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Mono(imidazolin-2-iminato) Titanium Complexes for Ethylene Polymerization at Low Amounts of Methylaluminoxane

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Supporting Information

ABSTRACT: The polymerization of ethylene with titanium complexes bearing one bulky imidazolin-2-iminato ligand (L) in the presence of MAO and/or TTPB as cocatalysts have been explored. The complex $LTiCl_3$ and its methylated forms were prepared to shed light on the nature of the active polymerization species. With some of these complexes, the best catalytic activity was obtained at an Al:Ti ratio of 8.

Many efforts have been devoted to research on homogeneous catalysts for the polymerization of olefins, starting from the breakthrough discovery of the cocatalyst methylaluminoxane (MAO) by Kaminsky and colleagues.[1] Most of the studies have been dedicated to the development of group-3 and -4 metallocenes, half-metallocenes, constrained-geometry complexes, and nonmetallocene catalysts for a large variety of monomers.[2] Although some complexes are known to be exceptionally active toward specific monomers, sophisticated studies were performed to design and tailor the desired polymer properties. The ability to polymerize different monomers is dependent on the geometry of the active catalyst. For example, metallocenes of the type L_2MX_2 [L = cyclopentadienyl (Cp), pentamethylcyclopentadienyl (Cp*); X = halogen; M = group 4 metal] in combination with different cocatalysts generate highly active species for polymerization of olefins (e.g., ethylene, propylene, 1-hexene).[2] On the other hand, activated 12-electron half-metallocenes of the type LMX_3 (L = Cp, Cp*; X = halogen; M = group 4 metal) can effectively produce polydienes and syndiotactic polystyrenes.[3] Interestingly, constrained-geometry complexes allow the copolymerization of different α-olefins.[4] It has been reported that the activator and the structures of the resulting ion pairs can have a profound influence on the single-site polymerization catalyst activity, stability, lifetime, chain-transfer mechanism, and possibly stereoregulation.[5] The formation of such ion pairs is based on activation of the complexes with a cocatalyst by removal of an alkyl group. The ratio and nature of each cocatalyst have a profound influence on the performance of the catalyst.[6] Perfluorinated aromatic boranes/or borates are usually utilized in stoichiometric amounts, whereas for MAO, a large excess (1000−10000-fold) is needed to activate and obtain the best reactivities of the complexes. Although very extensive research to understand the exact composition and structure of MAO has been carried out, this system is still not entirely well-understood.[7] However multinuclear NMR investigations of MAO indicated a possible cage structure under ambient conditions.[8] Interestingly, when $CpTiX_3$ was used for the polymerization of styrene with controlled amounts of MAO, activation was observed at a minimum MAO:metal ratio of 6:1. Additional amounts of MAO increased the activity of the complex, which was explained in terms of the formation of cages, as proposed by Barron.[9]

We have been interested in complexes with non-Cp ancillary ligands, particularly those containing an N-donor moiety. One such interesting family comprises complexes containing imidazolin-2-iminato (Im) ligands. This class of N-heterocycle-based N-donor compounds behave as $2\sigma,4\pi$ electron donors resembling the Cp ligand and can be described by the two limiting mesomeric structures shown in Figure 1, which in turn should lead to highly basic compounds with a strong electron-donating capacity.[10] The synthetic route is based on the Staudinger reaction of carbenes of the imidazolin-2-ylidene type with trimethylsilyl azide to form *N*-silyl-2-iminoimidazolines.[10] Moreover, the substituents on the ring may suitably be altered to allow fine-tuning of both the steric and electronic properties of the ligand.

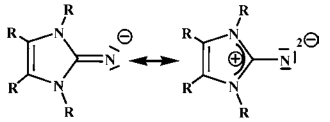

Figure 1. Mesomeric forms of imidazoline-2-iminato ligands.

It has been shown that titanium complexes of the type $CpTi(L)X_2$ (L = imidazolin-2-imide; X = Cl, CH_3) are active in the polymerization of ethylene and the copolymerization of ethylene with norbornene and 1-hexene,[11] whereas complexes of the type L_2TiX_2 (L = imidazolin-2-imide; X = Cl, CH_3) were found to be active in the living polymerization of propylene.[12]

Although the exact nature of MAO in an activated complex is unknown, various proposals have been offered, indicating that MAO may exist in an equilibrium among cages of different size.[7] This result implies the need for a large excess of MAO, as not every aluminum is active in the cage. Moreover, it has been

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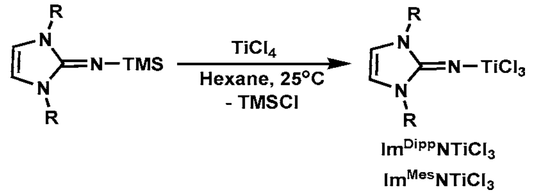
shown experimentally and theoretically that strong contact between the activated MAO anion and the cationic complex (ion pair) can inhibit the polymerization, though close contact is necessary in order to stabilize the cationic species formed after activation.[13] These results motivated us to study complexes of the type $LTiX_3$ (L = imidazolin-2-imide; X = Cl, CH_3) in which the one very bulky (large cone angle) ligand L is basic enough that it will not exchange with MAO. We present here the synthesis and X-ray characterization of four such complexes, their polymerization performance with ethylene, and the results of poisoning experiments. The conceptual expectations that we wanted to address in this study were the following: (i) If MAO is in close contact with the cationic complex to achieve good activity (avoiding the formation of oligomeric cationic structures), larger amounts of MAO should reduce the complex activity as a result of the formation of larger cages. (ii) An active complex should be obtained using very small MAO:catalyst ratios. (iii) If no close contact is operative, a large excess of MAO may improve the catalytic performance of the catalyst. However, a minimum amount of MAO should be needed to start the activation of the complex.

$TiCl_4$ was reacted with 1 equiv of the appropriate silylated neutral ligands (Scheme 1) to obtain the corresponding imidazolin-2-iminato complexes $Im^{Dipp}NTiCl_3$ and $Im^{Mes}NTiCl_3$ (Dipp = 2,6-diisopropylphenyl; Mes =1,3,5-trimethylphenyl). Since activation of the chloride complexes with MAO can form various active complexes (by replacement of one, two, or three chlorides and the formation of different counterion species), we prepared the methylated complexes $Im^{Dipp}NTiClMe_2$ and $Im^{Dipp}NTiMe_3$ to study the nature of the active species.

Scheme 1



According to the X-ray structure of the complex $Im^{Dipp}NTiCl_3$ (Figure 2), the titanium metal center exhibits a tetrahedral geometry. The Ti−N1 bond distance of 1.731(3) Å and the approximately linear C1−N1−Ti bond angle of 175.9(2)° indicate effective electron donation from the ligand to the metal atom. As shown by the X-ray structures of $Im^{Dipp}TiClMe_2$ (Figure 3) and $Im^{Dipp}NTiMe_3$ (Figure 4), as the number of methyl groups within the complex increases, the Ti−N1 bond distance increases and the C1−N1−Ti bond angle decreases to 1.762(4) Å and 172.8(4)°, respectively, in $Im^{Dipp}NTiClMe_2$ and 1.792(3) Å and 171.9(3)°, respectively, in $Im^{Dipp}NTiMe_3$. The X-ray structure of the complex $Im^{Mes}NTiCl_3$ exhibits a distorted tetrahedral geometry with features similar to those of $Im^{Dipp}NTiCl_3$, with a Ti−N1 bond distance of 1.720(10) Å and an almost linear C1−N1−Ti bond angle of 172.4(9)° (Figure 5).

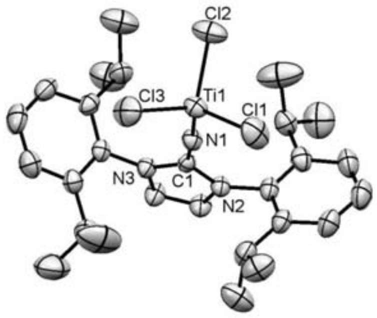


Figure 2. ORTEP drawing of $Im^{Dipp}NTiCl_3$ with 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Cl1−Ti = 2.2411(15), Cl2−Ti = 2.2415(14), Cl3−Ti = 2.2266(13), N1−Ti = 1.731(3), C1−N1 = 1.329(4), Cl1−Ti−Cl2 = 108.36(6), C1−N1−Ti = 175.9(2), N3−C1−N2 = 107.1(3).

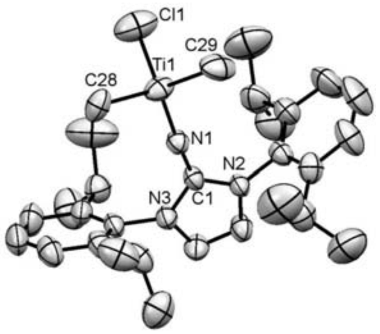


Figure 3. ORTEP drawing of $Im^{Dipp}NTiClMe_2$ with 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Cl1−Ti = 2.258(2), C28−Ti = 2.171(6), C29−Ti = 2.094(7), N1−Ti = 1.762(4), C1−N1 = 1.303(6), Cl1−Ti−C28 = 107.94(16), C28−Ti−C29 = 106.4(3), C29−Ti−Cl1 = 110.2(2), C1−N1−Ti = 172.8(4), N3−C1−N2 105.4(4).

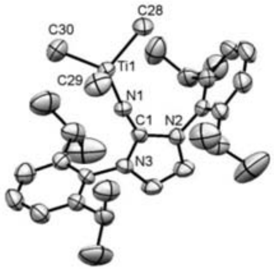


Figure 4. ORTEP drawing of $Im^{Dipp}NTiMe_3$ with 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): C28−Ti = 2.068(4), C29−Ti = 2.087(4), C30−Ti = 2.072(4), N1−Ti = 1.792(3), C1−N1 = 1.305(4), C29−Ti−C28 = 106.63(19), C28−Ti−C30 = 106.81(19), C1−N1−Ti = 171.9(3), N3−C1−N2 = 105.2(3).

The activities of these four complexes in combination with the cocatalysts MAO and trityl tetrakis(pentafluorophenyl)-borate (TTPB) were tested in the polymerization of ethylene. The activities, molecular weights of the polymers, and rates of insertion and chain termination are summarized in Table 1. The complex $Im^{Dipp}NTiCl_3$ can form active species at relatively moderate Al:Ti ratios (entries 1−3), but the polydispersities (PDs) of the obtained polymers indicate the plausible formation of more than one active species. Higher Al:Ti ratios (entries 4 and 5) allowed the formation of polymers with narrow PD, indicating that a single-site catalyst was operative. Excess MAO transforms the active complexes obtained at low concentrations of MAO into a single component at high MAO

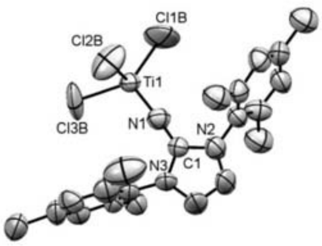


Figure 5. ORTEP drawing of Im^{Mes}NTiCl$_3$ with 50% probability ellipsoids. Selected bond distances (Å) and angles (deg): Cl3B−Ti = 2.214(19), N1−Ti = 1.720(10), C1−N1 = 1.311(14), C1−N1−Ti = 172.4(9), N3−C1−N2 = 106.2(8).

concentrations; however, it is evident that an Al:Ti ratio higher than 700 is unnecessary.

Although an increase in polymer molecular weight was observed as a function of the amount of MAO, higher activity was observed at Al:Ti = 100 (entry 2). This result indicates that a second complex with higher rates of insertion and chain termination is also operative. To better understand the nature of the active species formed at low MAO:catalyst ratios, we synthesized the methylated complex Im^{Dipp}NTiClMe$_2$, which would be the first precatalyst intermediate formed from the reaction of Im^{Dipp}NTiCl$_3$ with MAO. With Im^{Dipp}NTiClMe$_2$, the best catalytic activity was already achieved at very low Al:Ti ratios of 20. Higher amounts of MAO decreased the activity of the Im^{Dipp}NTiClMe$_2$ precatalyst.

It was expected that excess MAO would produce the same active species as obtained with Im^{Dipp}NTiCl$_3$, but the lower activity, rate of insertion, and rate of chain termination indicated that a different single-site catalyst was formed that presumably differed only in its counterion! To determine whether the chloride is attached to the complex in its active form, activation of the complex DippTiClMe$_2$ was performed with TTPB to produce the expected compound [Im^{Dipp}NTiClMe$^+$][B(C$_6$F$_5$)$_4$$^-$] (entry 10).[14] Interestingly, the activity and rates of insertion and chain termination for this compound were similar to those for Im^{Dipp}NTiClMe$_2$ (entry 6), corroborating the presence of a chloride moiety in the active site at low MAO ratios.

To shed light on the effect of the presence of a chloride in the complex and of the formed counterion, we also synthesized the fully methylated complex Im^{Dipp}NTiMe$_3$. This complex gave the best catalytic activity at Al:Ti = 20. In addition, its activation with TTPB afforded an active complex, but the resulting polymer had a lower molecular weight than the polymers obtained using the cocatalyst MAO because of the high rate of chain termination. This result indicates that a looser counterion must be operative with Im^{Dipp}NTiMe$_3$ and TTPB than with MAO.

On the basis of these results, we can assume that with low amounts of MAO, Im^{Dipp}NTiCl$_3$ gives mixtures of four possible active species: [Im^{Dipp}NTiClMe]$^+$[Cl-MAO]$^-$, [Im^{Dipp}NTiClMe]$^+$[Me-MAO]$^-$, [Im^{Dipp}NTiMe$_2$]$^+$[Cl-MAO]$^-$ and [Im^{Dipp}NTiMe$_2$]$^+$[Me-MAO]$^-$. Moreover, Im^{Dipp}NTiClMe$_2$ with MAO might afford the complexes [Im^{Dipp}NTiClMe]$^+$[Me-MAO]$^-$, [Im^{Dipp}NTiMe$_2$]$^+$[Cl-MAO]$^-$, and [Im^{Dipp}NTiMe$_2$]$^+$[Me-MAO]$^-$, while Im^{Dipp}NTiMe$_3$ can form only [Im^{Dipp}NTiMe$_2$]$^+$[Me-MAO]$^-$ (Figure 6).

Since the complex Im^{Dipp}NTiMe$_3$ gave the best catalytic activity at low Al:Ti ratios, it was intriguing to find out whether this result was due to the unavailability of the cocatalyst to abstract the chloride ion from Im^{Dipp}NTiClMe$_2$. This conceptual question was addressed by measuring the cone angle of the ligand in the three complexes (Im^{Dipp}NTiCl$_3$ = 259.0°, Im^{Dipp}NTiClMe$_2$ = 257.3°, Im^{Dipp}NTiMe$_3$ = 248.7°). We assumed that if we were able to synthesize a complex containing a similar bulky ligand with a lower cone angle in

Table 1. Ethylene Polymerization by the Catalysts Im^{Dipp}NTiCl$_3$, Im^{Dipp}NTiClMe$_2$, Im^{Dipp}NTiMe$_3$, and Im^{Mes}NTiCl$_3$ with MAO[a]

entry	catalyst	Ti:Al:TTPB[b]	A[c]	M_n[d]	M_w[d]	PD[d]	$R_i \cdot 10^{-4}$[e]	$R_t \cdot 10^{-8}$[e]
1	Im^{Dipp}NTiCl$_3$	1:10:0	15	62 600	184 500	2.9	0.8	3.5
2	Im^{Dipp}NTiCl$_3$	1:100:0	93	73 170	352 200	4.8	5.0	19.1
3	Im^{Dipp}NTiCl$_3$	1:400:0	60	120 400	426 300	3.5	3.2	7.5
4	Im^{Dipp}NTiCl$_3$	1:700:0	41	181 000	444 000	2.4	2.2	3.4
5	Im^{Dipp}NTiCl$_3$	1:1000:0	35	160 900	421 200	2.6	1.9	3.3
6	Im^{Dipp}NTiClMe$_2$	1:10:0	48	39 600	89 700	2.2	2.4	16.7
7	Im^{Dipp}NTiClMe$_2$	1:20:0	73	54 400	139 300	2.5	4.2	22
8	Im^{Dipp}NTiClMe$_2$	1:100:0	17	166 800	398 400	2.3	1.0	1.7
9	Im^{Dipp}NTiClMe$_2$	1:700:0	10	334 500	680 100	2.0	0.6	0.5
10	Im^{Dipp}NTiClMe$_2$	1:0:2	37	49 160	100 900	2.2	2.2	12.5
11	Im^{Dipp}NTiMe$_3$	1:10:0	48	163 000	315 800	1.9	3.0	5
12	Im^{Dipp}NTiMe$_3$	1:20:0	82	81 890	189 000	2.3	5.0	17
13	Im^{Dipp}NTiMe$_3$	1:100:0	66	115 530	273 160	2.3	4.0	10
14	Im^{Dipp}NTiMe$_3$	1:0:2	63	41 000	94 500	2.3	4.0	26
15	Im^{Mes}NTiCl$_3$	1:8:0	228	201 800	484 600	2.4	14	20
16	Im^{Mes}NTiCl$_3$	1:13:0	111	164 800	401 900	2.4	7.0	12
17	Im^{Mes}NTiCl$_3$	1:32:0	74	131 800	386 100	3.0	5.0	10
18	Im^{Mes}NTiCl$_3$	1:75:0	38	118 200	360 900	3.0	2.0	6
19	Im^{Mes}NTiCl$_3$	1:1000:0	17	169 800	482 400	2.8	1.0	2
20	Im^{Mes}NTiCl$_3$	1:8:2	95	51 400	23 200	5.0	6.0	32

[a]Conditions: 5 mg of catalyst, 6 mL of toluene, 6 atm ethylene, 1 h, 25 °C. [b]Ti:Al:TTPB molar ratio. [c]Activity in units of (kg of polyethylene) (mol of Ti)$^{-1}$ h^{-1}. [d]Data obtained by gel-permeation chromatography in 1,2,4-trichlorobenzene at 160 °C. [e]mol/min.

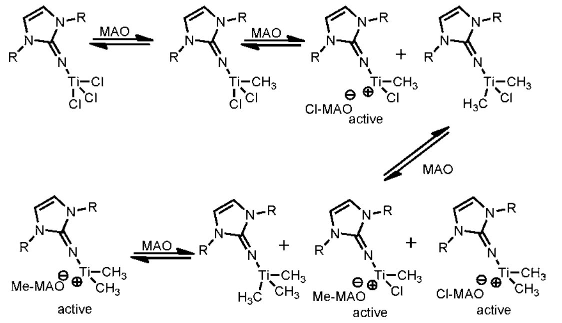


Figure 6. Activation of $Im^{Dipp}NTiCl_3$ with MAO to produce all possible combinations of complexes.

comparison with the Dipp moiety, this would allow the formation of a very active complex even at low MAO concentrations. Therefore, we decided to synthesize the complex $Im^{Mes}NTiCl_3$ (cone angle = 173.8°) as a test case. To our surprise, the best catalytic activity for this complex was obtained at a very low Al:Ti ratio of 8 (entry 15)! To the best of our knowledge, this is the first single-site catalyst reported to give its highest activity at such a low MAO:catalyst ratio. Lower Al:Ti ratios (6 or 4) also allowed the formation of polymers, but with lower activities. Using a greater excess of MAO decreased the polymer yield and increased the polymer PD. Using the mixture Al:TTPB (entry 20) drastically decreased the activity and the polymer molecular weight, indicating the different nature of the counterion.

It was important to investigate the number of active sites using the complex $Im^{Mes}NTiCl_3$ in order to determine the true MAO:catalyst ratio. Parallel poisoning experiments (using Al:Ti = 8) with water and by quenching the polymerization with CD_3OD showed that 30−50% of the precatalyst concentration was active.

In summary, we have synthesized the four complexes $Im^{Dipp}NTiCl_3$, $Im^{Dipp}NTiClMe_2$, $Im^{Dipp}NTiMe_3$, and $Im^{Mes}NTiCl_3$. These complexes gave moderate activities at very low Al:Ti ratios, especially the catalyst $Im^{Mes}NTiCl_3$, which gave its best catalytic activity at an Al:Ti ratio of 8. As far as we know, this is the first catalyst reported to display such a behavior. We are currently investigating more new metal complexes containing imidazolin-2-iminato ligands in the polymerization of α-olefins.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic details (CIF) and a table of bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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