Synthesis of titanium(IV) complexes containing 2,6-dimethylaniline substituted amino alcohols and their utilization in ethylene polymerizations

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Abstract

Two new Ti(IV) complexes of the type [(OCHRCH$_2$N-2,6-Me$_2$Ph)Ti(NMe$_2$)$_2$]$_2$ (where R = H, or ^{t}butyl) have been synthesized by protonolysis of Ti(NMe$_2$)$_4$ with the corresponding N-substituted amino alcohol ligand. The two complexes were studied as Ziegler–Natta type polymerization catalysts in the presence of an excess of methylaluminoxane (MAO). It was found that ethylene polymerization activity for both catalysts increased by increasing the polymerization temperature from 25 to 70°C. If the catalysts were pretreated with trimethylaluminum, the activities increased at 25°C, but slightly decreased at 70°C. Both complexes were found to be ineffective for the polymerization of propylene. An X-ray crystal structure of [(OCH$_2$CH$_2$N-2,6-Me$_2$Ph)Ti(NMe$_2$)$_2$]$_2$ shows the complex to be dimeric in the solid state, with bridging through the amino alcohol oxygen atoms. This complex crystallizes in the monoclinic system space group, $P2_1/n$ with $a = 9.181(6)$, $b = 13.766(3)$, $c = 13.002(3)$, $\beta = 93.08(3)$ and $Z = 4$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymerization; Titanium; Non-cyclopentadienyl; Ethylene

1. Introduction

The organometallic chemistry of titanium has been dominated by complexes containing cyclopentadienyl ligands [1]. This is reflected in the fact that most homogeneous Ziegler–Natta catalyst precursors are also based on the cyclopentadienyl framework [2a]. More recently, however, non-cyclopentadienyl based catalyst precursors have become more prominent in the literature [2b]. Some examples are titanium and zirconium complexes containing chelating dialkoxide ligands [3,4] and chelating diamido ligands [5–19]. These catalyst precursors have been used for the Ziegler–Natta polymerization of olefins. In some instances, living polymerization was observed [15].

As part of our program to synthesize novel Ziegler–Natta polymerization catalyst precursors, we have pre-

pared two titanium(IV) complexes containing chelating ligands with both an η^1-amido and an η^1-alkoxy linkage with the general formula [(OCHRCH$_2$N-2,6-Me$_2$Ph)Ti(NMe$_2$)$_2$]$_2$ (where R = H or ^{t}butyl) and have studied their ability to polymerize α-olefins in the presence of methylaluminoxane (MAO). This ligand design was chosen to discover how the effects of using a ligand, containing both a covalently bonded oxygen and nitrogen group would affect the catalytic properties of the complex. Previous research has concentrated mainly on symmetric ligands containing either two nitrogen or oxygen containing ligands.
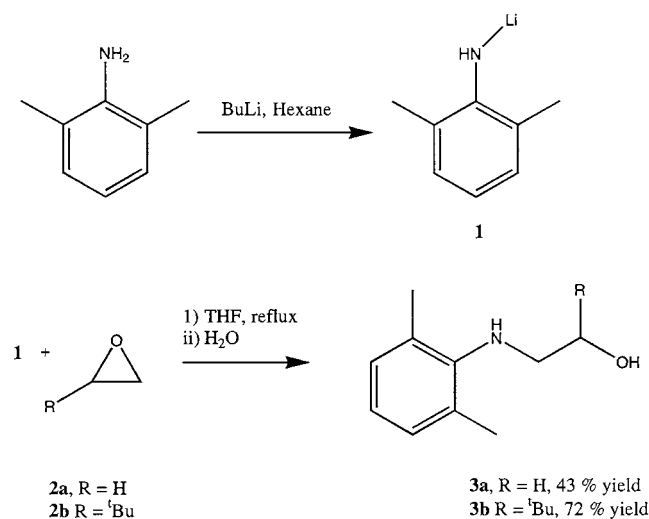
2. Results and discussion

2.1. Synthesis

The amino alcohol ligands were easily prepared in good yield by nucleophilic ring opening of epoxides. Reaction of the lithium salt of 2,6-dimethylaniline (1)

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Scheme 1.

with ethylene oxide (**2a**) or 3,3-dimethyl-1,2-epoxybutane (**2b**) in the presence of tetramethylethylenediamine (TMEDA), followed by hydrolysis, formed the amino alcohol ligands (Scheme 1). We were also able to prepare the unsubstituted amino alcohol (**3a**) by modification of a literature procedure [20]. Reaction of 2-chloroethanol with an excess of 2,6-dimethylaniline, followed by the addition of a base, formed the amino alcohol in good yield (Scheme 2).

The titanium(IV) complexes were synthesized via the aminolysis of tetrakis(dimethylamido) titanium in refluxing hexane (Scheme 3). The products formed were isolated as air-sensitive yellow or orange solids. The unsubstituted complex **4a** was isolated as crystalline orange needles, whereas for the 'butyl substituted complex **4b**, it was not possible to grow crystals suitable for X-ray work due to the high solubility of **4b** in hydrocarbon solvents. It formed only a yellow, microcrystalline powder.
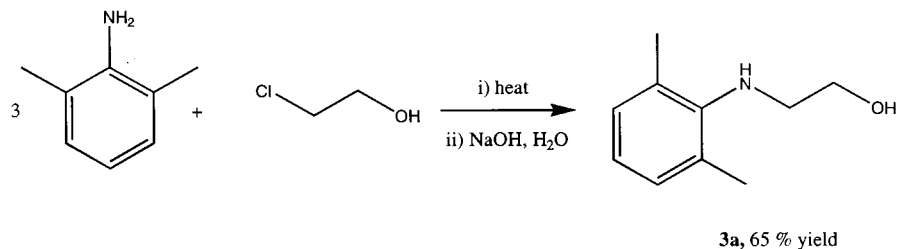
The proton NMR spectrum of **4b** was found to be temperature dependent. At all temperatures studied (-80 to $+60°C$), two dimethylamido groups were found to be magnetically non-equivalent. At ambient temperatures, one of the dimethylamido groups appears as a broad, featureless peak (δ 2.78). The low temperature-limiting spectrum ($-20°C$) exhibits two singlets

for this dimethylamido group (δ 2.39 and 3.10), whereas in the high temperature-limiting spectrum (60°C), the dimethylamido group appears as a sharp singlet (δ 2.73). We interpret this to be a consequence of restricted rotation about one of the $Ti-N_{(amido)}$ groups in **4b**. At all temperatures studied, the other dimethylamido group appeared as a sharp singlet (ca. δ 3.38). Additionally, the methyl substituents on the aromatic group are also non-equivalent, appearing as two singlets at all temperatures studied (ca. δ 2.33 and 2.59). This may be a consequence of restricted rotation about the $N-C_{ipso}$ bond[1].
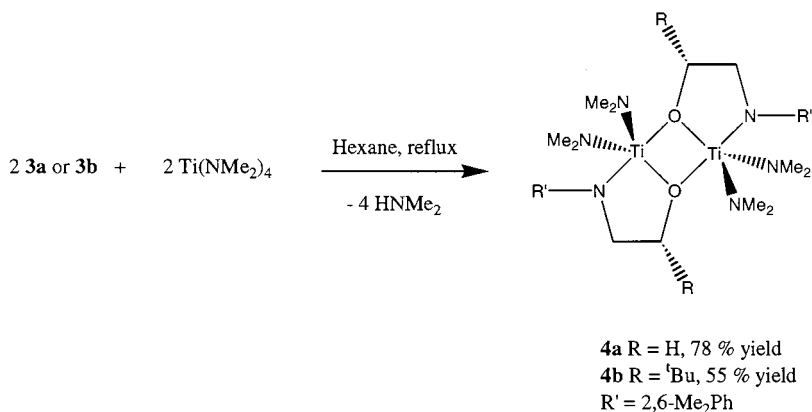
2.2. Polymerization studies

Complexes **4a** and **4b** were examined as potential Ziegler–Natta polymerization catalysts in the presence of MAO. Polymerizations of ethylene were carried out at two different temperatures, either with or without preactivation with trimethylaluminum (TMA). It has previously been reported that the preactivation of zirconium bis(dimethylamido) compounds with TMA methylates the complexes, and thus the complex is more easily activated with MAO [21]. The results are summarized in Table 1. Attempts to polymerize propylene under identical conditions resulted in no polymer being formed. Perhaps most notable is the effect of temperature on the polymerizations in the absence of TMA. In general, polymerization at room temperature afforded only a small amount of polymer, with activities in the low 10^4–10^5 range. Increasing the temperature to 70°C produced a significantly greater amount of polyethylene. We attribute this to the fact that these compounds are difficult to activate at ambient temperatures, i.e. alkylation of the titanium species is slow. This process is much more spontaneous at the higher temperature of 70°C. In the case where the complexes were preactivated with TMA, an increase in activity was observed at room temperature. The activities at 70°C are slightly lower when preactivated with TMA, indicating that the methylated titanium complexes are slightly less stable at these temperatures. In all cases,

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[1] Restricted rotation was also observed in several complexes containing a 2,6-diisopropylphenyl group [8,10,15–17,19].

Scheme 2.

$$2\ \mathbf{3a}\ \text{or}\ \mathbf{3b}\ +\ 2\ Ti(NMe_2)_4 \xrightarrow[-\ 4\ HNMe_2]{\text{Hexane, reflux}}$$

4a R = H, 78 % yield
4b R = ᵗBu, 55 % yield
R' = 2,6-Me₂Ph

Scheme 3.

Table 1
Ethylene polymerization with catalyst precursors **4a**, **4b**/MAO

Catalyst [a]	Preactivated with TMA [b]	Polymerization temperature (°C)	Polymer yield (g)	Activity [c]	m.p. of polymer (°C)	M_w of polymer [d] (g mol^{-1})
4a	No	25	0.011	1.2×10^4	134.1	6.8×10^5
4a	No	70	0.59	1.1×10^6	126.2	1.2×10^5
4b	No	25	0.102	1.1×10^5	134.0	2.5×10^5
4b	No	70	0.30	5.8×10^5	128.9	1.1×10^5
4a	Yes	25	0.18	1.9×10^6	135.9	7.3×10^5
4a	Yes	70	0.50	9.6×10^5	127.9	4.2×10^5
4b	Yes	25	0.12	1.3×10^5	131.7	1.8×10^5
4b	Yes	70	0.10	1.9×10^5	132.6	1.1×10^5

[a] Polymerization conditions; [Ti] = 50 μM; [Al]:[Zr] = 4000:1; monomer pressure = 15 psi; time of polymerization = 1 h.
[b] Catalyst preactivated with five equivalents of TMA for 20 min before polymerization initiation.
[c] Activity expressed in units of g polymer/(mol Ti·[C₂H₄] h).
[d] M_w determined by viscometry in decalin at 135°C.

the activities shown here are similar to the activities exhibited by the chelating alkoxide complexes described by Schaverien et al. which polymerize ethylene with activities in the range 10^5–10^6 gPE/mol cat h [3].

2.3. Crystal and molecular structure of $(OCH_2CH_2N$-2,6-$Me_2Ph)Ti(NMe_2)_2$ (**4a**)

Fig. 1 gives an ORTEP [22] plot of the complex **4a**, together with the atom labelling for the asymmetric unit. Table 2 shows the crystal data and structure refinement for **4a** and Table 3 lists selected bond distances and angles for the metal coordination environment.

The complex is a centrosymmetric dimer (the center of inversion being crystallographically imposed) with bridging oxygen atoms, and a distorted trigonal bipyramidal geometry around each titanium atom. The observation of bridging oxygen atoms to form dimeric and higher polymeric species is a common feature of titanium chemistry [23–25], and similar dimeric geometries have been reported for related complexes containing N-substituted amino-alcohols [25]. Fig. 2 shows com-

plex **5** [25], which is the closest structurally to that described here, the principal difference being the phenyl substituents on the chelate ring of the ligand. The bond
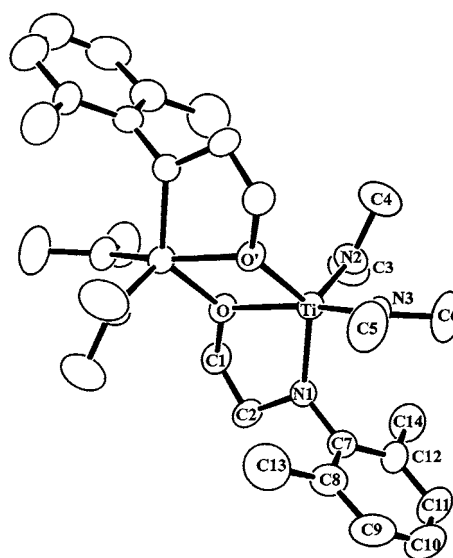

Fig. 1. Molecular structure of **4a**.

Table 2
Crystal data and structure refinement for **4a**

Empirical formula	$C_{14}H_{25}N_3OTi$
Formula weight	299.27
Temperature (K)	293(2)
Wavelength (Å)	0.71073, monochromated Mo Kα
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.181(6)
b (Å)	13.766(3)
c (Å)	13.002(3)
β (°)	93.08(3)
Z	4
D_{calc} (g cm^{-3})	1.211
Absorption coefficient (cm^{-1})	5.190
Total independent reflections measured	2009
Final R indices $[I > 2\sigma(I)]$ [a]	$R_1 = 0.0540$, $wR_2 = 0.0996$
Goodness-of-fit	$S = 1.12$

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

Table 3
Selected bond lengths (Å) and bond angles (°) for **4a** [a]

Bond lengths			
Ti–N(1)	1.938(5)	Ti–N(2)	1.882(6)
Ti–N(3)	1.891(5)	Ti–O	2.100(4)
Ti–O'	1.952(4)	Ti–Ti'	3.270(2)
O–C(1)	1.419(7)	C(1)–C(2)	1.497(9)
C(2)–N(1)	1.478(8)	N(1)–C(7)	1.429(8)
N(2)–C(3)	1.435(9)	N(2)–C(4)	1.466(8)
N(3)–C(5)	1.465(9)	N(3)–C(6)	1.454(8)
Bond angles			
N(2)–Ti–N(3)	101.3(3)	N(2)–Ti–N(1)	112.2(2)
N(3)–Ti–N(1)	99.1(2)	N(2)–Ti–O'	114.3(2)
N(3)–Ti–O'	94.8(2)	N(1)–Ti–O'	127.4(2)
N(2)–Ti–O	98.1(2)	N(3)–Ti–O	160.0(2)
N(1)–Ti–O	78.0(2)	O'–Ti–O	72.5(2)

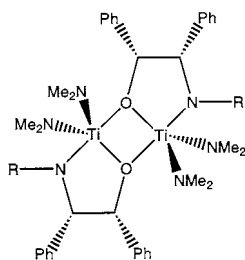[a] Symmetry transformations used to generate equivalent atoms: $-x, -y, -z+2$.

Fig. 2. Molecular structure of **5**.

distances and angles involving the titanium atom in **4a** are closely similar to those reported for **5** [25], the only change of any significance being the slightly larger difference in the Ti–O bond lengths, the equatorial oxygen (of the trigonal bipyramid) being 0.15 Å closer to the metal than the axial oxygen, and perhaps reflect-

ing the lower steric restrictions due to the chelate ring. There is no significant difference between the equatorial and axial Ti–NMe₂ distances, and as for **5** [25], these are a little shorter than the Ti–N(Ar) distance.

Unfortunately, we have been unable to grow adequate crystals of **4b** for X-ray analysis as **4b** is difficult to crystallize even when in a very pure state.

3. Summary and conclusions

We have prepared successfully two new titanium (IV) complexes based on ligands containing 2,6-dimethylaniline substituted amino alcohols. These catalysts have been shown to polymerize ethylene in the presence of an excess of MAO, exhibiting greater activities at 70°C than room temperature. We propose that methylation of the catalyst precursors is difficult at room temperature by MAO, or the TMA in it, but is spontaneous at 70°C. If the catalysts were preactivated (methylated) with trimethylaluminum (TMA) prior to the initiation of the polymerization, the activities were increased at room temperature compared to when the catalysts were not treated with TMA. The activities at higher temperatures were slightly decreased, probably due to the instability of the methylated titanium precursor at this temperature.

4. Experimental

4.1. General procedures

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 P₂O₅. 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.

Methylaluminoxane was purchased from Akzo. Butyllithium (1.6 M in hexanes), 2-chloroethanol and ethylene oxide were purchased from Aldrich and used without further purification. 2,6-Dimethylaniline was purchased from Aldrich and distilled from CaH₂, in vacuo, prior to use. 3,3-Dimethyl-1,2-epoxybutane was purchased from Lancaster and used without further purification. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was purchased from Aldrich and distilled from Na prior to use. Tetrakis(dimethylamido) tita-

nium was prepared by the literature method [26]. Celite was purchased from Fischer Scientific and used without pretreatment.

^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer with tetramethylsilane (Me$_4$Si) as an internal standard at ambient temperatures unless otherwise stated. Melting points of the polymers were obtained using a Perkin–Elmer model DSC-4 differential scanning calorimeter. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

4.2. Preparation of 2,6-Me$_2$PhNHLi (1)

Butyllithium (40.0 ml, 64 mmol) was slowly added to a solution of 2,6-dimethylaniline (7.75 g, 64 mmol) in hexane (75 ml) at 0°C. A white solid formed immediately. The mixture was warmed to room temperature (r.t.) and stirred for 2 h. The hexane was removed by cannula filtration and the resulting white solid dried in vacuo yielding a white, pyrophoric powder (8.03 g, 98% yield).

4.3. Preparation of 2,6-Me$_2$PhN(H)C$_2$H$_4$OH (3a)

Method (a): ethylene oxide (1.76 g, 40 mmol) was added to a solution of 1 (5.0 g, 39.3 mmol) in THF (50 ml) and the mixture was stirred at room temperature for 2 h. The mixture was hydrolyzed with water (50 ml) and the product extracted with diethyl ether (3 × 50 ml). The organic layers were combined, dried (MgSO$_4$) and the solvents removed. The resulting oil was distilled at 66–68°C (0.01 mmHg) to yield a colorless oil (2.77 g, 43% yield). ^{1}H-NMR (CDCl$_3$) δ 2.29 (s, 6H, Ar–CH$_3$), 3.05 (bs, 2H, NH/OH), 3.09 (t, 2H, CH$_2$), 3.73 (t, 2H, CH$_2$), 6.79–7.01 (m, 3H, aromatic-H). Method (b) [20]: 2,6-dimethylaniline (145 g, 1.2 mol) and 2-chloroethanol (29.0 g, 0.36 mol) were stirred at 100°C for 48 h. After the mixture was cooled to r.t., water (100 ml) was added and solid KOH was added until the mixture was basic to litmus. The organics were extracted in diethyl ether (3 × 100 ml). The organic layers were combined, dried (MgSO$_4$) and the residue distilled at 66–68°C (0.01 mmHg) to yield a colorless oil (38.7 g, 65% yield). ^{1}H-NMR data as above.

4.4. Preparation of 2,6-Me$_2$PhN(H)C$_2$H$_3$(^{t}Bu)OH (3b)

3,3-Dimethyl-1,2-epoxybutane (6.3 g, 62.9 mmol) was added to a solution of 1 (8.03 g, 62.9 mmol) and N,N,N′,N′-tetramethylethylenediamine (TMEDA) (9.49 ml, 62.9 mmol) in THF (75 ml). The solution was placed under reflux overnight. The mixture was hydrolyzed with water (75 ml) and the product extracted with diethyl ether (3 × 60 ml). The organic layers were combined, dried (MgSO$_4$), and the solvents removed.

The resulting solid was dried in vacuo and the product crystallized from pentane to afford the title compound as a pale yellow crystalline solid (9.98 g, 72% yield); m.p. 71–72°C. Anal. Calc. for C$_{14}$H$_{23}$NO: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.15; H, 10.58; N, 6.35%. ^{1}H-NMR (CDCl$_3$) δ 0.93 (s, 9H, ^{t}Bu), 2.31 (s, 6H, Ar–CH$_3$), 2.75 (bs, 1H, OH), 2.73–2.84 (t, 1H, –CH), 3.11–3.19 (dd, 1H, –CH$_2$), 3.31 (bs, 1H, NH), 3.39–3.46 (dd, 1H, –CH$_2$), 6.81–7.03 (m, 3H, aromatic-H).

4.5. Preparation of [(2,6-Me$_2$PhNC$_2$H$_4$O)Ti(NMe$_2$)$_2$]$_2$ (4a)

Ligand 3a (2.66 g, 16.1 mmol) was added in portions to a solution of Ti(NMe$_2$)$_4$ (3.60 g, 16.1 mmol) in hexane (50 ml) at 0°C. The mixture was placed under reflux overnight and the solution cooled to r.t. The mixture was filtered and the resulting orange solid dried in vacuo. The product was crystalized from toluene at −20°C as orange needles (3.76 g, 78.0% yield). Anal. Calc. for C$_{14}$H$_{25}$N$_3$OTi: C, 56.19; H, 8.42; N, 14.04. Found: C, 56.98; H, 8.50; N, 12.87%. ^{1}H-NMR (C$_6$D$_6$) δ 3.01 (s, 6H, Ar–CH$_3$), 3.46 (t, 2H, CH$_2$), 4.60 (t, 2H, –CH$_2$), 6.92–7.18 (m, 3H, aromatic-H).

4.6. Preparation of [(2,6-Me$_2$PhNC$_2$H$_3$(^{t}Bu)O)Ti(NMe$_2$)$_2$]$_2$ (4b)

Ligand 3b (2.00 g, 9.04 mmol) was added in portions to a solution of Ti(NMe$_2$)$_4$ (2.03 g, 9.04 mmol) in hexane (50 ml) at 0°C. The mixture was placed under reflux overnight and the reaction mixture was then cooled to r.t. The solution was filtered from any insoluble impurities and cooled to −78°C. The product was isolated as a highly hydrocarbon soluble yellow powder (1.76 g, 54.8% yield). Anal. Calc. for C$_{18}$H$_{33}$N$_3$OTi: C, 60.84; H, 9.36; N, 11.82. Found: C, 60.95; H, 9.59; N, 11.61%. ^{1}H-NMR (−20°C) (C$_7$D$_8$): δ 0.94 (s, 9H, ^{t}Bu), 2.33 (s, 3H, Ar–CH$_3$), 2.39 (s, 3H, NMe$_2$), 2.61 (s, 3H, Ar–CH$_3$), 3.05 (dd, 1H, –CH$_2$), 3.10 (s, 3H, NMe$_2$), 3.38 (s, 6H, NMe$_2$), 4.18 (dd, 1H, –CH$_2$), 4.37 (t, 1H, –CH), 6.96–7.13 (m, 3H, aromatic-H). ^{1}H-NMR (20°C) (C$_7$D$_8$): δ 0.94 (s, 9H, ^{t}Bu), 2.33 (s, 3H, Ar–CH$_3$), 2.59 (s, 3H, Ar–CH$_3$), 2.78 (bs, 6H, NMe$_2$), 3.08 (dd, 1H, –CH$_2$), 3.38 (s, 6H, NMe$_2$), 4.16 (dd, 1H, –CH$_2$), 4.38 (t, 1H, –CH), 6.95–7.10 (m, 3H, aromatic-H). ^{1}H NMR (60°C) (C$_7$D$_8$): δ 0.96 (s, 9H, ^{t}Bu), 2.32 (s, 3H, Ar–CH$_3$), 2.55 (s, 3H, Ar–CH$_3$), 2.73 (s, 6H, NMe$_2$), 3.06 (dd, 1H, –CH$_2$), 3.48 (s, 6H, NMe$_2$), 4.15 (dd, 1H, –CH$_2$), 4.39 (t, 1H, –CH), 6.81–7.10 (m, 3H, aromatic-H).

4.7. Polymerization procedure

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 the appropriate monomer (15 psi). The appropriate amount of methylaluminoxane (MAO) was added and the bottle was placed in a bath at the desired polymerization temperature and stirred for ten min. The catalyst precursor (preactivated with five equivalents of TMA for 20 min when necessary) in toluene was then added, 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.

4.8. Crystal structure determination

X-ray diffraction data for an orange needle-like crystal of **4a** were collected on an Enraf–Nonius CAD4 diffractometer at room temperature, using monochromated Mo Kα radiation and the $\omega/2\theta$ scan mode. Empirical absorption corrections, based on psi scans were made to the data. Details of unit cell dimensions etc. are summarized in Table 2.

The structure was solved by direct methods using SHELXS-86 [27] and refined by full-matrix least squares on F^2 using all 2009 independent reflections using the SHELXL-93 program [28]. The final residual, R_1 (based on F) for the 1329 reflections with $I \geq 2\sigma(I)$ was 0.054. 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 International Tables [29], and anomalous dispersion corrections were included [30]. The hydrogen atom scattering factor used, is that tabulated by Stewart et al. [31].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 152128 for compound **4a**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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