

Imido Titanium Ethylene Polymerization Catalysts Containing Triazacyclic Ligands

Nico Adams,[†] Henricus J. Arts,[‡] Paul D. Bolton,[†] Dan Cowell,[§] Stuart R. Dubberley,[†] Nic. Friederichs,[⊥] Craig M. Grant,[§] Mirko Kranenburg,^{||} Andrew J. Sealey,[†] Bing Wang,[⊥] Paul J. Wilson,[#] Martin Zuideveld,[‡] Alexander J. Blake,[#] Martin Schröder,[#] and Philip Mountford^{*,†}

Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K., DSM Research, P.O. Box 18, 6160 MD Geleen, The Netherlands, Millennium Pharmaceuticals Research and Development Ltd., Granta Park, Great Abington, Cambridge CB1 6ET, U.K., SABIC Europe, Research & Development, P.O. Box 319, 6160AH Geleen, The Netherlands, DSM Elastomers, Global R&D, P.O. Box 1130, 6160 BC Geleen, The Netherlands, and School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.

Received April 13, 2006

A comprehensive account of the synthesis, properties, and evaluation of a wide range of ethylene homopolymerization catalysts derived from imido titanium compounds supported by the triazacyclic ligands Me₃[9]aneN₃ and R₃[6]aneN₃ is described (Me₃[9]aneN₃ = 1,4,7-trimethyltriazacyclononane; R₃[6]aneN₃ = 1,3,5-trimethyl- or 1,3,5-tris(*n*-dodecyl)triazacyclohexane). Conventional preparative-scale reactions afforded the triazacycle-supported imido titanium compounds Ti(NR)(Me₃[9]aneN₃)Cl₂ (R = ^tBu (**1**), 2,6-C₆H₃Me₂, 2,6-C₆H₃ⁱPr₂, Ph, C₆F₅, or CH₂Ph (**6**)). Solid phase-supported analogues of **1** and **6** (linked by either the macrocycle or imido ligand to a 1% cross-linked polystyrene support) and representative Me₃[6]aneN₃ solution phase systems Ti(NR)(R₃[6]aneN₃)Cl₂ (R = Me or *n*-dodecyl) were also synthesized. At ambient temperature, solution phase Me₃[9]aneN₃ catalyst systems were more active for ethylene polymerization (methyl aluminoxane (MAO) cocatalyst) than their solid phase-supported or Me₃[6]aneN₃ analogues. A library of 41 other triazacyclononane-supported catalysts was prepared by the semiautomated, sequential treatment of Ti(NMe₂)₂Cl₂ with RNH₂ and Me₃[9]aneN₃. The ethylene polymerization capabilities of 46 compounds of the type Ti(NR)(Me₃[9]aneN₃)Cl₂ were evaluated at 100 °C (MAO cocatalyst) and compared in representative cases to the corresponding productivities at ambient temperature. Whereas either bulky N-alkyl or N-aryl imido substituents in the compounds Ti(NR)(Me₃[9]aneN₃)Cl₂ were sufficient to give highly active catalysts at ambient temperature, only those with bulky N-alkyl groups excelled at 100 °C. Polymer end group analysis indicated that polymeryl chain transfer to both AlMe₃ and ethylene monomer is an active mechanism in these systems. The use of MAO pretreated with BHT-H (BHT-H = 2,6-di-*tert*-butyl-4-methylphenol) led to higher productivities, increased polymer molecular weights, and more polymer chain unsaturations, but productivity decreased when a large excess of BHT-H was used. The reactions of the well-defined alkyl species Ti(N^tBu)(Me₃[9]aneN₃)Me₂, [Ti(N^tBu)(Me₃[9]aneN₃)(μ-Me)₂AlMe₂]⁺, and [Ti(N^tBu)(Me₃[9]aneN₃)Me]⁺ with BHT-H were examined, and the aryloxide compound [Ti(N^tBu)(Me₃[9]aneN₃)(BHT)][BAr^F₄] was isolated (Ar^F = C₆F₅). The X-ray structures of Ti(NR)(Me₃[9]aneN₃)Cl₂ (R = ^tBu, 2,6-C₆H₃Me₂, 2,6-C₆H₃ⁱPr₂, Ph, C₆F₅) and Ti(NR)(Me₃[6]aneN₃)Cl₂ (R = 2,6-C₆H₃ⁱPr₂, Ph, C₆F₅) are reported. The perfluorophenyl imido titanium compounds both exhibit well-defined supramolecular structures based on C···F intermolecular interactions.

Introduction

Homogeneous olefin polymerization catalysts have been a continuing focus of academic and industrial interest, and a diverse number of systems have been investigated with the purpose of optimizing catalyst performance and polymer properties.^{1–23} Of particular relevance to our present contribution is the ability of certain transition metal imido compounds (general

type L_nM=NR) to act as Ziegler-type olefin polymerization catalysts. The first systems of this type were derived from bis-(imido)chromium dichloride and dialkyl compounds Cr(NR)₂X₂ (R = ^tBu or 2,6-C₆H₃ⁱPr₂; X = Cl, Me, or CH₂Ph),^{24,25} and a number of other group 4, 5, and 6 systems have since been

* To whom correspondence should be addressed. E-mail: philip.mountford@chem.ox.ac.uk.

[†] University of Oxford.

[‡] DSM Research.

[§] Millennium Pharmaceuticals Research and Development Ltd.

[⊥] SABIC Europe, Research & Development.

^{||} DSM Elastomers.

[#] University of Nottingham.

(1) Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 47.

(2) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(3) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

(4) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413.

(5) Okuda, J.; Eberle, T. In *Metalloenes: synthesis, reactivity, applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: New York, 1998; Vol. 1.

(6) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429.

(7) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(8) Coates, G. W. *J. Chem. Soc., Dalton Trans.* **2002**, 467.

(9) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1.

reported.²³ A notable feature of group 6 bis(imido) and group 5 cyclopentadienyl-imido catalysts of the type $M(NR)_2X_2$ and $CpM(NR)X_2$, respectively, is their isolobal relationship²⁶ (discussed and documented elsewhere^{27–30}) with the quintessential group 4 metallocene-type systems Cp_2MX_2 . As part of our broad research program in titanium imido chemistry^{31–33} we have targeted compounds of the type $Ti(NR)(fac-L_3)Cl_2$ ($fac-L_3$ = triazacyclohexane,³⁴ triazacyclononane,^{35–37} or related^{35,38} tris-(3,5-dimethylpyrazolyl)methane^{39,40}) as potential polymerization precatalysts. These systems are also isolobal analogues of group 4 metallocenes, but their properties and reactivity depend significantly on the identity of the particular $fac-L_3$ ligand and imido N-substituent, R. Very recently, we described the synthesis, properties, and DFT bonding analysis of well-defined macrocycle-supported *tert*-butyl imido titanium monoalkyl cations $[Ti(N^tBu)(Me_3[9]aneN_3)R]^+$ ($R = Me$ or CH_2SiMe_3 ; $Me_3[9]aneN_3 = 1,4,7$ -trimethyltriazacyclononane), along with stoichiometric C–H bond and solvent activation reactions, insertion reactions, and addition product with $AlMe_3$.^{41,42} In this contribution we describe in full our studies of the ethylene

(10) Murphy, V.; Bei, X.; Boussie, T. R.; Brümmer, O.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M. K.; Longmire, J. M.; Schoemaker, J. A. W.; Turner, H. W.; Weinberg, H. *Chem. Rec.* **2002**, *2*, 278.

(11) Hagen, H.; Boersma, J.; van Koten, G. *Chem. Soc. Rev.* **2002**, *31*, 357.

(12) Erker, G. *Chem. Commun.* **2003**, 1469.

(13) Suzuki, Y.; Terao, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1493.

(14) Gambarotta, S. *Coord. Chem. Rev.* **2003**, *237*, 229.

(15) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(16) Leung, W.-H. *Eur. J. Inorg. Chem.* **2003**, 583.

(17) Mitani, M.; Saito, J.; Ishii, S.; Nakayama, Y.; Makio, H.; Matsukawa, N.; Matsui, S.; Mohri, J.; Furuyama, R.; Terao, H.; Bando, H.; H., T.; Fujita, T. *Chem. Rec.* **2004**, *4*, 137.

(18) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982.

(19) Gromada, J.; Carpentier, J.-F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397.

(20) Nakayama, Y.; Yasuda, H. *J. Organomet. Chem.* **2004**, *689*, 4489.

(21) Stephan, D. W. *Organometallics* **2005**, *24*, 2548.

(22) Speiser, F.; Braunstein, P.; Saussine, L. *Acc. Chem. Res.* **2005**, *38*, 784.

(23) Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, *347*, 355.

(24) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Clegg, W.; Elsegood, M. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1709.

(25) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Little, I. R.; Marshall, E. L.; Ribeiro da Costa, M. H.; Mastroianni, S. *J. Organomet. Chem.* **1999**, *591*, 78.

(26) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *21*, 711–800.

(27) Williams, D. S.; Schofield, M. H.; Anhaus, J. T.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6728.

(28) Glueck, D. S.; Green, J. C.; Michelman, R. I.; Wright, I. N. *Organometallics* **1992**, *11*, 4221.

(29) Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, *12*, 4560.

(30) Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1994**, 1607.

(31) Mountford, P. *Chem. Commun.* **1997**, 2127.

(32) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216–217*, 65.

(33) Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, *38*, 839.

(34) Wilson, P. J.; Blake, A. J.; Mountford, P.; Schröder, M. *J. Organomet. Chem.* **2000**, *600*, 71.

(35) Wilson, P. J.; Blake, A. J.; Mountford, P.; Schröder, M. *Chem. Commun.* **1998**, 1007.

(36) Male, N. A. H.; Skinner, M. E. G.; Bylikin, S. Y.; Wilson, P. J.; Mountford, P.; Schröder, M. *Inorg. Chem.* **2000**, *39*, 5483.

(37) Gardner, J. D.; Robson, D. A.; Rees, L. H.; Mountford, P. *Inorg. Chem.* **2001**, *40*, 820.

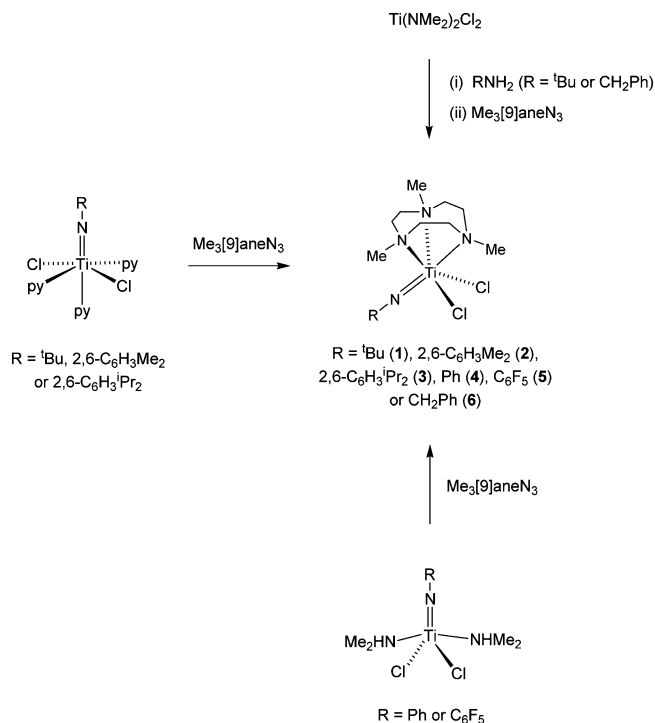
(38) Wilson, P. J.; Blake, A. J.; Mountford, P.; Schröder, M. *Inorg. Chim. Acta* **2003**, *345*, 44.

(39) Lawrence, S. C.; Skinner, M. E. G.; Green, J. C.; Mountford, P. *Chem. Commun.* **2001**, 705.

(40) Bigmore, H. R.; Dubberley, S. R.; Kranenburg, M.; Lawrence, S. C.; Sealey, A. J.; Selby, J. D.; Zuideveld, M.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2006**, 436.

(41) Bolton, P. D.; Clot, E.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3313.

Scheme 1. Synthetic Routes to Complexes of the Type $Ti(NR)(Me_3[9]aneN_3)Cl_2$



polymerization capabilities of two families of macrocycle-supported $Ti(NR)(fac-L_3)Cl_2$ systems. Part of this work has been communicated.^{35,43}

Results and Discussion

Synthesis of Selected Precatalysts $Ti(NR)(Me_3[9]aneN_3)Cl_2$. The available synthetic routes to the compounds $Ti(NR)(Me_3[9]aneN_3)Cl_2$ (**1–6**) are summarized in Scheme 1. Preliminary work focused on the tris(pyridine) complexes $Ti(NR)(Cl_2)(py)_3$ ($R = {}^tBu, 2,6-C_6H_3Me_2, 2,6-C_6H_3Pr_2$) reported by us previously⁴⁴ and shown to be very versatile precursors to a range of new imido titanium compounds by pyridine and/or chloride ligand substitution.^{31,33} Reaction of these compounds with $Me_3[9]aneN_3$ in CH_2Cl_2 at room temperature gave deep orange- or brown-colored solutions from which the target compounds $Ti(NR)(Me_3[9]aneN_3)Cl_2$ ($R = {}^tBu$ (**1**), $2,6-C_6H_3Me_2$ (**2**), $2,6-C_6H_3Pr_2$ (**3**)) were isolated in 85–87% yield. The analytical and spectroscopic data for these compounds, each of which has been structurally characterized, were consistent with the C_s symmetric structures proposed in Scheme 1. Full details are given in the Experimental Section. Encouraged by the preliminary ethylene polymerization capabilities of some of these compounds (see below), we decided to target a wider range of such complexes, with a particular emphasis on developing routes suitable for varying the imido N-substituent using semiautomated methods for the synthesis of a precatalyst library.

Although successful for the synthesis of compounds **1–3**, tris(pyridine) complexes of the general type $Ti(NR)Cl_2(py)_3$ were considered to be less suitable for the preparation of a wide range

(42) Bolton, P. D.; Clot, E.; Adams, N.; Dubberley, S. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2006**, *25*, 2806.

(43) Adams, N.; Arts, H. J.; Bolton, P. D.; Cowell, D.; Dubberley, S. R.; Friederichs, N.; Grant, C.; Kranenburg, M.; Sealey, A. J.; Wang, B.; Wilson, P. J.; Cowley, A. R.; Mountford, P.; Schröder, M. *Chem. Commun.* **2004**, 434.

(44) Blake, A. J.; Collier, P. E.; Dunn, S. C.; Li, W.-S.; Mountford, P.; Shishkin, O. V. *J. Chem. Soc., Dalton Trans.* **1997**, 1549.

of triazacyclononane-supported precatalysts for the following reasons. Only alkyl imido homologues (in particular *tert*-butyl derivatives) are readily accessible from TiCl_4 and an excess of RNH_2 since the side-products RNH_3Cl cannot be readily separated when R is an aryl group.⁴⁴ Although aryl imides $\text{Ti}(\text{NAr})\text{Cl}_2(\text{py})_3$ (Ar = aryl) can be prepared from $\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3$ by treatment with ArNH_2 , the products can be rather insoluble except for bulky Ar groups (e.g., 2,6-disubstituted phenyl rings) and also sometimes retain the displaced $^t\text{BuNH}_2$, thereby forcing further recrystallizations in the presence of an excess of pyridine. The pyridine *trans* to $\text{Ti}=\text{NR}$ is labile and can be readily lost to form rather insoluble μ -imido-bridged dimers $\text{Ti}_2(\mu\text{-NR})_2\text{Cl}_4(\text{py})_4$.^{44–46} To avoid all of these issues and to provide an alternative set of potential synthons in imido titanium chemistry, we recently reported a family of monomeric, five-coordinate compounds $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ (R = alkyl, aryl).⁴⁷ All of the 13 new compounds described (6 of which were structurally characterized) had good solubilities, and each was formed in excellent yield by the reaction of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ with the appropriate primary amine RNH_2 . The solid phase-supported synthon $\text{Ti}(\text{NCH}_2\text{PS})\text{Cl}_2(\text{NHMe}_2)_2$ (“PS” represents 1% cross-linked polystyrene resin) was also prepared.

Scheme 1 shows that both **1** and the new compounds $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (R = Ph (**4**), C_6F_5 (**5**), CH_2Ph (**6**)) can be prepared either from already-isolated $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ (R = Ph or C_6F_5 , giving **4** (99% yield) or **5** (79%)) or in a “one-pot” reaction from $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ and RNH_2 , first generating $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ in situ prior to addition of the macrocycle (R = ^tBu or CH_2Ph , giving **1** (85%) or **6** (96%)). The new compounds were fully characterized, and the data for samples of **1** prepared via the “one-pot” route were identical to those for the sample prepared from $\text{Ti}(\text{N}^t\text{Bu})\text{Cl}_2(\text{py})_3$. Conducting the reactions in C_6H_6 allowed for facile isolation of **1** and **4–6** since the solubilities of the compounds $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ in this solvent are rather low and they tend to precipitate in analytically pure form. As discussed further below, the “one-pot” synthetic route was eventually adopted for the synthesis of a library of such catalysts.

X-ray Crystal Structures of $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$. The solid-state structures of the compounds $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (R = ^tBu (**1**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**2**), 2,6- $\text{C}_6\text{H}_3^i\text{Pr}_2$ (**3**), Ph (**4**), C_6F_5 (**5**)) have been determined. The molecular structures of **1–4** are given in Figure 1, and a view of **5** is provided in the Supporting Information. The supramolecular structure of **5** and selected intermolecular $\text{C}\cdots\text{F}$ contacts are shown in Figure 2, and selected intramolecular bond distances and angles for all five structures are listed in Table 1. All five molecular structures feature a κ^3 -coordinated $\text{Me}_3[9]\text{aneN}_3$ ligand bound to an approximately octahedral titanium center, the coordination sphere of which is completed by two mutually *cis* chloride ligands and an imido group. The solid-state structures are consistent with the solution NMR data assuming free rotation about the $\text{N}(1)\text{–C}(10)$ bonds of **2** and **3** in solution.

In general terms, the distances and angles around the metal centers and within the ligands are within previously reported ranges,^{48,49} and the approximately linear imido linkages

($\text{Ti}(1)\text{–N}(1)\text{–C}(10) = 166.3(2)\text{–}171.22(12)^\circ$) suggest that these groups are acting as four-electron donors to the metal.^{50,51} The $\text{Ti}(1)\text{–N}(9)$ distances are all consistently longer than $\text{Ti}(1)\text{–N}(3)$ and $\text{Ti}(1)\text{–N}(6)$ due to the strong *trans* influence of imido ligands. The five structures form a useful homologous series for the comparison of the ground-state structural effects of the different types of imido ligands, which vary in their electron-releasing/withdrawing and steric properties. In general, the observed structural variations are analogous to those found in other homologous series of imido titanium dichloride compounds, namely, $\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3$ (R = ^tBu , Ph, 4- $\text{C}_6\text{H}_4\text{Me}$, 4- $\text{C}_6\text{H}_4\text{NO}_2$)⁴⁴ and $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ (R = ^iPr , Ph, C_6F_5 , 2- $\text{C}_6\text{H}_4\text{R}$ (R' = CF_3 , ^tBu)).⁴⁷

The orientation of the 2,6-disubstituted aryl substituents in **2** and **3** are somewhat different than those in **4** and **5** (Supporting Information, Figure S1). In the former compounds the ring carbons lie approximately in the same plane as $\text{Ti}(1)$, $\text{N}(9)$, and the midpoints between $\text{Cl}(1)$ and $\text{Cl}(2)$. In **4** and **5** the ring carbons are best considered to be approximately perpendicular to this plane. Inspection of the structures suggests that the observed orientation of the 2,6- $\text{C}_6\text{H}_3\text{R}_2$ (R = Me, ^iPr) rings best minimizes nonbonded contact between the *ortho* R-groups and the macrocycle N-methyl groups *cis* to the imido ligand (i.e., C(31) and C(61), Figure 1).

The *tert*-butyl imido ligand in **1** has the shortest $\text{Ti}(1)\text{–N}(1)$ bond, while the longest are found for the electron-withdrawing C_6F_5 or bulkier 2,6-disubstituted phenyl ligands. The electron-withdrawing effect of C_6F_5 is also presumably responsible for the comparatively short $\text{N}(1)\text{–C}(10)$ distance compared to those in **2–4**. The longest and shortest $\text{Ti}\text{–Cl}$ distances are found for the *tert*-butyl- and C_6F_5 -substituted systems, respectively, consistent with their relative electron-releasing properties, but there is no particular trend in $\text{Ti}\text{–Cl}$ distances for compounds **2–4**. Similarly, while the *trans* influences (see Table 1 for definition) of the imido ligands appear to be smallest for the C_6H_5 - and C_6F_5 -substituted imido ligands, there is no obvious trend among compounds having the bulkier substituents (**1–3**), and in fact it is the comparatively shorter $\text{Ti}(1)\text{–N}(9)$ distances in particular for **4** and **5** that appear to be mainly responsible for the smaller *trans* influences of the imido ligands in these two cases. The origins of the *trans* influence in octahedral imido titanium complexes have been described previously,⁵² and smaller influences are expected for less electron-releasing imido substituents. There appear to be no systematic trends in the angles subtended at the titanium centers. For instance the $\text{Cl}\text{–Ti}\text{–Cl}$ angles in **1** ($95.75(4)^\circ$) and **5** ($95.77(2)^\circ$) are experimentally identical despite the significantly different $\text{Ti}\text{–Cl}$ distances (av 2.393 and 2.357 Å, respectively). Notwithstanding any possible influences of intermolecular/crystal packing forces on the intramolecular distances and angles discussed, it appears that the different imido substituents have significant but comparatively small structural effects on the precatalysts.

While molecules of $\text{Ti}(\text{NPh})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (**4**) do not exhibit any particular supramolecular arrangement, those of $\text{Ti}(\text{NC}_6\text{F}_5)(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (**5**) form infinite stacks linked by $\text{C}(\delta^+)\cdots\text{F}(\delta^-)$ contacts in the range 3.078(2)–3.212(2) Å with four carbons (C(11), C(12), C(13), C(14)) and two fluorines (F(2), F(3)) of each C_6F_5 ring contributing (Figure 2). Intermolecular interactions between perfluorophenyl rings have

(45) Hazari, N.; Cowley, A. R.; Mountford, P. *Acta Crystallogr.* **2004**, *E60*, m1844.

(46) Nielson, A. J.; Glenny, M. W.; Rickard, C. E. *J. Chem. Soc., Dalton Trans.* **2001**, 232.

(47) Adams, N.; Bigmore, H. R.; Blundell, T. L.; Boyd, C. L.; Dubberley, S. R.; Sealey, A. J.; Cowley, A. R.; Skinner, M. E. G.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 2882.

(48) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746 (The United Kingdom Chemical Database Service).

(49) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 1&31.

(50) Cundari, T. R. *Chem. Rev.* **2000**, *100*, 807.

(51) Parsons, T. B.; Hazari, N.; Cowley, A. R.; Green, J. C.; Mountford, P. *Inorg. Chem.* **2005**, 8442.

(52) Kaltsoyannis, N.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1999**, 781.

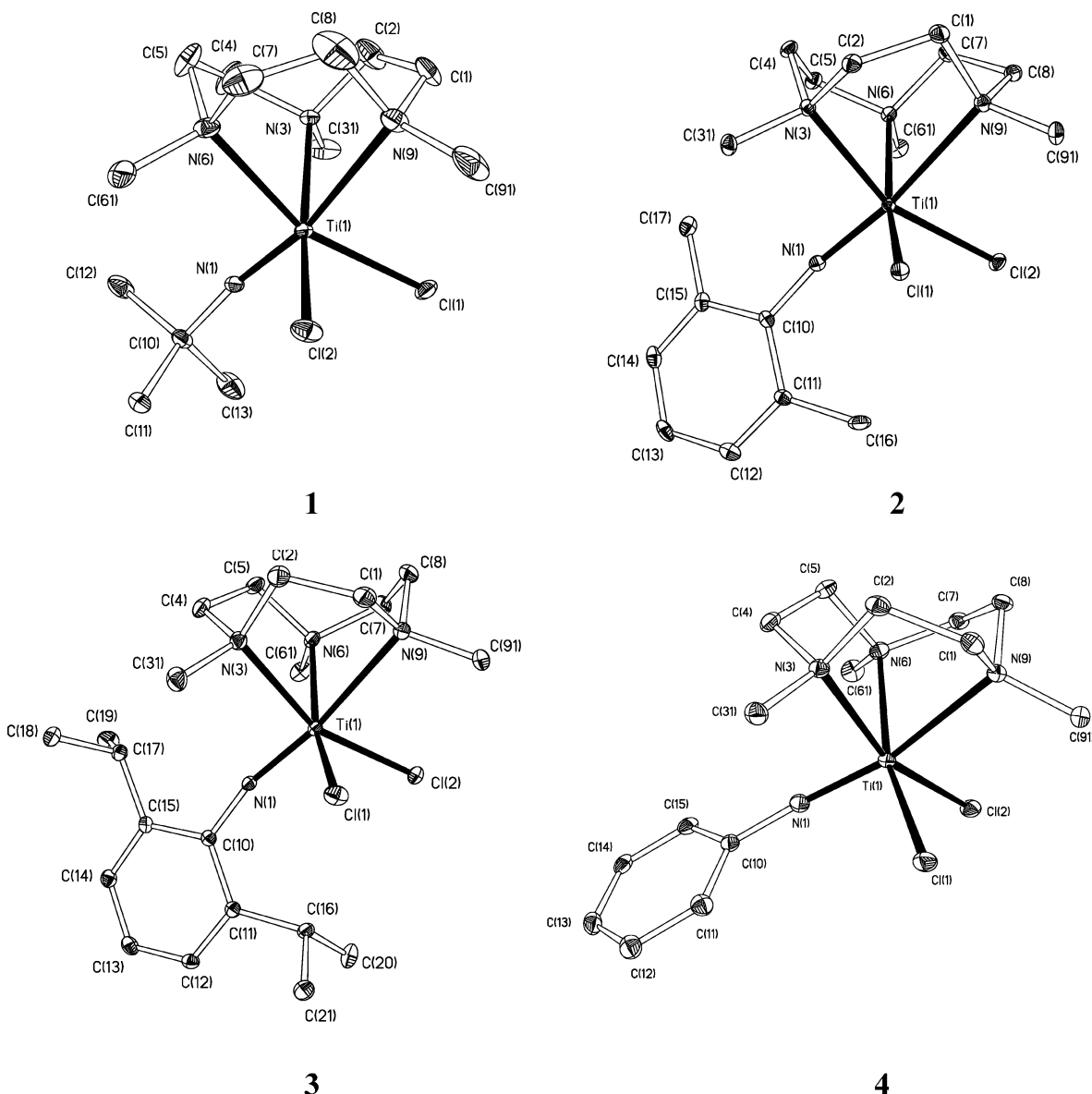


Figure 1. Displacement ellipsoid plots (20% probability) of $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ ($\text{R} = \text{}^i\text{Bu}$ (**1**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**2**), 2,6- $\text{C}_6\text{H}_3\text{}^i\text{Pr}_2$ (**3**), Ph (**4**)). H atoms are omitted.

recently received increased attention both computationally and experimentally.^{53–58} It has been proposed that intermolecular interactions between perfluorinated aromatic rings are slightly *more* attractive than the very well established ones between their hydro analogues (due mainly to an increased van der Waals component),⁵³ and the structures of **4** and **5** appear to support this. Note that in **5** the adjacent perfluorophenyl rings are considerably offset from each other (see Figures S2 and S3 in the Supporting Information).

Polystyrene-Supported Precatalysts. Immobilized single-site olefin polymerization catalysts have been of much interest because of their relevance to the industrial implementation of

this technology and the control of polymer morphology that can be achieved. A wide range of inorganic materials (e.g., silica, alumina, zeolites, magnesium chloride) and polymeric supports (e.g., polysiloxanes, polystyrene, polyolefins, dendrimers) has been used.^{59,60} Among these latter supports, polystyrene has attracted much attention due to its relative inertness, ease of functionalization, and the control afforded of the bead size and porosity. Polystyrene-supported zirconocene,⁶¹ constrained geometry,⁶² other group 4 half-sandwich,^{63–66} and iron or nickel

(53) Lorenzo, S.; Lewis, G. R.; Dance, I. *New J. Chem.* **2000**, *24*, 295.

(54) Blanchard, M. D.; Hughes, R. P.; Concolino, T. E.; Rheingold, A. L. *Chem. Mater.* **2000**, *12*, 1604.

(55) Deck, P. A.; Kroll, C. E.; Hollis, W. G.; Fronczek, F. R. *J. Organomet. Chem.* **2001**, *637–639*, 107.

(56) Deck, P. A.; Lane, M. J.; Montgomery, J. L.; Slobodnick, C.; Fronczek, F. R. *Organometallics* **2000**, *19*, 1013.

(57) Thornberry, M. P.; Slobodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 5352.

(58) Hair, G. S.; Cowley, A. H.; Gorden, J. D.; Jones, J. N.; Jones, R. A.; Macdonald, C. L. B. *Chem. Commun.* **2003**, 424.

(59) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347.

(60) Severn, J. R.; Chadwick, J. C.; Duchateau, R.; Friedrichs, N. *Chem. Rev.* **2005**, *105*, 4073.

(61) Stork, M.; Koch, M.; Klapper, M.; Mullen, K.; Gregorius, H.; Rief, U. *Macromol. Rapid Commun.* **1999**, *20*, 210.

(62) Kasi, R. M.; Coughlin, E. B. *Organometallics* **2003**, *22*, 1534.

(63) Kitawaga, T.; Uozumi, T.; Soga, K.; Takata, T. *Polymer* **1997**, *38*, 615.

(64) Zhu, H.; Jin, G.-X.; Hu, N. *J. Organomet. Chem.* **2002**, *655*, 167.

(65) Barrett, A. G. M.; de Miguel, Y. R. *Tetrahedron* **2002**, *58*, 3785.

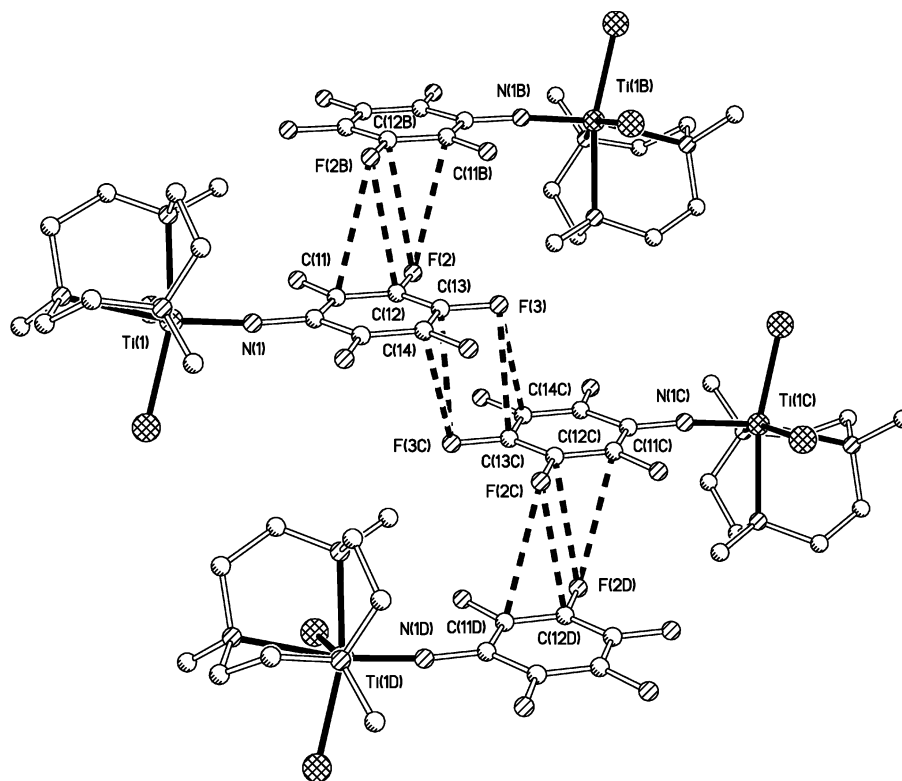


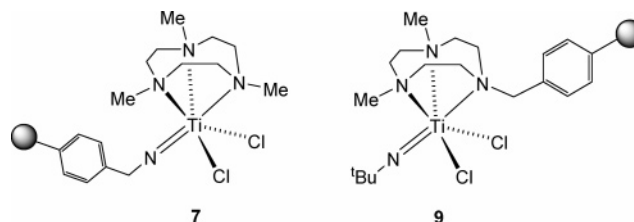
Figure 2. Partial packing diagram for $\text{Ti}(\text{NC}_6\text{F}_5)(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (**5**). H atoms are omitted and all atoms are drawn as spheres of arbitrary radius. Symmetry operators: B, $[2-x, -y, 1-z]$; C, $[2-x, -1-y, 1-z]$; D, $[x, y-1, z]$. The dashed lines indicate the closest points of intermolecular contact: $\text{C}(11)\cdots\text{F}(2\text{B}) = 3.198(2)$ Å; $\text{C}(12)\cdots\text{F}(2\text{B}) = 3.114(2)$ Å; $\text{C}(13)\cdots\text{F}(3\text{C}) = 3.078(2)$ Å; $\text{C}(14)\cdots\text{F}(3\text{C}) = 3.212(2)$ Å.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (R = ^tBu (**1**), 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**2**), 2,6- $\text{C}_6\text{H}_3\text{Pr}_2$ (**3**), Ph (**4**), C_6F_5 (**5**))

parameter	1	2	3	4	5
Ti(1)–N(1)	1.694(2)	1.736(2)	1.735(2)	1.717(2)	1.7420(13)
Ti(1)–N(3)	2.265(3)	2.281(2)	2.271(2)	2.2651(14)	2.2723(13)
Ti(1)–N(6)	2.270(3)	2.252(2)	2.267(2)	2.2787(14)	2.2532(12)
Ti(1)–N(9)	2.437(3)	2.426(2)	2.441(2)	2.3921(14)	2.3868(12)
Ti(1)–Cl(1)	2.394(1)	2.3889(8)	2.3613(10)	2.3832(5)	2.3565(4)
Ti(1)–Cl(2)	2.3915(9)	2.3787(9)	2.3904(10)	2.3859(5)	2.3581(4)
N(1)–C(10)	1.454(4)	1.387(3)	1.396(3)	1.387(2)	1.365(2)
<i>trans</i> influence (Å) ^a	0.172(4)	0.145(3)	0.170(3)	0.127(2)	0.114(2)
N(1)–Ti(1)–N(3)	97.3(1)	98.57(9)	98.77(9)	92.35(6)	93.38(5)
N(1)–Ti(1)–N(6)	96.6(1)	99.5(1)	99.47(9)	99.25(6)	96.39(5)
N(1)–Ti(1)–N(9)	169.1(1)	172.20(9)	171.78(8)	167.21(6)	167.41(5)
N(1)–Ti(1)–Cl(1)	100.34(9)	98.49(8)	99.60(7)	97.40(5)	101.46(4)
N(1)–Ti(1)–Cl(2)	98.49(9)	100.17(8)	98.94(7)	101.07(5)	99.41(4)
Cl(1)–Ti(1)–Cl(2)	95.75(4)	97.78(3)	97.36(4)	96.32(2)	95.77(2)
Ti(1)–N(1)–C(10)	171.0(2)	166.3(2)	166.5(2)	168.18(14)	171.22(12)

^a Defined as the difference between the Ti(1)–N(9) distance (i.e., *trans* to Ti=NR) and Ti(1)–N(3) and Ti(1)–N(6) distances.

α -diimine^{67–70} catalysts have been reported. Of particular relevance to our work are Gibson's⁷¹ and Nielson's⁴⁶ studies of polystyrene-supported imido vanadium⁷¹ and titanium⁴⁶ ethylene polymerization catalysts, respectively.



Catalysts of the type $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ can in principle be immobilized via either the imido ligand R-group or the macrocycle. We have established “proof of concept” results for both approaches and prepared $\text{Ti}(\text{NCH}_2\text{PS})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (**7**), the new supported macrocyclic ligand $\text{PSCH}_2\text{Me}_2[9]\text{aneN}_3$ (**8**), and its derivative $\text{Ti}(\text{N}^t\text{Bu})(\text{PSCH}_2\text{Me}_2[9]\text{aneN}_3)\text{Cl}_2$ (**9**) according to the further details given in the Supporting Information (“PS” represents 1% cross-linked polystyrene).

Triazacyclohexane-Supported Imido Titanium Precatalysts. 1,3,5-Triazacyclohexane ligands ($\text{R}_3[6]\text{aneN}_3$) have smaller ring sizes than their $\text{R}_3[9]\text{aneN}_3$ homologues, and their coordination chemistry in general is less extensively developed in comparison.^{34,72–79} Recently, Köhn and co-workers reported that MAO-activated chromium complexes of the type $\text{Cr}(\text{R}_3[6]-$

(72) Köhn, R.; Haufe, M.; Mihan, S.; Lilge, D. *Chem. Commun.* **2000**, 1927.

(73) Köhn, R. D.; Haufe, M.; Kociok-Köhn, G.; Filippou, A. C. *Inorg. Chem.* **1997**, *36*, 6064.

(74) Köhn, R. D.; Kociok-Köhn, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1877.

(75) Köhn, R. D.; Pan, Z.; Kociok-Köhn, G.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **2002**, 2344.

(76) Tredget, C. S.; Lawrence, S. C.; Ward, B. D.; Howe, R. G.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 3136.

(77) Armanasco, N. L.; Baker, M. V.; North, M. R.; Skelton, B. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1363.

(66) Zhang, Y.; Sita, L. R. *Chem. Commun.* **2003**, 2358.

(67) Zhang, D.; Jin, G.-X. *Appl. Catal. A* **2004**, *262*, 13.

(68) Liu, C.; Jin, G.-X. *New J. Chem.* **2002**, *10*, 1485.

(69) Boussie, T. R.; Coutard, C.; Turner, H.; Murphy, V.; Powers, T. S. *Angew. Chem., Int. Ed.* **1998**, *37*, 3272.

(70) Boussie, T. R.; Murphy, V.; Hall, K. A.; Coutard, C.; Dales, C.; Petro, M.; Carlson, E.; Turner, H. W.; Powers, T. S. *Tetrahedron* **1999**, *55*, 11699.

(71) Chan, M. C. W.; Chew, K. C.; Dalby, C. I.; Gibson, V. C.; Kohlmann, A.; Little, I. R.; Reed, W. *Chem. Commun.* **1998**, 1673.

Table 2. Ethylene Polymerization Data for Triazacycle-Supported Imido Titanium Catalysts (ambient temperature)^a

entry	precatalyst	precatalyst loading (μmol)	yield of PE (g)	productivity (kg mol ⁻¹ h ⁻¹ bar ⁻¹)	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	M_w/M_n
1	Ti(N ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (1)	2.5	9.5	630	1 140 000	264 000	4.3
2	Ti(N-2,6-C ₆ H ₃ Me ₂)(Me ₃ [9]aneN ₃)Cl ₂ (2)	20	0.92	8	736 000	12 900	57
3	Ti(N-2,6-C ₆ H ₃ ⁱ Pr ₂)(Me ₃ [9]aneN ₃)Cl ₂ (3)	2.5	1.8	120	440 000	55 500	7.9
4	Ti(NPh)(Me ₃ [9]aneN ₃)Cl ₂ (4)	20	0.04	<1	<i>c</i>	<i>c</i>	
5	Ti(NC ₆ F ₅)(Me ₃ [9]aneN ₃)Cl ₂ (5)	20	0.62	5	<i>c</i>	<i>c</i>	
6	Ti(NCH ₂ Ph)(Me ₃ [9]aneN ₃)Cl ₂ (6)	20	1.54	13	874 000	78 000	11
7	Ti(NCH ₂ PS)(Me ₃ [9]aneN ₃)Cl ₂ (7)	20	0.44 ^b	3	1 300 000	117 000	11
8	Ti(N ^t Bu)(P(SCH ₂ Me ₃ [9]aneN ₃)Cl ₂ (9)	20	0.03 ^b	<1	624 000	19 200	33
9	Ti(N ^t Bu)(Me ₃ [6]aneN ₃)Cl ₂ (10)	20	0.25	2	803 000	12 250	31
10	Ti(N-2,6-C ₆ H ₃ ⁱ Pr ₂)(Me ₃ [6]aneN ₃)Cl ₂ (11)	20	0.60	5	977 000	19 650	54
11	Ti(NC ₆ F ₅)(Me ₃ [6]aneN ₃)Cl ₂ (13)	20	0.37	3	1 040 000	16 750	64
12	Ti(N ^t Bu)(dd ₃ [6]aneN ₃)Cl ₂ (14)	20	0.27	2	812 500	16 450	50
13	Ti(N-2,6-C ₆ H ₃ ⁱ Pr ₂)(dd ₃ [6]aneN ₃)Cl ₂ (15)	20	0.12	1	647 000	11 050	59
14	Ti(N-2-C ₆ H ₄ CF ₃)(Me ₃ [9]aneN ₃)Cl ₂ (57)	2.5	3.2	220	2 245 000	937 000	2.4
15	Ti(N-2-C ₆ H ₄ ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (58)	2.5	8.6	580	532 000	165 000	3.3
16	Ti(N-2-C ₆ H ₄ ^t Bu)(Me ₃ [6]aneN ₃)Cl ₂ (59)	20	0.41	3	372 500	25 800	14

^a Conditions: 6 bar C₂H₄ on demand, Al:Ti = 1 500, 250 mL of toluene, 1 L reactor, 1 h, ambient temperature. ^b Corrected for weight of polystyrene support. ^c Polymer was very insoluble and gave a poor refractive index detector response.

aneN₃)Cl₃ are highly active homogeneous models of the Phillips-type catalysts.⁷² Therefore it was of interest to evaluate their effectiveness as supporting ligands in imido titanium polymerization catalysis.



R = ^tBu (**10**), 2,6-C₆H₃ⁱPr₂ (**11**),
Ph (**12**) or C₆F₅ (**13**)

R = ^tBu (**14**) or
2,6-C₆H₃ⁱPr₂ (**15**)

As part of a general survey of imido titanium coordination chemistry, we previously reported³⁴ the compounds Ti(NR)-(Me₃[6]aneN₃)Cl₂ (R = ^tBu (**10**), 2,6-C₆H₃ⁱPr₂ (**11**)) together with the X-ray structure of the *tert*-butyl derivative. However, no polymerization studies using these compounds have been reported, and so we included them in the current study. For comparison with the aryl imido triazacyclononane systems **4** and **5** we also prepared Ti(NR)(Me₃[6]aneN₃)Cl₂ (R = Ph (**12**), C₆F₅ (**13**)). Finally, since Köhn showed that the ethylene polymerization productivity of the tris(*n*-dodecyl)-1,3,5-triazacyclohexane complex Cr(dd₃[6]aneN₃)Cl₃ is ca. 60% higher than that of Cr(Me₃[6]aneN₃)Cl₃, we also prepared Ti(NR)(dd₃[6]aneN₃)Cl₂ (R = ^tBu (**14**), 2,6-C₆H₃ⁱPr₂ (**15**); dd = *n*-dodecyl). For further details of the syntheses and the X-ray structures see the Supporting Information.

Preliminary Ethylene Polymerization Studies. Ambient Temperature Screening of Triazacyclononane Systems. The solution phase precatalysts **1–6**, the solid-phase analogues **7** and **9**, and the R₃[6]aneN₃ systems **10–15** were screened for their ethylene homopolymerization capability at ambient temperature in toluene using methyl aluminoxane (MAO) cocatalyst (ratio Al:Ti = 1500:1). On the basis of the results of preliminary experiments, the more active systems **1** and **3** were reevaluated at a lower catalyst loading to minimize mass transport limitation effects. The results are summarized in Table 2.

Of the two alkyl imido (solution phase) systems Ti(NR)(Me₃[9]aneN₃)Cl₂ (R = ^tBu (**1**), CH₂Ph (**6**)), the *tert*-butyl analogue

is by far the most active, producing high M_w polyethylene (PE) with a polydispersity index (PDI) of 4.3. Single-site MAO-activated catalysts typically produce PE with PDIs of 2–2.5. The larger value for **1** may indicate changing reaction conditions (e.g., temperature rise as the polymerization proceeds, mass transport limitations, precipitation of insoluble PE) or the presence of more than one active species.¹⁸ Of the aryl imido systems **2–5**, it is again the compound with the bulkier imido R-group, namely, Ti(N-2,6-C₆H₃ⁱPr₂)(Me₃[9]aneN₃)Cl₂ (**3**), that affords the higher productivity. This catalyst system forms PE with a lower M_w than that formed with **1** and with a somewhat broader PDI.

The polystyrene-supported systems Ti(NCH₂PS)(Me₃[9]aneN₃)Cl₂ (**7**) and Ti(N^tBu)(P(SCH₂Me₃[9]aneN₃)Cl₂ (**9**) had lower activities than their solution phase analogues **6** and **1**, respectively. The PE formed with **7** had a higher M_w than that formed with **6**, suggesting that chain transfer is inhibited relative to chain propagation in this system. In contrast, the PE formed with **9** had a lower M_w than that obtained with **1**. However, given the very low productivity and mass of PE isolated in the case of **9**, it is unsafe to draw firm conclusions from this observation.

There is literature precedent for both enhanced and diminished catalyst productivities on going from solution phase systems to their supported analogues.⁶⁰ Of particular relevance to our work are contrasting observations made for two previous supported imido-based catalyst systems. Nielson found that polystyrene-supported imido titanium catalysts of the type Ti(NR)Cl₂(tmeda) had almost negligible activity compared to their solution phase analogues,⁴⁶ whereas Gibson found the opposite was true for cyclopentadienyl vanadium (+5) systems. This latter result was rationalized in terms of decreased bimolecular catalyst deactivation in the supported (site-isolated) system.⁷¹

There may be several reasons for the comparatively low productivities of the supported systems **7** and **9**. One very likely contributing factor is the much lower apparent swelling of the resins in toluene when they contain triazacyclononane-titanium dichloride moieties. This would doubtless block cocatalyst and/or monomer access to the metal centers. Higher productivities of supported imido titanium catalysts could potentially be achieved with a more rigid support. However, such studies were beyond the scope of the present study.

Ambient-Temperature Screening of Triazacyclohexane Systems. The performance of the triazacyclohexane systems **10–15** was disappointing in all cases assessed (given the very

(78) Armanasco, N. L.; Baker, M. V.; North, M. R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1145.

(79) Armanasco, N. L.; Baker, M. V.; North, M. R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1363.

Table 3. Ethylene Polymerization Data for Triazacyclononane-Supported Imido Titanium Catalysts (100 °C)

entry	precatalyst	conditions ^a	Al:Ti ratio	productivity (kg mol ⁻¹ h ⁻¹ bar ⁻¹)	<i>M</i> _w (g mol ⁻¹)	<i>M</i> _n (g mol ⁻¹)	<i>M</i> _w / <i>M</i> _n	vinyl end groups per chain ^b
1	Ti(N ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (1)	A	660	23 800	<i>c</i>	<i>c</i>		<i>c</i>
2	Ti(N-2,6-C ₆ H ₃ ⁱ Pr ₂)(Me ₃ [9]aneN ₃)Cl ₂ (3)	A	660	220	<i>c</i>	<i>c</i>		<i>c</i>
3	Ti(NPh)(Me ₃ [9]aneN ₃)Cl ₂ (4)	A	660	70	<i>c</i>	<i>c</i>		<i>c</i>
4	Ti(NC ₆ F ₅)(Me ₃ [9]aneN ₃)Cl ₂ (5)	A	660	70	<i>c</i>	<i>c</i>		<i>c</i>
5	Ti(N ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (1)	A	1600	96 600	100 000	37 000	2.7	0.37
6	Ti(N ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (1)	A	6500	13 100	11 000	5100	2.2	0.11
7	Ti(NCH ₂ C ₆ H ₁₁)(Me ₃ [9]aneN ₃)Cl ₂ (19)	B	1200	5890	152 700	15 200	10	0.59
8	Ti(NC ₅ H ₉)(Me ₃ [9]aneN ₃)Cl ₂ (21)	B	1200	4820	1 501 900	391 200	3.8	1.5 ^d
9	Ti(N ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (1)	B	1200	10 070	273 850	39 500	7.0	0.63
10	Ti(NCMe ₂ CH ₂ ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (23)	B	1200	8730	190 700	33 000	5.8	0.56
11	Ti(NAd)(Me ₃ [9]aneN ₃)Cl ₂ (24)	B	1200	10 340	152 900	22 900	6.7	0.85
12	Ti{N-3,5-C ₆ H ₃ (CF ₃) ₂ }(Me ₃ [9]aneN ₃)Cl ₂ (39)	B	1200	3370	50 300	10 400	4.8	0.68
13	Ti(N-2-C ₆ H ₄ CF ₃)(Me ₃ [9]aneN ₃)Cl ₂ (57)	A	1600	1230	863 000	195 500	4.4	<i>f</i>
14	Ti(N-2-C ₆ H ₄ ^t Bu)(Me ₃ [9]aneN ₃)Cl ₂ (58)	A	1600	690	667 000 ^e	25 700 ^e	26 ^e	<i>f</i>

^a Conditions: (A) 7 bar C₂H₄ on demand, 750 mL of PMH (or 1000 mL of heptanes for entries 5 and 6), 2 L autoclave, 0.05–5 μmol of precatalyst, 10 min, 100 °C; (B) 7 bar C₂H₄ on demand, 62 mL of PMH, parallel microreactor array, 0.16 μmol of precatalyst, 10 min, 100 °C. ^b Determined by NMR and/or FTIR spectroscopy (see the Supporting Information for further details). ^c Not recorded. ^d Estimate of ~1.5 RCH=CH₂ per chain may be inaccurate due to low number of unsaturations per 100 000 C and high *M*_w. ^e Bimodal. ^f Not determined (additional unknown absorptions obscured necessary spectral region).

poor performance of Ti(NPh)(Me₃[9]aneN₃)Cl₂, compound **12** was not tested). The low productivities in each instance were accompanied by very broad and complex molecular weight distributions, indicating extensive catalyst degradation to several species of limited activity. It is possible that the more open metal centers afforded by the smaller macrocycles lead more easily to bimolecular decomposition pathways, for instance via heterobimetallic or homobimetallic species, possibly with bridging imido ligands. Note, for example, that CpTi(N^tBu)Cl(py) readily loses pyridine to form the μ-imido-bridged dimer Cp₂Ti₂(μ-N^tBu)₂Cl₂, whereas the bulkier Cp*Ti(N^tBu)Cl(py) is perfectly stable in this regard.⁸⁰ Alternatively (or additionally) it is possible that the R₃[6]aneN₃ ligands are lost more readily in the triazacyclohexane systems. We note that Köhn has advanced evidence⁸¹ for transfer of up to 50% of the triazacyclic ligand from chromium to aluminum in certain Cr(R₃[6]aneN₃)Cl₃-based catalyst systems.

Higher Temperature Screening of Triazacyclononane Systems (Conventional Semibatch Reactors). While the triazacyclohexane systems are not promising candidates for development, the ambient temperature data (Table 2) for certain triazacyclononane precatalysts suggested that these could be viable systems for development under more commercially relevant conditions, in particular at higher operating temperatures. Preliminary experiments at 100 °C are shown in Table 3, entries 1–6.

The catalyst systems Ti(NR)(Me₃[9]aneN₃)Cl₂/MAO (R = ^tBu (**1**), 2,6-C₆H₃ⁱPr₂ (**3**), Ph (**4**), C₆F₅ (**5**)) were evaluated for ethylene polymerization in a conventional semibatch autoclave reactor at 100 °C with an initial Al:Ti ratio of 660:1 (Table 3, entries 1–4). While the *tert*-butyl imide **1** showed an excellent productivity of 23 800 kg mol⁻¹ h⁻¹ bar⁻¹, the three aryl imido systems were very disappointing. Focusing on the **1**/MAO system, it was found that increasing the relative amount of MAO (entry 5, Al:Ti ratio 1600:1) gave a 4-fold increase in productivity to 96 600 kg mol⁻¹ h⁻¹ bar⁻¹. NMR analysis of the linear PE produced showed an average of 0.37 vinyl end group per chain. This suggests¹⁸ that two predominant chain transfer mechanisms are operative in the **1**/MAO catalyst system, namely, chain transfer to AlMe₃ (present in ca. 20% amounts

w/w in the MAO used) and β-hydrogen transfer to ethylene monomer leading to RCH=CH₂ end groups (R = polymeryl). The PE produced had a PDI of only 2.7, indicative of a single site type catalyst.

Increasing the MAO:**1** ratio to 6500:1 (Table 3, entry 6) gave a substantial decrease in productivity and PE with a much lower *M*_w and an average of only 0.11 vinyl groups per chain. Since increasing the amount of MAO also increases the absolute amount of AlMe₃ in the system, this would lead to both an increased rate of chain transfer to AlMe₃ and suppression of catalyst activity due to increased equilibrium concentrations of AlMe₃ adducts of the type [Ti(N^tBu)(Me₃[9]aneN₃)(μ-Me)(μ-R)AlMe₂]⁺ (R = polymeryl or Me), which has been characterized crystallographically for R = Me.⁴¹

Regrettably, none of the complexes evaluated showed an affinity for propene polymerization or incorporation as comonomer.

Synthesis and Evaluation of a Library of Precatalysts Ti(NR)(Me₃[9]aneN₃)Cl₂. Ti(N^tBu)(Me₃[9]aneN₃)Cl₂/MAO (**1**/MAO) is the most productive imido-based Ziegler ethylene polymerization catalyst reported to date²³ and operates under commercially relevant conditions. Tables 2 and 3 also show clear evidence of dependence of productivity on the imido R-group (for example, precatalyst **1** (R = ^tBu) has a significantly higher productivity than **3** (R = 2,6-C₆H₃ⁱPr₂), especially at higher temperatures). The ambient temperature data indicated that polymer properties are influenced, and perhaps could eventually be controlled, by appropriate choice of imido N-substituent. Over the last 5 years in particular, high-throughput catalyst synthesis and screening techniques^{10,82,83} have started to become well established for the discovery and optimization of polymerization catalyst systems.^{84–92} Because the compounds Ti(NR)(Me₃[9]aneN₃)Cl₂ are easily prepared from our imido-dichloride synthons Ti(NR)Cl₂(NHMe₂)₂, we decided to target a library of such precatalysts and evaluate their polymerization capabilities using a high-throughput screening approach. No systematic survey of structure–activity relationships in imido-based Ziegler catalyst systems²³ has so far been described beyond our own preliminary communications.^{40,43}

Library Synthesis. A “one-pot” synthesis using the sequential addition of RNH₂ and then Me₃[9]aneN₃ to Ti(NMe₂)₂Cl₂

(80) Dunn, S. C.; Mountford, P.; Robson, D. A. *J. Chem. Soc., Dalton Trans.* **1997**, 293.

(81) Köhn, R. D.; Smith, D.; Mahon, M. F.; Prinz, M.; Mihan, S.; Kociok-Köhn, G. *J. Organomet. Chem.* **2003**, 683, 200.

(82) Murphy, V.; Volpe, A. F.; Weinberg, W. H. *Curr. Op. Chem. Biol.* **2003**, 7, 427.

(83) Stambuli, J. M.; Hartwig, J. F. *Curr. Op. Chem. Biol.* **2003**, 7, 420.

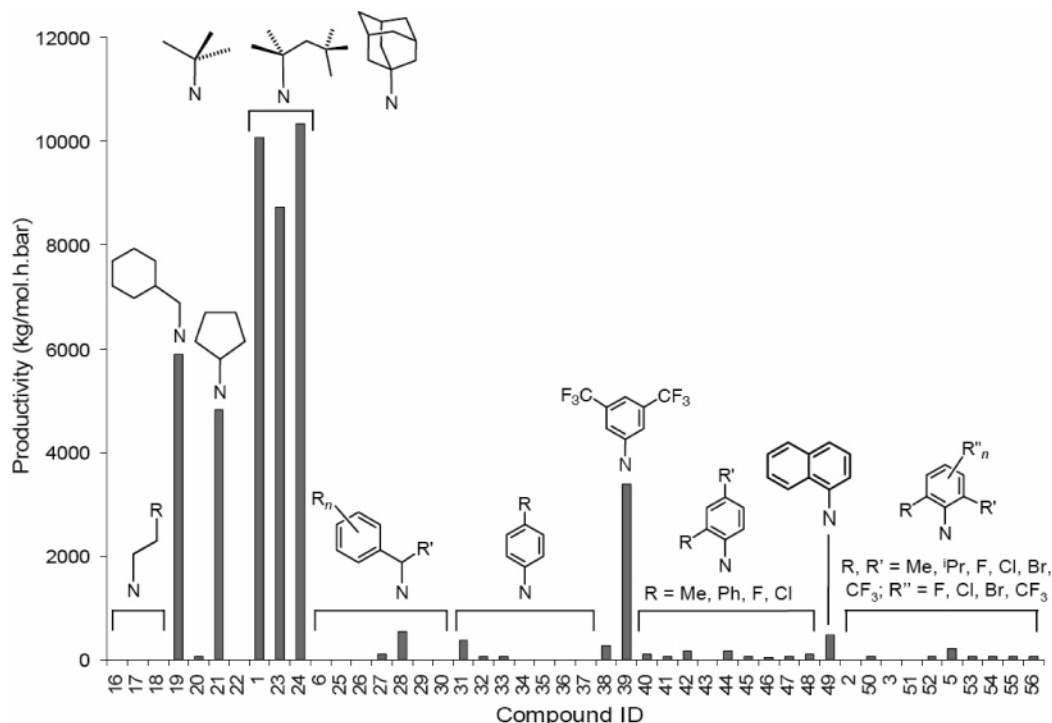


Figure 3. Summary of ethylene polymerization productivities at 100 °C for the library of catalysts $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$. Selected N–R groups are highlighted. See Table 3 and the Supporting Information for further details.

was selected since this route had already been used successfully for the preparation of $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ ($\text{R} = \text{tBu}$ or CH_2Ph , Scheme 1) and $\text{Ti}(\text{NR})(\text{R}'_3[6]\text{aneN}_3)\text{Cl}_2$ ($\text{R}' = \text{Me}$, $\text{R} = \text{Ph}$, C_6F_5 ; $\text{R}' = \text{dd}$, $\text{R} = 2,6\text{-C}_6\text{H}_3\text{iPr}_2$). From the point of view of using semiautomated technology, this method has the great advantage that all the reagents ($\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$, RNH_2 , and $\text{Me}_3[9]\text{aneN}_3$) and also the intermediates $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ are very benzene-soluble, whereas the target dichlorides $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ have quite limited solubility in this solvent and should precipitate, at least in sufficient quantities for characterization and subsequent use in polymerization screening. For otherwise “clean” reactions this therefore allows for ready separation and washing of the desired products and the use, where necessary, of an excess of certain reagents because they can be readily washed away. Full details of the method for library synthesis are provided in the Experimental Section, and the characterizing data and yields for all the compounds are given in the Supporting Information.

A library of 46 compounds of the type $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ was prepared using this “one-pot” semiautomated

route, and the isolated yields ranged from ca. 30 to 95 (av 61)%. These included the five previously prepared compounds **1–3**, **5**, and **6** for comparison. The NMR data and semibatch reactor polymerization capability of the compounds prepared in the semiautomated manner were identical to those of the conventionally prepared samples. The 41 new compounds (**16–56**) were characterized by satisfactory and clean ^1H NMR spectra in every case, and 39 of them gave correct molecular ions (or conclusive fragments arising from Cl, Me, or similar simple radical loss) in their high-resolution EI mass spectra (see the Supporting Information). None of the $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ intermediates was isolated, but in a previous paper we prepared and fully characterized 13 such species (including six X-ray structures), and we have also shown explicitly above that the compounds $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ ($\text{R} = \text{Ph}$, C_6F_5) and $\text{Ti}(\text{NtBu})(\text{dd}_3[6]\text{aneN}_3)\text{Cl}_2$ are formed by addition of $\text{R}'_3[n]\text{aneN}_3$ to such precursors ($\text{R}' = \text{Me}$ or dd ; $n = 6$ or 9).

Polymerization Testing and Polymer Properties. The precatalysts **1–3**, **5**, **6**, and **16–56** were screened for their ethylene polymerization capability at 100 °C using MAO cocatalyst ($\text{Al}:\text{Ti} = 1200:1$) in high-throughput, parallel microreactors. The productivities are displayed graphically in Figure 3. Further details of the productivities and PE properties for the most productive precatalysts, namely, **1**, **19**, **21**, **23**, **24**, and **39** (Figure 4), are given in Table 3. Full details of these PE analyses and all the catalyst productivities are given in the Supporting Information.

For ease of reference, the imido R-groups in Figure 3 are arranged as follows (from left to right): primary, secondary, and tertiary alkyl; benzyl; *para*-, *meta*-, *mono-ortho*-, and *di-ortho*-phenyl. It is clear that the productivity of $\text{Ti}(\text{NtBu})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (**1**, 10 070 $\text{kg mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$, Table 3, entry 9) using the microreactors is lower than that found on the 2 L conventional semibatch reactors at Al:Ti ratios of either 660 (23 800 $\text{kg mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$, Table 3, entry 1) or 1600 (96 600 $\text{kg mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$, Table 3, entry 5). This decrease in productivity is not an uncommon feature of this microreactor

(84) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626.

(85) Diamond, G. M.; Goh, C.; Leclerc, M. K.; Murphy, V.; Turner, H. W. *Symyx Technologies Inc.*, 2001.

(86) Hagemeyer, A.; Jandeleit, B.; Liu, Y.; Poojary, D. M.; Turner, H. W.; Volpe, J.; Anthony F.; Henry Weinberg, W. *Appl. Catal. A: Gen.* **2001**, *221*, 23.

(87) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038.

(88) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M. K.; Lund, C.; Murphy, V.; Shoemaker, J. A. W.; Tracht, U.; Turner, H.; Zhang, J.; Uno, T.; Rosen, R. K.; Stevens, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 4306.

(89) Kolb, P.; Demuth, D.; Newsam, J. M.; Smith, M. A.; Sundermann, A.; Schunk, S. A.; Bettonville, S.; Breulet, J.; Francois, P. *Macromol. Rapid Commun.* **2004**, *25*, 280.

(90) Mason, A. F.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, 10798.

(91) Kerton, F. M.; Whitwood, A. C.; Willans, C. E. *Dalton Trans.* **2004**, 2237.

(92) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 11037.

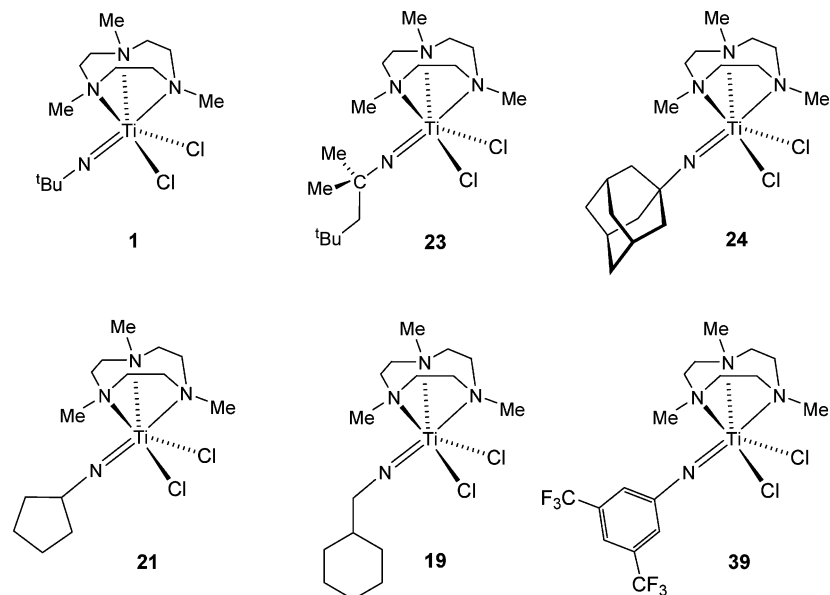


Figure 4. The most productive ethylene polymerization catalysts as assessed using high-throughput microreactors at 100 °C (see Figure 3 and Table 3 for further details).

system and may reflect differences in precatalyst and cocatalyst concentration and gas mixing. However, the general trends in the productivities as a function of imido N–R group determined using the high-throughput apparatus parallel those found in the 100 °C conventional semibatch reactor tests for **1**, Ti(N-2,6-C₆H₃ⁱPr₂)(Me₃[9]aneN₃)Cl₂ (**3**), and Ti(NC₆F₅)(Me₃[9]aneN₃)Cl₂ (**5**), with **3**/MAO and **5**/MAO giving zero or negligible yields of PE compared to **1** by both methods (Table 3 and Table S3 of the Supporting Information).

The structure–productivity profile described by Figure 3 shows clearly that (at 100 °C with MAO) bulky tertiary alkyl-substituted compounds Ti(NR)(Me₃[9]aneN₃)Cl₂ are consistently the most productive (i.e., **1**, **23**, and **24**). Furthermore, this self-consistency further validates the library screening technique (in addition to the identical structure–activity trends found for **1**, **3**, and **5** under both semibatch and microreactor screening). With the exception of **19** and **21** (Figure 4), all other primary and secondary N-alkyl-substituted precatalysts **16**–**22** give little or no PE. We note that compounds **19** and **21** contain a cycloalkyl group as or part of their substituents, although it is not clear why these would confer a special advantage. The benzyl-substituted imido precatalysts **6** and **25**–**30** all showed poor activities. It is interesting to note that Ti(NCH₂Ph)(Me₃[9]aneN₃)Cl₂ (**6**) is the unsaturated analogue of reasonably active **19**. None of the *para*-substituted phenyl imides **31**–**37** showed productivities of any merit. This is consistent with the conventional semibatch reactor results for Ti(NPh)(Me₃[9]aneN₃)Cl₂ (Table 3, entry 3). Compound **39** is interesting, as it appears to show that *meta*-positioned electron-withdrawing groups may assist catalyst productivity. The adjacent compound Ti{N-3,4,5-C₆H₂(OMe)₃}(Me₃[9]aneN₃)Cl₂ (**38**), with electron-releasing groups in the *meta*- and *para*-positions, has a productivity that is 10% of that of **39**. On the other hand, compounds Ti(N-4-C₆F₄CF₃)(Me₃[9]aneN₃)Cl₂ (**54**) and Ti(NC₆F₅)(Me₃[9]aneN₃)Cl₂ (**5**), for example, gave even lower productivities than **38**, and so simply using electron-withdrawing aryl groups in general appears to give no advantage. None of the mono-*ortho*- and di-*ortho*-phenyl-substituted imides had significant productivities.

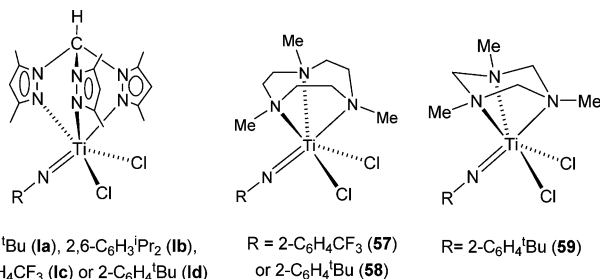
The PEs produced by compounds **1**, **19**, **21**, **23**, **24**, and **39** were predominantly linear with little branching (Table S4, Supporting Information). The PDIs (Table 3, entries 7–12) were

somewhat broad for single-site catalysts. This might again reflect the different conditions in the microreactors compared to the conventional semibatch reactors (compare Table 3, entries 5 and 9, for the catalyst system **1**/MAO). The PEs generally contain between 0.56 and 0.85 vinyl end group per polymer chain, so it is also clear that at least two different chain transfer mechanisms are operating. Except for that from **21**/MAO (Table 3, entry 8), the PE analysis indicates the formation of between ca. 300 and 500 polymer chains per precatalyst Ti center (assuming that all are activated and productive). The catalyst systems with the highest numbers of chains per Ti (namely, **39**/MAO (ca. 380) and **24**/MAO (ca. 530) also gave the higher vinyl end group content. The PE molecular weights for all samples except that from **21** were in the range ca. 50 000–270 000 kg mol^{−1}.

The PE formed with **21**/MAO was very different from that produced by the other catalyst systems. This PE has considerably higher *M_w* and only ca. 15 PE chains per precatalyst Ti center. At this time it is not possible to speculate further on this result.

High-Temperature versus Low-Temperature Structure–Productivity Relationships and Precatalysts with 2-C₆H₄R (R = CF₃, ⁱBu) Substituents. The ambient-temperature productivities for the precatalysts **1**–**6** (Table 2, entries 1–6) suggest that bulky aryl imido (e.g., **3**) as well as alkyl imido systems (e.g., **1**) should have reasonable productivities on moving to higher temperature testing. However, the productivities for Ti(NⁱBu)(Me₃[9]aneN₃)Cl₂ (**1**) and Ti(N-2,6-C₆H₃ⁱPr₂)(Me₃[9]aneN₃)Cl₂ (**3**) at 100 °C (Table 3, entries 1, 2; Figure 3) show that this expectation is unfulfilled. In this context it is interesting to note our very recent results for the MAO-activated tris(pyrazolyl)methane-supported titanium imido compounds Ti(NR){HC(Me₂pz)₃}Cl₂ (**I**, R = ⁱBu (**a**), 2,6-C₆H₃ⁱPr₂ (**b**), 2-C₆H₄CF₃ (**c**), 2-C₆H₄ⁱBu (**d**)).⁴⁰ Under identical ambient temperature conditions to those used for **1** and **3** (Table 2, entries 1, 3) the productivities of **Ia**–**Id** were 230, 810, 1170, and 930 kg mol^{−1} h^{−1} bar^{−1}, respectively. However, at 100 °C both **Ia** and **Ib** were virtually inactive, whereas **Ic** and **Id** had productivities of 133 700 (PDI = 3.8) and 152 500 (PDI = 2.4) kg mol^{−1} h^{−1} bar^{−1}. It therefore appears that dramatic changes in relative productivities (i.e., compounds with different N–R

groups) on going from ambient to higher temperature conditions are not unexpected in these classes of imido titanium catalyst systems.



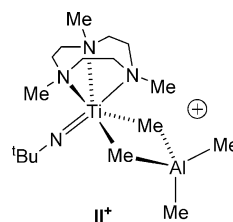
The “value-added” benefit (relative to *tert*-butyl) of the bulky *ortho*-aryl imido N-substituents in the tris(pyrzoly)methane precatalyst family **I** was attributed to fundamental differences in topology between the two different *fac*-N₃ ligands, HC(Me₂pz)₃ and Me₃[9]aneN₃.⁴⁰ Thus while κ³-bound HC(Me₂pz)₃ ligands have clefts between the Me₂pz rings, which are able to favorably direct the *ortho* substituent of an aryl imido ligand to protect the potentially reactive^{31–33} Ti=NR bond and/or highly electrophilic metal center, Me₃[9]aneN₃ has no such feature. Nevertheless, based on the successes of **1c** and **1d**, we prepared the new compounds Ti(N-2-C₆H₄R)(Me₃[9]aneN₃)Cl₂ (R = CF₃ (**57**), ^tBu (**58**)) and Ti(N-2-C₆H₄^tBu)(Me₃[9]aneN₃)Cl₂ (**59**) to test the effect of these bulkier aryl imido groups when used in conjunction with triazacyclic ligands. Compounds **57–59** were obtained in ca. 65–89% yield using the “one-pot” method starting from Ti(NMe₂)₂Cl₂ and the appropriate aniline and triazacycle.

As shown in Table 2 (entries 14, 15), the catalyst systems **57**/MAO and **58**/MAO have ambient temperature productivities of 220 and 580 kg mol⁻¹ h⁻¹ bar⁻¹, which compare favorably with those for **1** (630 kg mol⁻¹ h⁻¹ bar⁻¹) and **3** (120 kg mol⁻¹ h⁻¹ bar⁻¹) under identical conditions. The PDIs for the PEs formed with **57** (2.4) and **58** (3.3) are indicative of single-site-type behavior, and the PE for **57** had a particularly high *M_w*. Disappointingly, the productivity for the smaller triazacyclic system **59**/MAO (Table 2, entry 16) was still very low (4.1 kg mol⁻¹ h⁻¹ bar⁻¹) and gave PE with a relatively broad PDI. No further studies of this system were undertaken.

The catalyst systems **57**/MAO and **58**/MAO were evaluated at 100 °C in a conventional semibatch reactor (Table 3, entries 13, 14). The productivities (1230 and 690 kg mol⁻¹ h⁻¹ bar⁻¹, respectively) were only ca. 1% of that for Ti(N^tBu)(Me₃[9]aneN₃)Cl₂ (**1**) and were also remarkably poor in comparison to those of **1c** and **1d** (133 700 and 152 500 kg mol⁻¹ h⁻¹ bar⁻¹, respectively) under analogous conditions. The PE formed with **57** had a higher *M_w* than for **1** but featured a slightly broadened PDI (4.4); that for **58** was clearly bimodal (overall PDI = 24). The polymerization results for **57** and **58** confirm the general trend found for the mono- or di-*ortho*-substituted phenyl imides **2**, **3**, and **40–56** (Figure 3). In particular, the low productivity of **57** parallels that of Ti(N-2,6-C₆H₃(F)CF₃)(Me₃[9]aneN₃)Cl₂ (**51**), which yielded no PE when assessed using the parallel microreactors.

Effect of Added 2,6-Di-*tert*-butyl-4-methyl Phenol (BHT-H) and Its Reactions with Imido Titanium Alkyl Complexes. Commercial MAO typically contains significant amounts of “free” AlMe₃ (actually Al₂Me₆), which may act as both a chain transfer agent (“chain transfer to aluminium”) and inhibitor of catalyst activity through formation of adducts of the type [(L)M-(μ-Me)(μ-R)AlMe₂]⁺ (R = Me or polymeryl chain) with the

active species in polymerization,^{93–99} typically a monoalkyl cation “[(L)MR]⁺”.¹⁸ In certain catalyst systems the AlMe₃ can also degrade or otherwise modify the supporting ligand set.^{15,21} As mentioned above, several experimental observations point to an active role of AlMe₃ in catalyst systems based on Ti(NR)(Me₃[9]aneN₃)Cl₂/MAO. First the PE formed has, on average, significantly fewer vinyl end groups per chain (Table 3, entries 5–7 and 9–12) than would be expected if β-H transfer to monomer were the dominant chain transfer process, and the use of a very large excess of MAO (Al:Ti = 6500; Table 3 entry 6) gives PE having a drastically reduced *M_w* and even fewer vinyl groups per chain. Second, we have recently structurally characterized the AlMe₃ adduct [Ti(N^tBu)-(Me₃[9]ane)(μ-Me)₂AlMe₂]⁺ (**II**⁺) as its [BAR^F₄]⁻ salt (Ar^F = C₆F₅), showing that even with the bulky *tert*-butyl imido ligand the 14 valence electron cation [Ti(N^tBu)(Me₃[9]ane)Me]⁺ can interact strongly with AlMe₃.⁴¹ Third, we found that addition of an excess of AlMe₃ to the highly active catalyst system Ti(N-2-C₆H₄^tBu){HC(Me₂pz)₃}Cl₂ (**1d**)/MAO (ambient temperature) gave a ca. 55% decrease in productivity and distinctly bimodal PE (the two fractions arising from chain transfer to AlMe₃ (lower *M_w* part) and β-H transfer to monomer).¹⁰⁰



Polymerization Experiments Using MAO Modified by BHT-H. It has been known for some time that bulky aryloxy derivatives of AlMe₃, for example MeAl(BHT)₂ (readily formed^{101,102} from AlMe₃ and BHT-H, where BHT-H = 2,6-di-*tert*-butyl-4-methylphenol), can act as “noninteracting” scavengers.^{99,103–105} More recently, Busico et al. showed that addition of 2,6-di-*tert*-butylphenol to commercial MAO in appropriate quantities scavenged the “free” AlMe₃ as the expected bis(phenoxide).¹⁰⁶ Use of such a 2,6-di-*tert*-butylphenol/MAO cocatalyst with certain key metallocene and post-metallocene precatalysts afforded higher catalyst productivities

(93) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(94) Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1995**, *497*, 55.

(95) Bryliakov, K. P.; Babushkin, D. E.; Talsi, E. P.; Voskobynikov, A. Z.; Gritzko, H.; Schröder, L.; Damrau, H.-R. H.; Wieser, U.; Schaper, F.; Brintzinger, H. H. *Organometallics* **2005**, *24*, 894.

(96) Bryliakov, K. P.; Talsi, E. P.; Bochmann, M. *Organometallics* **2004**, *23*, 149.

(97) Petros, R. A.; Norton, J. R. *Organometallics* **2005**, *23*, 5105.

(98) Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; van Meurs, M. J. *Am. Chem. Soc.* **2004**, *126*, 10701.

(99) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161.

(100) Sealey, A. J. D. Ph.D. Thesis, University of Oxford, 2004.

(101) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409.

(102) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543.

(103) Williams, V. C.; Dai, C.; Li, Z.; Collins, S.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3695.

(104) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R.; Marder, T. B. *Organometallics* **2000**, *19*, 1619.

(105) Metcalfe, R. A.; Kreller, D. I.; Tian, J.; Kim, H.; Taylor, N. J.; Corrigan, J. F.; Collins, S. *Organometallics* **2002**, *21*, 1719.

(106) Busico, V.; Cipullo, R.; Cuttillo, F.; Friederichs, N.; Ronca, S.; Wang, B. *J. Am. Chem. Soc.* **2003**, *125*, 12402.

Table 4. Ethylene Polymerization Data for the Ti(N^tBu)(Me₃[9]aneN₃)Cl₂ (**1**)/MAO/BHT-H Catalyst System (100 °C)^a

entry	estimated BHT-H:total Al ratio (BHT-H:AlMe ₃ ratio)	yield of PE (g)	productivity (kg mol ⁻¹ h ⁻¹ bar ⁻¹)	M _w (g mol ⁻¹)	M _n (g mol ⁻¹)	M _w /M _n	vinyl end groups per chain ^b	internal unsaturations per chain ^b	total unsaturations per chain
1	0.0 (0)	5.63	96 600	100 000	37 000	2.7	0.37	0	0.37
2	0.4 (2)	5.46	93 600	120 000	40 000	3.0	0.40	0.06	0.46
3	0.8 (4)	8.48	145 400	235 000	67 000	3.5	0.53	0.24	0.77
4	1.2 (6)	4.41	75 400	280 000	125 000	2.2	0.91	0.16	1.09

^a Conditions: (A) 7 bar C₂H₄ on demand, 1000 mL of heptanes, Al:Ti ratio 1600, 0.05 μmol of **1**, polymerization run time 10 min, BHT-H and MAO premixed in reactor for 10 min prior to addition of **1** at 100 °C. ^b Determined by NMR and/or FTIR spectroscopy.

and/or average polymer molecular weight compared with nonmodified MAO alone.

Table 4 summarizes analogous experiments carried out on the Ti(N^tBu)(Me₃[9]aneN₃)Cl₂ (**1**)/MAO catalyst system. Entry 1 (which is the same as entry 5 in Table 3) uses “as supplied” MAO (Crompton, in which ca. 20% of the Al present is in the form of AlMe₃). Entries 2–4 report the effect of premixing the MAO with the stated amount of BHT-H for 10 min prior to injection of **1**. We address different aspects of the data in turn.

With regard to productivity, addition of 0.4 equiv (per total Al present) of BHT-H gave negligible change. However, addition of 0.8 and 1.2 equiv gave first an increase and then a decrease in productivity. The PDI values followed a similar trend, first increasing and then decreasing. In contrast, the total average number of unsaturations per chain (and also the number of vinyl end groups per chain) increases steadily with added BHT-H, as do the molecular weights. These general features may be readily interpreted. The increase in M_w and average number of unsaturations per chain is consistent with decreasing chain transfer to aluminum as “free” AlMe₃ is scavenged. The variation in PDI is also explained in this way, with lowest values for 0 equiv and 1.2 equiv added BHT-H, reflecting first one dominant chain transfer mechanism (i.e., chain transfer to aluminum) and then another (chain transfer to monomer). The decrease in productivity in entry 4 may indicate that addition of an excess of BHT-H has a detrimental effect on either the precatalyst and/or the activated species, or BHT-H may react with Al–Me groups of MAO itself, therefore diminishing its ability to activate the dichloride precatalyst.¹⁰⁶ It may also/alternatively indicate less efficient scavenging of impurities in this system since AlMe₃ is more effective in this regard than MeAl(BHT)₂.¹⁰³ Experiments to probe the underlying reaction chemistry of BHT-H with relevant neutral and cationic *tert*-butyl imido titanium compounds are described below. Interestingly, the systems presumably containing the lowest amounts of “free” AlMe₃ (entries 3 and 4) appear to contain more internal unsaturations per chain than in the other cases. The NMR data were unclear regarding the exact nature of these unsaturations, which may arise from “chain walking” for example. It is also interesting that while the experiment described in entry 2 (ratio of estimated “free” BHT-H to AlMe₃ = 2) has, in principle, sufficient BHT-H to scavenge all of the “free” AlMe₃, the beneficial effect on productivity continues in entry 3, and the increases in M_w and chain unsaturations continue through to entry 4. This may be associated with the ability of BHT-H to react with Al–Me bonds of MAO itself (or AlMe₃ gradually released from it).¹⁰⁶

Encouraged by the improved productivity of the Ti(N^tBu)-(Me₃[9]aneN₃)Cl₂ (**1**)/MAO catalyst system in the presence of BHT-H, we repeated the screening of Ti(N-2-C₆H₄^tBu)(Me₃[9]aneN₃)Cl₂ (**58**) under the same conditions as entry 14, Table 3, but this time pretreating the MAO with BHT-H (total Al: BHT-H = 1.0). Disappointingly, the activity was still very low (710 kg mol⁻¹ h⁻¹ bar⁻¹) compared to that of **1** and essentially

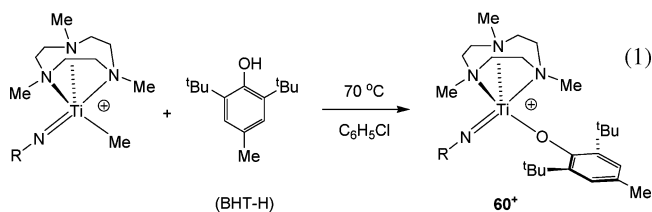
unchanged compared to that without BHT-H added (690 kg mol⁻¹ h⁻¹ bar⁻¹).

Reactions of Imido Titanium Compounds with BHT-H.

Previous work has shown that five-coordinate *tert*-butyl imido titanium compounds (L)Ti(N^tBu) can react readily with phenols to give the corresponding bis(aryloxides) (L)Ti(OAr)₂ and ^t-BuNH₂.^{33,107,108} Furthermore, Collins has shown that BHT-H reacts slowly with [Cp₂ZrMe]⁺ at room temperature (t_{1/2} ≈ 2 h) in C₆D₅Br to form [Cp₂Zr(BHT)]⁺.¹⁰⁹ Both types of protonolysis reaction would help account for the diminished productivity in entry 4 of Table 4. We therefore examined the reactions of the following species^{41–43} with BHT-H at room temperature and/or 70 °C: Ti(N^tBu)(Me₃[9]aneN₃)Cl₂ (**1**, the primary catalyst precursor), Ti(N^tBu)(Me₃[9]aneN₃)Me₂ (a likely dialkyl product of the reaction of **1** with MAO), [Ti(N^tBu)-(Me₃[9]aneN₃)Me]⁺ (a likely first-formed catalytically active species), and [Ti(N^tBu)(Me₃[9]aneN₃)(μ-Me)₂AlMe₂]⁺ (**II**⁺, a model for the AlMe₃-trapped active species resting state).

No reaction was observed between BHT-H and Ti(N^tBu)-(Me₃[9]aneN₃)Cl₂ (**1**) either at room temperature or at 70 °C. In contrast, the dimethyl derivative⁴³ Ti(N^tBu)(Me₃[9]aneN₃)Me₂ reacted completely within 10 min at room temperature. The only identifiable product of this reaction was free Me₃[9]aneN₃. Notably, ^tBuNH₂ was not one of the products. It appears that the *tert*-butyl group provides significant steric protection of the Ti=N^tBu bond and that it is the Ti–Me bonds that undergo attack by BHT-H.

The reaction between BHT-H and the in situ-generated cation^{41,42} [Ti(N^tBu)(Me₃[9]aneN₃)Me]⁺ (in C₆D₅Br) was slow at room temperature, and after 1 h the spectrum still showed resonances mainly for [Ti(N^tBu)(Me₃[9]aneN₃)Me]⁺ and BHT-H. However, heating at 70 °C for 1 h afforded a single new C_s symmetric species, and subsequent scale-up gave [Ti(N^tBu)-(Me₃[9]aneN₃)(BHT)][BAr^F₄] (**60**-BAr^F₄) as a fully characterized yellow powder in 68% isolated yield (eq 1).



The ¹H NMR spectrum of **60**⁺ featured resonances for a triazacyclononane ligand in a C_s symmetric complex along with those for a single BHT and N^tBu ligand. Although **60**⁺ is a five-coordinate cation, at room temperature the ¹H NMR spectrum shows no evidence for any fluxional behavior. This

(107) Swallow, D.; McInnes, J. M.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2253.

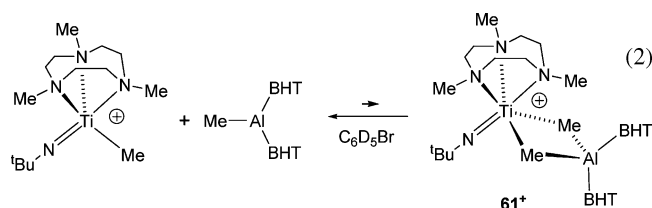
(108) Dubberley, S. R.; Friedrich, A.; Willman, D. A.; Mountford, P.; Radius, U. *Chem. Eur. J.* **2003**, *9*, 3634.

(109) Stapleton, R. A.; Galan, B. R.; Collins, S.; Simons, R. S.; Garrison, J. C.; Youngs, W. J. *J. Am. Chem. Soc.* **2003**, *125*, 9246.

is in contrast to the related five-coordinate cations $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{R}]^+$ ($\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3, \text{or Cl}$)^{41,42} and is probably due to the steric bulk of the *tert*-butyl groups of the aryloxy ligand. As mentioned, Collins and co-workers have reported the zirconocenium analogue of **60**⁺, namely, $[\text{Cp}_2\text{Zr}(\text{BHT})]^+$. The X-ray crystal structure of $[\text{Cp}_2\text{Zr}(\text{BHT})]^+$ featured a $\text{Zr}\cdots\text{H}-\text{C}$ agostic interaction between one of the *ortho tert*-butyl substituents and the metal center. Unfortunately, we were unable to obtain diffraction-quality crystals of **60-BAr**^F₄. Low-temperature ¹H NMR spectroscopy was used to seek evidence for an agostic interaction in **60**⁺. No decoalescence of any of the resonances was observed down to a temperature of -80 °C. Furthermore, there was no significant broadening of the singlet at 1.58 ppm for the *tert*-butyl protons of the aryloxy ligand relative to the other resonances. No evidence for an agostic interaction¹¹⁰ was detected in the expected region ($2800\text{--}2000\text{ cm}^{-1}$) of the IR spectrum of **60-BAr**^F₄.

In a final experiment BHT-H (2 equiv) was added to the AlMe_3 adduct⁴¹ $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\mu\text{-Me})_2\text{AlMe}_2]^+$ in $\text{C}_6\text{D}_5\text{Br}$. The ¹H NMR spectrum was monitored at room temperature over the course of 2 h, after which time the following species were present in the relative approximate proportions indicated: $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\mu\text{-Me})_2\text{AlMe}_2]^+$ (**II**⁺, 1.0), $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$ (2.5), $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\text{BHT})]^+$ (**60**⁺, 1.0), BHT-H (1.8), $\text{MeAl}(\text{BHT})_2$ (3.7). It therefore appears that BHT-H can trap the (previously) coordinated AlMe_3 of $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\mu\text{-Me})_2\text{AlMe}_2]^+$ as $\text{MeAl}(\text{BHT})_2$ to liberate $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$. However, this species in turn can react slowly with BHT-H to give **61**⁺.

The reactions of these various neutral and cationic imido titanium species with BHT-H indicate quite clearly that control of the amount of BHT-H present in the catalyst system, and the order in which the BHT-H and titanium precatalyst are added, is critical with regard to obtaining optimum levels of “free” monoalkyl cation active species.



Since the data in Table 4 imply that the BHT-modified AlMe_3 is less able to stabilize the cationic monoalkyl active species in polymerization, the interaction of in situ-generated $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}][\text{BAr}^{\text{F}}_4]$ with “noninteracting” $\text{MeAl}(\text{BHT})_2$ ^{101,102} was probed by NMR spectroscopy ($\text{C}_6\text{D}_5\text{Br}$). The resultant ¹H NMR spectrum showed resonances for the individual species $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$ and $\text{MeAl}(\text{BHT})_2$, except that those for the $\text{Ti}-\text{Me}$ (δ 0.66 ppm) and $\text{Al}-\text{Me}$ (δ -0.43 ppm) groups were significantly broadened. These observations are consistent with the dynamic process shown in eq 2, in which the equilibrium lies well to the left-hand side. Cooling the NMR sample in an attempt to shift the equilibrium in favor of the adduct **61**⁺ and slow the dynamic process caused $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}][\text{BAr}^{\text{F}}_4]$ to precipitate, and at 0 °C only resonances for $\text{MeAl}(\text{BHT})_2$ were visible. Warming the sample from 20 to 100 °C led first to increased broadening, and then (after ca. 60 °C) sharpening, of the $\text{Ti}-\text{Me}$ and

$\text{Al}-\text{Me}$ signals as the rate of methyl group exchange increased, but the proposed (entropically disfavored) equilibrium shifted more to the left-hand side. The lack of a significant interaction between $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$ and $\text{MeAl}(\text{BHT})_2$ contrasts strongly with that for AlMe_3 , in which the adduct $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\mu\text{-Me})_2\text{AlMe}_2]^+$ (**II**⁺) is instantaneously formed in quantitative yield.⁴¹ The NMR experiments therefore support the view that there is limited interaction between $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$ and $\text{MeAl}(\text{BHT})_2$ in the catalyst systems described in Table 4.

Conclusions

An extensive range of triazacycle-supported imido titanium compounds have been prepared and structurally characterized, and their ethylene polymerization capability has been assessed. Compounds with the smaller triazacyclohexane ligand, as well as polystyrene-supported systems, showed negligible activity. Compounds with the larger $\text{Me}_3[9]\text{aneN}_3$ ligand showed the best productivities at room temperature for both bulky alkyl- and aryl-imido ligands. Assessment of a library of $\text{Me}_3[9]\text{aneN}_3$ -supported compounds at 100 °C found that only compounds with bulky alkyl imido ligands gave the highest productivities at this temperature. Under the particular MAO-activation conditions assessed, the catalysts derived from $\text{Ti}(\text{NR})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ exhibit two types of chain transfer mechanism. Use of BHT-H scavenger in appropriate quantities increased the productivity and PE molecular weights associated with the catalyst system $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2/\text{MAO}$, and mainly PE terminated by β -hydrogen transfer to monomer was produced with the highest amounts of added BHT-H. The underlying organometallic chemistry in these systems was probed, and no reaction between BHT-H and the imido ligand was observed.

The present data suggest that a primary role of the imido N-substituent in these catalyst systems (and also the complementary $\text{Ti}(\text{NR})\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Cl}_2$ (**I**)/MAO⁴⁰) is to protect the $\text{Ti}=\text{NR}$ linkage and/or titanium center from attack by AlMe_3 . Bulkier N-R groups might also prevent homo-dimerization by low-coordinate monoalkyl cations and/or inhibit attack at the $\text{Ti}=\text{NR}$ bond by the ethylene substrate itself, a process recently proposed on the basis of DFT calculations to occur in the $\text{Cr}(\text{NR})_2\text{Cl}_2/\text{MAO}$ catalyst system.^{111,112} DFT and experimental studies of the reactions of well-defined imido titanium alkyl cations with AlMe_3 , olefins, and other unsaturated substrates are underway and will be reported in due course.

Experimental Section

General Methods and Instrumentation. All operations described herein are air- and moisture-sensitive and were carried out using standard Schlenk-line (Ar) and drybox (N_2) techniques. Protio- and deuterio-solvents were purified, dried, and distilled using conventional techniques. NMR samples were prepared under dinitrogen in Wilmad 505-PS tubes fitted with J. Young NMR/5 valves. Samples for magic angle spinning (MAS) NMR spectroscopy were prepared in 2 mm Zirconia rotors. Solution phase ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker DPX 300, Varian Unity Plus 500, and Varian Mercury-VX 300 spectrometers at 298 K unless otherwise stated. Spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ¹⁹F spectra were externally referenced to CFCl_3 ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. ¹H and ¹³C{¹H}

(110) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(111) Jensen, V. R.; Børve, K. J. *Organometallics* **2001**, *20*, 616.

(112) Jensen, V. R.; Børve, K. J. *Chem. Commun.* **2002**, 542.

MAS NMR spectra were recorded on a Chemagnetics 400 Infinity spectrometer. Spectra were referenced internally to tetramethylsilane. IR spectra were recorded on Perkin-Elmer 1600 and Perkin-Elmer 1710 spectrometers as Nujol mulls between CsBr, KBr, or NaCl windows unless otherwise stated, and data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded on a Micromass GCT TOF instrument using a solid probe inlet temperature program, and data are quoted in mass/charge ratio (m/z). Elemental analyses were carried out by the analytical laboratory of the School of Chemistry, University of Nottingham, Inorganic Chemistry Laboratory, University of Oxford, or by the Elemental Analysis Service at the London Metropolitan University. GPC analyses were carried out by Rapra Technology Ltd. in 1,2,4-trichlorobenzene solvent at 160 °C relative to polystyrene calibrants and using the appropriate Mark Houwink parameters for polyethylene. IR and NMR analyses of polymer samples were performed by the analytical services department of DSM Research or SABIC Europe, Research & Development.

Starting Materials. The compounds $\text{Me}_3[9]\text{janeN}_3$,¹¹³ $\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3$ ($\text{R} = \text{'Bu}$, 2,6- $\text{C}_6\text{H}_3\text{Me}_2$, 2,6- $\text{C}_6\text{H}_3\text{Pr}_2$),⁴⁴ $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ ($\text{R} = \text{'Bu}$, Ph, C_6F_5),⁴⁷ $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$,¹¹⁴ $\text{Ti}(\text{NR})(\text{Me}_3[6]\text{janeN}_3)\text{Cl}_2$ ($\text{R} = \text{'Bu}$, 2,6- $\text{C}_6\text{H}_3\text{Pr}_2$),³⁴ and $\text{MeAl}(\text{BHT})_2$ ¹⁰² were prepared according to the literature methods. Liquid primary amines for preparative scale experiments were predried over freshly ground CaH_2 and distilled prior to use. BHT-H was recrystallized from hexanes. MAO was obtained from Albermarle and Crompton. All other compounds and reagents were purchased and used without further purification.

Ti(NⁱBu)(Me₃[9]janeN₃)Cl₂ (1). From $\text{Ti}(\text{N}^i\text{Bu})\text{Cl}_2(\text{py})_3$. A solution of $\text{Me}_3[9]\text{janeN}_3$ (0.110 g, 0.642 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of $\text{Ti}(\text{N}^i\text{Bu})\text{Cl}_2(\text{py})_3$ (0.273 g, 0.639 mmol) in CH_2Cl_2 (15 mL). The initially deep orange solution became paler over 2 h, after which the volatiles were removed under reduced pressure to give an orange solid, which was washed with pentane (2×5 mL) and dried in vacuo. The crude material was dissolved in CH_2Cl_2 (8 mL) and the solution cooled to -25 °C for 3 days, which gave **1** as orange crystals, which were filtered off and dried in vacuo. Yield: 0.196 g (85%).

(b) From $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$. To a deep orange solution of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ (0.50 g, 2.4 mmol) in C_6H_6 (10 mL) was added 'BuNH_2 (0.25 mL, 2.4 mmol). Immediately after addition, the orange solution darkened and subsequently lightened over the space of several minutes to give a lemon yellow solution. After 16 h the solution was filtered and $\text{Me}_3[9]\text{janeN}_3$ (0.41 g, 2.4 mmol) was added, and the mixture was left to stir for another 16 h. Soon after addition of the ligand, a yellow solid began to precipitate. The solvent volume was reduced by two-thirds, and the solids were filtered off and washed with hexanes (3×10 mL). The resulting yellow powder was dried in vacuo. Yield: 0.73 g (85%). ¹H NMR (300.1 MHz, CDCl_3): 3.61 (2 H, m, CH_2 ring), 3.30 (6 H, s, NMe *trans* to NⁱBu), 3.18 (2 H, m, CH_2 ring), 3.10 (2 H, m, CH_2 ring), 2.94 (2 H, m, CH_2 ring), 2.80 (2 H, m, CH_2 ring), 2.57 (2 H, m, CH_2 ring), 2.51 (6 H, s, NMe *cis* to NⁱBu), 1.13 (9 H, s, ⁱBu). ¹³C-{¹H} NMR (75.5 MHz, CDCl_3): 69.2 (NCMe₃), 56.7 (CH_2 ring), 56.4 (CH_2 ring), 54.2 (CH_2 ring), 53.8 (NMe *cis* to NⁱBu), 48.1 (NMe *trans* to NⁱBu), 30.9 (NCMe₃). IR (CsBr plates, Nujol, cm^{-1}): 1498(w), 1462(s), 1377(m), 1351(w), 1298(w), 1244(m), 1206(w), 1155(w), 1120(w), 1074(w), 1065(w), 1002(m), 892(w), 784(m), 747(w), 730(w), 598(w), 584(w), 536(w), 438(w), 421(w). EI-MS: $m/z = 345$ (75%) [$\text{M} - \text{Me}$]⁺, 289 (100%) [$\text{M} - \text{N}^i\text{Bu}$]⁺. Anal. Found (calcd for $\text{C}_{13}\text{H}_{30}\text{Cl}_2\text{N}_4\text{Ti}$): C, 43.1 (43.2); H, 8.4 (8.4); N, 15.4 (15.5).

Ti(N-2,6-C₆H₃Me₂)(Me₃[9]janeN₃)Cl₂ (2). A solution of $\text{Me}_3[9]\text{janeN}_3$ (0.856 g, 5.00 mmol) in CH_2Cl_2 (5 mL) was added

to a stirred solution of $\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Me}_2)\text{Cl}_2(\text{py})_3$ (2.376 g, 5.00 mmol) in CH_2Cl_2 (25 mL). The resulting dark brown solution was stirred for 20 h, and the volatiles were removed under reduced pressure. The product was extracted into CH_2Cl_2 (15 mL) and then cautiously precipitated by the slow addition of hexane (30 mL) with vigorous stirring. The resulting brown precipitate was filtered off, washed with hexanes (5 mL), and dried in vacuo to give a brown powder. Yield: 1.76 g (86%). ¹H NMR (300.1 MHz, CDCl_3): 6.76 (2 H, d, ³ $J = 7.4$ Hz, *meta*- $\text{C}_6\text{H}_3\text{Me}_2$), 6.52 (1 H, t, ³ $J = 7.4$ Hz, *para*- $\text{C}_6\text{H}_3\text{Me}_2$), 3.91 (2 H, m, CH_2 ring), 3.34 (2 H, m, CH_2 ring), 3.33 (6 H, s, NMe *cis* to NAr), 3.12 (2 H, m, CH_2 ring), 3.10 (2 H, m, CH_2 ring), 2.78 (6 H, s, $\text{C}_6\text{H}_3\text{Me}_2$), 2.76 (2 H, m, CH_2 ring), 2.70 (3 H, s, NMe *trans* to NAr), 2.55 (2 H, m, CH_2 ring). ¹³C-{¹H} NMR (75.5 MHz, CDCl_3): 148.2 (*ipso*- $\text{C}_6\text{H}_3\text{Me}_2$), 133.6 (*ortho*- $\text{C}_6\text{H}_3\text{Me}_2$), 127.9 (*meta*- $\text{C}_6\text{H}_3\text{Me}_2$), 121.0 (*para*- $\text{C}_6\text{H}_3\text{Me}_2$), 57.8 (CH_2 ring), 57.2 (CH_2 ring), 54.7 (CH_2 ring), 54.3 (NMe *cis* to NAr), 49.2 (NMe *trans* to NAr), 22.1 ($\text{C}_6\text{H}_3\text{Me}_2$). Anal. Found (calcd for $\text{C}_{17}\text{H}_{30}\text{Cl}_2\text{N}_4\text{Ti}$): C 49.7, (49.9); H, 7.5 (7.4); N, 13.6 (13.7).

Ti(N-2,6-C₆H₃Pr₂)(Me₃[9]janeN₃)Cl₂ (3). A solution of $\text{Me}_3[9]\text{janeN}_3$ (0.856 g, 5.00 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of $\text{Ti}(\text{N-2,6-C}_6\text{H}_3\text{Pr}_2)\text{Cl}_2(\text{py})_3$ (2.657 g, 5.00 mmol) in CH_2Cl_2 (20 mL). The resulting dark brown solution was stirred for 14 h, and the volatiles were removed under reduced pressure. The product was extracted into CH_2Cl_2 (15 mL) and then cautiously precipitated by the slow addition of hexane (35 mL) with vigorous stirring. The resulting microcrystalline green-brown precipitate was filtered off, washed with hexanes (5 mL), and dried in vacuo to give a green-brown powder. Yield: 2.02 g (87%). ¹H NMR (300.1 MHz, CDCl_3): 6.90 (2 H, d, ³ $J = 7.6$ Hz, *meta*- $\text{C}_6\text{H}_3\text{Pr}_2$), 6.72 (1 H, t, ³ $J = 7.6$ Hz, *para*- $\text{C}_6\text{H}_3\text{Pr}_2$), 4.51 (2 H, sept, ³ $J = 6.9$ Hz, CHMe_2), 3.74 (2 H, m, CH_2 ring), 3.33 (2 H, m, CH_2 ring), 3.27 (6 H, s, NMe *cis* to NAr), 3.16 (2 H, m, CH_2 ring), 3.11 (2 H, m, CH_2 ring), 2.77 (2 H, m, CH_2 ring), 2.69 (3 H, s, NMe *trans* to NAr), 2.56 (2 H, m, CH_2 ring), 1.25 (12 H, d, ³ $J = 6.9$ Hz, CHMe_2). ¹³C-{¹H} NMR (75.5, CDCl_3 , MHz): 155.7 (*ipso*- $\text{C}_6\text{H}_3\text{Pr}_2$), 145.0 (*ortho*- $\text{C}_6\text{H}_3\text{Pr}_2$), 122.8 (*meta*- $\text{C}_6\text{H}_3\text{Pr}_2$), 121.3 (*para*- $\text{C}_6\text{H}_3\text{Pr}_2$), 58.3 (CH_2 ring), 57.3 (CH_2 ring), 54.4 (CH_2 ring), 54.0 (NMe *cis* to NAr), 49.1 (NMe *trans* to NAr), 27.4 (CHMe_2), 25.3 (CHMe_2). Anal. Found (calcd for $\text{C}_{21}\text{H}_{38}\text{Cl}_2\text{N}_4\text{Ti}$): C, 53.9 (54.2); H, 8.4 (8.2); N, 12.0 (12.0).

Ti(NPh)(Me₃[9]janeN₃)Cl₂ (4). To a solution of $\text{Ti}(\text{NPh})\text{Cl}_2(\text{NHMe}_2)_2$ (0.4 g, 1.33 mmol) in C_6H_6 (5 mL) was added $\text{Me}_3[9]\text{janeN}_3$ (0.26 mL, 1.33 mmol). Soon after addition, an orange solid began to precipitate. The mixture was stirred for 16 h, after which time the solids were filtered off, washed with hexanes (3×10 mL), and dried in vacuo. Yield: 0.50 g (99%). ¹H NMR (500.0 MHz, CD_2Cl_2): 7.06 (2 H, app t, app ³ $J = 8.2$ Hz, *meta*- C_6H_5), 6.92 (2 H, d, ³ $J = 8.8$ Hz, *ortho*- C_6H_5), 6.75 (1 H, t, ³ $J = 7.7$ Hz, *para*- C_6H_5), 3.48 (2 H, m, CH_2 ring), 3.23 (2 H, m, CH_2 ring), 3.21 (6 H, s, NMe *cis* to NPh), 3.02 (4 H, overlapping $2 \times$ m, CH_2 ring), 2.78 (2 H, m, CH_2 ring), 2.64 (3 H, s, NMe *trans* to NPh), 2.61 (2 H, m, CH_2 ring). ¹³C-{¹H} NMR (125.7 MHz, CD_2Cl_2): 128.6 (*ipso*- C_6H_5), 128.5 (*meta*- C_6H_5), 123.8 (*para*- C_6H_5), 121.4 (*ortho*- C_6H_5), 57.3 (CH_2 ring), 56.9 (CH_2 ring), 55.2 (CH_2 ring), 53.6 (NMe *cis* to NPh), 49.2 (NMe *trans* to NPh). IR (KBr pellet, cm^{-1}): 3064 (w), 3004 (w), 2928 (s), 2912 (s), 2858 (s), 2844 (s), 1576 (m), 1496 (m), 1294 (w), 1282 (w), 1280 (m), 1162 (w), 1072 (m), 1064 (m), 1008 (m), 962 (w), 896 (w), 788 (m), 772 (s), 750 (w), 670 (w), 584 (w), 520 (m), 442 (w), 426 (w). EI-MS: $m/z = 380$ (50%) [M]⁺, 288 (14%) [$\text{M} - \text{NPh} - \text{H}$]⁺. Anal. Found (calcd for $\text{C}_{15}\text{H}_{26}\text{Cl}_2\text{N}_4\text{Ti}$): C, 47.6 (47.3); H, 7.3 (6.9); N, 14.4 (14.7).

Ti(NC₆F₅)(Me₃[9]janeN₃)Cl₂ (5). To a solution of $\text{Ti}(\text{NC}_6\text{F}_5)\text{Cl}_2(\text{NHMe}_2)_2$ (0.62 g, 1.59 mmol) in C_6H_6 (10 mL) was added $\text{Me}_3[9]\text{janeN}_3$ (0.31 mL, 1.59 mmol). A yellow solid precipitated from solution soon after addition. The mixture was stirred for 16 h, after which time the solvent volume was reduced by two-thirds,

(113) Madison, S. A.; Batal, D. J. (Unilever PLC, UK.; Unilever N. V.) United States Patent 5,284,944, 1994.

(114) Froneman, M.; Cheney, D. L.; Modro, T. L. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1990**, *47*.

and the solids were filtered off, washed with hexanes (3×10 mL), and dried in vacuo. Yield: 0.59 g (79%). ^1H NMR (300.1 MHz CD_2Cl_2): 3.56 (2 H, m, CH_2 ring), 3.21 (6 H, overlapping $3 \times$ m, CH_2 ring), 3.15 (6 H, s, NMe *cis* to NC_6F_5), 3.01 (2 H, m, CH_2 ring), 2.75 (2 H, m, CH_2 ring), 2.74 (3 H, s, NMe *trans* to NC_6F_5). ^{19}F NMR (282.4 MHz, CD_2Cl_2): -152.1 (2 F, unresolved m, *ortho*- C_6F_5), -167.6 (2 F, unresolved m, *meta*- C_6F_5), -169.6 (1 F, unresolved m, *para*- C_6F_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): 57.4 (NMe *cis* to NC_6F_5), 55.4 (overlapping, $2 \times$ CH_2 ring), 53.5 (NMe *trans* to NC_6F_5), 49.7 (CH_2 ring), the C_6F_5 ring carbons were not observed due to ^{19}F coupling. IR (KBr plates, Nujol, cm^{-1}): 1320 (w), 1292 (w), 1262 (w), 1206 (w), 1156 (w), 1053 (m), 1038 (m), 1000 (m), 978 (m), 892 (w), 790 (m), 750 (w), 722 (m), 580 (br, w), 500 (w), 462 (w), 448 (w), 426 (m), 416 (w). EI-MS: m/z = 470 (45%) $[\text{M}]^+$, 435 (7%) $[\text{M} - \text{Cl}]^+$. Anal. Found (calcd for $\text{C}_{15}\text{H}_{21}\text{Cl}_2\text{F}_5\text{N}_4\text{Ti}$): C, 38.3 (38.3); H, 4.7 (4.5); N, 11.7 (11.9).

Ti(NCH₂Ph)(Me₃[9]aneN₃)Cl₂ (6). To a solution of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ (0.5 g, 2.4 mmol) in C_6H_6 (5 mL) was added PhCH_2NH_2 (0.25 mL, 2.4 mmol). Immediately after addition the orange color of the solution darkened noticeably. The solution was stirred for 16 h, and then $\text{Me}_3[9]\text{aneN}_3$ (0.47 mL, 2.4 mmol) was added. Almost immediately after addition, a pale yellow solid began to precipitate from the solution. The mixture was stirred for another 16 h, the solvent volume was reduced by two-thirds, and the solids were filtered off, washed with hexanes (3×10 mL), and dried in vacuo to yield pale cream colored **6**. Yield: 0.86 g (96%). ^1H NMR (500.0 MHz, CD_2Cl_2): 7.53 (2 H, d, $^3J = 7.3$ Hz, *ortho*- C_6H_5), 7.30 (2 H, app t, app $^3J = 7.8$ Hz, *meta*- C_6H_5), 7.17 (1 H, t, $^3J = 7.3$ Hz, *para*- C_6H_5), 4.53 (2 H, s, CH_2Ph), 3.31 (2 H, m, CH_2 ring), 3.13 (2 H, m, CH_2 ring), 3.06 (6 H, s, NMe *cis* to NCH_2Ph), 2.94 (4 H, overlapping $2 \times$ m, CH_2 ring), 2.69 (2 H, m, CH_2 ring), 2.50 (2 H, m, CH_2 ring), 2.49 (3 H, s, NMe *trans* to NCH_2Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CD_2Cl_2): 142.0 (*ipso*- C_6H_5), 128.3 (*meta*- C_6H_5), 127.6 (*ortho*- C_6H_5), 126.4 (*para*- C_6H_5), 68.6 (CH_2Ph), 57.1 (CH_2 ring), 56.8 (CH_2 ring), 54.9 (CH_2 ring), 53.5 (NMe *cis* to NCH_2Ph), 48.9 (NMe *trans* to NCH_2Ph). IR (KBr plates, Nujol, cm^{-1}): 3064 (w), 3020 (m), 3002 (m), 2958 (m), 2898 (s), 2866 (s), 2861 (s), 2768 (s), 1496 (vs), 1452 (vs), 1388 (w), 1336 (m), 1326 (m), 1298 (vs), 1244 (vs), 1186 (m), 1158 (m), 1124 (m), 1074 (vs), 1066 (vs), 1030 (m), 1004 (vs), 896 (s), 786 (vs), 744 (vs), 708 (vs), 690 (m), 618 (w), 586 (s), 458 (m), 426 (s), 442 (s), 412 (s). EI-MS: m/z = 395 (6%) $[\text{M}]^+$, 289 (100%) $[\text{M} - \text{CH}_2\text{Ph}]^+$, 218 (78%) $[\text{M} - \text{NCH}_2\text{Ph} - 2\text{Cl}]^+$. Anal. Found (calcd for $\text{C}_{16}\text{H}_{28}\text{Cl}_2\text{N}_4\text{Ti}$): C, 48.5 (48.7); H, 7.2 (7.2); N, 13.5 (14.2).

NMR Tube Scale Reaction of Ti(N^tBu)(Me₃[9]aneN₃)Cl₂ with BHT-H. $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (8.0 mg, 0.022 mmol) and BHT-H (4.9 mg, 0.022 mmol) were dissolved in CD_2Cl_2 (0.75 mL). ^1H NMR spectra after 10 min and 1 h showed resonances corresponding to unreacted $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ and BHT-H. After the sealed NMR tube was heated to 70 °C for 1 h the ^1H NMR spectrum remained unchanged.

NMR Tube Scale Reaction of Ti(N^tBu)(Me₃[9]aneN₃)Me₂ with BHT-H. $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}_2$ (2.5 mg, 0.008 mmol) and BHT-H (1.7 mg, 0.008 mmol) were dissolved in C_6D_6 (0.75 mL). The ^1H NMR spectrum after 10 min showed resonances corresponding to free $\text{Me}_3[9]\text{aneN}_3$ and a mixture of other unidentified products. The ^1H NMR spectrum was unchanged after 1 h at room temperature and after heating to 70 °C for 1 h.

[Ti(N^tBu)(Me₃[9]aneN₃)(BHT)][BAR^F₄] (60-BAR^F₄). To a solution of $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}_2$ (50 mg, 0.156 mmol) in $\text{C}_6\text{H}_5\text{Cl}$ (2 mL) was added $[\text{Ph}_3\text{C}][\text{BAR}^{\text{F}}_4]$ (144 mg, 0.156 mmol) in $\text{C}_6\text{H}_5\text{Cl}$ (2 mL) to give a bright orange solution. After 5 min BHT-H (34 mg, 0.156 mmol) was added. The reaction mixture was stirred for 1 h at 70 °C and then allowed to cool. The yellow solution was concentrated to approximately 1 mL, then pentane (4 mL) was added with stirring to give an orange oil. The supernatant was decanted and the oil washed with pentane (3×2 mL). When a

reduced pressure was applied to the oil, an orange powder was obtained. Yield: 127 mg (68%). ^1H NMR (499.9 MHz, CD_2Cl_2): 7.10 (2 H, $\text{C}_6\text{H}_2^t\text{Bu}_2\text{Me}$), 4.09 (2 H, m, CH_2 ring), 3.38 (2 H, m, CH_2 ring), 3.16 (6 H, s, NMe *cis* to N^tBu), 3.01 (2 H, m, CH_2 ring), 2.85 (2 H, m, CH_2 ring), 2.74 (2 H, m, CH_2 ring), 2.63 (2 H, m, CH_2 ring), 2.41 (3 H, s, NMe *trans* to N^tBu), 2.26 (3 H, s, $\text{C}_6\text{H}_2^t\text{Bu}_2\text{Me}$), 1.58 (18 H, s, $\text{C}_6\text{H}_2^t\text{Bu}_2\text{Me}$), 0.79 (9 H, s, ^tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CD_2Cl_2): 162.7 (*ipso*- $\text{C}_6\text{H}_2^t\text{Bu}_2\text{Me}$), 148.5 (br d, $^1J_{\text{C-F}} = 238$ Hz, *ortho*- C_6F_5), 138.6 (br d, $^1J_{\text{C-F}} = 247$ Hz, *para*- C_6F_5), 136.7 (br d, $^1J_{\text{C-F}} = 250$ Hz, *meta*- C_6F_5), 135.1 (*ortho*- $\text{C}_6\text{H}_2^t\text{Bu}_2\text{Me}$), 127.8 (*para*- $\text{C}_6\text{H}_2^t\text{Bu}_2\text{Me}$), 126.7 (*meta*- $\text{C}_6\text{H}_2^t\text{Bu}_2\text{Me}$), 72.7 (NCMe₃), 56.8 (CH_2 ring), 56.6 (CH_2 ring), 54.0 (CH_2 ring), 53.7 (NMe *cis* to ^tBu), 49.0 (NMe *trans* to ^tBu), 35.4 (CCMe₃), 31.6 (NCMe₃), 31.4 (CCMe₃). ^{19}F NMR (282.1 MHz, CD_2Cl_2): -133.5 (d, $^3J = 10.6$ Hz, *ortho*- C_6F_5), -164.0 (t, $^3J = 20.4$ Hz, *para*- C_6F_5), -167.9 (app t, app $^3J = 18.1$ Hz, *meta*- C_6F_5). IR (NaCl plates, Nujol, cm^{-1}): 1643 (m), 1514 (s), 1420 (m), 1265 (m), 1239 (m), 1216 (m), 1087 (s), 1001 (m), 980 (s), 844 (w), 775 (m), 756 (m), 684 (m), 662 (m). Anal. Found (calcd for $\text{C}_{52}\text{H}_{53}\text{BF}_{20}\text{N}_4\text{OTi}$): C 52.1 (52.5), H 4.4 (4.5), N 4.7 (4.7).

NMR Tube Scale Reaction of [Ti(N^tBu)(Me₃[9]aneN₃)Me]⁺ with MeAl(BHT)₂. To a solution of $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$ (generated in situ from $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}_2$ (7.0 mg, 0.022 mmol) and $[\text{Ph}_3\text{C}][\text{BAR}^{\text{F}}_4]$ (20.2 mg, 0.022 mmol)) in $\text{C}_6\text{D}_5\text{Br}$ (0.75 mL) was added $\text{MeAl}(\text{BHT})_2$ (10.5 mg, 0.022 mmol). After 10 min the ^1H NMR spectrum showed broadened resonances for $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$ and $\text{MeAl}(\text{BHT})_2$.

NMR Tube Scale Reaction of [Ti(N^tBu)(Me₃[9]aneN₃)(μ-Me)₂AlMe₂]⁺ (II⁺) with BHT-H (2 equiv). To a solution of $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\mu\text{-Me})_2\text{AlMe}_2]^+$ (II⁺) (generated in situ from $\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}_2$ (7.0 mg, 0.022 mmol), $[\text{Ph}_3\text{C}][\text{BAR}^{\text{F}}_4]$ (20.2 mg, 0.022 mmol), and Al_2Me_6 (2.1 μL, 0.022 mmol)) in $\text{C}_6\text{D}_5\text{Br}$ (7.5 mL) was added BHT-H (9.6 mg, 0.044 mmol). The ^1H NMR spectrum was monitored over the course of 2 h, after which time the following species were present in the relative approximate proportions indicated: $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\mu\text{-Me})_2\text{AlMe}_2]^+$ (II⁺, 1.0), $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)\text{Me}]^+$ (2.5), $[\text{Ti}(\text{N}^t\text{Bu})(\text{Me}_3[9]\text{aneN}_3)(\text{BHT})]^+$ (60⁺, 1.0), BHT-H (1.8), $\text{MeAl}(\text{BHT})_2$ (3.7).

Procedure for Ti(NR)(Me₃[9]aneN₃)Cl₂ Library Synthesis. In preparation of the parallel synthesis procedure, stock solutions of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$ (0.32 M), $\text{Me}_3[9]\text{aneN}_3$ (1.06 M), and the amine library (0.97 M) in benzene were prepared. Amines (1.94 mmol of amine per vial) were purchased as "CombiKits" from Aldrich and used as received. An M. Braun Labmaster glovebox was equipped with a Tecan Miniprep liquid handling robot, two low-vortex flatbed shakers, and a vacuum/ N_2 connection. The first step was carried out in sealable wells having a maximum volume capacity of 10 mL. In the first step, 3 mL of the titanium amide stock solution (corresponding to 200 mg of $\text{Ti}(\text{NMe}_2)_2\text{Cl}_2$, 0.97 mmol/well) was dispensed into each well, followed by 1 mL of the appropriate amine stock solution (corresponding to 0.97 mmol amine/well). The wells were sealed with a Teflon cover to prevent evaporation of the solvent and shaken for 16 h. After this time, the resulting solutions of $\text{Ti}(\text{NR})\text{Cl}_2(\text{NHMe}_2)_2$ were transferred to preweighed solid phase synthesis cartridges equipped with Teflon filters and housed in a specially constructed holder. The holder allowed the application of either an overpressure or a vacuum from underneath the cartridges. After the solution transfer had been completed, the plates were manually checked for signs of crystallization. If crystallization had occurred, the crystals were gathered and recombined with the corresponding solution. During the solution transfer, an overpressure was applied from underneath the cartridges to keep the solutions above the frit. Subsequently, 1 mL of $\text{Me}_3[9]\text{aneN}_3$ stock solution (containing 1.06 mmol of ligand) was dispensed into each cartridge under agitation. Addition of the macrocycle typically resulted in the formation of a thick precipitate of the corresponding $\text{Ti}(\text{NR})$ -

Table 5. X-ray Data Collection and Processing Parameters for Ti(N^tBu)(Me₃[9]aneN₃)Cl₂·CH₂Cl₂ (1·CH₂Cl₂) and Ti(NR)(Me₃[9]aneN₃)Cl₂ (R = 2,6-C₆H₃Me₂ (2), 2,6-C₆H₃ⁱPr₂ (3), Ph (4), C₆F₅ (5))

parameter	1·CH ₂ Cl ₂	2	3	4	5
empirical formula	C ₁₃ H ₃₀ N ₄ Cl ₂ Ti·CH ₂ Cl ₂	C ₁₇ H ₃₀ Cl ₂ N ₄ Ti	C ₂₁ H ₃₈ N ₄ Cl ₂ Ti	C ₁₅ H ₂₆ Cl ₂ N ₄ Ti	C ₁₅ H ₂₁ Cl ₂ F ₅ N ₄ Ti
fw	446.15	409.26	465.35	381.21	471.16
temp/K	150	150	150	150	150
wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
space group	<i>Pbca</i>	<i>Pna2₁</i>	<i>Pbca</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	15.104(6)	17.327(4)	16.130(9)	7.3615(2)	17.3911(2)
<i>b</i> /Å	14.515(6)	8.214(2)	16.049(6)	15.1070(4)	8.1056(1)
<i>c</i> /Å	19.933(7)	13.868(4)	18.348(8)	16.0577(6)	13.3658(2)
α/deg	90	90	90	90	90
β/deg	90	90	90	93.061(1)	96.218(1)
γ/deg	90	90	90	90	90
<i>V</i> /Å ³	4370(3)	1974.0(6)	4750(4)	1783.2(1)	1873.03(4)
<i>Z</i>	8	4	8	4	4
<i>d</i> (calcd)/Mg·m ⁻¹	1.36	1.38	1.302	1.42	1.67
abs coeff/mm ⁻¹	0.88	0.71	0.60	0.78	0.80
<i>R</i> indices ^a	<i>R</i> ₁ = 0.0470 <i>wR</i> ₂ = 0.0672 [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0319 <i>R</i> _w = 0.0310 [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0425 <i>wR</i> ₂ = 0.106 [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0283 <i>R</i> _w = 0.0213 [<i>I</i> > 3σ(<i>I</i>)]	<i>R</i> ₁ = 0.0262 <i>R</i> _w = 0.0262 [<i>I</i> > 3σ(<i>I</i>)]

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

Cl₂(Me₃[9]aneN₃) complex. The cartridges were shaken for 2 h, after which time the pressure underneath the cartridge was reversed to remove the reaction solvent, which was caught in the plate underneath. The resulting solids were washed with hexanes (3 × 1 mL), the cartridges stoppered, and the solids dried in vacuo. The compounds were characterized by ¹H NMR spectroscopy and EI-mass spectrometry (high resolution) where possible. Characterizing data and yields are given in the Supporting Information. The data for **1–4** and **6** were identical to those for samples prepared conventionally using Schlenk techniques.

Typical Procedure for Ambient-Temperature Ethylene Polymerization Studies. To a sealable metal reactor containing a glass insert was added MAO (Albermarle, 20 mL, 10% in toluene, w/w, 30 mmol) made up to 200 mL with toluene. The solution was stirred at 250 rpm for 5 min, and then the precatalyst (20 μmol) in toluene (50 mL) was added to the reactor and the mixture stirred for a further 30 min. The reaction vessel was placed under dynamic vacuum for 10 s, the stirring was increased to 750 rpm, and a dynamic pressure of ethylene (6 bar) was admitted. After 60 min, the reactor was isolated and the pressure was released. Methanol (5 mL) was added to the mixture, followed by water (50 mL) with stirring. The mixture was acidified to pH = 1 using a solution of 10% HCl (aq) in MeOH and stirred overnight. The precipitated polymers were filtered, washed with water (total volume ca. 1000 mL), and dried to constant weight at room temperature. Analogous procedures were used for the polystyrene-supported catalysts and solution phase catalysts at 2.5 μmol precatalyst loadings.

Conditions for Parallel Screening of the Catalyst Library Ti(NR)(Me₃[9]aneN₃)Cl₂. Proprietary equipment was used with the following conditions: 0.16 μmol of precatalyst with 192 μmol of MAO (Ti:Al = 1:1200) in 62 mL of PMH (2,2,4,4,6-pentamethylheptane); precatalyst injected at 100 °C and stirred under 7 bar dynamic ethylene pressure; polymerization time 10 min.

Conditions for Ethylene Polymerization Studies Using Semi-batch Reactors at 100 °C. MAO (Eurecen Al 5100/10T, 10% in toluene) was obtained from Crompton and used as received. BHT-H was obtained from Aldrich. The BHT-H was dissolved in toluene and dried in vacuo and subsequently stored under nitrogen. Ethylene and nitrogen are purified over deoxocatalyst (BTS catalyst BASF AG) and 4 Å molecular sieves. Heptane was purified by degassing with nitrogen and subsequently purified over 13× molecular sieves. Toluene was purified by distilling from sodium/benzophenone.

Typical Example of an Ethylene Polymerization. Polymerizations were carried out in a stainless steel autoclave, equipped with a magnetically coupled mechanical stirrer. The autoclave has an internal volume of 2 L, and for these experiments the reactor was

equipped with baffles and two interMIG stirrers, operated at 1400 rpm. A 500 mL amount of heptanes was dosed into the autoclave. Ethylene was dosed via a Brooks mass flow controller into the headspace, and the reactor pressure was set at 8 bar. The temperature was set at 100 °C. Subsequently the MAO was dosed together with an additional 350 mL of heptanes. In case BHT was used, this was premixed with the MAO in the reactor. After stirring the contents of the reactor for 10 min at 100 °C, a solution of the catalyst in approximately 1 mL of toluene was mixed with 50 mL of heptanes and subsequently pumped into the reactor. The catalyst feeding section was flushed with additional heptanes. After dosing the catalyst components, the total volume of added heptanes was 1 L. The reactor temperature was kept at 100 ± 2 °C by cooling with an oil system. The reactor pressure was kept constant via supplying ethylene. After 10 min, the mixture was drawn off via a bottom valve. A mixture of 2-propanol and Irganox 1076 was added. The reactor was rinsed with PMH at 150 °C until the washings were visibly clear from polymer. The complete polymer slurry, including the washings with PMH, was put in a vacuum oven and dried to constant weight at 50 °C. To minimize mass transfer limitations, the amount of catalyst was adjusted to obtain between 5 and 10 g of polymer.

Crystal Structure Determinations of Ti(N^tBu)(Me₃[9]aneN₃)Cl₂·CH₂Cl₂ (1·CH₂Cl₂), Ti(NR)(Me₃[9]aneN₃)Cl₂ (R = 2,6-C₆H₃Me₂ (2), 2,6-C₆H₃ⁱPr₂ (3), Ph (4), C₆F₅ (5)), Ti(N-2,6-C₆H₃ⁱPr₂)(Me₃[6]aneN₃)Cl₂ (11), Ti(NPh)(Me₃[6]aneN₃)Cl₂·0.5CH₂Cl₂ (12·0.5CH₂Cl₂), and Ti(NC₆F₅)(Me₃[6]aneN₃)Cl₂·CH₂Cl₂ (13·CH₂Cl₂). Crystal data collection and processing parameters are given in Table 5 (1–5) or Table S2 of the Supporting Information. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N₂ using an Oxford Cryosystems cryostream unit. Diffraction data were measured using either a Stoë Stadi-4 four-circle or a Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.¹¹⁵ The structures were solved by direct methods (SIR92¹¹⁶ or SHELXS-97¹¹⁷), and further refinements and all other crystallographic calculations were performed using SHELXL-97¹¹⁸ or the CRYSTALS program suite.¹¹⁹ Details of the structure solution and refinements are given in the Supporting Information (CIF data). A

(115) Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Academic Press: New York, 1997.

(116) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(117) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(118) Sheldrick, G. M.; Schneider, T. R. *Methods Enzymol.* **1997**, *277*, 319.

full listing of atomic coordinates, bond lengths and angles, and displacement parameters for all the structures has been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Acknowledgment. We thank the EPSRC, DSM Research, and Millenium Pharmaceuticals Ltd. for support and Albermarle for samples of MAO.

(119) Betteridge, P. W.; Cooper, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of **1–5** and **11–13**; displacement ellipsoid plot and two further views of the supramolecular arrangement for $\text{Ti}(\text{NC}_6\text{F}_5)(\text{Me}_3[9]\text{aneN}_3)\text{Cl}_2$ (**5**); further details of the polystyrene-supported and $\text{R}_3[6]\text{aneN}_3$ -supported catalyst systems **7–9**, **12–15**, and **59** (discussion, syntheses, and X-ray structures); characterizing data and yields for compounds **16–58**. This information is available free of charge via the Internet at <http://pubs.acs.org>.

OM0603316