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Synthesis and polymerization behavior of novel C_1 and C_s titanium *ansa*-cyclopentadienyl-amido catalysts for ethylene and propylene polymerization

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Four titanium *ansa*-cyclopentadienyl-amido complexes of the general formula $[C_5H_3RMe_2SiN(2,6\text{-}Me_2C_6H_3)]TiX_2$($R = H,Me,Bz,{}^tBu$;$X = NMe_2$ or Cl) have been synthesized. The complexes polymerize both ethylene and propylene in the presence of methylaluminoxane or $Ph_3CB(C_6F_5)_4$–triisobutylaluminum and were most active at lower temperatures. In general, the smaller the substituent on the cyclopentadienyl group, the more active the catalyst. The catalysts were found to be poorly stereoselective for the polymerization of polypropylene, with the tertiary-butyl substituted catalyst giving a polymer with the greatest [*mmmm*] (14.2%). The structure of $[C_5H_4Me_2SiN(2,6\text{-}Me_2C_6H_3)]Ti(NMe_2)_2$ was determined by X-ray diffraction. The complex crystallizes in the monoclinic system space group $P2_1/n$, with $a = 16.437(2)$, $b = 8.652(3)$, $c = 16.494(4)$, $\beta = 117.54(2)$ and $Z = 4$. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: polymerization; constrained geometry; ethylene; propylene

INTRODUCTION

The demonstration that stereorigid metallocenes polymerize propylene stereospecifically is the cornerstone of metallocene catalysis research. In particular: C_2 symmetric complexes lead to isotactic polymerization, e.g. see Refs 1 and 2; C_s symmetric complexes promote syndiotactic polymerization, e.g. see Ref. 3. Deviation from these symmetry characteristics can profoundly alter the polymerization stereospecificity. Several examples are cited below. The unsubstituted ethylene-1-(η^5-9-fluorenyl)-2-(η^5-1-indenyl)-zirconium dichloride[4] was synthesized and found to be moderately isospecific in propylene polymerization. Substitution in the indenyl moiety markedly increases the isotactic specificity: the 2,4,7-trimethyl indenyl derivative[5] afforded isotactic polypropylene having an $M_w = 27000$ and [*mmmm*] = 91%. The polymers formed contain isotactic chains with racemic triad junctions. The effects of polymerization temperature and monomer concentration support a mechanism of migratory insertion followed by return to initial configuration.

The C_s symmetric isopropylidene-2-(η^5-9-fluorenyl)-2-(η^5-1-cyclopentadienyl)zirconium dichloride is an important syndiotactic-specific catalyst.[6] The derivative containing a 3-tertiary butyl substituent on the cyclopentadienyl ring produces polypropylene with very long sequences of isotactic enchainment interspersed with racemic triads.[7–9] Even more striking is the case of bis(1-methylfluorenyl)zirconium dichloride,[10] which produces isotactic polypropylene (index = 90%) even though the complex is unbridged.

The *ansa*-monocyclopentadienyl-amido (CpA) group IV catalysts that have been developed by Dow and Exxon are well reported in the patent literature.[11–15] The ligands used in these complexes are based on the organoscandium complexes reported by Bercaw and co-workers.[16,17] A review by McKnight and Waymouth shows how intense research into CpA catalysts has been.[18]

The polymerization of propylene by CpA-type catalysts leads mainly to slightly syndiotactic polypropylene.[19–22] There are conflicting reports in the literature on CpA catalysts and the influence of the counteranion on stereospecificity. Canich reported that methylaluminoxane (MAO)-activated $[Me_2Si(Flu)(N^tBu)]ZrCl_2$ yielded a poly-

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mer with high isotacticities ([*mmmm*] = 93%).[11] McKnight *et al.* subsequently reported that they were unable to obtain stereoregular polymers under similar conditions.[23] Turner *et al.* also reported that conversion of this same zirconium dichloride compound to the dimethyl complex and activation with $[PhNMe_2H][B(C_6F_5)_4]$ gave syndiotactic polypropylene.[24] Clearly, the role of the counteranion on stereospecificity is complicated, and further research is necessary to draw definite conclusions.

The central objective of this work is to attempt alteration of the stereochemistry of propylene polymerization by changing the molecular structure of the industrially important constrained geometry catalysts that have received intense attention. We chose to study the effects (in terms of catalyst activity and stereoregularity of the polymers obtained) of monosubstitution on the cyclopentadienyl group, concomitant with the use of a 2,6-dimethylphenyl substituent on the η^1-amido linkage of the catalyst precursor. Our aim was to synthesize CpA-type catalyst precursors that had the same symmetry, and a similar steric environment to the isopropylidene-bridged fluorenyl/monosubstituted cyclopentadienyl complexes studied by Atwood and co-workers.[25–27]

EXPERIMENTAL

All experiments were performed under a dry argon atmosphere using standard Schlenk techniques. The argon was purified by deoxygenating with BTS catalyst and drying with molecular sieves and P_2O_5. Tetrahydrofuran (THF) was predried over sodium wire, distilled from sodium under argon, and finally distilled from Na–K alloy under argon. Diethyl ether was predried over sodium wire and distilled from Na–K alloy under argon. Toluene, hexane, and pentane were distilled from Na–K alloy under argon. Methylene chloride was distilled from calcium hydride. Deuterated solvents were stored over activated molecular sieves under an argon atmosphere.

MAO was purchased from Akzo. Butyllithium (1.6 M in hexanes), methyllithium (1.4 M in diethyl ether), and dimethyldichlorosilane were purchased from Aldrich and used without further purification. 2,6-Dimethylaniline (**1**) was purchased from Aldrich and distilled from calcium hydride, *in vacuo*, prior to use. Dicyclopentadiene and methyl cyclopentadiene dimer were also purchased from Aldrich and freshly cracked prior to use. Lead(II) chloride was purchased from Aldrich, dried at 120 °C *in vacuo* for 24 h, and stored under argon. 6,6-Dimethylfulvene,[28] tetrakis(dimethylamido)titanium,[29] benzylcyclopentadiene,[30] and titanium trichloride·tris THF[31] were prepared by literature methods. Celite was purchased from Fischer Scientific and used without pretreatment.

^1H NMR spectra were recorded on a Varian XL-200 spectrometer with tetramethylsilane (TMS) as an internal standard at ambient temperatures unless otherwise stated. All ^{13}C NMR spectra for the polypropylene samples were obtained on an AMX-500 spectrometer in 95% 1,2,4-trichlorobenzene–5% benzene-d_6 at 125 °C. Mass spectroscopic analyses were performed on a JEOL JMS-700 mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

Preparation of C_5H_5Li

A 1.6 M solution of butyllithium in hexane (96.3 ml, 151 mmol) was slowly added to a solution of cyclopentadiene (10.0 g, 151 mmol) in hexane (250 ml) at 0 °C. The white suspension was allowed to reach room temperature and was stirred for a further 4 h. The mixture was filtered via a cannula, washed with pentane (3 × 50 ml) and dried *in vacuo*, yielding a highly air-sensitive white solid (10.53 g, 97%).

Preparation of $(Me)C_5H_4Li$

The reaction was carried out as for C_5H_5Li using methylcyclopentadiene (5.03 g, 62.8 mmol) and 1.6 M butyllithium (40.0 ml, 62.8 mmol), yielding a highly air-sensitive white solid (4.60 g, 85%).

Preparation of $(Bz)C_5H_4Li$ (B_z = benzyl)

The reaction was carried out as for C_5H_5Li using benzylcyclopentadiene (5.20 g, 33.3 mmol) and 1.6 M butyllithium in hexane (21.20 ml, 33.3 mmol), yielding a highly air-sensitive white solid (5.06 g, 94%).

Preparation of $2,6\text{-}Me_2C_6H_3NHSiMe_2Cl$ (2)

2,6-Dimethylaniline (**1**) (121.18 g, 1 mol) was added over a period of 10 min to dimethyldichlorosilane (64.53 g, 0.5 mol) in hexane (500 ml) at 0 °C followed by placing the white suspension under reflux overnight. After cooling to room temperature, the mixture was filtered to remove **3** and the hexane removed. Distillation of the residue at 52–63 °C (0.03 mmHg) afforded 2,6-dimethylaniline (43.2 g). Distillation at 67–70 °C (0.03 mmHg) afforded **2** as an air-sensitive, colorless liquid (32.6 g, 30.4%). ^1H NMR ($CDCl_3$): δ 0.48 (s, 6H, Si*Me*$_2$), 2.30 (s, 6H, Ar$-$*CH*$_3$), 2.90 (bs, 1H, N*H*), 6.87–7.04 (m, 3H, Ar$-$*H*). Anal. Found: C, 55.92; H, 7.76; N, 6.53. Calc. for $C_{10}H_{16}ClNSi$: C, 56.18; H, 7.54; N, 6.55%.

Preparation of $C_5H_5Me_2SiNH\text{-}2,6\text{-}Me_2C_6H_3$ (4a)

Solid C_5H_5Li (1.00 g, 13.9 mmol) was quickly added as a solid to **2** (2.98 g, 13.9 mmol) in THF (50 ml) at 0 °C. After warming to room temperature, the mixture was allowed to stir overnight. The solvent was removed *in vacuo*, the product extracted in pentane (3 × 20 ml), and the solvent removed to give a yellow oil. Distillation of the residue at 97–107 °C (0.01 mmHg) afforded **4a** as an air-sensitive, colorless mixture of isomers (1.48 g, 44%). ^1H NMR ($CDCl_3$): δ 0.08–0.32 (m, 6H, Si*Me*$_2$), 2.15–2.33 (m, 6H, Ar$-$*CH*$_3$), 2.99–3.06 (m, 2H, Cp-*H*), 3.55 (bs, 1H, N*H*), 6.66–7.00 (m, 6H, Cp$-$*H*/Ar$-$*H*). HRMS (EI) *m/z* calc. for $C_{22}H_{27}NSi$: 243.1443. Found: 243.1446.

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Preparation of $C_5H_4(Me)Me_2SiNH$-2,6-$Me_2C_6H_3$ (4b)

A solution of $(Me)C_5H_4Li$ (1.05 g, 12.2 mmol) in THF (50 ml) was added to a solution of **2** (2.55 g, 12.2 mmol) in THF (70 ml) at 0 °C. After warming to room temperature, the mixture was allowed to stir overnight. The solvent was removed *in vacuo* and the product extracted in pentane (3 × 50 ml). The pentane was removed, followed by distillation of the residue at 102–107 °C (0.01 mmHg) to yield **4b** as an air-sensitive, pale yellow mixture of isomers (1.89 g, 60%). ^1H NMR ($CDCl_3$): δ 0.11–0.38 (m, 6H, Si*Me*$_2$), 2.08 (bs, 3H, Cp$-$*CH*$_3$), 2.18–2.30 (m, 6H, Ar$-$*CH*$_3$), 2.85–2.99 (m, 2H, Cp$-$*H*), 3.41 (bs, 1H, N*H*), 6.08–7.02 (m, 7H, Cp$-$*H*/Ar$-$*H*). HRMS (EI) *m/z* calc. for $C_{22}H_{27}NSi$: 257.1600. Found: 257.1626.

Preparation of $C_5H_4(Bz)Me_2SiNH$-2,6-$Me_2C_6H_3$ (4c)

A solution of $(Bz)C_5H_4Li$ (2.27 g, 14.0 mmol) in THF (50 ml) was added to a solution of **2** (2.93 g, 14.0 mmol) in THF (70 ml) at 0 °C. After warming to room temperature, the mixture was allowed to stir overnight. The solvent was removed *in vacuo* and the product extracted in pentane (3 × 50 ml). The pentane was removed, followed by distillation of the residue at 168–171 °C (0.01 mmHg) to yield **4c** as an air-sensitive, pale yellow mixture of isomers (2.78 g, 60%). ^1H NMR ($CDCl_3$): δ 0.08–0.28 (m, 6H, Si*Me*$_2$), 2.19–2.28 (m, 6H, Ar$-$*CH*$_3$), 2.82–2.99 (m, 2H, Cp$-$*H*), 3.61–3.78 (m, 2H, $-$*CH*$_2-$), 6.09–7.32 (m, 7H, Cp$-$*H*/Ar$-$*H*). HRMS (EI) *m/z* calc. for $C_{22}H_{27}NSi$: 333.1913. Found: 333.1873.

Preparation of $C_5H_4(^tBu)Me_2SiNH$-2,6-$Me_2C_6H_3$ (4d)

A 1.4 M solution of methyllithium in diethyl ether (16.43 ml, 23.0 mmol) was added to a solution of 6,6-dimethylfulvene (2.44 g, 23.0 mmol) in THF (75 ml) at 0 °C. The yellow mixture was warmed to room temperature and stirred for 2 h. After cooling the solution to 0 °C, **2** (4.93 g, 23.0 mmol) was added and the mixture was placed under reflux overnight. After cooling to room temperature, the solvents were removed *in vacuo* and the product extracted in pentane (3 × 30 ml). The pentane was removed and the residue distilled at 123–135 °C (0.01 mmHg) to yield **4d** as an air-sensitive, pale yellow mixture of isomers (4.16 g, 60%). ^1H NMR ($CDCl_3$): δ 0.05–0.34 (m, 6H, Si*Me*$_2$), 1.19–1.23 (m, 9H, ^{t}*Bu*), 2.24–2.31 (m, 6H, Ar$-$*CH*$_3$), 2.96–3.03 (m, 2H, Cp$-$*H*), 3.45 (bs, 1H, N*H*), 6.09–7.05 (m, 7H, Cp$-$*H*/Ar$-$*H*). HRMS (EI) *m/z* calc. for $C_{19}H_{29}NSi$: 299.2069. Found: 299.2046.

Preparation of $[C_5H_4Me_2SiN(2,6\text{-}Me_2C_6H_3)]$-$Ti(NMe_2)_2$ (5)

Neat **4a** (1.19 g, 4.89 mmol) was added to a solution of $Ti(NMe_2)_4$ (1.16 ml, 4.89 mmol) in hexane (25 ml) at 0 °C. The yellow solution was warmed to room temperature, followed by heating the mixture to reflux overnight. After cooling to room temperature, the red solution was filtered away from any insoluble impurities and cooled to −20 °C, resulting in the formation of air-sensitive orange crystals of **5** (1.46 g, 79%). ^1H NMR (C_6D_6): δ 0.38 (s, 6H, Si*Me*$_2$), 2.15 (s, 6H, Ar$-$*CH*$_3$), 2.83 (s, 12H, N*Me*$_2$), 6.21–6.30 ('dt', 4H, Cp$-$*H*), 6.90–7.18 (m, 3H, Ar$-$*H*). Anal. Found: C, 60.59; H, 8.42; N, 10.90. Calc. for $C_{19}H_{31}N_3SiTi$: C, 60.46; H, 8.28; N, 11.13%. HRMS (EI) *m/z* calc. for $C_{19}H_{31}N_3SiTi$: 377.1769. Found: 377.1794.

Preparation of $[C_5H_4Me_2SiN(2,6\text{-}Me_2C_6H_3)]TiCl_2$ (6a)

Neat chlorotrimethylsilane (1.17 ml, 9.28 mmol) was added to a solution of **5** (1.00 g, 2.65 mmol) in hexane (35 ml) and the mixture allowed to stir overnight. The suspension was filtered, washed with hexane (3 × 25 ml) and the resulting solid crystallized from methylene chloride at −20 °C, yielding air-sensitive yellow crystals of **6a** (0.59 g, 62%). ^1H NMR ($CDCl_3$): δ 0.58 (s, 6H, Si*Me*$_2$), 2.03 (s, 6H, Ar$-$*CH*$_3$), 6.75–6.77 ('t', 2H, Cp$-$*H*), 6.95–7.10 (m, 3H, Ar$-$*H*), 7.19–7.21 ('t', 2H, Cp$-$*H*). Anal. Found: C, 50.02; H, 5.36; N, 3.86. Calc. for $C_{15}H_{19}Cl_2NSiTi$: C, 50.02; H, 5.32; N, 3.89%.

Preparation of $[C_5H_3(Me)Me_2SiN(2,6\text{-}Me_2C_6H_3)]$-$TiCl_2$ (6b)

A 1.6 M solution of butyllithium in hexane (9.36 ml, 14.7 mmol) was added to a solution of **4b** (1.89 g, 7.34 mmol) in hexane (50 ml) at 0 °C. After warming to room temperature, THF (50 ml) was added and the pale yellow solution was allowed to stir for 5 h. The dilithium salt solution was then added to a suspension of $TiCl_3 \cdot 3THF$ (2.72 g, 7.34 mmol) in THF (30 ml) at −78 °C. After allowing the mixture to reach room temperature, the mixture was placed under reflux for 15 min until all the $TiCl_3 \cdot 3THF$ had reacted. The mixture was again cooled to 0 °C, solid $PbCl_2$ (2.04 g, 7.34 mmol) was added, and the mixture was stirred at room temperature for 45 min. After removal of the solvent *in vacuo*, the product was washed with hexane (3 × 30 ml) and the product extracted in toluene (50 ml). Following filtration, the solution was concentrated to one-third its original volume and cooled to −20 °C, yielding **6b** as yellow microcrystals (1.13 g). A further crop of product was obtained by cooling the hexane washings to −20 °C and collecting the yellow crystals obtained (0.83 g, total yield 71%). ^1H NMR ($CDCl_3$): δ 0.56 (s, 3H, Si*Me*$_2$), 0.57 (s, 3H, Si*Me*$_2$), 2.02 (s, 3H, Ar$-$*CH*$_3$), 2.05 (s, 3H, Ar$-$*CH*$_3$), 2.50 (s, 3H, Cp$-$*Me*), 6.49–6.51 ('t', 1H, Cp$-$*H*), 6.61–6.65 ('t', 1H, Cp$-$*H*), 6.91–6.93 ('t', 1H, Cp$-$*H*), 6.97–7.10 (m, 3H, Ar$-$*H*). Anal. Found: C, 51.12; H, 5.59; N, 3.60. Calc. for $C_{16}H_{21}Cl_2NSiTi$: C, 51.35; H, 5.66; N, 3.74%.

Preparation of $[C_5H_3(Bz)Me_2SiN(2,6\text{-}Me_2C_6H_3)]$-$TiCl_2$ (6c)

A 1.6 M solution of butyllithium in hexane (8.47 ml, 13.3 mmol) was added to a solution of **4c** (2.21 g, 6.63 mmol)

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in THF (75 ml) at 0 °C. After warming to room temperature, the yellow solution was allowed to stir for 5 h. The dilithium salt solution was then added to a suspension of $TiCl_3 \cdot 3THF$ (2.46 g, 6.63 mmol) in THF (50 ml) at −78 °C. After the mixture had been allowed to reach room temperature, it was refluxed for 15 min until all the $TiCl_3 \cdot 3THF$ had reacted. The mixture was again cooled to 0 °C, solid $PbCl_2$ (1.84 g, 6.63 mmol) added, and the mixture was stirred at room temperature for 45 min. After removal of the solvent *in vacuo*, the product was washed with hexane (3 × 30 ml) and the product extracted in toluene (50 ml). Following filtration, the solution was concentrated to one-third its original volume, hexane added (15 ml), and the solution cooled to −20 °C, yielding **6c** as a yellow powder (1.63 g, 55%). ^1H NMR ($CDCl_3$): δ 0.55 (s, 3H, Si*Me*$_2$), 0.56 (s, 3H, Si*Me*$_2$), 2.02 (s, 3H, Ar−*CH*$_3$), 2.07 (s, 3H, Ar−*CH*$_3$), 4.18 (s, 1H, Bz−C*H*$_2$), 4.20 (s, 1H, Bz−C*H*$_2$), 6.55–6.57 ('t', 1H, Cp−*H*), 6.63–6.67 ('t', 1H, Cp−*H*), 6.87–6.89 ('t', 1H, Cp−*H*), 6.94–7.38 (m, 8H, Ar−*H*). HRMS (EI) *m/z* calc. for $C_{22}H_{25}NCl_2SiTi$: 449.0616. Found: 449.0617.

Preparation of $[C_5H_3(^tBu)Me_2SiN(2,6\text{-}Me_2C_6H_3)]TiCl_2$ (6d)

A 1.6 M solution of butyllithium in hexane (8.53 ml, 13.4 mmol) was added to a solution of **4d** (2.01 g, 6.71 mmol) in THF (30 ml) at 0 °C. After warming to room temperature, the yellow solution was stirred for 2.5 h. The dilithium salt solution was then added to a suspension of $TiCl_3 \cdot 3THF$ (2.49 g, 6.71 mmol) in THF (30 ml) at −78 °C. After the green mixture had warmed to room temperature, solid $PbCl_2$ (1.87 g, 6.71 mmol) was added and the mixture was stirred at room temperature for 45 min. After removal of the solvent *in vacuo*, the product was extracted in hexane (3 × 30 ml). Following filtration, the solution was concentrated to one-third its original volume and cooled to −20 °C, yielding **6d** as yellow microcrystals (1.89 g, 68%). ^1H NMR ($CDCl_3$): δ 0.54 (s, 3H, Si*Me*$_2$), 0.58 (s, 3H, Si*Me*$_2$), 1.40 (s, 9H, ^{t}Bu), 2.01 (s, 3H, Ar−*CH*$_3$), 2.06 (s, 3H, Ar−*CH*$_3$), 6.50–6.52 ('t', 1H, Cp−*H*), 6.71–6.74 ('t', 1H, Cp−*H*), 6.93–7.08 (m, 3H, Ar−*H*), 7.10–7.12 ('dd', 1H, Cp−*H*). Anal. Found: C, 54.94; H, 6.58; N, 3.26. Calc. for $C_{19}H_{27}Cl_2NSiTi$: C, 54.82; H, 6.54; N, 3.36%.

Crystal structure determination

X-ray diffraction data for a tan-colored prismatic crystal of **5** were collected on an Enraf–Nonius CAD4 diffractometer at room temperature, using monochromated Mo Kα radiation and the ω–2θ scan mode. Unit-cell dimensions were determined from a least squares fit of 25 carefully centered reflections in the 10–15° range in θ. Empirical absorption corrections, based on ψ scans were made to the data. Details of the unit-cell dimensions and other parameters are summarized in Table 4.

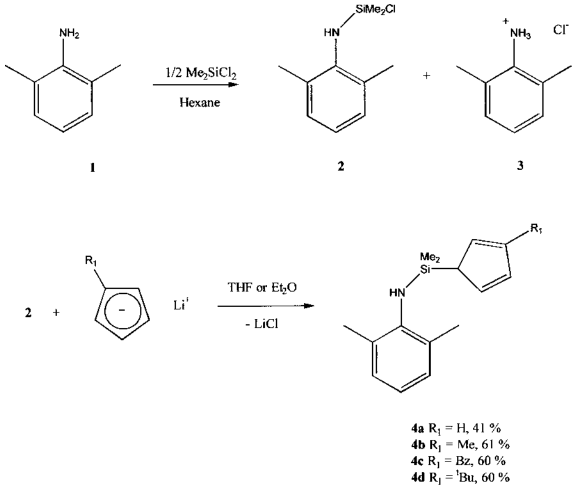
The structure was solved by direct methods using SHELXS-86[32] and refined by full-matrix least squares on F^2 for the 2812 independent reflections with $I \geq 2\sigma(I)$ using the SHELXL-93 program.[33] The final residual R_1 (based on F) for these reflections was 0.0436, and that on all 3656 independent reflections was 0.068. Hydrogen atoms based on a riding model with a C−H distance of 1.05 Å were included in the refinement. Neutral atom scattering factors for non-hydrogen atoms were taken from Ref.[34,] and anomalous dispersion corrections were included.[35] The hydrogen atom scattering factor used is that tabulated by Stewart *et al.*[36]

Polymerization procedures

A 250 ml glass pressure-bottle was sealed under an argon atmosphere. Freshly distilled toluene (50 ml) was added via a syringe, and pressurized with ethylene or propylene (15 psi (1.0 bar)). MAO or triisobutylaluminum (TIBA) was added and the bottle was placed in a bath at the desired polymerization temperature and stirred for 10 min. The catalyst precursor in toluene was then added (preactivated with trimethylaluminum (TMA) when necessary), $Ph_3CB(C_6F_5)_4$ (trityl) added when necessary, and the mixture was stirred until the desired reaction time was reached. The reaction mixture was subsequently quenched with 2% HCl in methanol (200 ml), filtered, and dried in a vacuum oven at 70 °C.

RESULTS AND DISCUSSION

The amine-containing ligands (**4a–d**) can be readily prepared in a two-step synthesis (Scheme 1). Reaction of 2,6-dimethylaniline (**1**) with half an equivalent of Me_2SiCl_2 in refluxing hexane forms two products, **2** and **3**, which were easily separated by filtration and distillation under reduced pressure. The yield of **2** is quite low (30%), but unreacted **1** (36%) can easily be recovered during the distillation. Additional **1** can also be recovered by treatment of **3** with aqueous KOH. Reaction of **2** with the corresponding lithium salt of the substituted (or unsubstituted) cyclopentadienyl



Scheme 1.

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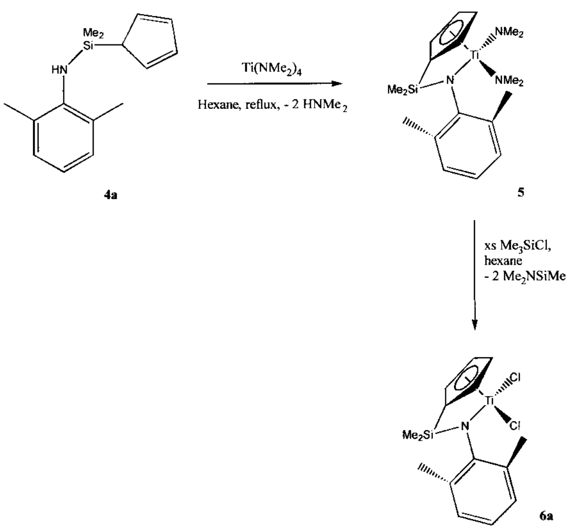


Scheme 2.

moiety affords the ligands (**4a**, R = H; **4b**, R = Me; **4c**, R = Bz; **4d**, R = ^{t}Bu) in *ca* 40–60% yields as mixtures of isomers, after distillation under reduced pressure.

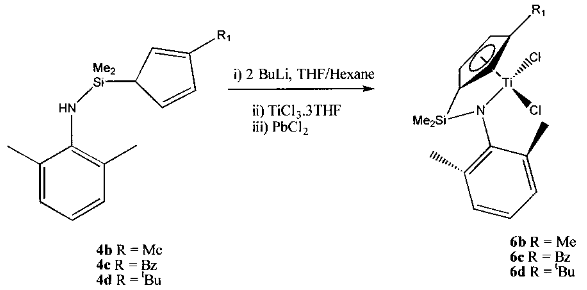
The unsubstituted ligand (**4a**) was readily converted to the corresponding titanium complex by aminolysis with tetrakis(dimethylamido)titanium to give **5** in good yield. Crystals suitable for X-ray diffraction studies could be grown by slow cooling of a saturated solution of **5** in hexane. Subsequent reaction of **5** with an excess of Me_3SiCl in hexane afforded the corresponding dichloride complex (**6a**), also in good yield (Scheme 2).

Analogous reactions utilizing the above procedure with the substituted ligands (**4b–d**) were unsuccessful, probably due to the increased steric bulk and reduced acidity of the cyclopentadienyl group, and a mixture of undesired products was obtained.

In an early report, researchers at Dow indicated that it was possible to metallate ligands to produce titanium *ansa*-cyclopentadienyl-amido complexes with $TiCl_3(THF)_3$ followed by oxidation to titanium(IV) with AgCl.[14] It has also been shown that $PbCl_2$ is a particularly effective oxidizing agent.[37] We were able to utilize these synthetic methodologies for the conversion of ligands **4b–d** to the corresponding complexes **6b–d**.

The ligands (**4b–d**) were deprotonated with two equivalents of butyllithium in a mixture of THF–hexane followed by addition to $TiCl_3\cdot 3THF$. The product was then subsequently oxidized to titanium(IV) with $PbCl_2$ and the products crystallized as yellow solids in *ca* 70% yield (Scheme 3).

The new catalyst precursors **5** and **6a–d** were found to polymerize ethylene in the presence of an excess of MAO. The results are summarized in Table 1. The activities for all five of the catalyst precursors were very similar except for catalyst precursor **6d**, which showed low activities. The activity shown by **5** when preactivated with TMA was very similar to that of complexes **6a–c**.



Scheme 3.

Propylene was also polymerized by the catalyst precursors **5** and **6a–d** over a range of temperatures. Higher-temperature polymerizations were attempted in the presence of MAO, whereas the lower-temperature polymerizations were attempted in the presence of a mixture of trityl–TIBA. The results are summarized in Table 2.

As can be seen from Table 2, the polymerization activities drop considerably as the polymerization temperature increases. For all of the above catalysts, no polymer was produced at temperatures of 70 °C. Also, only the relatively sterically unrestricted catalysts, **5**, **6a** and **6b**, form reasonable amounts of polymer at room temperature. All of the catalysts studied form reasonable amounts of polymer at −20 °C. In general, as the steric bulk on the cyclopentadienyl group is increased, the polymerization activities decrease, i.e. in order of increasing activity:

$$^{t}\mathrm{BuCp} \ll \mathrm{BzCp} < \mathrm{MeCp} < \mathrm{Cp}$$

According to the X-ray molecular structure of **5**, the substituent at C3 would not directly influence the sterics at either coordination position. The lower activity of complex **6d** may be due to an electronic effect.

Table 1. Polymerization of ethylene with **5**/**6a–d** activated with MAO

Catalyst precursor[a]	Polymer yield (g)	Activity[b]
5[c]	0.53	1.1×10^6
6a	0.68	1.5×10^6
6b	0.55	1.2×10^6
6c	0.49	1.1×10^6
6d	0.057	6.2×10^4

[a] Polymerization conditions: [Ti] = 50 μM; [Al]:[Ti] = 4000:1; monomer pressure, 15 psi (1.0 bar), time of polymerization, 0.5 h; $T_p = 50\,°C$.
[b] Activity expressed in units of grams polymer/(molTi·$[C_2H_4]$·h).
[c] The complex was preactivated with ten equivalents of TMA for 20 min prior to the polymerization.

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Table 2. Propylene polymerization results for catalyst precursors **5, 6a–d**

Catalyst precursor[a]	Cocatalyst	Temperature (°C)	Polymer yield (g)	Activity[b]
5[c]	MAO	25	0.57	3.4×10^5
5[c]	MAO	70	trace	–
6a	Trityl–TIBA	−20	2.19	7.6×10^5
6a	Trityl–TIBA	25	0.88	5.3×10^5
6a	MAO	25	0.96	5.7×10^5
6a	MAO	70	trace	–
6b	Trityl–TIBA	−20	2.44	8.5×10^5
6b	Trityl–TIBA	25	0.22	1.3×10^5
6b	MAO	25	0.31	1.9×10^5
6b	MAO	70	trace	–
6c	Trityl–TIBA	−20	0.34	1.2×10^5
6c	Trityl–TIBA	25	0.09	5.4×10^4
6c	MAO	25	0.05	3.0×10^4
6c	MAO	70	trace	–
6d	Trityl–TIBA	−20	0.056	1.9×10^4
6d	Trityl–TIBA	25	trace	–
6d	MAO	25	trace	–
6d	MAO	70	trace	–

[a] *Polymerization conditions:* *[Ti] = 50* μM; [MAO]:[Ti] = 4000:1 or [TIBA]:[Ti] = 20:1; [trityl]:[Ti] = 1:1; monomer pressure, 15 psi (1.0 bar); time of polymerization, 1 h.

[b] Activity expressed in units of grams polymer/(molTi · [C_3H_6] · h).

[c] The complex was preactivated with ten equivalents of TMA for 20 min prior to the polymerization.

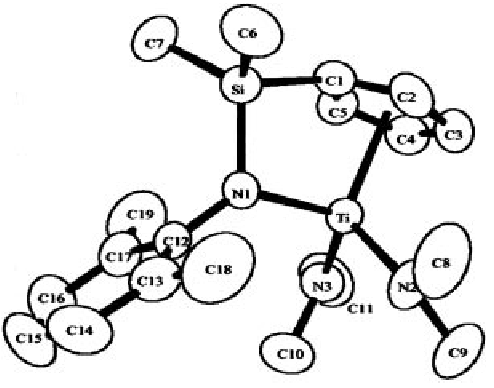

Figure 1. Molecular structure of **5**.

The pentad distributions for the polypropylene obtained from complexes **6a–d** are summarized in Table 3. There are no large differences between any of the catalysts **6a** to **6c**. However, the polypropylene obtained with **6d** has a noticably higher isotactic content.

Figure 1 gives an ORTEP[39] plot of complex **5** together with the atom labeling scheme. Table 4 summarizes details of the crystal data and refinement results. Table 5 lists selected bond distances and angles for the coordination environment of the titanium atom. The complex is monomeric in the solid state, and the geometry around the titanium is pseudo tetrahedral with the *ansa*-monocyclopentadienyl-amido ligand acting in a bidentate mode. Comparison of the bond distances and angles in Table 5 with those reported for the closely related molecule $[(C_5H_4Si(CH_3)_2(N-{}^tBu)]$-$Ti(N(CH_3)_2)_2$ reveals only minor and probably chemically insignificant differences.[40] For instance, the distance from titanium to the amido nitrogen N(1) at 1.97 Å is marginally shorter than in the complex reported here (2.00 Å), perhaps reflecting the change from a quaternary sp^3 carbon in the *tert*-butyl substituent to an sp^2-bonded carbon in the 2,6-dimethyl phenyl group. As in the previously reported example,[40] the orientations of the two dimethylamido ligands with respect to the Ti N(2) N(3) plane are quite different and are reflected in the different Ti—N(2) and Ti—N(3) distances. The constraints imposed by the chelating $(C_5H_4)Si(CH_3)_2N[2,6\text{-}(CH_3)_2C_6H_3]$ ligand are characterized both by the Si—C(1)—Cp(c) angle of 151.0° and by small but significant distortions in the Cp ring.

Table 3. Pentad distributions for polypropylenes obtained From complexes **5** and **6a–d**

Complex[a]	Cocatalyst	Temp. (°C)	*mmmm*[b]	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*mrmr*	*rrrr*	*mrrr*	*mrrm*
5	MAO	25	1.0	6.9	5.5	11.7	28.0	14.8	9.0	16.0	7.1
6a	Trityl–TIBA	−20	0.8	5.6	5.3	11.7	28.3	15.9	8.7	16.7	7.0
6a	MAO	25	1.0	7.4	5.6	11.6	29.8	14.1	7.7	17.1	5.8
6b	Trityl–TIBA	−20	5.7	10.7	6.4	13.7	22.95	12.3	8.1	12.9	7.3
6b	Trityl–TIBA	25	5.4	10.3	5.8	13.6	23.4	12.2	8.1	13.3	7.8
6b	MAO	25	6.1	11.0	6.0	13.7	24.4	12.3	6.9	13.1	6.5
6c	Trityl–TIBA	−20	4.2	9.3	4.2	12.0	25.3	13.9	7.1	14.0	10.2
6d	Trityl–TIBA	−20	14.2	13.4	3.4	15.3	23.6	8.3	5.4	10.9	5.4

[a] Polymerization conditions as shown in Table 2.

[b] Pentad distribution expressed as percentage; see Ref. 38 for an explanation of [*mmmm*], [*rrrr*], etc.

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Table 4. Crystal data and structure refinement for **5**

Empirical formula	$C_{19}H_{31}N_3SiTi$
Formula weight	377.46
Temperature (K)	293(2)
Wavelength (Å)	0.71073, monochromated Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	16.437(2)
b (Å)	8.652(3)
c (Å)	16.494(4)
β (deg)	117.54(2)
Z	4
Density (calc.) (g cm^{-3})	1.205
Absorption coefficient (cm^{-1})	4.74
Total independent reflections measured	3656
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0436$, $wR_2 = 0.1127$
Goodness of fit	$S = 1.089$

[a] $R_1 = \sum||F_o|| - ||F_c||/\sum||F_o||$. $wR_2 = [\sum(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]^{1/2}$.

SUMMARY AND CONCLUSIONS

We have successfully prepared four new 'constrained geometry'-type titanium(IV) catalysts. These catalysts polymerized ethylene and propylene with varying degrees of activity. The most active species were the catalysts that had the least amount of steric bulk on the cyclopentadienyl moiety, i.e. in increasing activity: ^{t}BuCp < BzCp < MeCp < Cp.

The polypropylenes that were obtained from these catalysts were essentially atactic by ^{13}C NMR. We assume from these findings that the introduction of a β-substituent on the cyclopentadienyl ring in complexes **6d–d** does not have much influence on the stereochemistry of propylene insertion, as it does on other site-switching catalysts.

Table 5. Selected bond lengths (Å) and angles (deg) for **5**[a]

Ti–N(3)	1.899(3)	Ti–N(2)	1.927(3)
Ti–N(1)	2.001(3)	Ti–Cp(c)	2.079
Si–N(1)	1.730(3)	Si–C(1)	1.859(4)
N(1)–C(12)	1.413(4)		
N(3)–Ti–N(2)	101.7(1)	N(3)–Ti–N(1)	108.2(1)
N(1)–Ti–N(2)	107.4(1)	N(1)–Ti–Cp(c)	105.0
N(2)–Ti–Cp(c)	118.46	N(3)–Ti–Cp(c)	115.5
Si–C(1)–Cp(c)	151.0	Si–N(1)–Ti	103.9(1)
C(12)–N(1)–Ti	130.2(1)	Si–N(1)–C(12)	124.9(2)
C(1)–Si–N(1)	93.6(1)		

[a] Cp(c) denotes the centroid of the cyclopentadienyl ring.

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REFERENCES

1. Ewen JA. *J. Am. Chem. Soc.* 1984; **106**: 6355.
2. Rieger B, Mu X, Mallin DT, Rausch MD and Chien JCW. *Macromolecules* 1990; **23**: 3559.
3. Fierro R, Yu Z-T, Rausch MD, Dong S-Z, Alvares D and Chien JCW. *J. Polym. Sci. Part A, Polym. Chem.* 1994; **32**: 661.
4. Rieger B, Jany G, Fawzi R and Steimann M. *Organometallics* 1994; **13**: 647.
5. Thomas EJ, Chien JCW and Rausch MD. *Macromolecules* 2000; **33**: 1546.
6. Ewen JA, Jones RL, Razavi A and Ferrera JD. *J. Am. Chem. Soc.* 1988; **110**: 6255.
7. Razavi A, Peters L, Nafpliotis L, Vereecke D, Dendauw K, Atwood J and Thewald U. *Macromol. Symp.* 1995; **89**: 345.
8. Razavi A and Atwood JL. *J. Organomet. Chem.* 1995; **497**: 105.
9. Razavi A and Atwood JL. *J. Organomet. Chem.* 1996; **520**: 115.
10. Razavi A and Atwood JL. *J. Am. Chem. Soc.* 1993; **115**: 7529.
11. Canich JAM (Exxon). US Patent 5-026-798, 1991.
12. Canich JAM and Licciardi GF (Exxon). US Patent 5-057-475, 1991.
13. Canich JAM (Exxon). Eur. Pat. Appl. 0-420-436-A1, 1991.
14. Stevens JC, Timmers FJ, Wilson DR, Schmidt GF, Nickias PN, Rosen RK and Knight GW, Lai S-y (Dow). Eur. Pat. Appl. 0-416-815-A2, 1991.
15. Stevens JC and Neithamer DR (Dow). Eur. Pat. Appl. 0-418-044-A2, 1991.
16. Bercaw JE. In *3rd Chemical Congress of North America*, Toronto, Canada, June 1988.
17. Shapiro PJ, Bunel EE, Schaefer WP and Bercaw JE. *Organometallics* 1990; **9**: 867.
18. McKnight AL and Waymouth RM. *Chem. Rev.* 1988; **98**: 2587 and referencesated therein.
19. Stevens JC, Timmers FJ, Wilson DR, Schmidt GF, Nickias PN, Rosen RK and Knight GW, Lai S-y (Dow). Eur. Pat. Appl. 0-416-815-A2, 1991.
20. Pannell RB, Canich JAM and Hlatky GG (Exxon). PCT Int. Appl. WO 3/00500, 1994.
21. LaPointe RE, Stevens JC, Nickias PN and McAdon MH (Dow). Eur. Pat. Appl. 0-520-732-A1, 1992.
22. Canich JAM (Exxon). US Patent 5-504-169, 1996.
23. McKnight AL, Masood MA, Waymouth RM and Straus DA. *Organometallics* 1997; **16**: 2879.
24. Turner HW, Hlatky GG and Canich JAM (Exxon). PCT Int. Appl. WO 93/19103, 1993.
25. Ewen JA, Elder MJ, Jones RL, Haspeslagh JL, Atwood JL, Bott SG and Robinson K. *Makromol. Chem. Macromol. Symp.* 1991; **48–49**: 253.
26. Razavi A, Napfliotis L, Peters L, Vereecke D, Den Dauw K, Atwood JL and Thewald U. *Macromol. Symp.* 1995; **89**: 345.
27. Razavi A and Atwood JL. *J. Organomet. Chem.* 1996; **520**: 115.
28. Stone KJ and Little RD. *J. Org. Chem.* 1984; **49**: 1849.
29. Bradley DC and Thomas IM. *Proc. Chem. Soc.* 1959; 225.
30. Singh P, Rausch MD and Bitterwolf TE. *J. Organomet. Chem.* 1988; **352**: 273.
31. Manzer LE. *Inorg. Synth.* 1982; **21**: 135.
32. Sheldrick GM. *Acta Crystallogr. Sect. A* 1990; **46**: 467.
33. Sheldrick GM. *SHELXL-93*: program for crystal structure refinement.

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34. International Tables for X-ray Crystallography, vol. IV. Kynoch Press: Birmingham, UK, 1974; 99–149.
35. Cromer DT and Lieberman DJ. *J. Chem. Phys.* 1970; **53**: 1891.
36. Stewart RF, Davidson RF and Simpson WJ. *J. Chem. Phys.* 1965; **42**: 3175.
37. Luinstra GA and Teuben JH. *J. Chem. Soc. Chem. Commun.* 1990; 1470.
38. Brintzinger HH, Fischer D, Mülhaupt R, Rieger B and Waymouth R. *Angew. Chem. Int. Ed. Engl.* 1993; **115**: 1143.
39. Farrugia LJ. *J. Appl. Crystallogr.* 1997; **30**: 565.
40. Carpenetti DW, Kloppenburg L, Kupec JT and Peterson JL. *Organometallics* 1996; **15**: 1572.

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