Chiral *ansa*-Titanocene Imido Complexes: Novel Synthesis and Effective Initiator for Syndiospecific Polymerization of MMA

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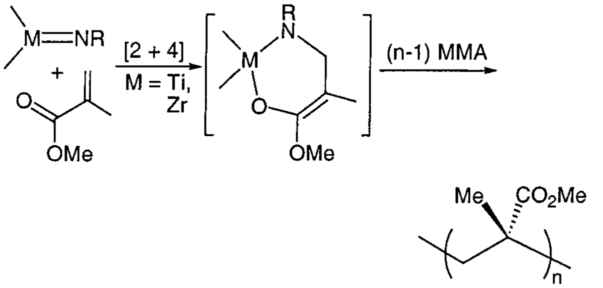
Summary: Reaction of $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)TiCl_2$ with lithium indenide and methyllithium in a one-pot fashion produces a chiral ansa-titanocene imido complex, which is an effective initiator for syndiospecific polymerization of MMA.

Group 4 imido complexes[1] have attracted considerable attention[2−4] over the past decade, in part because the M═NR imido moiety exhibits substantial reactivity toward a wide range of unsaturated organic substrates such as alkynes, imines, and certain alkenes. These reactions typically proceed through formal [2 + 2] cycloadditions, but nonterminal imido complexes such as vinylimido titanocenes undergo [4 + 2] cycloadditions with ketones, nitriles, and imines.[5] Enantioselective reactions between chiral, enantiopure zirconocene imido complexes and allenes have also been recently reported by Andersen, Bergman, and co-workers.[2b]

Controlled polymerization of methyl methacrylate (MMA) by lanthanocene[6] and metallocene[7] initiators has been well-documented. Either a neutral metal (Zr or Sm) enolate or a cationic Zr enolate is believed to participate in the propagation with a mechanism analogous to group-transfer polymerization.[8] We were investigating alternative initiation pathways for polymerization of polar vinyl monomers using metallocene/Lewis acid hybrid catalysts.[9] Inspired by earlier studies of the group 4 imido chemistry[1−5] and MMA polymerization by metallocene and related initiators,[6,7] we reasoned group 4 imido complexes could initiate MMA polymerization via an apparent [2 + 4] cycloaddition pathway (eq 1). We wish to report here the first chiral *ansa*-titanocene imido complex, conveniently synthesized from an industrially important constrained-geometry titanium complex in a one-pot fashion. This titanium imido complex is active for polymerization of MMA and is highly active with addition of an aluminum activator, affording syndiotactic PMMA.



(1)

Reaction of $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)TiCl_2$ (CGC-$TiCl_2$)[10] with lithium indenide ((Ind)Li) in THF from −78 °C to room temperature followed by direct addition of methyllithium produced a single diastereomer, a chiral *ansa*-titanocene imido complex (**1**; Scheme 1).[11] Diastere-

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Table 1. MMA Polymerization Results by 1

entry no.	$Al(C_6F_5)_3$/ Ti mole ratio	[M]/[I] ratio	T_p (°C)	t_p	yield (%)	$10^4 M_n$[b]	M_w/M_n	[*rr*][c] (%)	[*mr*] (%)	[*mm*] (%)
1	0	200	25	24 h	27	1.02	2.45	62.1	30.6	7.3
2	1	400	25	1 min	84	2.77	2.18	69.1	26.5	4.4
3[a]	1	400	25	1 min	81	2.76	2.12	68.7	26.8	4.5
4	1	400	−78	5 min	3.2	1.10	2.25	88.5	11.5	0.0
5	2	400	−78	5 min	100	2.52	2.37	87.9	12.1	0.0

[a] For entry 3, initiator **1** was first mixed with 1 equiv of the activator (in situ generation of **2**), whereas for entries 2, 4, and 5, MMA monomer was first activated with $Al(C_6F_5)_3$. [b] Determined by GPC relative to polystyrene standards. [c] Determined by ^1H NMR spectroscopy.

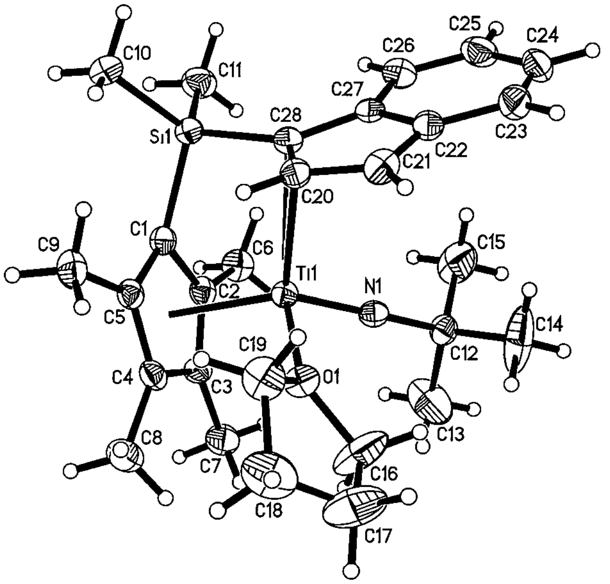
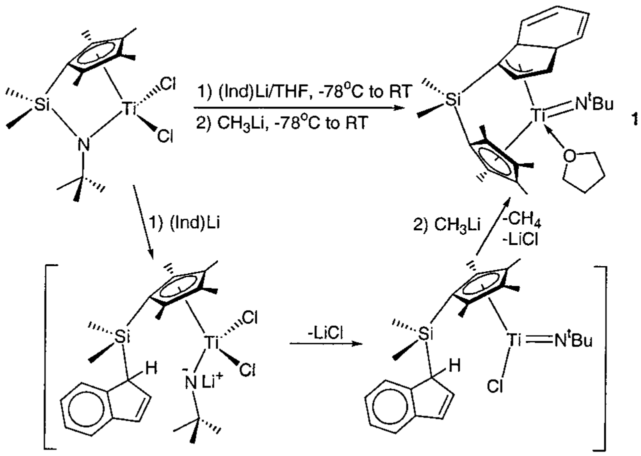


Figure 1. Crystallographic structure of **1**. Selected bond lengths (Å) and angles (deg): Ti−N = 1.708(3); Ti−C20 = 2.422(3); Ti−C28 = 2.478(3); Ti−C21 = 3.155; Ti−O = 2.138(2); N−C12 = 1.465(4); Ti−N−C12 = 176.0(2).

Scheme 1



omerization was not observed when heating a toluene solution of **1** up to 90 °C. The reaction was not investigated mechanistically, but the overall reaction represents an unprecedented route to *ansa*-titanocene imido complexes from commercially available constrained-geometry complexes.

The crystal structure of **1** (Figure 1)[12] features a bridged, η^5-coordinated tetramethylcyclopentadienyl ring, a bridged, ring-slipped η^2-indenyl moiety, and a near-linear terminal Ti=N−^{t}Bu linkage. The Ti−N−C12 angle is 176.0(2)°, suggesting sp hybridization about nitrogen and implying that the N^{t}Bu group is a four-electron donor to the metal center. The Ti=N bond distance is 1.708(3) Å and is well within the range of other structurally characterized titanium *tert*-butylimido bond lengths, such as $Ti(=N^tBu)Cl_2(py)_3$ (1.705(3) Å),[13] Cp*Ti(=N^{t}Bu)Cl(py) (1.698(4) Å),[14] and κ^3N-$(2\text{-}C_5H_4N)CMe_3(CH_2NSiMe_3)_2Ti(=N^tBu)(py)$ (1.724(2) Å).[15]

Attempts to generate a base-free derivative of **1** by sublimating **1** at 10^{-6} Torr/150 °C or by reacting **1** with $B(C_6F_5)_3$[16] resulted in decomposition and formation of a mixture of several species. Interestingly, the reaction of **1** with $Al(C_6F_5)_3$[17] effectively produced the zwitterionic complex **2**[18] rather than the anticipated base-free derivative (Scheme 2).

1 directly initiates polymerization of MMA at room temperature, producing syndiotactic-enriched PMMA despite low activity (entry 1, Table 1). Triad tests of the resulting polymer fit neither a site-controlled mechanism nor a chain-end-controlled mechanism. This result is in sharp contrast to that for $Me_2C(Cp)(Ind)ZrMe^+$, a chiral zirconocene cation having similar ligation but with a terminal methyl group, which produces isotactic PMMA via a site-controlled mechanism.[7a] Activity of the

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(11) ^1H NMR (C_6D_6, 23 °C): δ 7.97 (d, *J* = 6.8 Hz, 1 H, Ind), 7.90 (d, *J* = 6.8 Hz, 1 H, Ind), 7.46 (d, *J* = 3.6 Hz, 1 H, Ind), 7.25 (m, 2 H, Ind), 6.05 (d, *J* = 3.6 Hz, 1 H, Ind), 3.50 (m, 4 H, α-CH_2, THF), 2.57 (s, 3 H, Me_4C_5), 2.28 (s, 3 H, Me_4C_5), 1.99 (s, 3 H, Me_4C_5), 1.42 (s, 3 H, Me_4C_5), 1.16 (m, 4 H, β-CH_2, THF), 1.11 (s, 3 H, Me_2Si), 0.73 (s, 3 H, Me_2Si), 0.62 (s, 9 H, ^{t}Bu). ^{13}C NMR (C_6D_6, 23 °C): δ 154.73, 139, 79, 125.21, 123.00, 121.86, 119.39, 118.63, 116.75, 105.63 (Ind), 77.15 (α-CH_2), 69.18 (N*C*Me_3), 31.71 (NC*Me*$_3$), 25.72 (β-CH_2), 17.40, 14.56, 13.86, 11, 53 (*Me*$_4C_5$), 5, 79, 2.35 (*Me*$_2$Si). Anal. Calcd for $C_{28}H_{41}ONSiTi$: C, 69.54; H, 8.54; N, 2.89. Found: C, 68.99; H, 8.40; N, 2.81.

(12) Crystallographic data for **1**: triclinic, space group $P\bar{1}$; $a = 9.769(3)$ Å, $b = 10.560(4)$ Å, $c = 13.324(4)$ Å, $\alpha = 87.225(6)°$, $\beta = 89.690(6)°$, $\gamma = 72.208(7)°$ at 173(2) K; $V = 1307.2(7)$ Å^3; $Z = 2$; $D_{calcd} = 1.229$ Mg/m^3, absorption coefficient 0.393 mm^{-1}, $F(000) = 520$, 6160 reflections collected, 3757 independent reflections, R1 = 0.0466 ($I > 2\sigma(I)$), wR2 = 0.1222.

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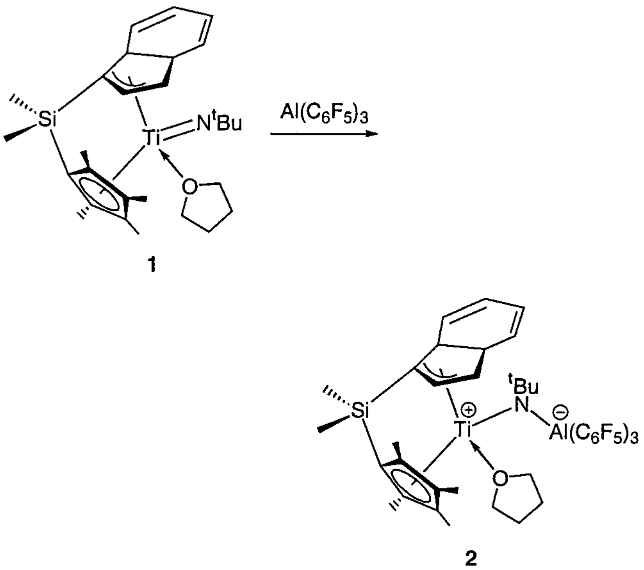
(18) ^1H NMR (C_7D_8, 23 °C): δ 8.05 (s, 1 H, Ind), 7.87 (d, *J* = 7.8 Hz, 1 H, Ind), 7.09 (m, 2 H, Ind), 6.75 (m, 1 H, Ind), 6.43 (s, 1 H, Ind), 3.08 (m, 2 H, α-CH_2, THF), 2.69 (m, 2 H, α-CH_2, THF), 2.19 (s, 3 H, Me_4C_5), 2.17 (s, 3 H, Me_4C_5), 1.58 (s, 3 H, Me_4C_5), 1.20 (s, 3 H, Me_4C_5), 1.03 (s, 9 H, ^{t}Bu), 0.82 (m, 4 H, β-CH_2, THF), 0.61 (s, 3 H, Me_2Si), 0.46 (s, 3 H, Me_2Si). ^{19}F NMR (C_7D_8, 23 °C): δ −120.15 (d, $^3J_{F-F}$ = 18.7 Hz, 6 F, *o*-F), −155.78 (t, $^3J_{F-F}$ = 19.7 Hz, 3 F, *p*-F), −162.73 (tt, 6 F, *m*-F).

Scheme 2



MMA polymerization can be substantially enhanced by either monomer activation or catalyst activation with the strong Lewis acid Al(C_6F_5)$_3$. Thus, addition of Al(C_6F_5)$_3$ to MMA followed by addition of **1** (Al/Ti/MMA = 1/1/400) results in a highly active system with TON = 20 256/h (entry 2), representing a rate enhancement of ~10^4. Likewise, preactivation of **1** with Al(C_6F_5)$_3$ (in situ generation of **2**) generates a similarly highly active system (TON = 19 488/h, entry 3). Initiator efficiencies ($I^* = M_n(\text{calcd})/M_n(\text{exptl})$) for these two runs exceed 100% (i.e., ~120%), indicative of the added Al(C_6F_5)$_3$ also functioning as a chain-transfer agent in these polymerizations. Lowering the polymerization temperature to −78 °C resulted in much lower activity but considerably higher syndiotacticity (entry 4). The activity can be drastically increased by adjusting the Al/Ti ratio from 1 to 2 at $T_p = -78$ °C, resulting in a quantitative polymer yield in 5 min at a high [M]/[I] ratio of 400 (entry 5).

In summary, we have developed a novel synthetic route to a new chiral, C_1-symmetric titanocene imido complex directly from a constrained-geometry complex. The titanocene imido complex itself is active for MMA polymerization, whereas addition of the activator Al(C_6F_5)$_3$ substantially enhances the polymerization activity producing syndiotactic PMMA. Further studies on mechanistic details of the polymerization as well as applications of this synthesis and polymerization to other group 4 imido complexes are in progress.

Acknowledgment. We thank Ms. Susie M. Miller for the X-ray diffraction analysis and Boulder Scientific Co. for a gift of B(C_6F_5)$_3$.

Supporting Information Available: Text and tables giving crystallographic data for **1** and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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