, *J* = 1.6, 13 Hz, NCH_2 gauche to OCH proton), 1.06(d, 9H, *J* = 6.3 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 63.76 (OCH), 63.37 (NCH_2), 20.21 ($CHCH_3$).

10a: yield 96%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 4.91 (br s, 3H, $-OH$), 3.93 (m, 2H, OCH), 3.70 (m, 1H), 3.50 (m, 1H), 2.70 (m, 1H), 2.32 (m, 5H), 1.08 (d, 6H, *J* = 6.3 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 64.00 (OCH), 63.30 (OCH_2), 59.37 ($OCHCH_2$), 57.41 (OCH_2CH_2), 20.11 ($CHCH_3$).

11a: yield 94%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 5.01 (br s, 3H, $-OH$), 3.84 (m, 1H, OCH), 3.64 (m, 2H), 3.45 (m, 2H), 2.70 (m, 2H), 2.33 (m, 4H), 1.07 (d, 3H, *J* = 6.2 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 64.35 (OCH), 63.32 (OCH_2), 59.43 ($OCHCH_2$), 57.38 (OCH_2CH_2), 19.96 ($CHCH_3$).

Syntheses of Complexes (η^5-C_5Me_5R)Ti(TAA) (6−12). These compounds, listed in Scheme 2, were prepared in a manner analogous to the procedure for **2** using the scale of 2.0 mmol of (η^5-C_5Me_5)$TiCl_3$ (**6**): yield 84%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 4.53 (m, 3H, OCH), 2.70 (dd, 3H, *J* = 3.8, 12 Hz, NCH_2), 2.54 (t, 3H, $^3J_{HH}$ = 11 Hz, NCH_2), 1.84 (s, 15H, $C_5(CH_3)_5$), 0.99 (d, 9H, *J* = 6.0 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 121.7 ($C_5(CH_3)_5$), 75.32 (OCH), 63.01 (NCH_2), 22.59 ($CHCH_3$), 11.08 ($C_5(CH_3)_5$); EI-MS (intensity) *m*/*z* 371 (93%, M^+), 327 (92%, M^+ − OCHMe), 283 (100%, M^+ − 2OCHMe), 236 (73%, M^+ − Cp*), 228 (95%, $M^+ - (OCHCH_2)_3N$), 199 (49%, $M^+ - (OCHMeCH_2)_2NCH_2CH_2O$), 182 (71%, Cp*$Ti^+$); exact mass calcd for $C_{19}H_{33}O_3NTi$ 371.1940. found: 371.1941. Anal. Calcd: C, 61.45; H, 8.96; N, 3.77. Found: C, 61.60; H, 9.10; N, 3.72.

7: yield 81%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 4.54 (m, 2H, OCH), 4.36 (td, 1H, *J* = 3.9, 12 Hz, OCH_2), 4.06 (dd, 1H, *J* = 6.2, 12 Hz, OCH_2), 3.05 (m, 1H), 2.77−2.50 (m, 5H), 1.84 (s, 15H, $C_5(CH_3)_5$), 0.97 (dd, 6H, *J* = 1.3, 6.0 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 121.7 ($C_5(CH_3)_5$), 75.51 (OCH), 75.42 (OCH), 70.39 (OCH_2), 63.31 ($OCHCH_2$), 62.28 ($OCHCH_2$), 56.59 (OCH_2CH_2), 22.50 ($CHCH_3$), 11.05 ($C_5(CH_3)_5$); EI-MS (intensity) *m*/*z* 357 (78%, M^+), 313 (78%, M^+ − OCHMe), 269 (100%, M^+ − 2OCHMe), 222 (19%, M^+ − Cp*), 214 (68%, $M^+ - (OCHCH_2)_3N$); exact mass calcd for $C_{18}H_{31}O_3NTi$ 357.1783, found 357.1786. Anal. Calcd: C, 60.50; H, 8.74; N, 3.92. Found: C, 60.62; H, 9.01; N, 3.80.

8: yield 82%; ^{1}H NMR (300.13 MHz, $CDCl_3$, ppm) δ 4.55 (m, 1H, OCH), 4.35 (m, 2H), 4.10 (dd, 2H, *J* = 6.1, 12 Hz), 3.04 (m, 2H), 2.74 (m, 2H), 2.52 (t, 2H, $^3J_{HH}$ = 11 Hz), 1.85 (s, 15H, $C_5(CH_3)_5$), 1.00 (d, 3H, *J* = 5.9 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm) δ 122.1 ($C_5(CH_3)_5$), 75.67 (OCH), 70.62 (OCH_2), 70.50 (OCH_2), 62.63 ($OCHCH_2$), 56.92 (OCH_2CH_2), 55.97 (OCH_2CH_2), 22.47 ($CHCH_3$), 11.03 ($C_5(CH_3)_5$); EI-MS (intensity) *m*/*z* 343 (94%, M^+), 299 (99%, M^+ − OCHMe), 269

Table 1. Crystallographic Data for the Structural Analysis

	2	**4**	**5**	**6**	**8**
empirical formula	$C_{15}H_{25}NO_3Ti$	$C_{21}H_{29}NO_3Ti$	$C_{22}H_{31}NO_3Ti$	$C_{19}H_{33}O_3NTi$	$C_{17}H_{29}O_3NTi$
fw	315.25	391.35	405.35	371.36	343.31
cryst syst	triclinic	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)
a (Å)	8.000(3)	8.528(3)	12.649(6)	8.6020(10)	8.674(2)
b (Å)	8.694(2)	11.427(5)	12.628(7)	14.2711(20)	12.066(3)
c (Å)	12.818(3)	11.511(4)	15.435(7)	16.7553(3)	17.448(8)
α (deg)	74.67(2)	68.69(4)	66.86(4)	90.00	90
β (deg)	74.49(2)	70.42(3)	66.81(4)	91.855(16)	90
γ (deg)	70.73(3)	87.00(4)	80.59(5)	90.00	90
V (Å^3)	795.5(4)	981.4(6)	2083.9(19)	2055.82(53)	1826.1(10)
Z	2	2	2	4	4
D_{calcd} (g cm^{-3})	1.316	1.324	1.292	1.20	1.25
λ(Mo Kα)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
F(000)	336	416	864	800	736
μ (cm^{-1})	5.44	4.56	4.32	4.31	4.80
cryst size (mm)	0.25 × 0.28 × 0.28	0.29 × 0.29 × 0.29	0.28 × 0.28 × 0.28	0.19 × 0.20 × 0.25	0.20 × 0.18 × 0.25
θ range (deg)	$2< \theta <25$	$2< \theta <25$	$2< \theta <25$	$1< \theta <25$	$2< \theta <25$
scan type	$\omega/2\theta$	ω/θ	ω/θ	$\omega/2\theta$	$\omega/2\theta$
h; k; l	±9; −10 to +9; ±15	±10; ±13; −12 to +13	−14 to +15; ±14; −16 to +18	±10; ±16; ±19	±10; ±14; ±20
total no. of rflns	2058	2583	5329	3546	2719
no. of data with $I > 2\sigma(I)$	1154	1450	3027	1988	2152
no. of params refined	185	239	497	433	208
R1($I > 2\sigma(I)$)[a]	0.0832	0.0933	0.0833	0.0746	0.0973
wR2($I > 2\sigma(I)$)[b]	0.1606	0.1499	0.1535	0.1646	0.2051
GOF($I > 2\sigma(I)$)	1.237	1.247	1.137	1.201	1.213
peak and hole (e Å^{-3})	0.45, −0.33	0.34, −0.45	0.45, −0.54	0.53, −0.56	1.94, −1.77
Flack param				-0.03(8)	-0.06(12)
x	0.0730	0.0549	0.0713	0.0848	0.1446
y	0.5987	0.0000	2.5614	0.0840	0.0000

[a] The structure was refined in F_o^2 using all data; the value of R1 is given for comparison with older refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$. R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [b] wR2 = $[\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

(100%, M$^+$ − (OCHMeCH$_2$)N), 241 (49%, M$^+$ − (OCH$_2$CH$_2$)$_2$N), 226 (48%, M$^+$ − (OCH$_2$CH$_2$)N(CH$_2$CHMeO)), 214(96%, M$^+$ − (OCH$_2$CH$_2$)N(CH$_2$CHMeO)(CH$_2$)); exact mass calcd for $C_{17}H_{29}O_3NTi$ 343.1627, found 343.1626. Anal. Calcd: C, 59.48; H, 8.51; N, 4.08. Found: C, 59.40; H, 8.56; N, 4.00.

9: yield 84%; ^{1}H NMR (400.13 MHz, CDCl$_3$, ppm) δ 4.53 (m, 3H, OC*H*), 2.70 (dd, 3H, J = 3.8, 12 Hz, NC*H*$_2$), 2.54 (t, 3H, $^3J_{HH}$ = 11 Hz, NC*H*$_2$), 1.84 (s, 15H, C$_5$(C*H*$_3$)$_5$), 0.99 (d, 9H, J = 6.0 Hz, CHC*H*$_3$); ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$, ppm) δ 121.7 (*C*$_5$(CH$_3$)$_5$), 75.32 (O*C*H), 62.97 (N*C*H$_2$), 22.59 (CH*C*H$_3$), 11.08 (C$_5$(*C*H$_3$)$_5$); EI-MS (intensity) m/z 343 (88%, M$^+$), 299 (90%, M$^+$ − OCHMe), 269 (100%, M$^+$ − (OCHMeCH$_2$)N), 241 (55%, M$^+$ − (OCH$_2$CH$_2$)$_2$N), 226 (70%, M$^+$ − (OCH$_2$CH$_2$)N(CH$_2$CHMeO)), 214 (79%, M$^+$ − (OCH$_2$CH$_2$)N(CH$_2$CHMeO)(CH$_2$)); exact mass calcd for $C_{19}H_{33}O_3NTi$ 371.1940; found 371.1940. Anal. Calcd: C, 61.45; H, 8.96; N, 3.77. Found: C, 61.55; H, 9.18; N, 3.76.

10: yield 71%; ^{1}H NMR (400.13 MHz, CDCl$_3$, ppm) δ 4.54 (m, 2H, OC*H*), 4.36 (td, 1H, J = 3.9, 12 Hz, OC*H*$_2$), 4.06 (dd, 1H, J = 6.2, 12 Hz, OC*H*$_2$), 3.05 (m, 1H), 2.77−2.50 (m, 5H), 1.85 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.00 (dd, 6H, J = 1.5, 6.0 Hz, CHC*H*$_3$); ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$, ppm) δ 122.0 (*C*$_5$(CH$_3$)$_5$), 75.54 (O*C*H), 75.45 (O*C*H), 70.44 (O*C*H$_2$), 63.38 (OCH*C*H$_2$), 62.36 (OCH*C*H$_2$), 56.64 (OCH$_2$*C*H$_2$), 22.50 (CH*C*H$_3$), 11.04 (C$_5$(*C*H$_3$)$_5$); EI-MS (intensity) m/z 357 (95%, M$^+$), 313 (98%, M$^+$ − OCHMe), 269 (100%, M$^+$ − 2OCHMe), 222 (79%, M$^+$ − Cp*), 214 (99%, M$^+$ − (OCHCH$_2$)$_3$N); exact mass calcd for $C_{18}H_{31}O_3NTi$ 357.1783, found 357.1785. Anal. Calcd: C, 60.50; H, 8.74; N, 3.92. Found: C, 60.52; H, 8.59; N, 3.88.

11: yield 84%; ^{1}H NMR (300.13 MHz, CDCl$_3$, ppm) δ 4.55 (m, 1H, OC*H*), 4.35 (m, 2H), 4.09 (dd, 2H, J = 6.1, 12 Hz), 3.04 (m, 2H), 2.74 (m, 2H), 2.52(t, 2H, $^3J_{HH}$ = 11 Hz), 1.85 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.01 (d, 3H, J = 5.9 Hz, CHC*H*$_3$); ^{13}C{^{1}H} NMR (75.1 MHz, CDCl$_3$, ppm) δ 122.2 (*C*$_5$(CH$_3$)$_5$), 75.68 (O*C*H), 70.63 (O*C*H$_2$), 70.51 (O*C*H$_2$), 62.65 (OCH*C*H$_2$), 56.94 (OCH$_2$*C*H$_2$), 55.99 (OCH$_2$*C*H$_2$), 22.47 (CH*C*H$_3$), 11.03 (C$_5$(*C*H$_3$)$_5$); EI-MS (intensity) m/z 343 (83%, M$^+$), 299 (100%, M$^+$ − OCHMe), 269 (89%, M$^+$ − (OCHMeCH$_2$)N), 241 (29%, M$^+$ − (OCH$_2$CH$_2$)$_2$N), 226 (22%, M$^+$ − (OCH$_2$CH$_2$)N (CH$_2$CHMeO)), 214 (62%, M$^+$ − (OCH$_2$CH$_2$)N(CH$_2$CHMeO)(CH$_2$)); exact mass calcd for $C_{17}H_{29}O_3NTi$ 343.1627, found 343.1630. Anal. Calcd: C, 59.48; H, 8.51; N, 4.08. Found: C, 59.52; H, 8.56; N, 4.30.

12: yield 75%; ^{1}H NMR (300.13 MHz, CDCl$_3$, ppm) δ 4.60−4.35 (m, 3H), 3.16 (dd, 1H, J = 6.8, 13 Hz), 2.96 (dd, 1H, J = 3.9, 12 Hz), 2.74−2.66 (m, 3H), 2.60−2.48 (m, 3H), 1.86 (d, 15H), 1.16 (d, 3H, J = 6.7 Hz), 1.13−0.96 (m, 9H); ^{13}C{^{1}H} NMR (75.1 MHz, CDCl$_3$, ppm) δ 121.76, 121.70, 76.57, 75.93, 75.32, 75.20, 69.13, 65.16, 64.14, 63.00, 25.11, 22.59, 22.19, 11.07.

X-ray Structural Determination. Crystals suitable for X-ray crystallography were obtained by slow cooling of toluene/pentane solutions of **2**, **4**−**6**, and **8** in a refrigerator (−15 °C). A set of independent reflections was measured on an Enraf-Nonius CAD4TSB diffractometer at 293 K with λ(Mo Kα radiation) = 0.710 73 Å. All data were corrected for Lp effects, and ψ-scan absorption corrections were applied. The structures were solved by a semiinvariant direct method (SIR 92 in MoleN) and refined by full-matrix least-squares calculations (SHELXL 93) with anisotropic thermal parameters for all non-hydrogen atoms.[13] Hydrogens were placed at their geometrically calculated positions (d_{C-H} = 0.96 for methyl hydrogens, d_{C-H} = 0.97 for methylene hydrogens, d_{C-H} = 0.93 for phenyl hydrogens) and refined riding on the corresponding carbon atoms with isotropic thermal parameters (1.5U for methyl hydrogens, 1.2U for methylene hydrogens, 1.5U for phenyl hydrogens). All calculations were performed on a Silicon Graphics Indigo2XZ workstation. The detailed data are listed in Table 1.

(13) User's Manual of: Sheldrick, G. M. SHELXL-93: A Computer Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

Polymerization Procedure. Styrene polymerizations were carried out in a 250 mL Schlenk flask with magnetic stirring. Toluene, the polymerization solvent, was distilled from sodium−potassium alloy under an argon atmosphere just before use. Styrene monomer was distilled from calcium hydride and stored in a refrigerator. Polymerizations were carried out as following: toluene, styrene, MMAO, and the titanium compound were injected into a 250 mL Schlenk flask with magnetic stirring in that order at the desired temperature of 70 °C. After the desired reaction time was reached, the reaction was terminated by the addition of 50 mL of methanol and the addition of 50 mL of 10% HCl in methanol was followed. The resulting precipitated polymer was collected, washed three times each with 500 mL of methanol, and dried in vacuo at 70 °C for 12 h. The polymer was extracted with refluxing 2-butanone for 12 h, and the resulting insoluble portion was determined as the sPS portion (SI) of the polymer obtained. Syndiotacticity of the insoluble portion was confirmed by measuring ^{13}C NMR spectra at 100 °C in 1,1,2,2-tetrachloroethane-d_2. For each given polymerization run, two or three serial experiments were carried out to confirm the reproducibility of the formation of the polymer, and the average values of these serial experimental results are given.

Results and Discussion

Preparation of Ligands. The preparation of **6a** from 2 M ammonia solution in methanol and (*S*)-propylene oxide was previously reported by Nugent.[7] Nugent's synthetic route was also analogously applied to the syntheses of **7a**−**11a**. Slightly more than the appropriate equivalent of enantiopure propylene oxide and 1 equiv of amine in methanol solution were mixed in a 10 mL screw-cap vial and allowed to stand overnight at room temperature. The mixture was then heated for several days at 50 °C to ensure a complete reaction. NMR studies in benzene-d_6 indicate that the reaction is essentially complete after 3 days. The corresponding enantiopure homochiral ligands could be isolated in pure form by removal of the solvent at reduced pressure. **6a** and **9a** were obtained in the solid form, but the ligands **7a**, **8a**, **10a**, and **11a** were obtained only as sticky oils.

Synthesis of Metal Complexes 1−12. (η^5-C_5Me_4R)$TiCl_3$ (R = Me, H, Et, Pr^i, Ph, Tol) were obtained in more than 95% yield as reddish solids from the reactions of $TiCl_4$ with C_5Me_4R(TMS) in toluene.[12] They were purified by recrystallization from toluene/pentane. Like other titanium complexes containing a single η^5 ligand, all (η^5-C_5Me_4R)$TiCl_3$ compounds are slightly moisture-sensitive. They are all readily soluble in toluene and dichloromethane. The reaction of a solution of (η^5-C_5Me_4R)$TiCl_3$ in CH_2Cl_2 with trialkanolamine ligand in the presence of triethylamine afforded the yellow crystalline solids **1**−**12** in yields of 71−84% (see Schemes 1 and 2). The attempted use of trilithiated species instead of neutral trialkanolamine in toluene was not successful, and a mixture of several unidentified compounds was obtained, suggesting that mild reaction conditions of HCl elimination are essential for the synthesis of **1**−**12**.

The yellow crystalline solids **1**−**12** are freely soluble in toluene, methylene chloride, and ethereal solvent and slightly soluble in hydrocarbon solvents such as hexane. Further characteristics worthy of mention for the compounds **1**−**12** are their air and thermal stability and the ease of their handling and purification.[14] In addition, all compounds have a volatile nature and the EI mass spectra of the compounds exhibit molecular peaks for the corresponding complexes.

NMR Studies. In the case of **2**−**5**, methylene signals of the triethanolatoamine ligand in the ^1H and $^{13}C\{^1H\}$ NMR spectra are shifted downfield compared to the signals for free triethanolamine, presumably due to the high Lewis acidity of the titanium metal. The extent of downfield shift in ^1H NMR spectra is greater for OCH_2 resonances (0.8 ppm) than for CH_2N resonances (0.4 ppm). Two virtual triplets are seen, indicating the presence of average C_{3v} symmetry in solution at ambient temperature and thus rapid conformational change within the structural unit. This pattern is a general feature of monomeric atrane and azatrane complexes.[6,15] It is interesting to note that the coupling constants (5.6 Hz) of these triplets for **1**−**5** are independent of the kinds of Cp rings.

For **6a** and **9a**, the NCH_2 and OCH proton signals typically appear as two doublets of doublets and multiplets, respectively, while only three $^{13}C\{^1H\}$ NMR peaks are observed, clearly showing the enantiopurity of them. However, commercially available tri-2-propanolamine (**12a**) turns out to be a mixture of about 40% (*R*,*R*,*R*)/(*S*,*S*,*S*) enantiomeric pair and about 60% (*R*,*R*,*S*)/(*S*,*S*,*R*) enantiomeric pair, as judged by nine $^{13}C\{^1H\}$ NMR resonances at 65.7, 66.5, 65.9, 65.5, 63.7, 63.1, 20.5, 20.4, and 20.2 ppm. The ligands **7a**, **8a**, **10a**, and **11a** display particularly informative $^{13}C\{^1H\}$ NMR spectra consistent with the homochiral ligand: one kind of methine *C*H peak, one kind of methyl *C*H_3 peak, and three kinds of methylene *C*H_2 peaks are observed. Their ^1H NMR spectra are much less informative, due to the presence of large numbers of different C*H*$_2$ and C*H* protons with a complicated coupling pattern. However, the stoichiometry of the reaction was ascertained from the integral ratio of the ^1H NMR spectra.

The NMR spectra of an enantiomeric pair of **6** and **9** are similar in the aspect of peak position and intensity and are consistent with the trigonal-bipyramidal structure of C_3 symmetry in solution. The three arms of the trialkanolamine ligand are magnetically equivalent in ^1H and $^{13}C\{^1H\}$ NMR spectra. In the ^1H NMR spectra, the NCH_2 methylene protons are diastereotopic, giving an AB spin system (2.70 and 2.54 ppm). Unlike **6** and **9**, the NMR spectra of the compounds **7**, **8**, **10**, and **11** show a trigonal-bipyramidal structural nature with no symmetric elements such as mirror plane and rotational axis. The three arms of the trialkanolamine ligand are magnetically nonequivalent in ^1H and $^{13}C\{^1H\}$ NMR spectra. The NMR spectra of enantiomeric pairs **7** and **10** and **8** and **11** are also similar with respect to peak position and intensity. In comparison to the free trialkanolamine precursors, all signals are shifted downfield, which is a consequence of the complexation with Lewis acidic titanium metal. The greater extent of downfield

(14) In general, the syntheses and purification of the compounds Cp*Ti$(OR)_3$ are difficult due to their air instability and high boiling points: Kucht, A.; Kucht, H.; Barry, S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1993**, *12*, 3075.

(15) (a) Duan, Z.; Naiini, A. A.; Lee, J.-H.; Verkade, J. G. *Inorg. Chem.* **1995**, *34*, 5477. (b) Pinkas, J.; Wang, T.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1994**, *33*, 4202. (c) Schubart, M.; O'Dwyer, L.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Inorg. Chem.* **1994**, *33*, 3893. (d) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452. (e) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.

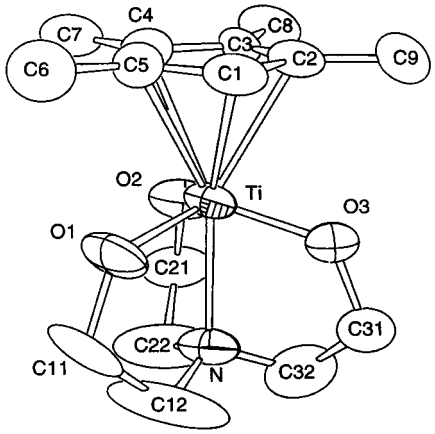

Figure 1. ORTEP drawing of the compound **2**, showing 50% probability thermal ellipsoids and atom labeling.

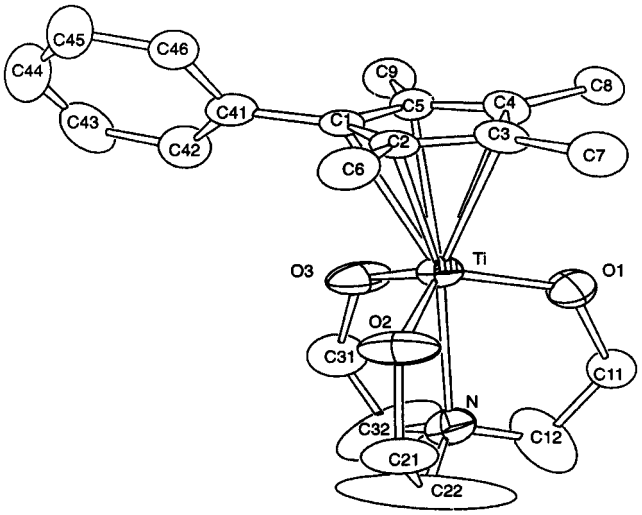

Figure 2. ORTEP drawing of the compound **4**, showing 50% probability thermal ellipsoids and atom labeling.

shifts of OCH or OCH_2 NMR resonances as compared to those of NCH_2 resonances suggests a strong bond between the O atom and Ti atom and a weak interaction between the N atom and the Ti atom upon complexation. The solution structures, therefore, are consistent with the solid-state structures described below.

Crystal Structures of 2, 4−6, and 8. ORTEP[16] representations of **2, 4−6**, and **8** are shown in Figures 1−5, and selected bond distances and angles are summarized in Table 2. For the systems **5** and **6**, only one of two molecules that show similar structural features in the asymmetric unit is presented. In contrast to the often observed oxygen-bridged dimeric structural feature of titanatranes,[6] the crystal structures of these five compounds show monomeric character, which is consistent with their NMR spectra, presumably because of the bulky nature of the Cp′ ancillary ligand. The Ti atom adopts essentially an η^5 bonding posture with the Cp′ ring and a tetradentate bonding mode with the TEA or TAA ligand via a transannular interaction from the bridgehead N atom to Ti. The overall coordination geometry of the complexes is slightly distorted trigonal bipyramidal. The amino nitrogen and Cp′ ligand occupy the axial positions of a trigonal-bipyramidal coordination array. The Ti atom is displaced from the plane formed by the three equatorial oxygen atoms in the direction of the Cp′ ring by approximately 0.47 Å. The centroid of the Cp′ ring, Ti atom, and N atom lie on the pseudo 3-fold axis and approach linearity with deviations of 0.34−1.46°. The three five-membered rings adopt an envelope conformation, similar to all the previously investigated monomeric atranes and azatranes.[6,15] All Cp′ rings exhibit highly regular η^5 coordination. The distances between the Cp′ centroid and

(16) Johnson, C. K. ORTEP; Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

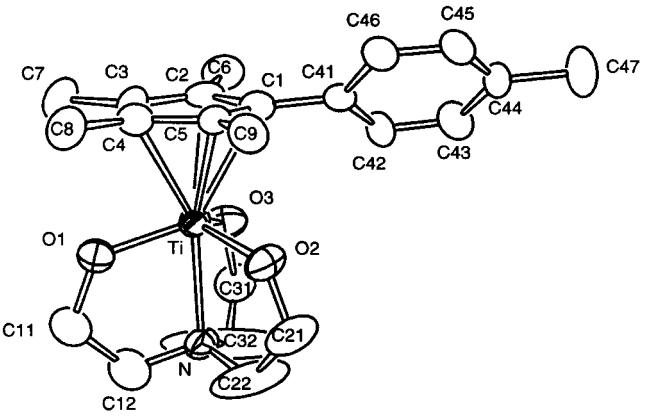

Figure 3. ORTEP drawing of the compound **5**, showing 50% probability thermal ellipsoids and atom labeling.

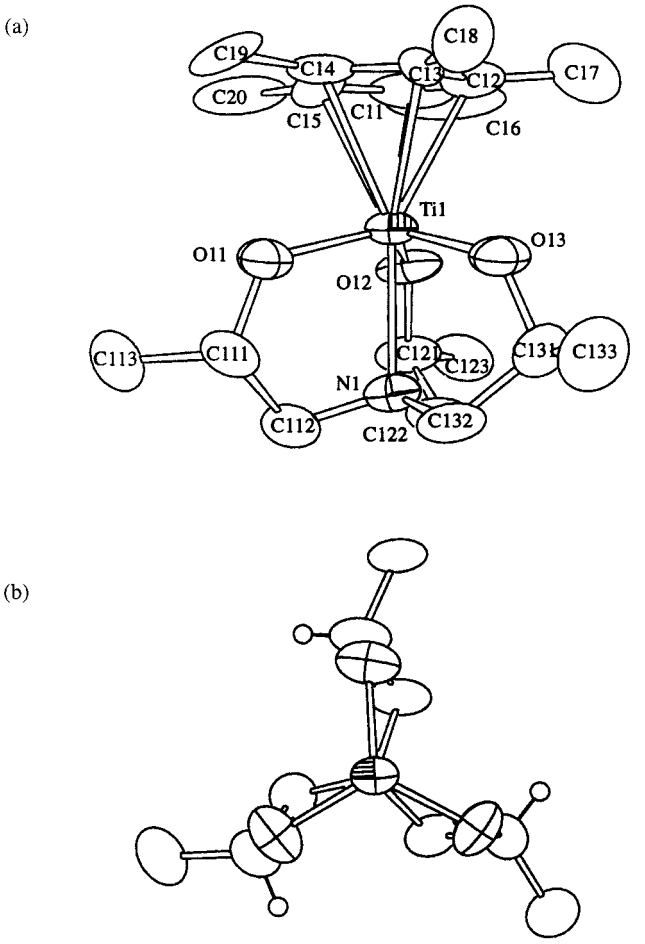

Figure 4. (a) ORTEP drawing of the compound **6**, showing 50% probability thermal ellipsoids and atom labeling. (b) Top view of compound **6** through its 3-fold axis (the Cp* ligand is omitted for clarity).

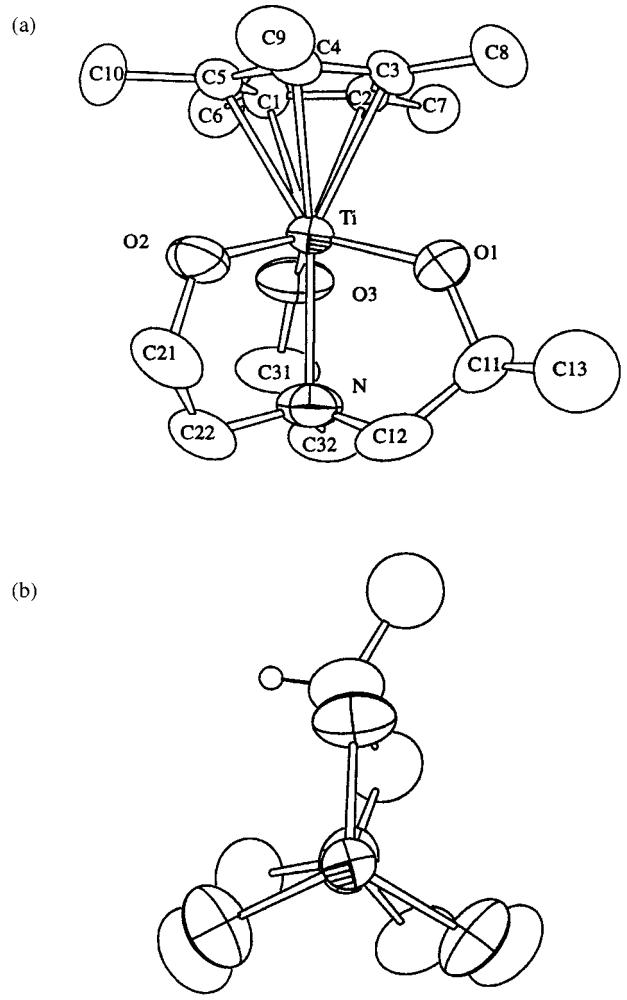

Figure 5. (a) ORTEP drawing of the compound **8**, showing 50% probability thermal ellipsoids and atom labeling. (b) Top view of the compound **8** through its 3-fold axis (the Cp* ligand is omitted for clarity).

Ti for **2, 4**−**6**, and **8** are in the range 2.119−2.139 Å, which are longer than that (2.119(10) Å) found in the compound **1**. The Ti to Cp′ carbon distances, listed in Table 2, fall in the range observed for other known Ti−Cp complexes.[18] The average Ti−O distances of 1.870, 1.868, 1.880, 1.867, and 1.880 Å for **2, 4**−**6**, and **8**, respectively, are similar to those observed for other structurally characterized titanatranes[6] and titanium alkoxides.[17] The transannular Ti−N bond distances for **2** (2.307(7) Å), **4** (2.331(8) Å), **5** (2.322 Å), **6** (2.328 Å), and **8** (2.314(5) Å) fall at the long end of the range (2.264(3)−2.342(9) Å) found in the eight other[3,6,7,9] structurally characterized titanium trialkanolamine derivatives. This observation confirms the existence of the transannular interaction. Figures 4 and 5 illustrate that all the methyl substituents at O*C* carbons for the compounds **6** and **8** adopt the Cahn−Ingold−Prelog *S* configuration. The absolute configuration is confirmed by the Flack parameters[19] of −0.03 for **6** and −0.06 for **8**. Thus, the stereochemistry of the ligands is retained after the complexation with titanium metal.

Syndiospecific Polymerization of Styrene. A wide variety of sPS catalytic systems based on titanium or zirconium organometallic complexes have been reported in the literature.[20] The examples include $Cp'TiX_3$ ($Cp' = C_5H_5$, C_5Me_5 and X = halide, alkyl, alkoxy),[21] (indenyl)$TiCl_3$,[22] and substituted indenyl derivatives,[23] which are among the most active catalysts. Recently, we reported that the **1**/MMAO catalyst system is highly active and syndiospecific for the polymerization of styrene as compared to Cp^*TiCl_3/MMAO.[9] To investigate the effect of the substituents in the cyclopentadienyl ligand and the chiral substituents in the tetradentate ligand of the precatalyst **1** on the polymerization behavior, the compounds **2**−**12** are examined as catalysts for syndiospecific polymerization of styrene in the presence of MMAO. The polymerization results are summarized in Table 3 along with those for the **1**/MMAO catalyst system in terms of the activity of the catalyst, conversion, syndiotacticity, and T_m value. The sPS samples were analyzed by GPC and DSC. Furthermore, to assess the significance of the quoted activity values, we also carried out control polymerization experiments using the trichloride analogue of **1**−**5**/MMAO systems under the same polymerization conditions. Table 3 shows that precatalysts containing the TEA ligand are much better catalyst systems for sPS than corresponding Cl-based precatalysts in terms of activity, T_m, SI, and molecular weight.

The catalytic efficiency in terms of activity decreases in the order of **1**/MMAO > **2**/MMAO ≫ **4**/MMAO > **3**/MMAO > **5**/MMAO, indicating that the electronic and steric effects of the substituent in the new titanatranes (C_5Me_4R)Ti(TEA) are best optimized when R is methyl group. In addition, the catalytic activity decreases in the order of **1**/MMAO > **9**/MMAO > **7**/MMAO ≈ **10**/MMAO ≈ **6**/MMAO > **8**/MMAO ≈ **11**/MMAO > **12**/MMAO, indicating that the steric effect of the substituent in the new titanatranes (C_5Me_5)Ti(N(CH_2CR^1HO)-(CH_2CR^2HO)(CH_2CR^3HO)) is the dominant factor in determining the activity for sPS.

The molecular weights of all the resulting polymers obtained by **1**−**12**/MMAO are in the range M_w = 31 400−292 000 with M_w/M_n = 1.77−4.07. In particular, the molecular weights of all the resulting polymers by **6**−**11**/MMAO are in the range M_w = 31 400−34 100 with M_w/M_n = 1.8−1.98. Polydispersity index (PDI) values of ca. 2 were seen for all the catalytic systems, except for **1**/MMAO, which gave a PDI of 4.07. This is presumably due to the formation of polymer precipitate prior to the termination of the polymerization, which was observed only for the **1**/MMAO system at 70 °C. It

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 2, 4−6, and 8

(η^5-C_5Me_4H)Ti(TEA) (**2**)					
Ti−O(1)	1.880(6)	Ti−O(2)	1.856(7)	Ti−O(3)	1.874(7)
Ti−N	2.307(7)	Ti−C(1)	2.411(9)	Ti−C(2)	2.460(9)
Ti−C(3)	2.461(8)	Ti−C(4)	2.445(10)	Ti−C(5)	2.453(11)
Ti−CENT	2.134(9)				
CENT−Ti−O(3)	104.89(3)	CENT−Ti−O(1)	105.09(3)	CENT−Ti−O(2)	103.53(3)
O(2)−Ti−N	75.2(3)	CENT−Ti−N	178.67(3)	O(1)−Ti−N	75.5(3)
		O(3)−Ti−N	75.8(3)		
(η^5-C_5Me_4Ph)Ti(TEA) (**4**)					
Ti−O(1)	1.869(6)	Ti−O(2)	1.869(7)	Ti−O(3)	1.867(8)
Ti−N	2.331(8)	Ti−C(1)	2.483(9)	Ti−C(2)	2.468(9)
Ti−C(3)	2.420(9)	Ti−C(4)	2.456(9)	Ti−C(5)	2.440(9)
Ti−CENT	2.139(9)				
CENT−Ti−O(3)	105.07(3)	CENT−Ti−O(1)	104.46(3)	CENT−Ti−O(2)	104.35(3)
O(2)−Ti−N	75.7(3)	CENT−Ti−N	179.74(3)	O(1)−Ti−N	75.3(3)
		O(3)−Ti−N	75.1(3)		
(η^5-C_5Me_4Tol)Ti(TEA) (**5**)					
Ti−O(1)	1.876(7)	Ti−O(2)	1.879(6)	Ti−O(3)	1.882(7)
Ti−N	2.312(8)	Ti−C(1)	2.432(9)	Ti−C(2)	2.434(10)
Ti−C(3)	2.404(10)	Ti−C(4)	2.464(9)	Ti−C(5)	2.466(8)
Ti−CENT	2.124(9)				
CENT−Ti−O(3)	105.25(3)	CENT−Ti−O(1)	104.13(3)	CENT−Ti−O(2)	103.48(3)
O(2)−Ti−N	76.2(3)	CENT−Ti−N	179.56(3)	O(1)−Ti−N	75.7(3)
		O(3)−Ti−N	75.2(3)		
Ti′−O(1′)	1.873(6)	Ti′−O(2′)	1.880(7)	Ti′−O(3′)	1.888(7)
Ti′−N′	2.331(8)	Ti′−C(1′)	2.428(9)	Ti′−C(2′)	2.439(10)
Ti′−C(3′)	2.422(10)	Ti′−C(4′)	2.460(9)	Ti′−C(5′)	2.473(9)
Ti′−CENT	2.125(9)				
CENT−Ti′−O(3′)	105.18(3)	CENT−Ti′−O(1′)	104.03(3)	CENT−Ti′−O(2′)	104.14(3)
O(2′)−Ti′−N′	75.3(3)	CENT−Ti′−N′	179.66(3)	O(1′)−Ti′−N′	76.0(3)
		O(3′)−Ti′−N′	75.1(3)		
(Pentamethylcyclopentadienyl)titanium (*S*,*S*,*S*)-Tri-2-propanolaminate (**6**)					
Ti1−O(11)	1.878(9)	Ti1−O(12)	1.869(7)	Ti1−O(13)	1.873(9)
Ti1−N1	2.336(6)	Ti1−C(11)	2.447(9)	Ti1−C(12)	2.407(14)
Ti1−C(13)	2.449(11)	Ti1−C(14)	2.462(14)	Ti1−C(15)	2.448(14)
Ti1−CENT	2.129(13)				
CENT−Ti1−O(13)	104.99	CENT−Ti1−O(11)	103.95	CENT−Ti1−O(12)	104.59
O(12)−Ti1−N1	76.2(2)	CENT−Ti1−N1	179.12	O(11)−Ti1−N1	74.9(4)
		O(13)−Ti1−N1	75.5(4)		
Ti2−O(21)	1.865(10)	Ti2−O(22)	1.860(6)	Ti2−O(23)	1.857(11)
Ti2−N2	2.319(7)	Ti2−C(21)	2.445(15)	Ti2−C(22)	2.423(9)
Ti2−C(23)	2.42(2)	Ti2−C(24)	2.396(14)	Ti2−C(25)	2.464(12)
Ti2−CENT	2.120(14)				
CENT−Ti2−O(23)	105.72	CENT−Ti2−O(21)	104.00	CENT−Ti2−O(22)	105.72
O(22)−Ti2−N2	75.6(3)	CENT−Ti2−N2	179.43	O(21)−Ti2−N2	76.0(4)
		O(23)−Ti2−N2	73.8(5)		
(Pentamethylcyclopentadienyl)titanium (*S*)-2-Propanoldiethanolaminate (**8**)					
Ti−O(1)	1.878(5)	Ti−O(2)	1.873(5)	Ti−O(3)	1.888(5)
Ti−N	2.314(5)	Ti−C(1)	2.461(8)	Ti−C(2)	2.416(6)
Ti−C(3)	2.436(5)	Ti−C(4)	2.427(6)	Ti−C(5)	2.445(8)
Ti−CENT	2.119(7)				
CENT−Ti−O(3)	104.10	CENT−Ti−O(1)	106.04	CENT−Ti−O(2)	103.32
O(2)−Ti−N	75.8(2)	CENT−Ti−N	178.54	O(1)−Ti−N	75.4(2)
		O(3)−Ti−N	75.3(2)		

is interesting to note that the **12**/MMAO system can produce sPS with high molecular weight compared with **6**/MMAO and **9**/MMAO systems. The syndiotacticity of all the resulting polymers exceeds 96.8%, as determined by ^{13}C NMR spectra of the 2-butanone-insoluble portion at 110 °C in 1,1,2,2-tetrachloroethane-d_2. The signals for methylene, methine, and ipso phenyl carbons of sPS appear at 40.51, 43.68, and 145.36 ppm, respectively. The chemical shifts of the methine and ipso phenyl carbons are sensitive to the microstructure of sPS and are used to interpret the stereospecificity of sPS, and thus, the appearance of only one methine and one ipso phenyl carbon signal at those particular positions is a clear indication of the syndiotacticity.[24] In addition, all catalytic systems, except **2**/MMAO, afford polystyrenes

(24) (a) Mani, R.; Burns, C. M. *Macromolecules* **1991**, *24*, 5476. (b) Dias, M. L.; Giarrusso, A.; Porri, L. *Macromolecules* **1993**, *26*, 6664.

Table 3. Styrene Polymerization Catalyzed by 1−12/MMAO[a]

catalyst	amt of PS (g)	$10^{-7}A$[b]	conversn (%)[c]	T_m[d]	SI[e] (%)	M_w[f]	M_n[f]	M_w/M_n[f]
(η^5-C_5Me_5)$TiCl_3$	3.00	2.12	66	272.7	95.4	182 300	87 000	2.09
1	4.01	2.83	88	273.4	98.2	292 000	71 700	4.07
(η^5-C_5Me_4H)$TiCl_3$	1.50	1.06	33	260.4	86.7	15 300	8 300	1.85
2	3.25	2.29	71	261.9	96.8	43 200	22 500	1.92
(η^5-C_5Me_4Et)$TiCl_3$	0.72	0.51	16	265.9	40.3	25 300	9 600	2.62
3	1.46	1.03	32	274.1	98.3	65 700	34 600	1.90
(η^5-C_5Me_4Ph)$TiCl_3$	1.32	0.93	29	269.4	69.7	22 000	12 400	1.77
4	1.98	1.40	44	273.7	98.7	123 500	68 800	1.80
(η^5-C_5Me_4Tol)$TiCl_3$	0.59	0.42	13	260.1	32.2	30 300	11 400	2.65
5	1.17	0.83	26	271.8	97.5	133 600	74 600	1.79
6	2.23	1.57	50	273.9	98.7	31 400	17 100	1.84
7	2.31	1.63	51	273.6	98.4	33 700	18 500	1.82
8	1.92	1.35	42	273.3	98.5	34 000	18 900	1.80
9	2.61	1.84	57	274.8	98.8	31 600	17 200	1.84
10	2.29	1.61	50	275.4	99.0	33 400	17 900	1.86
11	1.83	1.29	40	273.6	98.8	34 100	17 200	1.98
12	0.92	0.65	20	273.5	97.4	135 800	48 400	2.81

[a] Polymerization conditions: [styrene] = 0.436 M (5 mL); **[**Ti**]** = 0.195 mM; Al/Ti = 1000; time 10 min; T_p = 70 °C. [b] A = activity = (g of sPS)/((mol of Ti)(mol of styrene) h). [c] Conversion = ((g of polymer)/(g of monomer)) × 100. [d] Determined by DSC. [e] SI = 2-butanone-insoluble portion whose tacticity was established by ^{13}C NMR in 1,1,2,2-tetrachloroethane-d_2. [f] Determined by GPC.

with T_m values of greater than 271 °C, even at a high polymerization temperature of 70 °C. Overall, the **1**−**12**/MMAO catalytic systems produce highly syndiotactic polystyrenes with good activity.

In conclusion, we have synthesized various kinds of new titanatranes containing Cp ancillary ligands and trialkanolamine auxiliary ligands. They are good and efficient catalysts for the syndiospecific polymerization of styrene in terms of activity, T_m value, and syndiotacticity.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for **2**, **4**−**6**, and **8** and figures giving ^1H and $^{13}C\{^1H\}$ NMR spectra for **2**−**8** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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