SHORT PAPER

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Ethene polymerisation with titanium half-sandwich amido-complexes[†]

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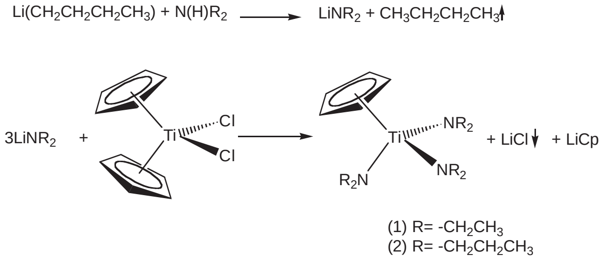
The complexes [CpTi(NR_2)$_3$] were tested in ethene polymerisation and the effect of the alkyl-amine groups on their activities was explored.

Keywords: half-sandwich, metal amido complexes, ethene polymerisation

Half-sandwich metal amido-complexes are potential catalytic precursors for homogeneous olefin polymerization.[1–4] Amine groups directly linked to the metal atom may affect both the catalytic activity and polymer properties through their steric and/or electronic influence, as well as playing a fundamental role in the stability of active species during polymerisation. This latter characteristic has great importance for understanding catalytic behaviour in homogenous olefin polymerisation.

In this work, using two different alkyl-amines as substituents (–NCH_2CH_3 and –$NCH_2CH_2CH_3$) in half-sandwich titanium complexes of the type [CpTi(NR_2)$_3$], a comparison of the amido-substituent effect on the catalyst performance toward ethene polymerisation was made. Compounds **1** and **2** were synthesised by reaction of an excess of $LiNR_2$ (R = –CH_2CH_3 or –$CH_2CH_2CH_3$) and an equivalent of [(η^5-C_5H_5)$_2$$TiCl_2$] in hexane (Scheme 1). This synthetic route is an alternative to the traditional amine elimination route used before for Cp-amido complexes. [3-6]



Scheme 1
Synthesis of [CpTi{(N(CH_2CH_3)$_2$}]$_3$] (1) and [CpTi{N($CH_2CH_2CH_3$)$_2$}$_3$] (2).

Homogenous polymerisation of ethene was carried out by activation of complexes **1** and **2** with MAO. The results of their activities are collected in Table 1. The polyethenes obtained showed high melting temperature (between 134 and 137 °C), corresponding to high density PE (HDPE). Optimum activity values of Al/Ti molar ratios were empirically determined. Both catalysts showed a maximum of the activity at a ratio Al/Ti = 4000. As found before in different catalytic systems, [3,4,7,8] increasing the MAO amount leads to lower activity, because of the poisoning effect by MAO at high Al/Ti ratios. On the other hand, a low MAO amount is not sufficient for total conversion to the active species.

Table 1 Polymerisation of ethene with **1** and **2** at different MAO/Ti molar ratio.

Catalyst	Al/Ti	Activity /gPE/gTi*h*atm	T_m /°C
1	2000	572	137
2	2000	243	136
1	4000	1522	136
2	4000	1259	134
1	6000	1259	135
2	6000	1111	134

The activity of **2** is always lower than **1**, with this becoming significant at low ratios of Al/Ti. There are several possible reasons for this. Firstly, *n*-propyl chain will favour terminal agostic interactions more than an ethyl chain. Secondly, the N^nPr_2 group is bulkier than the NEt_2 group, which may lead to slightly lower activation rates, or steric hindrance of the polymerisation. Thirdly, the $N^{n}Pr_2$ group is more electron-donating than the NEt_2 group, leading to a slightly less electrophilic active species.

Results reported herein indicate that an electronic effect, by using bulky and different chain length of amines, on the olefin polymerisation activities is expected in this kind of complexes.

Experimental

All manipulations were performed under a nitrogen atmosphere. Solvents were dried by refluxing over convenient drying agents. The structures of all isolated compounds were fully characterised by FTIR (Perkin-Elmer 1725 spectrometer), ^{1}H and ^{13}C NMR *(*Bruker 400). Chemical shifts are in ppm relative to TMS. The titanium content was determined by a colorimetric method.[9]

Compound **1** was synthesised in the following way: a solution of LiN(CH_2CH_3)$_2$ (from 7 mmol of *n*-butyllithium and 6 mmol of diethylamine in hexane) was added slowly to 0.498 g (2 mmol) of [(η^5-C_5H_5)$_2$$TiCl_2$] in hexane (40 ml). After stirring for 72 h, the mixture was filtered with a celite column and the volatiles removed in vacuum. Yield 88% (0.581 g). ^{1}H NMR ($CDCl_3$, ppm) δ = 1.02 (t, 18H, $\mathit{CH_3}CH_2$), 3.6, 3.9 (dq, 12H, $CH_3\mathit{CH_2}$), 6.2 (s, 5H, $CH_{aromatics}$ of C_5H_5). ^{13}C NMR ($CDCl_3$, ppm) δ = 13.6 ($\mathit{CH_3}CH_2$); 47.8 ($CH_3\mathit{CH_2}$); 112.8 ($C_{aromatics}$ of C_5H_5).

Compound **2** was synthesised in an analogous way to **1**, from dipropylamine (0.95 ml; 6.9 mol), *n*-butyllithium (2.76ml; 6.9 mol) and a suspension in hexane of [(η^5-C_5H_5)$_2$$TiCl_2$**]** (0.582 g; 2.3 mol). Yield 87% (0.706 g). ^{1}H NMR ($CDCl_3$, ppm) δ = 0.85 (t, 18H, $\mathit{CH_3}CH_2$); 1.4 (m, 12H, $CH_3\mathit{CH_2}$CH2N); 3.3 (m, 12H, $CH_3CH_2\mathit{CH_2}N$); 6.1 (s, 5H, $CH_{aromatics}$ of C_5H_5). ^{13}C NMR ($CDCl_3$, ppm) δ = 12 ($\mathit{CH_3}CH_2$); 22 ($CH_2\mathit{CH_2}N$); 110 ($C_{aromatics}$ of C_5H_5).

The ethene polymerisations were performed at 1 bar total pressure in a 100 ml glass reactor kept in a thermostatic bath at 25 ºC ±1 ºC. Toluene (40 ml) and the amount of MAO required to obtain Al/Ti molar ratios of 2000, 4000 and 6000, respectively, were mixed under

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

dinitrogen. Then nitrogen was removed by vacuum and the reaction mixture was saturated with ethene. Polymerisation started when a titanium complex solution containing typically 2 μmol in 2 ml of toluene was injected. The reactions were stopped after 0.5 h by venting the reactor and quenching the polymerisation with a solution of HCl/methanol. The polymers were washed in methanol for several hours, filtered and dried in vacuum at 40 °C overnight. Melting temperatures of polymers were measured by DSC.

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