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Discovery and evaluation of highly active imidotitanium ethylene polymerisation catalysts using high throughput catalyst screening†

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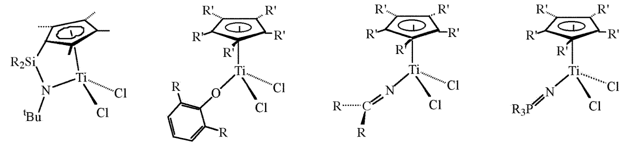
A family of *ca.* 50 imidotitanium precatalysts [Ti(NR)(Me_3[9]aneN$_3$)Cl$_2$] (R = alkyl or aryl; Me_3[9]aneN$_3$ = 1,4,7-trimethyltriazacyclononane) were prepared in good yields using semi-automated procedures; high-throughput screening techniques identified seven highly active ethylene polymerisation precatalysts with activities in the range *ca.* 3 400 to 10 000 kg(PE) mol^{-1} h^{-1} bar^{-1}.

Among the several types of Group 4 "post-metallocene" olefin polymerisation precatalysts[1] of note are half-sandwich complexes of the type [Ti(η-C$_5$R$_5$)(X)R$_2$] where X is a monoanionic O- or N-coordinated π-donor ligand (Chart 1).[2] All four families **A**–**D** have olefin polymerisation characteristics that depend critically on the substituents of the C$_5$R$_5$ and X ligands. Along with suitable steric protection around the O- and N-donor atoms, an important factor in the polymerisation activities of the ketimide **C** and phosphinimide **D** systems is the π-donor ability of the R$_2$CN and R$_3$PN ligands, with imido-type (RN=M) resonance contributions being deemed to be desirable.[2c,d] However, although imido compounds have a reasonable track record for ethylene polmerisation in Groups 5 and 6,[3a–c] activities for Group 4 systems have been surprisingly low.[3d] We report here the first highly active Group 4 imido ethylene polymerisation catalysts.



A **B** **C** **D**

Chart 1

Alkylation of [Ti(N^{t}Bu)(Me_3[9]aneN$_3$)Cl$_2$] **1**[4] affords [Ti(N^{t}Bu)(Me_3[9]aneN$_3$)R$_2$] (R = Me **2a** or CH$_2$SiMe$_3$ **2b**); the X-ray structure of **2a** is shown in Fig. 1.‡ Reaction of **2a** with either [CPh$_3$][B(Ar^F)$_4$] or B(Ar^F)$_3$ (Ar^F = C$_6$F$_5$) in C$_6$D$_5$Br afforded [Ti(N^{t}Bu)(Me_3[9]aneN$_3$)Me]$^+$ and the anions [B(Ar^F)$_4$]$^-$ **3** and [MeB(Ar^F)$_3$]$^-$ **4** respectively. The ^{19}F NMR spectra of **3** and **4** indicated the presence of solvent-separated ion pairs in both complexes.[5] Reaction of **2b** with [CPh$_3$][B(Ar^F)$_4$] gave [Ti(N^{t}Bu)(Me_3[9]aneN$_3$)(CH$_2$SiMe$_3$)]$^+$, and subsequent addition of ethylene to the NMR tube afforded a copious white precipitate. Polymerisation of ethylene at room temperature with 2.5 μmol of **2a** and 1 equiv. of [CPh$_3$][B(Ar^F)$_4$] activator (5 bar C$_2$H$_4$; T_0 = 24 ± 3 °C; 60 min., 250 cm^3 toluene; 5 mmol Al^{i}Bu$_3$) afforded 15.7 g polyethylene. This corresponds to a very high activity figure of 1260 kg(PE) mol^{-1} h^{-1} bar^{-1}, competitive with values reported for dialkyl compounds of the type **C** and **D** under comparable conditions.[2c,d] Additionally, we examined the polymerisation capability of the dichloride **1** with MAO cocatalyst (MAO = methylaluminoxane) under higher temperature conditions (Ti : Al 1 : 1600; 7 bar C$_2$H$_4$; T = 100 °C; 1–2 μmol of **1** in 1000 cm^3 PMH (pentamethylheptane); 5–10 mins) and recorded excellent activities of *ca.* ≥10^5 kg(PE) mol^{-1} h^{-1} bar^{-1}. In contrast, room temperature ethylene polymerisation by **1** with MAO cocatalyst (Ti : Al 1500; 5 bar C$_2$H$_4$; T_0 = 24 ± 3 °C; 20 μmol **1** in 250 cm^3 toluene) gave a modest activity of 22 kg(PE) mol^{-1} h^{-1} bar^{-1}. The corresponding arylimido compounds [Ti(N-2,6-C$_6$H$_3$R$_2$)(Me_3[9]aneN$_3$)Cl$_2$]† (R = H, Me, ^{i}Pr) had activities of 0.4, 9 and 80 kg(PE) mol^{-1} h^{-1} bar^{-1} respectively under these conditions, establishing at low temperature a dependence of activity on the imido N–R substituent.

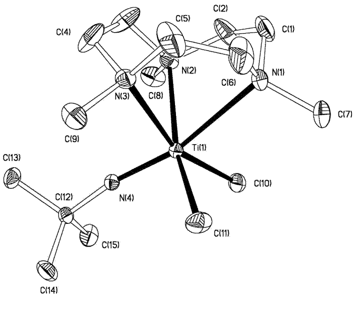
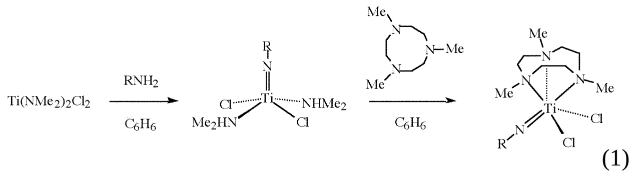


Fig. 1 Structure of [Ti(N^{t}Bu)(Me_3[9]aneN$_3$)Me$_2$] **2a**.

To evaluate the effects of a diverse range of imido N-substituents on polymerisation by [Ti(NR)(Me_3[9]aneN$_3$)Cl$_2$] at the more industrially relevant higher temperatures we devised an improved synthetic strategy (eqn. (1)) compatible with HTS (high throughput screening) methodologies.[6] Reaction of [Ti(NR)Cl$_2$(NHMe$_2$)$_2$][7] (easily soluble in benzene) with Me_3[9]aneN$_3$ cleanly and quantitatively afforded the moderately benzene-soluble [Ti(NR)(Me_3[9]aneN$_3$)Cl$_2$] which could be easily isolated by simple filtration and washing. Using this methodology we set out to prepare and evaluate a series of imidotitanium compounds [Ti(NR)(Me_3[9]aneN$_3$)Cl$_2$] *via* semi-automated parallel syntheses using 50 commercially available amines.‡



(1)

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† Electronic supplementary information (ESI) available: supporting characterising data and a listing of the polymerisation activities for the 47 compound precatalyst collection. See http://www.rsc.org/suppdata/cc/b3/b313921b/

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For the 47 successful syntheses the average isolated yield was *ca.* 60%, (avg. 250 mg quantities); all of these 47 compounds were greater than 95% pure by ^{1}H NMR spectroscopy and 45 gave molecular ions or related fragments within 5–10 ppm of the expected *m/z* value in their high-resolution mass spectra. Five of the compounds were independently prepared using conventional techniques and their ^{1}H NMR spectra were indistinguishable from those prepared in the semi-automated manner. The 47 precatalysts were screened for ethylene polymerisation with MAO at 100 °C (the temperature variations during polymerisation are usually within a couple of tenths of a degree). The activity data are illustrated in Fig. 2, and experimental details are summarised in Table 1.‡

Of the 47 $[Ti(NR)(Me_3[9]aneN_3)Cl_2]$ compounds screened, 7 (15%) had high activities in the range *ca.* 3,400–10,340 kg(PE) mol^{-1} h^{-1} bar^{-1}. The most active catalysts are found for bulky, electron-donating alkyl N-substituents (compound ID = 34, 41 (**1**) and 45), in line with trends reported for cyclopentadienyl-phosphinimides **D**. Surprisingly, the bulky ring 2,6-disubstituted arylimido compound $[Ti(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)(Me_3[9]aneN_3)Cl_2]$ (ID = 15) showed no activity, whereas at room temperature the same compound was nearly four times as active as the *tert*-butylimido analogue **1**. This indicates that thermal stability factors may also be important for these imido-based catalyst systems. The high activities recorded for NR = N-2-C_6H_4Br (ID 2) and N-3,5-$C_6H_3(CF_3)_2$ (ID 7) could reflect a special stability at the chosen reaction conditions.

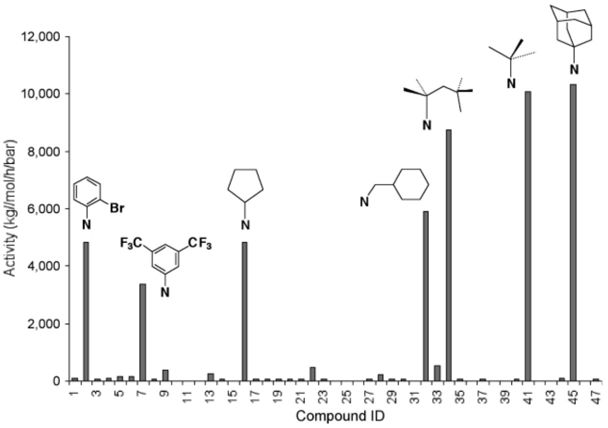

Fig. 2 Ethylene polymerisation activities for 47 imidotitanium precatalysts‡ $[Ti(NR)(Me_3[9]aneN_3)Cl_2]$. Selected R-groups (ID): 2-C_6H_4Br (ID = 2), 3,5-$C_6H_3(CF_3)_2$ (ID = 7), *c*-C_5H_9 (ID = 16), $CH_2C_6H_{11}$ (ID = 32), $CMe_2CH_2{}^tBu$ (ID = 34), ^{t}Bu **1** (ID = 41), Ad (ID = 45).

Table 1 Selected details of precatalyst productivities and polymer properties (IDs correspond to the catalyst list in Fig. 2 and the ESI).[a]

			GPC analysis		
ID	PE (g)	Activity[b]	*Mw*	*Mn*	*Mw/Mn*
45	1.93	10 340	145 950	24 450	6.0
41 (**1**)	1.88	10 070	273 850	39 500	7.0
34	1.63	8 730	190 700	33 000	5.8
32	1.10	5 890	152 700	15 200	10
2	0.90	4 820	119 400	19 400	6.2
7	0.63	3 380	50 300	10 400	4.8
16	0.90	4 820	1 501 900	391 200	3.8

[a] Conditions: 0.16 μmol precatalyst with 192 μmol MAO in 62 mL PMH (Ti:Al = 1:1200); precatalyst injected at 100 °C under 7 bar ethylene pressure; polymerisation time 10 minutes. [b] kg mol^{-1} h^{-1} bar^{-1}

As shown in Table 1 most of the polymer samples produced have reasonable molecular weights but slightly broad polydispersities (M_w/M_n). Generally a single-site catalyst is able to produce a polymer with $M_w/M_n \sim 2$, but in our system we believe that there is some interaction with residual $AlMe_3$ (or some other aluminium alkyls) in the MAO. Thus polymerisation with $[Ti(N^tBu)(Me_3[9]aneN_3)Cl_2]$ and MAO that had been heated *in vacuo* (60 °C, 12 h) to diminish the $AlMe_3$ content afforded improved activities (25% gain *cf.* conventional MAO), and polymer with higher M_w (480 000 *vs.* 192 000) and narrower polydispersity (M_w/M_n = 2.5 *vs* 5.8). Such results would be consistent with reducing chain transfer to aluminium processes. IR analysis of the polymers† showed them to be predominantly linear.

In summary we have discovered the first highly active Group 4 imido ethylene polymerisation catalysts. We have also made the first systematic study of imido ligand substitution patterns on polymerisation activity and polymer properties, and we have shown how low temperature structure–activity trends in these systems must not be assumed to persist at elevated temperatures. Well-defined dialkyl precatalysts (*e.g.* **2a** and **2b**) provide a platform to probe more systematically the roles of temperature, cocatalyst and imido group in the absence of MAO/$AlMe_3$ effects. The general synthetic route outlined in eqn. 1 is amenable for use with a range of other supporting co-ligands.

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‡ CCDC 223647. See http://www.rsc.org/suppdata/cc/b3/b313921b/ for crystallographic data in .cif or other electronic format.

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