

C_2 - and C_s -symmetric diamidodichlorotitanium complexes: Syntheses, structures and 1-hexene polymerization catalysis

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Abstract

The complexes l -[CMe₂{CHMeN(2-Pr^{*i*}-C₆H₄)₂TiCl₂] (**2**) and u -[CMe₂{CHMeN(2,6-Pr^{*i*}₂-C₆H₃)₂TiCl₂] (**3**), C_2 - and C_s -symmetric analogues, respectively, of McConville's C_{2v} hexene polymerization precatalyst [(CH₂)₃{N(2,6-Pr^{*i*}₂-C₆H₃)₂TiCl₂] (**1**), were prepared by high-dilution salt-elimination from the lithium amides and characterized spectroscopically and crystallographically. Complex **2**, though less active than **1**, was a highly active catalyst of polymerization of 1-hexene when activated by MAO. Complex **3** was inactive under similar conditions. NMR analysis confirmed that there were more *mmmm* pentads in polymer produced by **2** than in the statistically atactic material produced by **1**, though the isotacticity index was not high. The results are interpreted in terms of an isotactic/atactic block structure, caused by *syn/anti* fluxion of the two 2-isopropylphenyl rings in **2**. Kinetic profiles and polydispersities were consistent with a slow initiation step involving monomer, followed by rapid propagation, with some chain transfer to aluminium and only a small extent of β -hydride elimination. The rubber-like polymers were indistinguishable by thermal analysis from those prepared by Ziegler–Natta catalyst systems.

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1. Introduction

Despite the half-century elapsed since the seminal discoveries of Ziegler [1] and Natta et al. [2] and the later strides of Kaminsky et al. [3], Bochmann [4], Ewen [5], Chien et al. [6], Brintzinger and co-workers [7], Chen and Marks [8], Coates and Waymouth [9] and others in metallocene catalysis, the employment of group 4 metal ion complexes as catalysts of alkene polymerization remains an intensively researched issue. This is due to the combination of high academic interest with huge commercial importance. More recent workers have sought to replace metallocenes with nitrogen ligated catalysts,

in attempts to control the persistent problem of β -hydrogen elimination from metallocene catalysts, and improve co-monomer incorporation rates. The 'constrained geometry' catalysts commercialized by Dow represent a hybrid situation [10]. Recent developments have been summarized in a number of reviews [11]; Kol and co-workers [12] have recently published data on C_2 -amino-alkoxide-titanium and zirconium complexes giving highly isotactic polyhexene, but pure N-ligation was pioneered by McConville and co-workers [13], with the employment of 1,3-diamido ligands with bulky aryl substituents. The ligand bulk calmed the inherently high reactivity associated with the low electron count and co-ordination number of the metal ion in **1**, and allowed efficient catalysis of 1-hexene polymerization while preventing termination by β -hydrogen transfer. With the use of borate co-catalysts, chain transfer to aluminium was also eliminated, allowing

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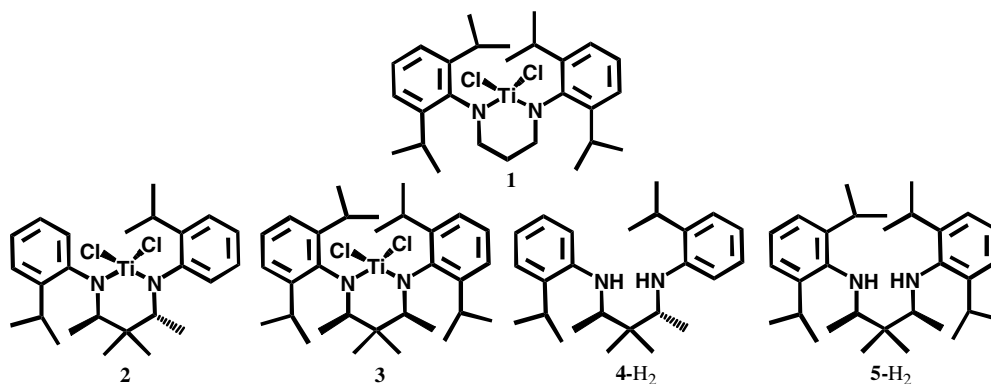
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polymerizations to proceed with living character [14]. While strides have been made in post-metallocene catalysis, including further examples of living systems [15], and systems capable of stereocontrol (though with more modest activities than those found with **1**) [16], within the subclass of 1,3-diamidotitanium complexes, there have been no prior reports of the introduction of lowered symmetry into the ligand backbone. Heretofore, a C_{2v} environment has been prevalent. Given the significance of C_2 and C_s symmetries in metallocene polymerization catalysis [5], we reasoned that it would be desirable to introduce these lowered symmetries to post-metallocene 1,3-diamido systems. We recently disclosed [16] the syntheses of C_2 - and C_s -symmetric variants of the bulky diaryl 1,3-diamido ligands employed by McConville, and here we report the preparation and evaluation as hexane polymerization catalysts of titanium complexes, **2** and **3**, of these new diamido ligands, **4** and **5**.

dilution. Complexes **2** and **3** were thus obtained by concurrent slow addition of 0.03 M hexane solutions of $TiCl_4$ and **4/5-Li**₂ to a stirred reaction flask containing pure *n*-hexane. In this fashion, yields were boosted from 2% to 26% (**2**) or 29% (**3**). Soxhlet extraction of the brown residue failed to boost yields further. Solvent must be rigorously freed of both moisture and oxygen, to guard against the usual hydrolysis, and an unusual oxidative ring-closure of **4/5-Li**₂ to N–N' cyclized pyrazolidines [16].

2.2. Structure

Single crystals of the orange-red compounds **2** and **3** were grown from hexane solution, and subjected to crystallographic analysis. Figs. 1 and 2 depict the molecular structures of C_2 **2** and C_s **3**, respectively.



2. Results and discussion

2.1. Synthesis

Synthesis of **1** has been reported to proceed by elimination of trimethylsilylchloride (TMSCl) from the reaction of $TiCl_4$ with the bis-trimethylsilyl-substituted 1,3-diamine, prepared from reaction of TMSCl with the dilithiated diamine. The bis-trimethylsilylation of **4-Li**₂ and **5-Li**₂, which possess higher degrees of backbone bulk, would not proceed [17], rendering the TMSCl elimination route inapplicable to the case of complexes of **4** and **5**. The alternative direct salt-elimination route, reaction of the diamidolithium species **4-Li**₂ and **5-Li**₂ with $TiCl_4$, was employed. While this method, as McConville has reported [13], gives large amounts of a brown powder by-product, tentatively formulated as lithium halide adducts of the desired species, and/or co-ordination polymers resulting from non-chelate bridging of the diamido ligands, we found that the yield could be boosted by performing the reaction at higher

The gross structural features of **1**, **2** and **3** proved, as expected, to be similar. While all are monomeric, pseudo-tetrahedral at titanium, and essentially planar at nitrogen, there are significant differences in chelate ring conformations, and slight differences in metrical parameters. Selected bond lengths and angles for **2** and **3** are shown in Table 1, with previously published data for **1** for comparison.

There is a small increase in the chelate ring C–N distances on increasing bulk as in **3**. This is probably a reflection of the chelate ring conformations. In **1**, there is a slight boat conformation. This is more pronounced in **2**, giving rise to one axial and one equatorial methyl group, as well as the inevitable axial/equatorial positions in the Me_2C hinge unit, and a sharpening of the N–Ti–N angle. The phenyl groups are pointed away from the bough of the boat. In **2**, there is an *anti*-disposition of isopropyl groups on each ring, re-enforcing the pseudo- C_2 symmetry of the reaction space [18]. The phenyl group adjacent to the axial ring in **2** is tilted significantly from the near-orthogonal angles found in **1**,

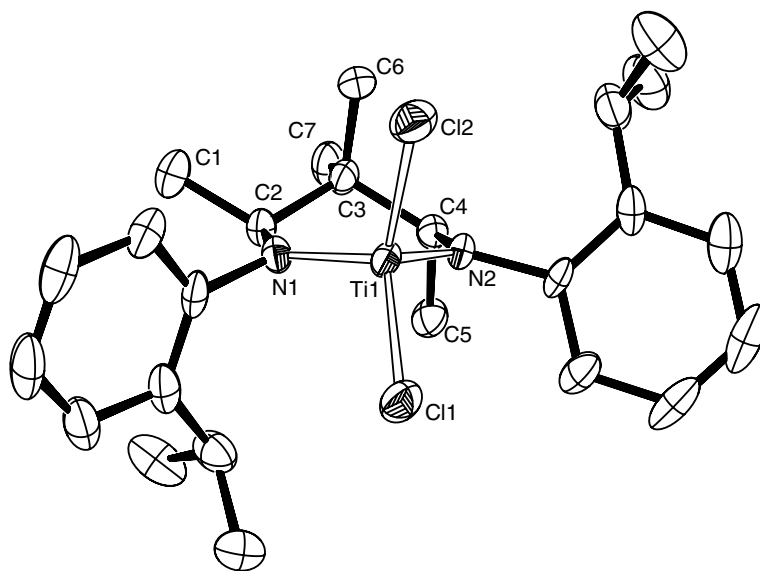


Fig. 1. ORTEP representation (50% ellipsoids) of the molecular structure of **2**. Hydrogen atoms are omitted.

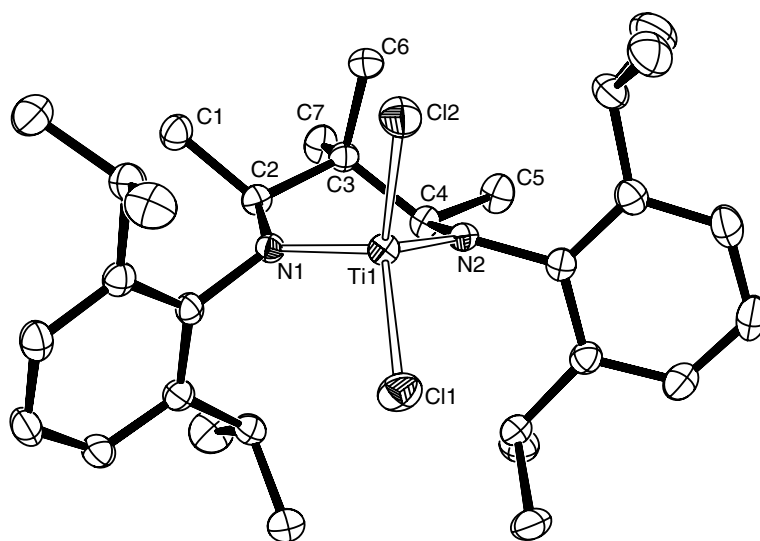


Fig. 2. ORTEP representation (50% ellipsoids) of the molecular structure of **3**. Hydrogen atoms are omitted.

Table 1
Selected bond lengths (Å) and angles (°) for **2** and **3**, with comparative data for **1**

	1 ^a	2	3
Ti–N	1.839(5) 1.856(5)	1.831(4) 1.847(4)	1.855(2) 1.860(2)
Ti–Cl	2.257(2) 2.240(2)	2.2705(14) 2.2596(14)	2.2382(6) 2.2777(6)
N–C (chelate ring)	1.465(8) 1.469(8)	1.474(6) 1.483(6)	1.496(2) 1.502(2)
Cl–Ti–Cl	107.77(9)	108.11(6)	107.00(2)
N–Ti–N	99.2(2)	92.46(16)	97.70(2)
Aryl ring tilts ^b	90, 86	82, 65	80, 74

^a Data from Ref. [13].

^b Defined as the angle between C(CN)₂Ti and aryl mean ring planes.

suggesting the possibility of induction of asymmetry to polymer chain propagation. The deviation from orthogonality is less dramatic in **3**, because both the 1- and the 3-methyl groups can be accommodated in equatorial positions. This serves to fix the metallacycle conformation, since boat inversion would place a total of three methyl groups in axial positions. Because of this fixing, the two methyls in the 2-position are sharply distinct in the ¹H NMR spectrum of **3**. For **2**, this resonance is broad. Furthermore, there is a single, broad resonance in ¹H and ¹³C NMR for the 1- and 3-methyls in **2**. Ring inversion is therefore occurring. This would exchange the axial-equatorial disposition of the 1- and 3-methyls. However, a symmetry-equivalent conformer would be generated only if the isopropylphenyl groups

Table 2
Activities of **2** in 1-hexene polymerization

Run	Run time (min)	Yield (g)	Activity ^c (g mmol ⁻¹ h ⁻¹)	M _w (g mol ⁻¹)	M _n (g mol ⁻¹)	PDi
1 ^a	15	0.46	920	17100	7380	2.3
2 ^a	30	1.03	1030	23500	11600	2.0
3 ^a	45	2.34	1560	22600	11300	2.0
4 ^a	60	4.00	2000	25100	12700	2.0
6 ^a	120	8.80	2200	29900	15400	1.9
7 ^b	60	0	–	–	–	–

^a 60 °C.

^b 22 °C.

^c Conditions: 2.0 μmol of **2** and 500 equiv. of MAO in 30 ml of 1-hexene and 2 ml of hexane at 1 atm.

rotated in concert. Attempts to probe these processes by low-temperature ¹H NMR spectroscopy were inconclusive; only general broadening was observed before precipitation.

It is clear from the presence of two isopropyl methine resonances, and four isopropyl methyl resonances, that the aryl rings in **3** are fixed in solution on the NMR spectroscopic timescale. This was also seen in **1** [13]. It is not possible to say whether this is the case in **2**. The most significant structural difference in **2** and **3** versus **1** comes from the Me₂C hinge unit. Whether or not the ring is flexing faster than the monomer insertion rate, at least one 3-methyl group will always be axial, blocking the titanium reaction space in concert with the *ortho* isopropyl groups on the aryl rings.

2.3. 1-Hexene polymerization

The studies of Ewen in metallocene polymerization teach that a C₂-symmetry reaction space should produce isotactic poly(α-olefin) whereas a *meso* reaction space may yield atactic polymer [5]. To test whether the C_s and C₂ symmetries of the post-metallocene precatalysts **2** and **3** could offer similar control [19], or, for **2** block tacticity arising from slow *syn/anti* isomerization of isopropyl group position, polymerization of 1-hexene was studied. This substrate was chosen because it allowed direct comparison with the original published polymeriza-

tion data for **1** [13]. Activity results are shown in Table 2.

The products were invariably highly viscous oils with rubber-like character. They exhibited a T_g indistinguishable from that of Ziegler–Natta polyhexene (–52 °C) [21]. The effect of the extra substitution on polymerization activity is dramatic. Complex **3**, which shares with **1** the 2,6-bis-isopropyl-phenyl substituents on nitrogen, is inactive for MAO-catalyzed polymerization of 1-hexene. Notional removal of one of the isopropyl groups on each phenyl generates **2** from **3**. Activities for **2** reached 2.2 kg (mmol Ti)⁻¹ h⁻¹, which is defined as ‘very high’ on the Gibson scale [11]. However, it is lower and quite different in character from that found in **1**. As well as being less spectacularly active [**1** was reported to give activities of 115 kg (mmol Ti)⁻¹ h⁻¹], there are differences in kinetic profile [13]. Activity data for **1** was collected over the first 30 s of polymerization time. Similar treatment of catalyst **2** gave an initially slow rate, even after pre-contacting catalyst and co-catalyst pairings prior to the addition of monomer; the activity vs time plot (Fig. 3) shows that the activity of the catalyst system increased during the first hour of the polymerization run before starting to plateau during the second hour.

Colour change from orange-red to yellow was observed almost instantaneously on mixing precatalyst **2** with MAO, suggesting that Me/Cl exchange was as fast as would be expected from similar cases [13]. Detailed studies of 1-hexene polymerization using zirconium metallocenes indicate that initiation is defined as the insertion of the first monomer unit, and *not* the generation of ion pairs [22]. Subsequent insertions, i.e. chain propagation events, are significantly faster. Furthermore, the rate-limiting step may be co-ordination of monomer with partial displacement of anion, rather than migratory insertion itself [22]. It is possible that a similar situation obtains for **2**, but with a more dramatic difference in rate between first insertion (initiation) and propagation. Initiation is *much* slower in **2** than in **1**, suggesting that first insertion/monomer addition is hindered by the backbone methylation. It was also found that activity was severely curtailed unless temperatures were raised to 60 °C. This is consistent with an activation step requiring partial separation of the putative

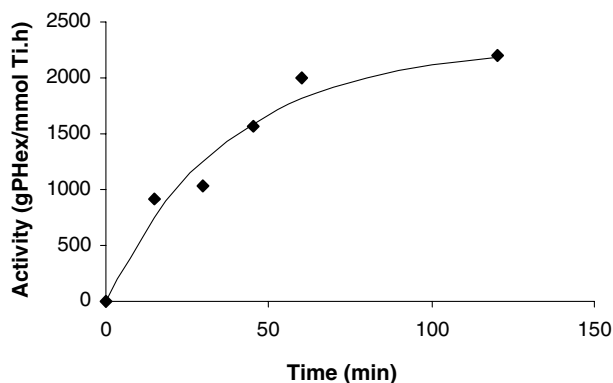
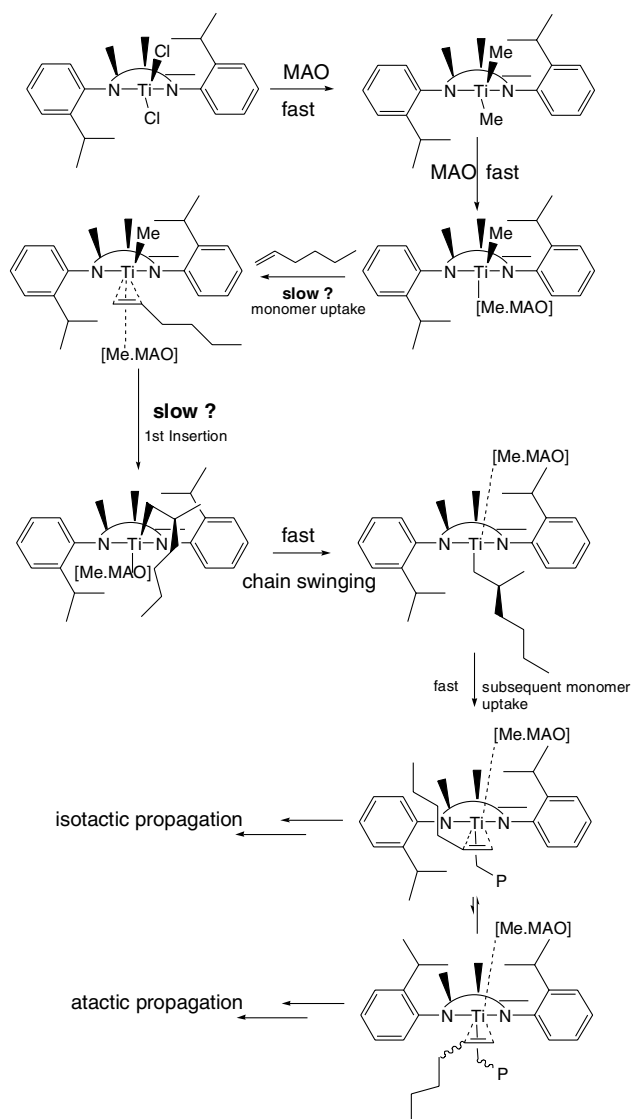
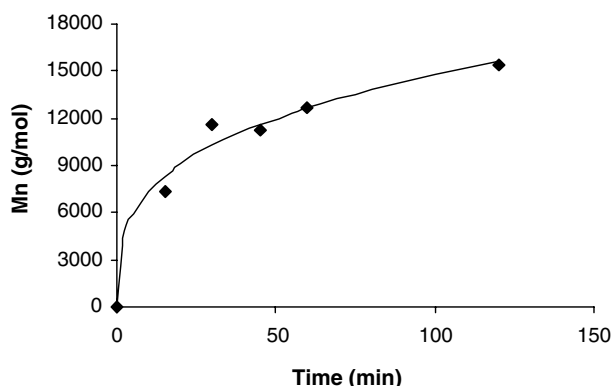


Fig. 3. Activity vs. time graph for hex-1-ene polymerization using **2**/MAO.



Scheme 1.

LTiMe/(MeMAO) ion pair. As the polymer grows, the active site becomes more encumbered, and the interaction with (MeMAO) anion becomes weaker. It is plausi-

Fig. 4. M_n vs. time graph for hex-1-ene polymerization using **2**/MAO.

ble that it is only cleaved sufficiently under the influence of incoming monomer, since the dramatic reduction in activity on moving from **1** to **2** to the more bulky **3** implies an associative process. This is consistent with modern understanding from metallocene systems [11,22]. For **3**, monomer is prevented by the excessive bulk from access to the tight ion pair, whereas for **2** some access is available. This model of slow initiation from tightly paired LTiMe/(MeMAO) followed by rapid propagation from more loosely paired LTi(polymeryl)/(MeMAO), as outlined in Scheme 1, also fits the modest polydispersities of around 2, which decrease with longer reaction time.

Plotting the number average molecular weight, M_n , of the polyhex-1-ene against time (Fig. 4) shows that M_n is not directly proportional to time. The polymerization is not 'living'.

Several factors may contribute to the non-linear relationship between M_n and time: (i) slow catalyst initiation, (ii) increasing reaction mixture viscosity (particularly after 1 h of reaction) and (iii) polymer chain termination. The molecular weights were not high. End-group analysis by quantitative ^{13}C NMR using a 10 mm probe revealed that there was in fact some termination by β -hydride elimination. This termination mechanism (reportedly absent from **1**), which plagues otherwise highly active metallocene [5] and FI catalysts [23], was however restricted even with a single isopropyl group on each aryl substituent. The moderate polydispersities and molecular weights were suggestive of chain transfer to aluminium as was seen in **1**. Such a mechanism generates new active sites, and so fits the increasing productivity/time relation. However, living character has been reported in (atactic) propene polymerization using **1** and dried MAO under conditions similar to those used for **2** and **3**, but for the temperature (0°C), vide infra [24].

The ^{13}C NMR (Fig. 5) revealed that there was a difference in microstructure between the polyhexenes produced by **1** and **2**. The polymer produced by **2**, while being far short of the very high degrees of isotacticity available with *ansa*-metallocenes [20], displayed significantly greater extents of *mmmm* pentad, ca. 40%, than that produced by **1**. It is clear that *mm* triads predominate.

The relative abundances of the various pentads would seem consistent with a mixture such as might be expected if the *anti*-disposition of isopropyl groups displayed in the solid state structure of **2**, giving isotactic segments, were exchanging with a *syn*-disposition, giving atactic segments. Though we were able to partially resolve heptad splitting on the *mmmm* pentad (Fig. 5), the pentad and heptad structure of polyhexene is not well-enough resolved or characterised to allow a less tentative interpretation. The rubber-like, amorphous nature of all polyhexenes

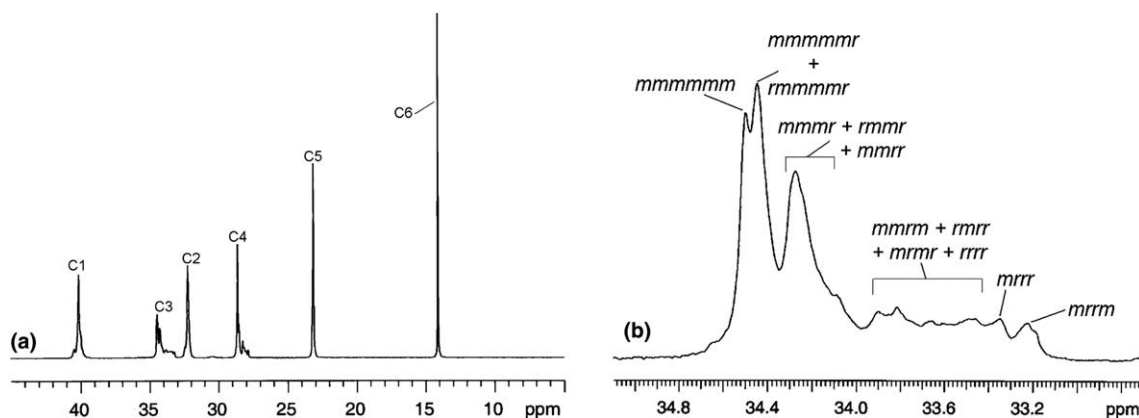


Fig. 5. (a) ^{13}C NMR of polyhexene produced by **2** at 126 MHz in deuteriochloroform at 35 °C; (b) expansion of the C3 peak, with pentad and heptad labelling.

[12,20–23] precludes an alternative diagnosis of block tacticity by mechanical property or microscopic study. This level of control was attained at higher temperatures than have been used in other stereoselective 1-hexene polymerizations [20–22]. While one might expect better isotacticity index at lower temperature, the polymerization did not proceed at room temperature. In those cases where it did proceed at room temperature with good selectivity, higher co-ordination numbers, and hence electron counts, than those in **1**, **2** and **3** were prevalent, which would lower the barrier to anion partial separation [12,22].

In summary, the extra backbone substitution has partially hindered the polymerization pathway for **2** and closed it down fully for **3**. This finding fits with intriguing results published by Soga and co-workers [25]. They found when using **1** with $\text{Al}(\text{Bu}^i)_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, for propylene polymerization, at low propylene pressures they obtained predominantly atactic polypropylene; at high pressures, or in the presence of the non-polymerizable additive cyclohexene, they obtained isotactic polypropylene, with much improved turnover, and with a polymer microstructure indicative of enantiomeric site control. Leaving aside for a moment the issue of how the C_{2v} precatalyst **1** could give rise to an enantiomeric site, the most direct conclusion must be that there are two competing mechanisms, the more productive of which must involve two moles of co-ordinated monomer (or one of spectator alkene cyclohexene) in the transition state. Such ‘trigger’ mechanisms are not new, and in metallocene catalysis there have been several instances of rate laws with an order in monomer greater than 1 [26]. While Busico et al. has published a persuasive critique of the trigger hypothesis of metallocene catalysis based upon polymer microstructure analysis [27], in the case of the diamidotitanium complexes, even the microstructure data fits the trigger hypothesis [25]. Indeed, given the putative bis-amido-polymeryl-alkene Ti(IV) intermediate electron count of only 12, the need for a further pair of elec-

trons to free the hold of the metal on the substrate monomer and polymer chain seems reasonable. Further, a second propene monomer cannot be incorporated without destroying the C_{2v} symmetry of the reaction space, thus providing an explanation for the apparent enantiomeric site. However, it is doubtful whether such a mechanism could occur for the bulkier substrate 1-hexene; indeed no stereocontrol was found in neat 1-hexene by McConville and co-workers [13]. The extra methyl substitution in the backbone of **3** relative to **1** must wholly preclude the possibility of such a mechanism by blocking the site of co-ordination of alkene, perhaps even of a single molar equivalent of alkene. The polyhexene stereocontrol achieved by **2**, while being more modest than that achieved for polypropylene at high pressure by **1** [25], must have been due to the enantiomeric site generated by the C_2 ligand. The hypothesis of block tacticity due to *syn/anti* exchange of isopropyl groups in **2** is now ripe for testing with polypropylene, where precedent exists from the bis-indenyl systems of Waymouth [9].

3. Experimental

3.1. General

All manipulations were carried out under a protective argon blanket, either in a double manifold argon/vacuum line or argon-filled recirculating glovebox. Argon was dried over phosphorus pentoxide supported on vermiculite.

Solvents were freshly distilled under argon from suitable drying agents (hexane, toluene, benzene–sodium/benzophenone). Hex-1-ene was distilled from Na/K alloy and stored over 4 Å molecular sieves. CDCl_3 was stored over 4 Å molecular sieves.

Diamines **4-H₂** and **5-H₂** [16], and crystalline MAO [28] were prepared according to literature procedures.

Unless otherwise stated, all other reagents were obtained from standard commercial vendors and used as received.

Melting points were determined in glass capillaries under argon. Elemental analyses were performed by the microanalytical group in the Chemistry Department at UMIST. Moisture sensitive samples were provided in ampoules sealed under argon.

^1H NMR spectra were recorded on a Bruker DPX 300 MHz NMR spectrometer. ^{13}C NMR spectra (^1H decoupled) were recorded on a Bruker DPX 300 MHz spectrometer operating at 75 MHz, except for polymer NMR which were recorded on a Varian Unity 500 MHz NMR spectrometer operating at 126 MHz. Chemical shifts are given in ppm and referenced to residual H solvent shifts or ^{13}C NMR solvent shifts.

Single crystal X-ray diffraction data were collected on either *Nonius MACH3* (**2**) or *Nonius Kappa CCD* (**3**) diffractometers. Data collection, solution and refinement procedures and programs have been detailed for both geometries in a previous paper [29].

Infrared spectra were recorded on a Nicolet Nexus-FTIR spectrometer using NaCl plates and nujol mulls. GPC analyses of polyhex-1-ene samples were performed by Rapra Technology Ltd., Shawberry, Shrewsbury, on a Polymer Laboratories PL220 instrument in 1,2,4-trichlorobenzene at 160 °C, relative to narrow polystyrene standards (PLgel guard plus 2 × mixed bed-B, 30 cm, 10 μm). DSC analyses were carried out using a Mettler Toledo DSC822^c/200 STAR^c system.

3.2. Synthesis

3.2.1. Dichloro[2,4-(2,6-diisopropylphenylamino)-3,3-dimethyl-2,4-pentane]-titanium(IV) (**3**)

BuLi (11.8 ml of a 1.58 M hexane solution, 18.7 mmol) was added dropwise to a stirring solution of **5-H₂** (4.00 g, 8.9 mmol) in hexane (30 ml) at 22 °C. After overnight stirring, further hexane (220 ml) was added to the resultant solution of **5-Li₂**. The **5-Li₂** hexane solution and a solution of TiCl_4 (0.97 ml, 8.9 mmol, diluted in 250 ml of hexane) were added separately, dropwise at the same rate over 1 h at 22 °C, to a 1 L flask containing hexane (200 ml). The reaction mixture was stirred vigorously throughout the addition period. A brown precipitate formed after 15 min. The mixture was stirred overnight. The mixture was filtered and the brown filtrand was washed with hexane (3 × 10 ml). The majority of the solvent (600 ml) was removed under reduced pressure from the orange filtrate to yield an orange solid which was isolated by filtration. Recrystallization of the orange solid from hexane yielded dark orange diamond-shaped crystals of **3**. Yield: 1.44 g, 29%. M.p.: 288–290 °C. ^1H NMR (300 MHz; C_6D_6): δ 0.79 (6H, bd, $^3J_{\text{HH}} = 6.8$ Hz, $\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 0.92 (3H, s, $\text{NCHMeC}(\text{MeMe})\text{CHMeN}$); 1.29 (6H, d,

$^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 1.30 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 1.50 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 1.61 (3H, s, $\text{NCHMeC}(\text{MeMe})\text{CHMeN}$); 1.69 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 3.26 (2H, septet, $^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 4.03 (2H, septet, $^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 4.55 (2H, q, $^3J_{\text{HH}} = 6.8$ Hz, $\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 7.17–7.30 (6H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; C_6D_6): δ 16.4 ($\text{NCHMeC}(\text{MeMe})\text{CHMeN}$); 16.6 ($\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 24.6, 25.1, 26.5 and 27.3 (MeCHMe); 27.5 ($\text{NCHMeC}(\text{MeMe})\text{CHMeN}$); 28.7 and 30.2 (MeCHMe); 48.2 ($\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 78.8 ($\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 125.9 and 130.1 (aromatic CH); 144.1, 148.1 and 153.5 ($\text{C}(\text{CHMe}_2)$ and C-NH, aromatic carbons). Elemental analysis, Calcd. for $\text{TiCl}_2\text{C}_{31}\text{H}_{48}\text{N}_2$: C, 65.6; H, 8.5; N, 4.9; Cl, 12.5. Found: C, 65.4; H, 8.7; N, 4.7; Cl, 12.1%.

3.2.2. Dichloro[2,4-(2-isopropylphenylamido)-3,3-dimethyl-2,4-pentane]titanium(IV) (**2**)

Complex **2** was prepared as for **3**, using **4-H₂** in place of **5-H₂**. In this case, a fine suspension of **4-Li₂** was formed in hexane. A brown precipitate gradually formed when **4-Li₂** reacted with TiCl_4 . The mixture was stirred at 22 °C overnight. The mixture was filtered and the brown filtrand was washed with hexane (3 × 5 ml). The solvent was removed under reduced pressure from the bright orange filtrate to yield an orange oil. The ^1H NMR of the orange oil indicated that the oil contained **2**, contaminated with 1,2-(2-isopropylphenyl)-3,4,4,5-tetramethyl pyrazolidine. The orange oil was redissolved in hexane (5 ml) and cooled to –20 °C. An orange-red solid, **2**, precipitated. The solid was filtered off and recrystallised from toluene/hexane (4:1) at –25 °C to yield deep orange cuboid crystals. M.p.: 180–182 °C. Yield: 0.72 g, 26%. ^1H NMR (300 MHz; C_6D_6): δ 0.89 (6H, just-resolved d, $\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 1.20 (6H + 6H, d and s overlapped, $\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$ and MeCHMe); 1.40 (6H, d, $^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 3.55 (2H, septet, $^3J_{\text{HH}} = 6.8$ Hz, MeCHMe); 3.71 (2H, apparent bs, $\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 6.95–7.43 (8H, non-first-order m, aromatic protons). ^{13}C NMR (75 MHz; C_6D_6): δ 15.4 ($\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 23.7 (MeCHMe); 24.8 ($\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 25.6 (MeCHMe); 28.1 (MeCHMe); 47.4 ($\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$); 126.5, 127.7, 130.1 and 130.9 (aromatic CH); 147.8 ($\text{C}(\text{CHMe}_2)$, aromatic C); unobserved ($\text{NCHMeC}(\text{Me}_2)\text{CHMeN}$) and (C-NH, aromatic C). Elemental analysis, Calcd. for $\text{TiCl}_2\text{C}_{25}\text{H}_{36}\text{N}_2$: C, 62.1; H, 7.5; N, 5.8; Cl, 14.7. Found: C, 62.3; H, 7.6; N, 5.8; Cl, 14.3%.

3.3. Crystallography

A dark orange diamondoid crystal of $\text{C}_{31}\text{H}_{48}\text{Cl}_2\text{N}_2\text{Ti}$ (**3**) (0.20 × 0.15 × 0.10 mm³) was mounted on a Nonius

Kappa CCD diffractometer, $\lambda = 0.71073 \text{ \AA}$. 35 707 reflections were measured ($2.98^\circ < \theta < 27.49^\circ$) of which 7001 were independent ($R_{\text{int}} = 0.0706$). Monoclinic cell, $P2_1/c$, $a = 18.8665(3)$, $b = 9.9678(2)$, $c = 18.0529(3) \text{ \AA}$; $\beta = 115.532(1)^\circ$; $Z = 4$. Data underwent semi-empirical absorption correction ($\mu = 0.475$) from equivalents. Refinement on F^2 with hydrogens treated using a riding model gave $R_1 = 0.0402$ (for 5384 reflections with $I > 2\sigma I$), $wR_2 = 0.1011$ (all data).

A deep orange cuboid crystal of $\text{C}_{25}\text{H}_{36}\text{Cl}_2\text{N}_2\text{Ti}$ (**2**) ($0.35 \times 0.20 \times 0.20 \text{ mm}^3$) was mounted on a Nonius MACH 3 diffractometer, $\lambda = 0.71073 \text{ \AA}$. 4836 reflections were measured ($1.68^\circ < \theta < 24.98^\circ$) of which 4514 were independent ($R_{\text{int}} = 0.0446$). Monoclinic cell, $P2_1/c$, $a = 8.4806(10)$, $b = 20.172(2)$, $c = 15.487(2) \text{ \AA}$; $\beta = 102.791(10)^\circ$; $Z = 4$. An absorption correction (Ψ -Scan, $\mu = 0.552$) was applied. Refinement on F^2 with hydrogens treated using a riding model gave $R_1 = 0.0619$ (for 3006 reflections with $I > 2\sigma I$), $wR_2 = 0.1686$ (all data).

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, No. 251184 for **2**, No. 251183 for **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [fax: +44 (1223) 336 033] or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

4. Hexene polymerization

Homogeneous 1-hexene polymerizations were carried out in a 50 ml Schlenk reactor vessel which was heated to the required temperature using a circulating water jacket. The titanium(IV) diamide precatalyst (2 μmol in 2 ml of hexane) and 500 equiv. of solid MAO were premixed for 1 h at 22°C . The catalyst mixture quickly turned from orange to yellow. The catalyst system was then heated to the required temperature and hex-1-ene (30 ml, at the same temperature) was added. The resulting pale yellow solution was stirred for the required time period and then quenched with 1.0 M HCl (20 ml). The organic phase was extracted with hexane ($3 \times 50 \text{ ml}$), the solvent removed and the viscous polymer dried under vacuum at 22°C for 8 h. The weight of the polymer was used in the calculation of activity and a small amount was used for GPC and DSC analyses. In DSC experiments (heating rate: $5.0^\circ\text{C min}^{-1}$), all the polyhex-1-ene samples showed an exothermic perturbation at -52°C . Polymer ^{13}C NMR spectra were recorded from 10% wt solutions in CDCl_3 , in 10 mm tubes at 35°C ; all showed identical ^{13}C NMR spectra.

The polymer yields and molecular weights are recorded in Table 2.

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