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Titanium complexes bearing bidentate benzimidazole-containing ligands and their behavior in ethylene polymerization

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ABSTRACT

A series of potentially bidentate benzimidazolyl ligands of the type (Bim)CH_2D (where Bim = benzimidazolyl and D = NMe_2 **L1**, NEt_2 **L2**, NPr^i_2 **L3**, OMe **L4** and SMe **L5**) has been reacted with Ti(NMe_2)$_4$ to give five- and six-coordinate Ti(IV) complexes of the type [(Bim)CH_2D]Ti(NMe_2)$_3$ and [(Bim)CH_2D]$_2$Ti(NMe_2)$_2$, respectively. The X-ray structures of [(Bim)CH_2OMe]Ti(NMe_2)$_3$, [(Bim)CH_2NMe_2]$_2$Ti(NMe_2)$_2$ and [(Bim)CH_2OMe)]$_2$Ti(NMe_2)$_2$ are reported along with an evaluation of their behavior in ethylene polymerization.

1. Introduction

Early transition metals bearing various amide derived ligands have been extensively studied in the development of post-metallocene polymerization catalysts [1–7]. In contrast, benzimidazolyl compounds, although widely investigated in biochemistry [8–10] and other (non-catalytic) applications, [11,12] have been little studied as ligands for the stabilization of olefin polymerization systems [13–16]. In a recent study we have found that chromium and vanadium complexes supported by bis(benzimidazolyl)amine ligands are highly active for olefin oligomerization and polymerization, respectively [16,17]. Encouraged by these promising results, we were interested to explore the potential of benzimidazolyl-containing ligands attached to other transition metal centers and derivatives of the Group 4 metals presented attractive targets. Here we report the synthesis and characterization of a family of potentially bidentate benzimidazole-containing ligands incorporating hard and soft pendant donors and their complexes with titanium; the latter have been examined as pre-catalysts for olefin polymerization.

2. Results and discussion

2.1. Synthesis of ligands

The benzimidazolylmethylamine pro-ligands, (Bim)CH_2NR_2 **L1**–**L3**, were obtained by condensation of 2-choromethylbenzimidazole with the appropriate amine (Scheme 1i) [18]. It should be noted that although 2-chloromethylbenzimidazole is commercially available, improved yields and purities were achieved when this precursor was freshly synthesized [18].

To evaluate the effect of differing heteroatom donors, 2-(methoxymethyl)benzimidazole (**L4**) and 2-(methylthiomethyl)benzimidazole (**L5**) were also synthesised [19] by condensation of phenylenediamine with the required acid (Scheme 1).

2.2. Synthesis of [(Bim)CH_2D]Ti(NMe_2)$_3$ complexes

To determine an appropriate titanium precursor for the preparation of complexes of the type [(Bim)CH_2D]Ti(NMe_2)$_3$, NMR scale reactions (benzene-d_6) were carried out using a 1:1 mixture of (benzimidazolyl-2-methyl)dimethylamine **L1** and Ti(NMe_2)$_4$. The ^{1}H NMR spectrum showed that reactions of the pro-ligand with $TiCl_4$, Ti(CH_2Ph)$_4$ or Ti(NMe_2)Cl_2 afforded a mixture of products and, in the case of Ti(O^iPr)$_4$, no reaction was observed. In contrast, the reaction with Ti(NMe_2)$_4$ gave a single product which included titanium-bonded $HNMe_2$ indicating that the benzimidazole ligand had undergone deprotonation to afford a monoanionic ligand. An analogous reaction on a preparative scale gave **1** in 67% isolated yield. This procedure was readily extended to the preparative scale syntheses of **2–4** as orange or yellow, air- and moisture-sensitive solids in 67–83% yield (Scheme 2).

Although the formation of the thioether-containing complex **5** was successful in an NMR-scale reaction at room temperature, it did not prove possible to isolate this product cleanly upon scale-up. Unlike for its hard donor relatives, it appeared to be more thermally sensitive, possibly a consequence of the relatively weak Ti–S interaction.

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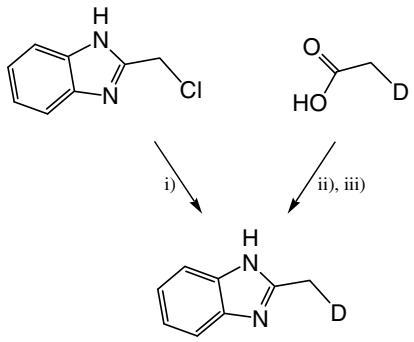
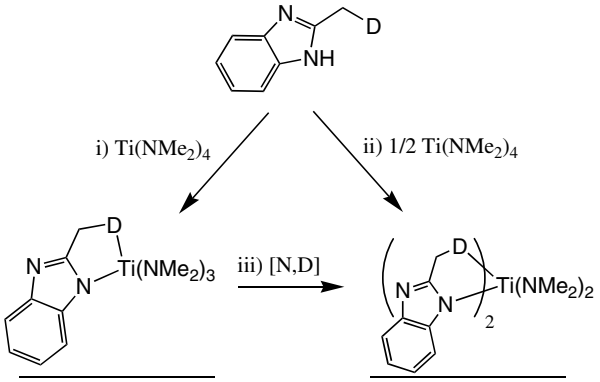


No.	Donor
L1	NMe_2
L2	NEt_2
L3	N^iPr_2
L4	OMe
L5	SMe

Scheme 1. Synthesis of (Bim)CH_2D compounds **L1**–**L5**. Reagents and Conditions: for D = NR_2[10]: (i) 2 equiv. HNR_2[18], MeOH/Et_2O, reflux 3 h; for D = OMe, SMe[8]: (ii) *o*-phenylendiamine, 4 M HCl, 24 h reflux, (iii) 6 M NH_4OH (aq).



Comp	Donor
1	$N(Me)_2$
2	$N(Et)_2$
3	$N(^iPr)_2$
4	OMe
5[a]	SMe

Comp	Donor
6	$N(Me)_2$
7	OMe
8[a]	SMe

[a] Compound prepared on NMR scale

Scheme 2. Synthetic procedures for complexes **1–8**.

2.3. The molecular structure of $[(Bim)CH_2OMe]Ti(NMe_2)_3$

Crystals of **4** suitable for a single-crystal *X*-ray structure determination were grown from a saturated pentane/DCM solution. The solid-state structure revealed the presence of two crystallographically independent molecules denoted by **4(I)** and **4(II)** (molecule **4(I)** is shown in Fig. 1, molecule **4(II)** in the SI). The metal coordination geometry is best described as trigonal bipyramidal with O(1) and N(40) occupying axial sites, the τ parameter being 0.88 and 0.81 for molecules **4(I)** and **4(II)**, respectively. The metal centre lies ca. 0.26 Å out of the {N(4), N(20), N(30)} equatorial plane in the direction of N(40) in both **4(I)** and **4(II)**. The five-membered N,O chelate ring is only slightly folded into an envelope conformation, the oxygen lying ca. 0.16 Å [0.28 Å in **4(II)**] out of the {TiC_2N} plane which is coplanar to within ca. 0.03 Å [0.02 Å in **4(II)**].

Room temperature ^{1}H NMR spectra of **1**–**5** are relatively simple (see Fig. 2 as an example) and consistent with highly fluxional amido ligands. In each case, singlet resonances are observed for the six methyl groups of the dimethylamido donors, the methylene protons of the ligand backbone and the dimethylamino donor of the benzimidazolyl chelate; characteristic ^{1}H–^{1}H couplings are observed for the phenylene unit of the benzimidazolyl moiety. A significant downfield shift for the protons of the NMe_2 unit relative to the signal observed for the pro-ligand confirms that the neutral donor is bonded to the metal.

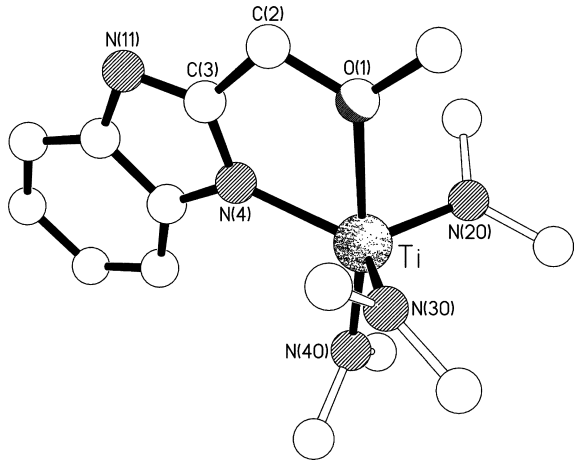


Fig. 1. Molecular structures of **4(I)** (H atoms omitted for clarity). Key bond lengths (Å) and angles (°): **4(I)**) Ti–O(1) 2.2539(15), Ti–N(4) 2.0826(15), Ti–N(20) 1.8935(16), Ti–N(30) 1.8930(17), Ti–N(40) 1.9204(17), O(1)–Ti–N(4) 72.10(6), O(1)–Ti–N(40) 172.23(6), N(4)–Ti–N(20) 120.69(7), N(20)–Ti–N(30) 114.74(7), N(30)–Ti–N(40) 96.00(8), **4(II)**) Ti–O(1) 2.2333(14), Ti–N(4) 2.0891(16), Ti–N(20) 1.8858(17), Ti–N(30) 1.9094(17), Ti–N(40) 1.9156(16), O(1)–Ti–N(4) 71.63(5), O(1)–Ti–N(40) 169.34(6), N(4)–Ti–N(20) 121.01(7), N(20)–Ti–N(30) 112.71(7), N(30)–Ti–N(40) 96.58(7).

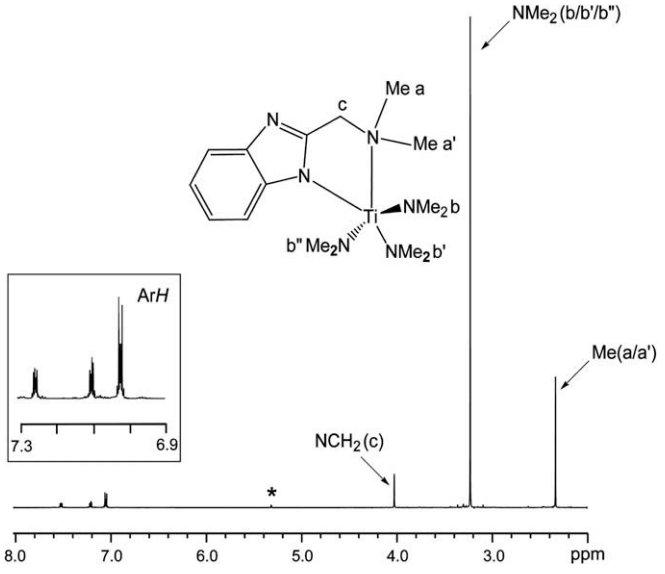


Fig. 2. ^{1}H NMR spectra of **1** in DCM-d_2(*).

2.4. Synthesis of $[(Bim)CH_2D]_2Ti(NMe_2)_2$ complexes

Bis-chelate derivatives could be obtained by treatment of $[(Bim)CH_2D]Ti(NMe_2)_3$ with a further equivalent of the pro-ligand, or by direct treatment of $Ti(NMe_2)_4$ with 2 equivalent of the pro-ligand. For example, **6** could be prepared in 80% yield by reacting **1** with 1.0 equivalent of (Bim)CH_2NMe_2, while **7** was obtained in 74% yield by reacting 2.0 equivalents of (Bim)CH_2OMe with $Ti(NMe_2)_4$. The thioether product **8** was notably less stable than **6** and **7** and could not be isolated in pure form, although its formation could be observed in NMR-scale reactions.

2.5. The molecular structures of $[(Bim)CH_2D]_2Ti(NMe_2)_2$ complexes

Single crystals of $[(Bim)CH_2NMe_2]_2Ti(NMe_2)_2$ **6** and $[(Bim)CH_2OMe]_2Ti(NMe_2)_2$ **7** were grown from a saturated benzene solution and by slow evaporation of a chloroform solution, respectively; the structures are shown in Figs. 3 and 4. The molecular structure of **6** shows the metal to have a distorted octahedral coordination [*cis* angles in the range 70.44(5) to 104.31(6)°, and *trans* angles of 155.30(5), 161.97(5) and 165.30(5)°] with the two dimethylamido ligands mutually *cis*; the two most acute *cis* angles are associated with the bite angle of the $(Bim)CH_2NMe_2$ chelate ligands. The coordination sphere is C_1-symmetric with the imidazole nitrogen N(4) lying *trans* to the neutral amine N(21) and the other imidazole donor N(24) positioned *trans* to a dimethylamido N(50) ligand. As was seen in the structure of $[(Bim)CH_2NMe_2]Ti(NMe_2)_3$ **4**, the two five-membered chelate rings in **6** have envelope conformations, with the amino nitrogens N(1) and N(21) lying *ca.* 0.78 and 0.69 Å out of their respective $\{TiC_2N\}$ planes which are coplanar to within *ca.* 0.03 and 0.01 Å, respectively.

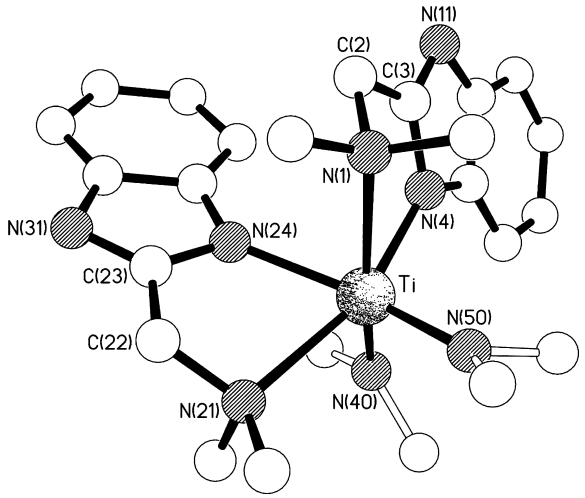


Fig. 3. Molecular structure of **6** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ti–N(1) 2.5180(15), Ti–N(4) 2.0834(14), Ti–N(21) 2.4703(15), Ti–N(24) 2.1630(14), Ti–N(40) 1.9068(14), Ti–N(50) 1.9145(14), N(1)–Ti–N(40) 165.30(5), N(4)–Ti–N(21) 161.97(5), N(24)–Ti–N(50) 155.30(5), N(1)–Ti–N(4) 71.91(5), N(40)–Ti–N(50), 99.78(6), N(21)–Ti–N(24) 70.44(5).

In contrast to **6**, the molecular structure of **7** has a *trans*-N_2, C_2-symmetric structure with the two methoxy donors and the dimethylamido ligands both mutually *cis*. The geometry at the metal center is distorted octahedral with *cis* angles in the range 72.72(4) to 104.87(5)° and *trans* angles of 145.14(4), 168.90(4) and 170.38(4)°, the two most acute *cis* angles are, as expected, associated with the bite angle of the five-membered *N,O* chelate rings. These two chelate rings have envelope conformations with the oxygen lying *ca.* 0.31 and 0.34 Å, respectively out the associated $\{TiC_2N\}$ planes which are each coplanar to within *ca.* 0.06 Å. In this regard the benzimidazolyl ligands in **7** mirror the benzimidazolyl ligand in **4**. The Ti–O bond lengths are noticeably shorter (*ca.* 0.22 Å) than the Ti–N(1) bond in **6**.

Attempts to prepare the diethylamino derivative, $[(Bim)CH_2NEt_2]_2Ti(NMe_2)_2$, afforded only a mixture of products; however crystals suitable for a single-crystal X-ray analysis could be obtained from the reaction mixture. The structure determination revealed an unexpected compound, **A**, in which the α-carbon [C(12)] of one of the diethylamino donors has lost a proton, eliminating $HNMe_2$, and coordinating to the metal centre as a 3-membered {Ti,C,N} metallacyclic ring [20,21] (Fig. 5). This benzimidazolyl ligand is effectively dianionic and tridentate. In contrast to **6**, the benzimidazolyl nitrogen N(4) and N(21) are mutually *trans*. The two five-membered *N,N'* chelate rings both have envelope conformations, but whereas for the N(1), N(4) ring it is the metal that lies *ca.* 0.24 Å out of the $\{C_2N_2\}$ plane (which is coplanar to within *ca.* 0.02 Å), for the N(21), N(24) ring, N(21) lies *ca.* 0.53 Å out of the $\{C_2NTi\}$ plane that is coplanar to within *ca.* 0.02 Å. Unfortunately we were unable to isolate this compound in an analytical pure form, nor synthesize it selectively.

NMR spectroscopy provides a convenient method of assessing the solution state geometries of the $[(Bim)CH_2D]_2Ti(NMe_2)_2$ complexes. For the C_1 symmetric, all-*cis* complex **6**, distinct signals would be expected for each methyl group of the dimethylamino and dimethylamido donors. However, at room temperature, the ^1H NMR spectrum in toluene-d_8 (Fig. 6a) shows a single resonance for the methyl units of the dimethylamino donors, as well as a single resonance for the methyls of the dimethylamido groups, suggesting that an averaging process is taking place in solution. On

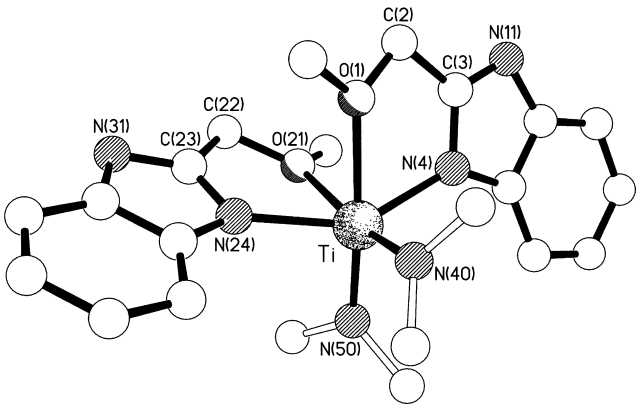


Fig. 4. Molecular structure of **7** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ti–O(1) 2.2150(9), Ti–O(21) 2.2569(10), Ti–N(4) 2.1132(11), Ti–N(24) 2.1093(11),Ti–N(40) 1.9010(11), Ti–N(50) 1.8946(11), O(1)–Ti–N(50) 170.38(4), N(4)–Ti–N(24) 145.14(4), N(40)–Ti–O(21) 168.90(4), O(1)–Ti–N(4) 73.18(4), N(40)–Ti–N(50) 99.09(5), O(21)–Ti–N(24) 72.72(4).

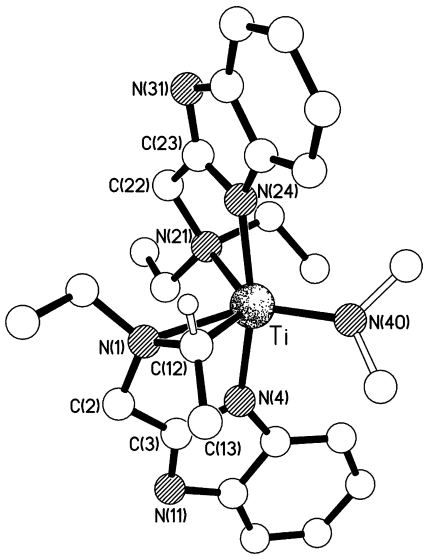


Fig. 5. Molecular structure of **A** (H atoms omitted for clarity). Key bond lengths (Å) and angles (°): Ti–N(1) 2.219(3), Ti–N(4) 2.0799(19), Ti–N(21) 2.306(2), Ti–N(24) 2.0681(19), Ti–N(40) 1.897(2), Ti–C(12) 2.116(3), N(1)–C(12) 1.416(3), N(1)–Ti–N(40) 137.70(9), C(12)–Ti–N(21) 127.39(10), N(24)–Ti–N(4) 164.75(7), N(1)–Ti–N(4) 77.45(8), N(40)–Ti–C(12) 101.68(11), N(21)–Ti–N(24) 74.73(7).

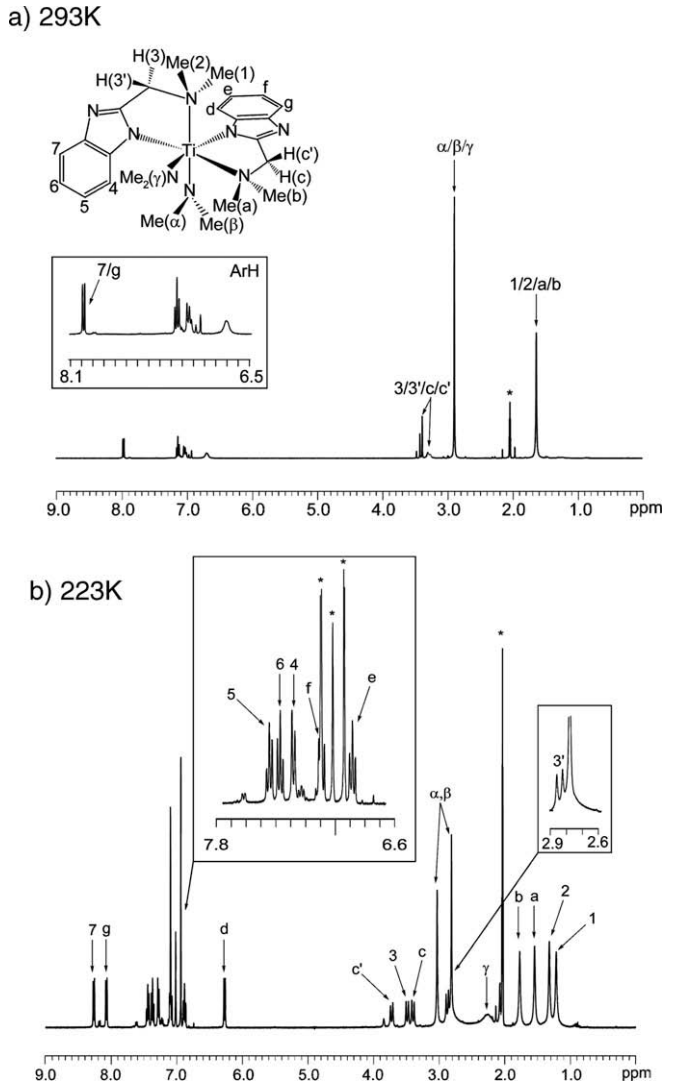
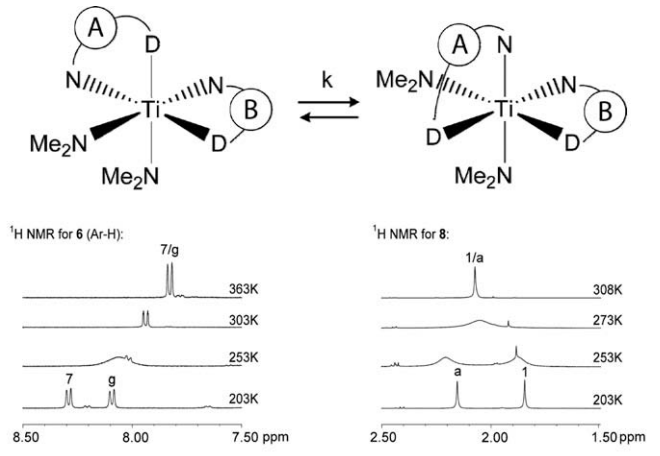


Fig. 6. ^{1}H NMR spectra (toluene-d_8(*)) of **6**: (a) at 293 K; (b) at 223 K.

cooling a sample to 223 K the exchange is slowed sufficiently to distinguish most of the signals attributable to the C_1 symmetric species (Fig. 7b) [22]. To determine the activation parameters for the averaging process, VT ^{1}H NMR spectra were recorded over the temperature range 203–375 K in toluene-d_8. The fluxional process could be followed using a number of resonances but, for ease, signals well-separated from other resonances were chosen. Activation parameters, determined from Eyring plots (see SI) derived from signals attributable to the benzimidazolyl aromatic protons *7* and *g* and the dimethylamino protons *1* and *a*, are tabulated in Fig. 8, along with those for the methylthioether analogue **8**. [23] ^{1}H NMR spectra of **8** at 203 K and 293 K are shown in Fig. 8.

Positive $\Delta S^{\ddagger}$ values were determined for both **6** and **8** indicating that the transition state (TS) is less ordered than the ground state and implicating a dissociative mechanism. Based on these observations, the ligand exchange is believed to arise from dissociation followed by re-association of one of the weakly bound NMe_2 or SMe donors. For **7**, the NMR data at room temperature (see SI) are consistent with a C_2 symmetric species in solution; in this case the symmetry of the complex does not permit the fluxional processes to be followed by NMR spectroscopy.

The observed rates of exchange for **6** and **8**, at 16×10^4 and 1.6×10^4 s^{-1}, respectively, are perhaps the opposite way round to what would be expected intuitively, i.e. it is not unreasonable



	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K.mol)	$\Delta G^{\ddagger}_{298K}$ (kca//mol)	$k_{obs(298K)}$ (10^3s^{-1})
6	21±1	37±4	10±3	16
8	17±1	17±2	12±1	1.6

Fig. 7. Key activation parameters for the exchange of the ligands in **6** and **8**; selected portions of the ^{1}H NMR spectra of **6** (toluene-d_8) and **8** (DCM-d_2) are shown.

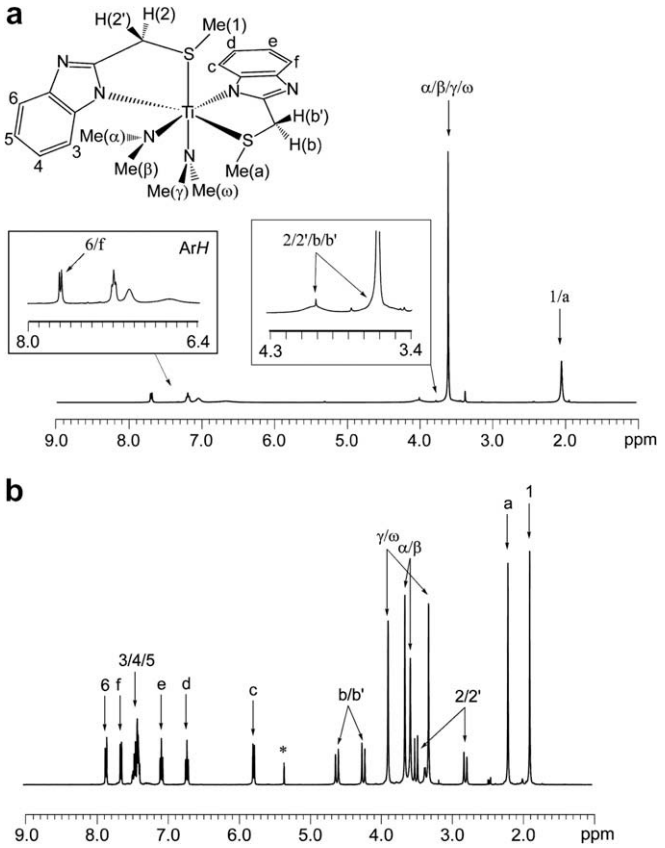


Fig. 8. The ^{1}H NMR spectra (DCM-d_2) of **8** is shown at (a) 293 K and (b) 203 K.

to anticipate a stronger interaction between the titanium center and the nitrogen donor rather than with the softer sulfur donor.

Table 1
Ethylene polymerizations using 2[a].

Run	Precat. (μmol)	Alkylator (mmol)	Cocatalyst (mmol)	Temp. (°C)	Yield (g)	Activity[b]	M_n[c] (kg/mol)	M_w[c] (kg/mol)	M_w/M_n[c]
1	40	TMA (0.4)	MAO (8)	25	0.12	4.0	11.2	263	23.5
2	40	TIBAL (0.4)	MAO (8)	25	0.18	6.0	7.2	235	32.6
3	40		MAO (8)	25	0.16	5.3	10.9	221	20.3
4	40	TMA (0.4)	DMAO (8)	25	0.20	6.7	20.4	525	25.7
5	40	TIBAL (0.4)	DMAO (8)	25	0.50	16.7	27.0	409	15.1
6	20	TIBAL (0.2)	DMAO (4)	25	0.30	20.0	57.5	813	14.1
7	20	TIBAL (0.4)	DMAO (4)	25	0.23	15.3	19.5	297	15.2
8	10	TIBAL (0.2)	DMAO (2)	25	0.14	18.8	48.7	434	8.9
9	10	TIBAL (0.2)	DMAO (2)	45	0.24	32.2	19.8	262	13.2
10	10	TIBAL (0.2)	DMAO (2)	60	0.40	53.7	12.8	161	12.6
11	10	TIBAL (0.2)	DMAO (2)	75	0.50	67.1	9.7	81.2	8.4
12	10	TIBAL (0.2)	DMAO (2)	90	0.35	47.0	6.5	42.5	6.6

[a] Polymerization conditions: Schlenk, toluene (100 ml), 1.5 bar ethylene, 30 min.
[b] Activities g/mmolTi bar h.
[c] Determined by GPC. TMA = trimethylaluminium; TIBAL = triisobutylaluminium; MAO = methylaluminoxane; DMAO = dried MAO.

However, inspection of the activation parameters shows that while $\Delta H^{\ddagger}$ is greater for the N donor complex **6**, $\Delta S^{\ddagger}$ is lower for the thioether donor complex **8** and it is this entropy effect that largely accounts for the rate difference.

2.6. Ethylene polymerization studies

Activation of amido complexes usually requires an alkylating agent to exchange the amido units for alkyl ligands, and an activator to then form the active cationic species. Thus, combinations of triisobutylaluminum (TIBAL) and trimethylaluminum (TMA) with methylaluminoxane (MAO) or dry-methylaluminoxane (DMAO) [24] were screened to optimize the ethylene polymerization conditions for precatalyst **2** (see Table 1).

When MAO was employed as the co-catalyst, with either TMA or TIBAL as co-activators, very low productivities were observed (4–6 g/mmol h bar, runs 1–3). Dried MAO had a beneficial effect on the productivities, with TIBAL affording significantly higher values than TMA (compare run 4 with 5). However, further increases in TIBAL concentration were found to have a detrimental effect on the productivities (runs 6, 7). Interestingly, an increase in temperature was found to have a positive effect (runs 8–12) with the optimal productivity being obtained at 75 °C (67 g/mmol h bar). The molecular weight (M_n) of the polyethylene formed using **2**/MAO was *ca.* 10 000 Da. with broad polydispersity indices (PDI) in all cases. Using DMAO as cocatalyst, the molecular weight is increased and with slightly narrower PDIs.

Using the optimized conditions found for **2**, the bidentate and bis(bidentate) complexes **1–7** were all found to be moderately active for ethylene polymerization (Table 2). No clear effect of the neutral donor was observed, although the bis(bidentate) complexes **6** and **7** were found to have slightly lower productivities than their mono-chelate relatives. Complexes (**1**–**4**, **6** and **7**) afforded molecular weights (M_n) in the range 7–11 kg/mol with PDIs in the range 7.1–9.2.

Table 2
Ethylene polymerization results using complexes **1–7**[a].

Run	Precat.	Yield (g)	Activity[b]	M_n[c] (kg/mol)	M_w[c] (kg/mol)	M_w/M_n[c]
13	1	0.50	67.5	7.5	56.1	7.5
11	2	0.50	67.1	9.7	81.2	8.4
14	3	0.52	69.4	7.1	50.5	7.1
15	4	0.58	77.6	11.1	102	9.2
16	6	0.25	33.6	9.2	73.9	8.2
17	7	0.41	54.5	8.8	62.5	7.1

[a] Polymerisation conditions: Schlenk, 10 μmol cat., 20 equiv. TIBAL, 200 equiv. DMAO, toluene (100 ml), 1.5 bar ethylene, 75 °C, 30 min.
[b] Activities g/mmol h bar.
[c] Determined by GPC.

2.7. Conclusion

A new family of titanium complexes supported by chelating benzimidazolyl-containing ligands has been described along with a study of their solid and solution state behavior. Moderately active catalysts for ethylene polymerization are formed upon treatment of the titanium complexes with TIBAL/dried-MAO. Extensions of these studies to systems containing tridentate benzimidazolyl-derived ligands will be described in a future report.

3. Experimental

All manipulations of water and/or moisture sensitive compounds were performed by means of standard high vacuum Schlenk and cannula techniques. Air and moisture sensitive compounds were stored in a nitrogen filled glove-box at room temperature, unless stated otherwise. All solvents used for air and moisture sensitive compounds were stored in glass ampoules under a nitrogen atmosphere. Pentane, heptane and toluene were dried by passing through a cylinder containing commercially available Q-5 reactant (13 wt.% Cu(II)O on alumina) and activated alumina (pellets, 3 mm), and stored over a potassium mirror. Diethyl ether was distilled from sodium benzophenone ketyl and stored over a potassium mirror. THF and DCM were distilled from potassium metal and powdered calcium hydride, respectively, and stored over 4 Å molecular sieves. All solvents were thoroughly deoxygenated before use. All deuterated NMR solvents were dried and stored over 4 Å sieves. The following precursors were prepared according to published procedures or modifications thereof: $Ti(NMe_2)Cl_2$ [25], $Ti(CH_2Ph)_4$ [26]. $Ti(O^iPr)_4$, $Ti(NMe_2)_4$, and were purchased from Aldrich Chemicals. Ethylene (CP grade) was purified by passing it through an Oxy-trap and gas drier (Alltech Associates). 1-Hexene and norbornene were distilled twice over potassium and stored over a potassium mirror. All other reagents were purchased from Aldrich Chemicals or Acros Organics (and used without further purification) except for MAO which was purchased from Crompton.

NMR spectra were recorded on Bruker AC-250, DRX-400, AM-500, Avance-400 and Avance-500 spectrometers. Mass spectra were run on either a VG Autospec or a VG Platform II spectrometer. Elemental analyses were performed at the London Metropolitan University.

3.1. Synthesis of pro-ligands

General procedure A [18]*:* To a solution of the corresponding amine in a 6:1 mixture of ether and ethanol (10–20 ml) was added 2-chloromethylbenzimidazole in small portions, keeping the temperature below 15 °C. After the reaction had subsided the mixture was heated under reflux for 3 h. After standing overnight at room temperature, ether was added (100–200 ml), the mixture chilled, and the precipitate of ammonium chloride removed. The filtrate was washed with water, dried with sodium sulphate and then evaporated. The product was recrystallised from methanol and dried under vacuum at 60 °C.

General procedure B [8,19]*:* To a solution of the corresponding acid in 4 M HCl (aq.) (100–200 ml) was added *o*-phenylenediamine. The mixture was heated under reflux for 18 h. The pH of the resultant green solution was neutralised with 4 M NH_4OH. The resulting white precipitate was collected, recrystallised three times from methanol/water and then washed with water. The resulting solid was dried under vacuum at 60 °C for 15 h.

3.1.1. 2-(Dimethylaminomethyl)-1H-benzimidazole, (*L1*)

Following the general procedure **A**, reaction of dimethylamine (2.42 g, 53.70 mmol) and 2-chloromethylbenzimidazole (4.47 g, 26.80 mmol) afforded **L1** as a yellow solid. Yield 1.80 g (38.1%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 12.32 (1H, bs, N*H*), 7.48–7.45 (2H, bm, Ar*H*), 7.13–7.10 (2H, m, Ar*H*), 3.64 (2H, s, NCH_2), 2.22 (6H, s, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 152.3 (C_{Ar}q), 142.9 (C_{Ar}q), 134.7 (C_{Ar}q), 121.3 (C_{Ar}H), 118.3 (C_{Ar}H), 111.4 (C_{Ar}H), 57.0 (NCH_2), 45.2 (N(CH_3)$_2$).MS (CI, NH_3) *m/z* = 176 [M+H]$^+$. $C_{10}H_{13}N_3$ (176.23): C 68.54, H 7.48, N 23.98. Found C 68.59, H 7.52, N 24.01%. IR (KBr; cm^{-1}): 2940 (s), 1621 (w), 1589 (w), 1540 (w), 1456 (s), 1273 (s), 746 (s).

3.1.2. 2. 2-(Diethylaminomethyl)-1H-benzimidazole, (*L2*)

Following the general procedure **A**, reaction of diethylamine (12.50 ml, 120.32 mmol) and 2-chloromethylbenzimidazole (10.00 g, 60.02 mmol) gave **L2** as a yellow solid. Yield 7.80 g (63.7%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.88 (1H, bs, N*H*), 7.75–7.72 (1H, bm, Ar*H*), 7.45–7.43 (1H, bm, Ar*H*), 7.28–7.18 (2H, m, Ar*H*), 3.90 (2H, s, NCH_2), 2.65 (4H, q, $^3J_{HH}$ = 7.1 Hz, N(CH_2CH$_3$)$_2$), 1.09 (6H, t, $^3J_{HH}$ = 7.1 Hz, N(CH$_2$CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 154.3 (C_{Ar}q), 143.6 (C_{Ar}q), 133.3 (C_{Ar}q) 122.5 (C_{Ar}H), 121.9 (C_{Ar}H), 119.2 (C_{Ar}H), 110.6 (C_{Ar}H), 52.0 (NCH_2), 45.9 (N(CH_2CH$_3$)$_2$), 12.0 (N(CH$_2$CH_3)$_2$). MS (CI, NH_3) *m/z* = 204 [M+H]$^+$. $C_{12}H_{17}N_3$ (203.28): C 70.90, H 8.43, N 20.67. Found C 70.99, H 8.37, N 20.60%. IR (KBr; cm^{-1}): 2966 (s), 1618 (w), 1560 (w), 1522 (w), 1420 (s), 1274 (s), 753 (s).

3.1.3. 2-(Diisopropylaminomethyl)-1H-benzimidazole, (*L3*)

Following the general procedure **A**, reaction of diisopropylamine (17.10 ml, 120.27 mmol) and 2-chloromethylbenzimidazole (10.00 g, 60.02 mmol) gave **L3** as a yellow solid. Yield 10.00 g (72.0%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 11.76 (1H, bs, N*H*), 7.46–7.44 (2H, m, Ar*H*), 7.09–7.07 (2H, m, Ar*H*), 3.80 (2H, s, NCH_2), 3.00 (2H, sept, $^3J_{HH}$ = 6.6 Hz, N(C*H*(CH$_3$)$_2$), 1.00 (6H, t, $^3J_{HH}$ = 6.6 Hz, N(CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 156.3 (C_{Ar}q), 143.5 (C_{Ar}q), 134.3 (C_{Ar}q), 121.2 (C_{Ar}H), 120.6 (C_{Ar}H), 118.8 (C_{Ar}H), 111.2 (C_{Ar}H), 48.8 (N(*C*H(CH$_3$)$_2$), 43.6 (NCH_2), 20.4 (N(CH$_2$(*C*H$_3$)$_2$). MS (CI, NH_3) *m/z* = 232 [M+H]$^+$. $C_{14}H_{21}N_3$ (231.34): C 72.69, H 9.15, N 18.16. Found C 72.75, H 9.17, N 18.21%. IR (KBr; cm^{-1}): 2969 (s), 1619 (w), 1590 (w), 1527 (w), 1421 (s), 1272 (s), 742 (s).

3.1.4. 2-(Methoxymethyl)-1H-benzimidazole, (*L4*)

Following the general procedure **B**, reaction of methoxyacetic acid (10.00 g, 111.01 mmol) and *o*-phenylenediamine (12.00 g, 110.96 mmol) afforded **L4** as a white solid. Yield 8.00 g (44.3%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 12.51 (1H, bs, N*H*), 7.51–7.49 (2H, bm, Ar*H*), 7.16–7.13 (2H, m, Ar*H*), 4.62 (2H, s, OCH_2), 3.34 (3H, s, OCH_3). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 151.4 (C_{Ar}q), 142.0 (C_{Ar}q), 136.0 (C_{Ar}q), 121.7 (C_{Ar}H), 115.2 (C_{Ar}H), 67.65 (OCH_2), 58.1 (OCH_3). MS (CI, NH_3) *m/z* = 163 [M+H]$^+$. $C_9H_{10}N_2O$ (162.19): C 66.65, H 6.21, N 17.27. Found C 66.57, H 6.25, N 17.34%. IR (KBr; cm^{-1}): 3000 (s), 1619 (w), 1588 (w), 1540 (w), 1434 (s), 1272 (s), 747 (s).

3.1.5. 2-(Methylthiomethyl)-1H-benzimidazole, *L5*

Following the general procedure **B**, reaction of methylthioacetic acid (5.48 g, 51.60 mmol) and *o*-phenylenediamine (5.58 g, 51.60 mmol) gave **L5** as a white solid. Yield 4.00 g (43.3%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 12.32 (1H, bs, N*H*), 7.48–7.46 (2H, bm, Ar*H*), 7.14–7.10 (2H, m, Ar*H*), 3.85 (2H, s, SCH_2), 2.09 (3H, s, SCH_3). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 151.9 (C_{Ar}q), 142.0 (C_{Ar}q), 135.0 (C_{Ar}q), 121.5 (C_{Ar}H), 117.9 (C_{Ar}H), 111.4 (C_{Ar}H), 30.3 (SCH_2), 15.0 (SCH_3). MS (CI, NH_3) *m/z* = 179 [M+H]$^+$. $C_9H_{10}N_2S$ (162.19): C 60.64, H 5.65, N 15.72. Found C 60.56, H 5.74, N 15.74%. IR (KBr; cm^{-1}): 2917 (s), 1623 (w), 1589 (w), 1531 (w), 1428 (s), 1275 (s), 749 (s).

3.2. Synthesis of complexes

General procedure C: A solution of benzimidazolyl pro-ligand in toluene (20–40 ml) was added to a solution of Ti(NMe$_2$)$_4$ in toluene (20–40 ml) at −78 °C. The red mixture was allowed to warm to room temperature over 15 h. The solvent was removed under reduced pressure, the solid washed with pentane (2 × 20 ml) and resulting solid was dried under vacuum.

3.2.1. Synthesis of [2-(Dimethylaminomethyl)-benzimidazolato-κN1]Ti(NMe$_2$)$_3$ (*1*)

Following the general procedure **C**, reaction of 2-(Dimethylaminomethyl)-1H-benzimidazole (0.50 g, 2.85 mmol) and Ti(NMe$_2$)$_4$ (0.72 ml, 2.85 mmol) gave **1** as an orange solid. Yield 0.7 g (67%). ^{1}H NMR (500 MHz, DCM-d_2, 298 K): δ *7.53–7.51* (1H, m, Ar*H*), 7.22–7.20 (1H, m, Ar*H*), 7.07–7.05 (2H, m, Ar*H*), 4.03 (2H, s, NCH_2), 3.23 (18H, s, TiN(CH_3)$_2$), 2.34 (6H, s, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, DCM-d_2, 298 K): δ 162.0 (C_{Ar}q), 146.4 (C_{Ar}q), 143.6 (C_{Ar}q), 121.0 (C_{Ar}H), 120.7 (C_{Ar}H), 117.6 (C_{Ar}H), 116.0 (C_{Ar}H), 61.3 (*C*H$_2$), 48.8 (N(*C*H$_3$)$_2$), 44.3 (TiN(*C*H$_3$)$_2$). $C_{16}H_{30}N_6Ti$ (364.32): C 54.24, H 8.53, N 23.72. Found C 54.18, H 8.48, N 23.72%.

3.2.2. Synthesis of [2-(Diethylaminomethyl)-benzimidazolato-κN1]Ti(NMe$_2$)$_3$ (*2*)

Following the general procedure **C**, reaction of 2-(diethylaminomethyl)-1H-benzimidazole (1.0 g, 5.00 mmol) and Ti(NMe$_2$)$_4$ (1.34 ml, 5.00 mmol) gave **2** as an orange solid. Yield 1.3 g (68%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.66 (1H, bd, $^3J_{HH}$ = 8.0 Hz, Ar*H*), 7.18–7.07 (3H, m, Ar*H*), 4.12 (2H, s, NCH_2), 3.23 (18H, s, N(CH_3)$_3$), 2.68 (2H, q, $^3J_{HH}$ = 7.2 Hz, NCH_2CH$_3$), 1.01 (3H, t, $^3J_{HH}$ = 7.2 Hz, NCH$_2$CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 162.0 (C_{Ar}q), 145.6 (C_{Ar}q), 143.1 (C_{Ar}q), 120.9 (C_{Ar}H), 120.7 (C_{Ar}H), 117.6 (C_{Ar}H), 115.5 (C_{Ar}H), 53.7 (*C*H$_2$), 46.3 (N*C*H$_2$CH$_3$), 45.5 (N(CH$_3$)$_2$), 8.4 (NCH$_2$*C*H$_3$). $C_{18}H_{34}N_6Ti$ (382.37): C 56.54, H 8.96, N 21.98. Found C 56.49, H 8.85, N 21.91%.

3.2.3. Synthesis of [2-(Diisopropylaminomethyl)-benzimidazolato-κN1]Ti(NMe$_2$)$_3$ (*3*)

Following the general procedure **C**, reaction of 2-(diisoprpylaminomethyl)-1H-benzimidazole (1.16 g, 4.95 mmol) and Ti(NMe$_2$)$_4$ (1.32 ml, 4.95 mmol) gave **3** as an orange solid. Yield 1.7 g (83%). ^{1}H NMR (500 MHz, DCM-d_2, 298 K): δ *7.57–7.56* (1H, m, Ar*H*), 7.16–7.14 (1H, m, Ar*H*), 7.05–7.03 (2H, m, Ar*H*), 3.80 (2H, s,

NCH_2), 3.30 (18 H, s, $N(CH_3)_2$), 3.14 (2H, sept, $^3J_{HH}$ = 6.5 Hz, $NCH(CH_3)_2$), 1.04 (12H, d, $^3J_{HH}$ = 6.5 Hz, $NCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, DCM-d_2, 298 K): δ 164.4 ($C_{Ar}q$), 145.8 ($C_{Ar}q$), 142.3 ($C_{Ar}q$), 120.8 ($C_{Ar}q$), 120.6 ($C_{Ar}H$), 118.1 ($C_{Ar}H$), 114.2 ($C_{Ar}H$), 49.7 ($CH(CH_3)_2$), 46.9 (CH_2), 44.4 ($N(CH_3)_2$), 20.8 ($CH(CH_3)_2$). $C_{18}H_{34}N_6Ti$ (382.37): C 58.53, H 9.33, N 20.48. Found C 58.60, H 9.23, N 20.57%.

3.2.4. Synthesis of [2-(Methoxymethyl)-benzimidazolato-κN1]Ti(NMe$_2$)$_3$ (**4**)

Following the general procedure **C**, reaction of 2-(methoxymethyl)-1H-benzimidazole (0.50 g, 1.42 mmol) and $Ti(NMe_2)_4$ (0.38 ml, 1.42 mmol) gave **4** as a yellow solid. Yield 1.00 g (74%). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.67 (1H, bd, Ar*H*), 7.17–7.10 (3H, m, Ar*H*), 5.12 (2H, s, OCH_2), 3.62 (3H, s, OCH_3), 3.28 (18H, s, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K): δ 159.6 ($C_{Ar}q$), 145.9 ($C_{Ar}q$), 142.7 ($C_{Ar}q$), 121.1 ($C_{Ar}H$), 120.8 ($C_{Ar}H$), 117.7 ($C_{Ar}H$), 115.6 ($C_{Ar}H$), 72.4 (OCH_2), 60.6 (OCH_3), 45.7 ($N(CH_3)_2$). $C_{15}H_{27}N_5OTi$ (341.17): C 52.79, H 7.97, N 20.52. Found C 52.75, H 8.01, N 20.48%.

3.2.5. ^1H NMR data for in situ generated [2-(thiomethoxymethyl)-benzimidazolato-kN1]Ti(NMe$_2$)$_3$ (**5**)

^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.66 (1H, bd, Ar*H*), 7.07–7.23 (3H, m, Ar*H*), 3.82 (2H, s, SCH_2), 3.34 (6H, s, $N(CH_3)_2$), 3.15 (12H, s, $N(CH_3)_2$), 1.73 (3H, br. s, SCH_3).

General procedure D: A solution of the benzimidazolyl pro-ligand in toluene (20–40 ml) was added to solution of 1 eq. of the corresponding [N,D]Ti(NMe$_2$)$_3$ complex in toluene at −78 °C. The mixture was allowed to warm to room temperature over 15 h. The solution was filtered and the solvent removed under reduced pressure. The resulting solid was washed with pentane (2 × 20 ml) and dried under vacuum.

General procedure E: A solution benzimidazolyl pro-ligand in toluene (20–40 ml) was added to solution of ½ eq. of $Ti(NMe_2)_4$ in toluene at −78 °C. The mixture was allowed to warm to room temperature over 15 h, filtered, and the solvent was removed under reduced pressure. The resulting solid was washed with pentane (2 × 20 ml) and dried under vacuum.

3.2.6. Synthesis of bis[2-(dimethylaminomethyl)-benzimidazolato-κN1]Ti(NMe$_2$)$_2$ (**6**)

Following the general procedure **D**, reaction of 2-(dimethylaminomethyl)-1H-benzimidazole (0.21 g, 1.2 mmol) and **1** (0.43 ml, 1.2 mmol) gave **6** as a red solid. Yield 0.51 g (88%). ^1H NMR (500 MHz, toluene-d_8, 293 K): δ 7.96 (2H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(7/g)*), 7.14–7.12 (2H, m, Ar*H*), 7.05–7.03 (2H, m, Ar*H*), 6.69–6.67 (1H, bm, Ar*H*), 3.39 (2H, d, $^2J_{HH}$ = 14.0 Hz NCH(*H)(c'/c, 2'/2)*, 3.29 (2H, bd, $^2J_{HH}$ = 14.0 Hz NC(*H*)H *(c'/c, 2'/2)*), 2.88 (12H, s, $NCH_3(\alpha,\beta,\gamma)$), 1.63 (6H, s, $NCH_3(a/b, 1/2)$). ^1H NMR (500 MHz, toluene-d_8, 223K): δ 8.23 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(7)*), 8.04 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(g)*), 7.42 (1H, t, $^3J_{HH}$ = 8.0 Hz, Ar*H(5)*), 7.36 (1H, t, $^3J_{HH}$ = 8.0 Hz, Ar*H(6)*), 7.26 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(4)*), 7.08 (1H, t, $^3J_{HH}$ = 8.0 Hz, Ar*H(f)*), 6.86 (1H, t, $^3J_{HH}$ = 8.0 Hz, Ar*H(e)*), 6.25 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(d)*), 3.71 (1H, d, $^2J_{HH}$ = 14.0 Hz, NC(*H)(c')*H(c)), 3.47 (1H, d, $^2J_{HH}$ = 14.0 Hz, NC(*H)(3)*H(3')), 3.37 (1H, d, $^2J_{HH}$ = 14.0 Hz, NC*H(c)*H(c')), 3.06 (3H, s, $NCH_3(\alpha/\beta)$), 2.85 (1H, d, $^2J_{HH}$ = 14.0 Hz, NC(*H)(3')*H(3)), 2.81 (3H, s, $NCH_3(\alpha/\beta)$), 2.56 (6H, br, $NCH_3(\gamma)$), 1.81 (3H, s, $NCH_3(b)$), 1.56 (3H, s, N $CH_3(a)$), 1.32 (3H, s, $NCH_3(2)$), 1.22 (3H, s, $NCH_3(1)$). $^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8, 223 K): δ 160.5 ($C_{Ar}q$(i)), 160.2 ($C_{Ar}q$(9)), 147.0 ($C_{Ar}q$(j)), 146.6 ($C_{Ar}q$(10)), 143.7 ($C_{Ar}q$(h)), 143.6 ($C_{Ar}q$(8)), 122.0 ($C_{Ar}H$(e)), 121.6 ($C_{Ar}H$(6)), 121.4 ($C_{Ar}H$(5)), 121.0 ($C_{Ar}H$(f)), 119.8 ($C_{Ar}H$(7)), 118.7 ($C_{Ar}H$(g)), 115.5 ($C_{Ar}H$(4)), 114.9 ($C_{Ar}H$(d)), 63.5 (NCH(c)), 63.0 (NCH(3)), 53.3 ($N(CH_3(\alpha/\beta))$, 50.7 (NCH_3(b)), 50.4 (NCH_3(a)), 47.9 (NCH_3(2)), 47.7 (NCH_3(1)), 47.0 ($N(CH_3(\alpha/\beta))$. $C_{24}H_{36}N_8Ti$ (484.46): C 59.50, H 7.49, N 23.13. Found C 59.58, H 7.39, N 22.91%.

3.2.7. Synthesis of bis[2-(methoxymethyl)-benzimidazolato-κN1]Ti(NMe$_2$)$_2$ (**7**)

Following the general procedure **E**, reaction of 2-(methoxymethyl)-1H-benzimidazole (0.36 g, 2.2 mmol) and $Ti(NMe_2)_4$ (0.33 ml, 1.23 mmol) gave **7** as an orange solid. Yield 0.74 g (74%). ^1H NMR (500 MHz, DCM-d_2, 293 K): δ *7.73–7.71* (2H, m, Ar*H*), 7.53–7.52 (2H, m, Ar*H*), 7.23–7.18 (4H, m, Ar*H*), 5.05 (1H, d, $^2J_{HH}$ = 13.0 Hz, C(*H*)$HOCH_3$), 5.03 (1H, d, $^2J_{HH}$ = 13.0 Hz, CH(*H*)OCH_3), 3.57 (12H, s, $N(CH_3)_2$), 3.17 (6H, s, OCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8, 223 K): δ 157.0 ($C_{Ar}q$), 245.9 ($C_{Ar}q$), 141.9 ($C_{Ar}q$), 121.3 (CH_{Ar}), 121.1 (CH_{Ar}), 118.3 (CH_{Ar}), 115.0 (CH_{Ar}), 74.0 (CH_2OCH_3), 61.4 (CH_2OCH_3), 48.7 ($N(CH_3)_2$). $C_{22}H_{30}N_6O_2Ti$ (458.38): C 57.65, H 6.60, N 18.33. Found C 57.60, H 6.56, N 18.18%.

3.2.8. Synthesis of bis[2-(methylthioethermethyl)-benzimidazolato-κN1]Ti(NMe$_2$)$_2$ (**8**)

The reaction was performed on an NMR scale following the general procedure **C** in a drybox; 2-(Methylthiomethyl)-1H-benzimidazole (16.9 mg, 0.1 mmol) was combined with $Ti(NMe_2)_4$ (12 mg, 0.05 mmol) in C_6D_6. ^1H NMR (500 MHz, DCM-d_2, 293 K): δ 7.70 (2H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(6/f)*), 7.20 (2H, bt, $^3J_{HH}$ = 7.0 Hz, Ar*H*), 7.07–7.06 (2H, bm, Ar*H*), 6.69–6.68 (2H, bm, Ar*H*), 4.05–4.03 (2H, bm, NC(*H*)H*(2/2',b/b')*), 3.62 (12H+2H, s + bm, $NCH_3(\alpha,\beta,\gamma,\omega)$+NCH *(H)(2/2',b/b')*), 2.07 (6H, s, $S(CH_3(1,a))$. ^1H NMR (500 MHz, DCM-d_2, 203 K): δ 7.83 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(6)*), 7.62 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(f)*), 7.46–7.36 (3H, m, Ar*H(3,4,5)*), 7.05 (1H, t, $^3J_{HH}$ = 8.0 Hz, Ar*H(e)*), 6.69 (1H, d, $^3J_{HH}$ = 8.0 Hz, Ar*H(d)*), 5.75 (1H, t, $^3J_{HH}$ = 8.0 Hz, Ar*H(c)*), 4.59 (1H, d, $^2J_{HH}$ = 16.0 Hz, NC(*H*)H*(b/b')*), 4.19 (1H, d, $^2J_{HH}$ = 16.0 Hz, NCH(*H)(b/b')*), 3.85 (3H, br, $N(CH_3)CH_3(\gamma/\omega)$), 3.61 (3H, br, $N(CH_3)CH_3(\alpha/\beta)$), 3.53 (3H, br, $NCH_3(CH_3)(\alpha/\beta)$), 3.45 (1H, d, $^2J_{HH}$ = 16.0 Hz, NC(*H*)H*(2/2')*), 3.28 (3H, br, $NCH_3(CH_3)(\gamma/\omega)$), 2.75 (1H, d, $^2J_{HH}$ = 16 Hz, NC(*H*)H*(2/2')*), 2.15 (3H, s, $SCH_3(a)$), 1.85 (3H, s, $SCH_3(1)$). $^{13}C\{^1H\}$ NMR (126 MHz, DCM-d_8, 203 K): δ 161.9 ($C_{Ar}q$(h)), 160.8 ($C_{Ar}q$(8)), 146.7 ($C_{Ar}q$(i)), 145.4 ($C_{Ar}q$(9)), 142.8 ($C_{Ar}q$(g)), 142.5 ($C_{Ar}q$(7)), 121.5 ($C_{Ar}H$(3/4/5)), 121.0 ($C_{Ar}H$(3/4/5)), 120.6 ($C_{Ar}H$(d)), 120.1 ($C_{Ar}H$(e)), 118.1 ($C_{Ar}H$(6)), 117.3 ($C_{Ar}H$(f)), 115.2 ($C_{Ar}H$(3/4/5)), 113.9 ($C_{Ar}H$(c)), 53.44 ($N(CH_3(\gamma/\omega))$, 51.4 ($N(CH_3(\alpha/\beta))$, 46.3 ($N(CH_3(\gamma/\omega))$, 42.4 ($N(CH_3(\alpha/\beta))$, 35.6 (NCH(b/b')), 35.0 (NCH(2/2')), 18.2 (SCH_3(a)), 16.7 (SCH_3(1)).

3.3. Ethylene polymerization procedure

A known quantity of pre-catalyst (5–10 mg) was transferred to a Schlenk flask in a glove-box. Toluene was added (100 ml), followed by a known amount of aluminium alkyl (TMA, TIBAL) and the mixture stirred at room temperature for 15 min. The co-catalyst (MAO, DMAO) was added and the vessel placed in a water bath at the desired temperature and the Schlenk was flushed with 0.5 bar of ethylene (1.5 bar overall pressure). Polymerizations were terminated by venting the overpressure, and addition of 10 ml 2 M $HCl_{(aq)}$. The polyethylene was precipitated from the reaction mixture by addition of MeOH (200 ml). After filtration the polymer was washed with a large quantity of MeOH and dried under vacuum at 60 °C for 12 h.

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Appendix A. Supplementary material

CCDC 671182, 671184, 671185 and 671183 contain the supplementary crystallographic data for compounds **4**, **6**, **7** and **A**. These data can be obtained free of charge from The Cambridge Crystallo-

graphic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.057.

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