CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc Europe

DOI: 10.1002/chem.201301176

A Highly Efficient Titanium Catalyst for the Synthesis of Ultrahigh-Molecular-Weight Polyethylene (UHMWPE)

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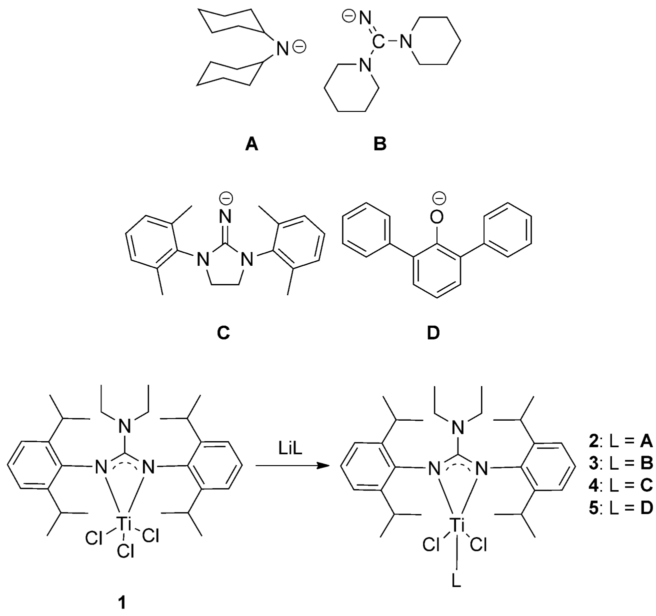
Ultrahigh-molecular-weight polyethylene (UHMWPE) is a unique polymer with outstanding physical and mechanical properties and a molecular weight of 2–6 × 10^6 g mol^{-1}. It is known for its chemical inertness, lubricity, and impact and abrasion resistance. Therefore, UHMWPE has a variety of important commercial uses, including polymer components in knee and hip replacements,[1] pickers for textile machinery, microporous films for battery separators,[2] the lining for coal chutes and dump trucks, runners for bottling production lines, and bumpers and siding for ships and harbors.[3]

We are investigating Group 4 metal based polymerization catalysts stabilized by very bulky monoanionic bidentate N ligands.[4] Recently, our group discovered a guanidinato titanium catalyst system that is able to polymerize ethylene by coordinative chain-transfer polymerization.[5] It is highly active in the presence of very high chain-transfer-agent to catalyst ratios and undergoes polyethylene chain transfer to triethylaluminum. These results encouraged us to develop a new titanium-based polymerization catalyst class [GuaTiLCl_2] (Gua = 1,2-bis(2,6-diisopropylphenyl)-3,3-diethylguanidinato; L = additional monoanionic ligand, for instance, imidazolidine-2-imide, guanidide, phenoxide, or amide; Scheme 1). The bulky guanidinato ligand (Gua) is monoanionic and a second monoanionic ligand can be introduced to alter the properties of the already highly active polymerization catalyst **1** (Scheme 1). Some of the additional ligands L, such as aryloxides[6] and guanidinates[7] or closely related ketimides[8] and phosphoraneimides,[9] are already documented in the olefin polymerization chemistry literature, but were never combined with guanidinato ligands. Herein, we report the synthesis and structure of dichloro titanium complexes of the type [GuaTiLCl_2] and their use in ethylene polymerization. One of the catalysts introduced is able to produce UHMWPE with a very high activity.

The titanium precursor complex **1** (Scheme 1) was easily prepared by reaction of diethylamido titanium trichloride[10] with *N,N'*-bis(2,6-diisopropyl)carbodiimide through methanediimine insertion into the titanium–amide bond.[5] Lithium 1,1,3,3-bis(pentamethylene)guanidide Li**B** was prepared in situ by reaction of piperidyl lithium with 1-piperidinecarbonitrile,[11] whereas sterically protected 1,3-bis(2,6-dimethylphenyl)imidazolidin-2-imine H**C** was prepared from the corresponding 1,2-dianilinoethane and cyanogen bromide in toluene according to literature procedures.[12] The two other monoanionic monodentate ligands used are 2,6-diphenylphenoxide (**D**) and dicyclohexylamide (**A**; Scheme 1), both of which are prepared from their commercially available protonated forms by deprotonation of the hydroxyl or amine function, respectively. The guanidinato titanium dichloride complexes **2**–**5** were prepared by simple salt elimination reactions from the titanium precursor **1** and the Li salts of the ligands (Scheme 1). All complexes were analyzed by NMR spectroscopy, elemental analysis, and single-crystal structure analysis. Crystals suitable for X-ray analysis were obtained by layering concentrated solutions in toluene with hexane or by recrystallization from toluene. The molecular structures of complexes **2**–**5** are presented in Figures 1 and 2. Selected bond lengths and angles are listed in Table 1. Crystallographic details are available in the Supporting Information (Table S1).



Scheme 1. Monodentate ancillary ligands (top); synthesis of the complexes **2**–**5** (bottom).

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301176.

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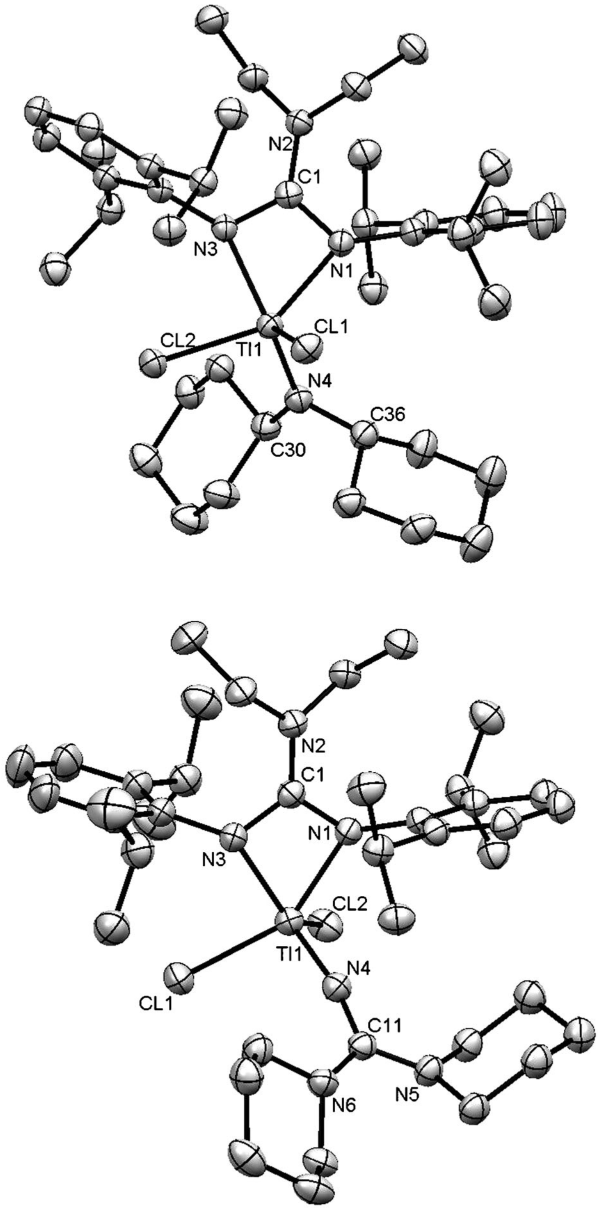

Figure 1. Molecular structures of **2** (top) and **3** (bottom). Carbon-bonded hydrogen atoms and one toluene molecule in the asymmetric unit of complex **3** are omitted for clarity.

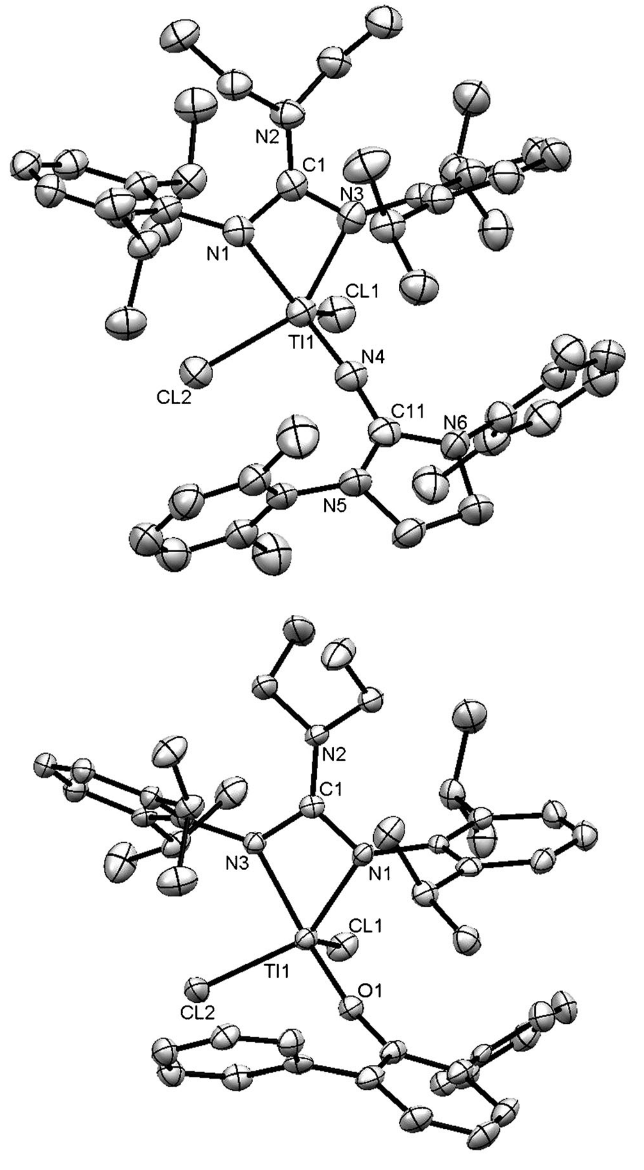

Figure 2. Molecular structures of **4** (top) and **5** (bottom). Complex **4** crystallized with two independent molecules per asymmetric unit. Carbon-bonded hydrogen atoms are omitted for clarity.

Complexes **2** and **3** crystallize in the monoclinic space group $P2_1/n$, complex **4** in the monoclinic space group $C2/c$ and complex **5** in the monoclinic space group $P2_1$. The geometry around the titanium centers in all four complexes is roughly trigonal bipyramidal including the guanidinate ligand, an ancillary ligand, and two chloro ligands. The equatorial positions are occupied by Cl1, Cl2, and one of the guanidinate nitrogen donors (N1 in complex **2**, **3**, and **5** and N3 in complex **4**). The axial positions are occupied by the second nitrogen donor of the guanidinate ligand and the ancillary ligand donor atom. The distortion of the trigonal bipyramid results from the very small bite angle of the chelating guanidinate (range 62–64°), caused by the high steric demand of the 2,6-diisopropyl moieties. The angles around the guanidinate central atom are distorted because of coordination to the titanium center. The N-C-N angle between the ligating nitrogen atoms is considerably smaller than 120° (106–110°), whereas the remaining angles are greater than 120° (124–128°). However, the sum of the angles around the central carbon atom in each chelating guanidinate ligand is 360° indicating no deviation from planarity.[13] Complex **5** shows the same bond length of 1.353(4) Å for all three C–N bonds; they are therefore indistinguishable, indicating considerable delocalization of the uncoordinated nitrogen atom lone pair into the ligand π system.[14] This is in contrast to the crystallographic data of complexes **2**, **3**, and **4** in which the C–N bond to the uncoordinated nitrogen atom (1.359(2)–1.376(5) Å) is slightly longer than those to the coordinated nitrogen atoms (1.337(5)–1.3533(19) Å).

Table 1. Selected bond lengths [Å] and angles [°].

complex	2	3	4	5
Ti1–Cl1	2.2851(5)	2.3462(5)	2.2788(13)	2.2185(9)
Ti1–Cl2	2.3232(5)	2.3035(5)	2.3216(14)	2.2824(10)
Ti1–N1	2.0839(13)	2.0787(13)	2.150(3)	2.047(3)
Ti1–N3	2.1011(13)	2.1239(13)	2.097(4)	2.055(2)
Ti1–N4	1.8663(13)	1.7662(14)	1.765(3)	–
Ti1–O1	–	–	–	1.8100(19)
C1–N1	1.3431(19)	1.348(2)	1.337(5)	1.353(4)
C1–N2	1.368(2)	1.359(2)	1.376(5)	1.353(4)
C1–N3	1.3533(19)	1.350(2)	1.336(5)	1.353(4)
C11–N4	–	1.327(2)	1.326(5)	–
C11–N5	–	1.355(2)	1.353(5)	–
C11–N6	–	1.367(2)	1.360(5)	–
N4–C30	1.483(2)	–	–	–
N4–C36	1.493(2)	–	–	–
N1-C1-N3	110.05(13)	109.21(13)	110.2(4)	106.6(3)
N1-Ti1-N3	63.73(5)	63.10(5)	62.15(13)	63.85(10)
Ti1-N4-C11	–	168.05(12)	170.5(3)	–
Cl1-Ti1-Cl2	95.108(18)	95.867(18)	94.86(5)	101.10(4)
$\Sigma<$(C1)	359.99	359.99	360.0	360.0
$\Sigma<$(C11)	–	359.99	359.8	–
$\Sigma<$(N4)	359.98	–	–	–

Closer examination of the ancillary monodentate ligand shows that the sum of the bond angles around C11 is 359.99° (for complex **3**) and 359.8° (for complex **4**), which confirms that the carbon atoms are sp^2 hybridized. An advantage of the monodentate guanidide ligands is that they can donate more than two electrons to the titanium center because of the presence of lone pairs and C=N double bonds. The additional π bonds increase the Ti–N bond order and strength, and simultaneously decrease the electron deficiency of the titanium center, thereby enhancing the stability of the complex. Furthermore, because electron donation is maximized for a linear Ti–N=C arrangement, the angles in complexes **3** and **4** are found to be around 170° (170.5° for **4** and 168.1° for **3**). Complex **5** also shows the linear Ti-O-C arrangement with an angle of 170.7(2)°. Moreover, the zwitterionic resonance structures of the two monoanionic guanidides in complexes **3** and **4** suggest increased negative charge on the metal-binding nitrogen atom. The bond lengths in the ancillary ligand and at the metal center confirm this. Whereas the titanium–nitrogen bond lengths are 1.765(3) and 1.7662(14) Å in the two guanidide complexes **4** and **3**, respectively, the titanium-oxygen bond length is significantly larger (1.8100(19) Å) in the aryloxide complex **5** and the titanium–amide bond length is 1.8663(13) Å in complex **2**. The N–C bond lengths N4–C30 (1.483(2) Å) and N4–C36 (1.493(2) Å) in the amide complex **2** are significantly longer than $C(sp^3)$–N single bonds,[15] but the sum of the bond angles around N4 is 359.98° and the Ti1–N4 bond length is 1.8663(13) Å , which clearly confirms the sp^2 hybridization of N4.

To compare their efficiencies in ethylene polymerization, all of the synthesized complexes were activated with methylalumoxane (MAO; Table 2, entries 1–6). Complex **1**, without any ancillary ligand, was used as the reference system for the polymerization performances of the new catalysts **2**–**5**. The polymerization data for complex **1** activated with MAO showed a high activity of 1670 $kg\,mol^{-1}\,h^{-1}\,bar^{-1}$, a polydispersity index (PDI) of 2.5 and a molecular weight of 21 000 $g\,mol^{-1}$. Complex **2** did not show any polymerization activity after activation with MAO, whereas the control experiment with (*N,N*-dicyclohexylamido)titanium trichloride gave some polymerization activity. Comparison of the polymerization results of complexes **3** and **1**, both activated with MAO, showed nearly identical data. Molecular weights of about 20 000 $g\,mol^{-1}$ and PDIs of 2.5 were obtained (Figure 3).

Table 2. Ethylene homopolymerization with complexes **1**–**5** (Ti complex (2 μmol), toluene (150 mL), ethylene (2 bar), 50 °C, 15 min run time).[a]

	Cat.	Co-cat.	n(Co-cat.) [μmol]	m(Polymer) [g]	Activity [$kg\,mol^{-1}\,h^{-1}\,bar^{-1}$]	M_w [$g\,mol^{-1}$][b]	M_w/M_n[b]
1	**1**	MAO	1300	1.67	1670	21 000	2.5
2	[c]	MAO	1300	0.18	180	417 000	14.5
3	**2**	MAO	1300	–	–	–	–
4	**3**	MAO	1300	0.45	450	19 000	2.5
5	**4**	MAO	1300	0.97	970	1 259 000 (2 385 000)	93.3
6	**5**	MAO	1300	1.35	1350	188 000 (412 000)	20.8
7	**1**	d-MAO	1000	1.36	1360	172 000	3.3
8	[c]	d-MAO	1000	0.36	360	1 465 000	123.3
9	**2**	d-MAO	1000	–	–	–	–
10	**3**	d-MAO	1000	2.10	2100	280 000	20.9
11	**4**	d-MAO	1000	5.56	5560	1 546 000	3.8
12	**4**[d]	d-MAO	1000	0.88	8800	2 488 000	3.4
13	**5**	d-MAO	1000	0.76	760	369 000	1.8

[a] Numbers in brackets display the high-molecular-weight fraction of bimodal distributions. [b] Determined by HT-GPC analysis. [c] (*N,N*-Dicyclohexylamido)titanium trichloride. [d] 0.2 μmol Ti complex.

This agreement indicates an immediate transfer of the ancillary guanidinate ligand of complex **3** to the alkyl aluminum that is usually present in small amounts in MAO. Activation of complex **4** with MAO leads to a bimodal distribution (Table 2, entry 5). This indicates that two active sites are operating during the polymerization process. The lower

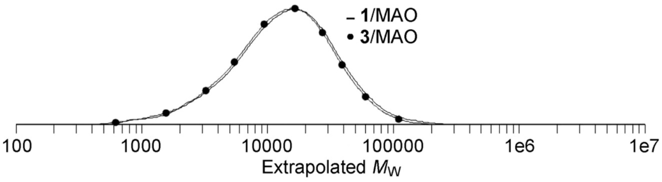

Figure 3. M_w distribution plots of polymers (Table 2, entries 1 and 4).

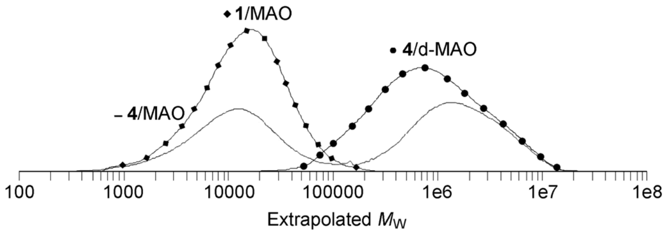

Figure 4. M_w distribution plots of polymers (Table 2, entries 1, 5, and 11).

molecular-weight fraction is identical to that observed for precatalyst **1**/MAO (Table 2, entry 1, Figure 4). The very high-molecular-weight fraction indicates the potential of the catalyst to produce UHMWPE.

The gel permeation chromatography (GPC) data provide explicit evidence for ligand transfer of the imidazolidin-2-imido ligand to the alkyl aluminum. In comparison to the catalyst system **3**/MAO, for which immediate ligand transfer is observed, the catalyst system **4**/MAO showed gradual ligand transfer to aluminum alkyls during the 15 min polymerization run. The slower transfer may be due to the higher steric demand of the imidazolidin-2-imido ligand compared to the ancillary guanidinate ligand in catalyst system **3**.

After activation with MAO, catalyst precursor **5** also gave a polymer with a bimodal distribution of chain lengths. The GPC spectra are consistent with those obtained by using catalyst precursor **4** and indicate that after activation with MAO the low-molecular-weight fraction obtained is similar to the one obtained with **1**/MAO (Table 2, entry 1) and the high-molecular-weight fraction is similar to that obtained with **5**/dry methylalumoxane (d-MAO; Table 2, entry 13, Figure S1 in the Supporting Information). Even the small amounts of free TMA in MAO suffice to transfer the ancillary aryloxide to aluminum. To completely inhibit the ligand transfer described above, all catalyst precursors were tested with d-MAO as the activator, from which free TMA was removed (Table 2, entries 7–13). Under these conditions, complex **1** gave a higher molecular-weight fraction together with a broader PDI because efficient chain transfer to aluminum was suppressed. Complex **2** showed no polymerization activity, whereas the control experiment with (*N,N*-dicyclohexylamido)titanium trichloride showed an increase in the molecular weight and an extremely broad polydispersity. The activity of catalyst system **3** significantly increased with the use of d-MAO as the activator, as did the molecular weight of the polymer obtained. Complexes **4** and **5** yielded monomodal molecular-weight distributions after activation with d-MAO. The GPC spectrum of **5**/d-MAO showed a PDI of 1.8, the narrowest observed for all of the systems tested. Furthermore, the activity of catalyst system **4**/d-MAO increased dramatically, as did the molecular weight of the polymer obtained. By lowering the amount of active catalyst from 2 to 0.2 μmol, to avoid diffusion control, the activity and molecular weight can be further enhanced, reaching $8800\,\mathrm{kg\,mol^{-1}\,h^{-1}\,bar^{-1}}$ and UHMWPE of $2500\,\mathrm{kg\,mol^{-1}}$.

In summary, the reaction of the lithiated amine, guanidine, imidazolidin-2-imine, or phenol with [GuaTiCl$_3$] (**1**) selectively led to the desired nonbridged titanium dichlorides. The "addition" of a second anionic ligand drastically alters the polymerization behavior of the precursor complex **1** . Some complexes are completely inactive and others show about one order of magnitude higher activity than the already highly active precursor **1**. Furthermore, drastically different polymer products can be obtained, for instance UHMWPE. The many bulky monoanionic non-cyclopentadienyl ligands developed in recent years might be useful candidates to further develop nonbridged, mixed ligand Group 4 metal complexes combining high polymerization activity and unusual selectivity patterns.

Acknowledgements

Financial support from the German National Academic Foundation is gratefully acknowledged.

Keywords: mixed ligand complexes · N ligands · polymerization · titanium · polyethylene

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Received: March 27, 2013