2428 *Organometallics* **2001,** *20,* 2428−2430

Polymerization of Ethylene by the Electrophilic Heteroscorpionate-Containing Complexes [$TiCl_3$(bdmpza)] and [$TiCl_2$(bdmpza){$O(CH_2)_4Cl$}] (bdmpza = Bis(3,5-dimethylpyrazol-1-yl)acetate)

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Received October 13, 2000

Summary: Novel heteroscorpionate-containing titanium complexes, $TiCl_3$(bdmpza) and $TiCl_2$(bdmpza){$O(CH_2)_4Cl$} (bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate), have been prepared. Toluene solutions of these complexes with methylaluminoxane catalyze the polymerization of ethylene and show a high catalytic activity.

The development of new "single site" group 4 catalyst precursors aimed at optimizing polymerization catalysis is one of the most attractive subjects in the field of organometallic chemistry.[1] The most recent strategy in catalyst design and modification involved the development of non-cyclopentadienyl-based complexes of group 4 metals, with particular attention focused on nitrogen- and/or oxygen-containing ligands. A number of chelating diamide[2] and dialkoxide[3] complexes have been described in detail, and many of these systems are excellent catalyst precursors for the polymerization of α-olefins. Given the impact of ligand design, we recently reported[4] the preparation of a new monoanionic multidentate ligand, namely bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza), which belongs to the family known as "scorpionate" ligands,[5] and also described the coordinative ability of this system toward several niobium precursors. Herein, we report the preparation of heteroscorpionate-containing titanium complexes, an interesting nucleophilic THF ring-opening process to give an alkoxide species, and also a preliminary study of the ethylene polymerization activities for these complexes.

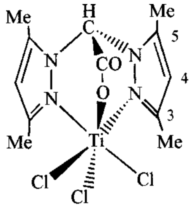

Figure 1. Proposed structure of complex **1**.

The complex [$TiCl_3$(bdmpza)] (**1**) was synthesized by the reaction of $TiCl_4(THF)_2$ and [{$Li(H_2O)$(bdmpza)}$_4$] in CH_2Cl_2 at low temperature.[6] Complex **1** was characterized spectroscopically.[7] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** exhibit one set of resonances for the pyrazole rings, as would be expected for the presence of two equivalent pyrazolyl rings in the molecule. These results agree with an octahedral structural disposition, as depicted in Figure 1, where a κ^3-N,N,O coordination for the bdmpza ligand is proposed. Several tris(pyrazol-1-yl)borate group 4 metal complexes have been described previously.[8] However, as far as we are aware, complexes **1**−**3** constitute the first examples of this class of compound with a heteroscorpionate ligand.[9] An interesting phenomenon regarding the reactivity of complex **1** was observed when a THF solution of the complex was refluxed. Under these conditions the complex [{$TiCl_2$(bdmpza){$O(CH_2)_4Cl$}}] (**2**) was isolated after the appropriate workup.[10] The formation of this complex can be envisaged as being the result of a nucleophilic THF ring-opening reaction on the cationic THF-containing

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[1] *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996.

[2] See, for example: (a) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (b) Scollard, J. D.; McConville, D. H.; *J. Am. Chem. Soc.* **1996**, *118*, 10008. (c) Tinkler, S.; Deeth, R. J.; Duncalf, D. J.; McCamley, A. *Chem. Commun.* **1996**, 2623. (d) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415. (e) Gibson, V. C.; Kimberely, B. S.; White, A. J. R.; Williams, D. J.; Houd, P. *Chem. Commun.* **1998**, 313. (f) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199. (g) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308.

[3] See, for example: (a) Sarsfiled, M. J.; Ewart, S. W.; Tremblay, T. L.; Roszak, A. W.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3097. (b) Fokken, S.; Spaniol, T. P.; Okuda, J.; Serentz, F. G.; Mullhaupt, R. *Organometallics* **1997**, *16*, 4240.

[4] Otero, A.; Fernández-Baeza, J.; Tejeda, J.; Antiñolo, A.; Carrillo-Hermosilla, F.; Diez-Barra, E.; Lara-Sanchez, A.; Fernández-López, M.; Lanfranchi, M.; Pellinghelli, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 3537.

[5] Trofimenko, S. *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

[6] Preparation of **1**: a solution of $TiCl_4(THF)_2$ (0.800 g, 2.39 mmol) in CH_2Cl_2 (50 mL) was cooled to −30 °C, and [{$Li(H_2O)$(bdmpza)}$_4$] (0.608 g, 0.60 mmol) was added with vigorous stirring. The solution turned from yellow to red, and a white precipitate was formed. After 12 h at −30 °C the mixture was filtered, giving a red solution which was evaporated to dryness; complex **1** was obtained as a red solid (yield 91%).

[7] Spectroscopic data for **1** are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 6.71 (s, 1 H, CH), 6.07 (s, 2 H, H^4), 2.69 (s, 6 H, Me^3), 2.51 (s, 6 H, Me^5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 66.6 (CH), 155.3, 141.1 ($C^{3\text{ or }5}$), 108.7 (C^4), 15.9 (Me^3), 11.1 (Me^5), 162.0 (CO_2^-). IR (Nujol mull, cm^{-1}): 1705 $\nu_{as}(CO_2^-)$, 1464 $\nu_s(CO_2^-)$, 360 ν(Ti−Cl). Mass spectrum (FAB (*m/z* assignment, % intensity)): 364D [M − Cl], 25, 313D [M − 2Cl − O], 100. Anal. Calcd for $C_{12}H_{15}Cl_3N_4O_2Ti$: C, 35.9; H, 3.7; N, 13.9. Found: C, 36.1; H, 3.9; N, 14.1.

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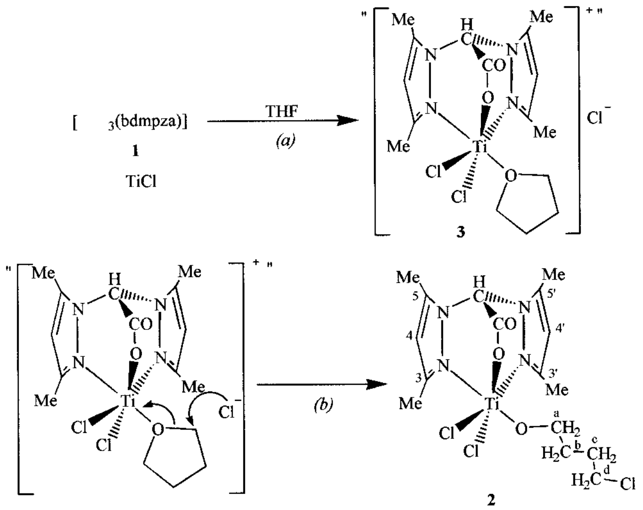
Scheme 1. Proposed Reaction Pathway for the Formation of Complex 2



species [TiCl$_2$(THF)(bdmpza)]Cl (**3**), which itself results from coordination of a THF molecule and subsequent loss of a Cl$^-$ ligand from **1** (Scheme 1). This proposal appears reasonable, given that several cationic d^0 titanium cyclopentadienyl species that contain THF or related coordinating solvents, namely [Cp$_2$Ti(R)(L)]$^+$, have previously been described.[11] The next step in the process would involve a nucleophilic attack by the free Cl$^-$, step b in Scheme 1, on the activated C−O bond of the coordinated THF, which would give rise to complex **2**. Complex **3** was isolated and characterized spectroscopically.[12] Similar reactivity was previously found by Jordan et al.[13] in the reaction between the [Cp$_2$Zr(R)(THF)]$^+$ species and certain nucleophilic reagents, namely NR$_3$ and PMe$_2$Ph. Furthermore, nucleophilic attack of a chloride anion on a coordinated THF molecule has been previously observed in other examples where THF is bound to an electrophilic center, namely boron and uranium.[14] The single-crystal X-ray analysis of **2** was undertaken.[15] The molecular structure, atomic numbering scheme, and selected bond lengths and angles for **2** are shown in Figure 2. The structure consists of a heteroscorpionate ligand bonded to the titanium atom through the two nitrogen atoms and the oxygen from the acetate group. In addition, the titanium center is coordinated to two chlorine atoms and an oxygen from the opened THF ring; with this disposition the titanium atom is a chiral center. In the solid state,[16] due to the centrosymmetric space group, both enantiomers are present and one of them, namely *OC*-6-32(A), is depicted in Figure 2. The Ti1−O3 bond distance (1.731(5) Å) is significantly shorter than the Ti1−O1 bond distance (1.984(4) Å), a difference that could indicate the existence of partial Ti−O double-bond character.

Preliminary studies on the ethylene polymerization activation for complexes **1** and **2** in the presence of methylaluminoxane (MAO) were carried out at various temperatures and with different Al/Ti ratios (see results in Table 1).[17a]The catalytic activity is very sensitive to the MAO/Ti ratio, and a linear increase of the polymerization activity with increasing Al/Ti molar ratio is observed. The exchange of a chloride by an alkoxide ligand from **1** and **2** does not markedly affect the observed activities. Complex **1** exhibits slightly higher activities than complex **2**, which may be related to

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(8) (a) Kouba, J. K.; Wreford, S. S. *Inorg. Chem.* **1976**, *15*, 2313. (b) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1982**, *21*, 840. (c) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1983**, *22*, 1064. (d) Reger, D. L.; Tarquini, M. E.; Lebioda, L. *Organometallics* **1983**, *12*, 1763. (e) Kresinski, R. A.; Isam, L.; Hamor, J. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1835. (f) Antiñolo, A.; Carrillo-Hermosilla, F.; Corrochano, A. E.; Fernández-Baeza, J.; Lanfranchi, M.; Otero, A.; Pellinghelli, M. A. *J. Organomet. Chem.* **1999**, *577*, 174.

(9) Selected examples of heteroscorpionate complexes: (a) Higgs, T. C.; Carrano, C. J. *Inorg. Chem.* **1997**, *36*, 291. (b) Higgs, T. C.; Carrano, C. J. *Inorg. Chem.* **1997**, *36*, 298. (c) Higgs, T. C.; Spartalian, K.; O'Connor, C. J.; Matzanke, B. F.; Carrano, C. J. *Inorg. Chem.* **1998**, *37*, 2263 (d) Higgs, T. C.; Ji, D.; Czernuszewicz, R. S.; Matzanke, B. F.; Schunemann, V.; Trautwein, A. X.; Helliwell, M.; Ramirez, W.; Carrano, C. J. *Inorg. Chem.* **1998**, *37*, 2383.

(10) Preparation of **2**: a solution of [TiCl$_3$(bdmpza)] (**1**; 0.500 g, 1.24 mmol) in THF (50 mL) was refluxed for 8 h. The solution was concentrated under vacuum and, after extraction with dicholoromethane (40 mL) and evaporation of the solvent, a yellow solid (yield 93%) was isolated. Spectroscopic data for **2** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.59 (s, 1 H, CH), 6.07 (s, 2 H, H^4), 2.72 (s, 3 H, Me^3), 2.57 (s, 3 H, Me$^{3'}$), 2.45 (s, 6 H, Me$^{5,5'}$), 4.92 (m, 2H, H^a), 2.07 (m, 4H, H^{b,c}), 3.67 (t, 2H, H^d). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 66.5 (CH), 154.7, 153.3, 141.4, 140.5 (C$^{3\text{ or }3'\text{ or }5\text{ or }5'}$), 108.6, 108.0 (C$^{4\text{ or }4'}$), 15.2, 14.8 (Me$^{3,3'}$), 11.1, 10.1 (Me$^{5,5'}$), 163.4 (CO$_2^-$), 86.2 (C^a), 28.8 (C^b), 28.9(C^c), 44.6 (C^d). IR (Nujol mull, cm^{-1}): 1699 ν_{as}(CO$_2^-$), 1459 ν_s(CO$_2^-$), 376 ν(Ti−Cl). Mass spectrum (FAB (*m*/*z* assignment, % intensity)): 437D [M − Cl], 28. Anal. Calcd for C$_{16}$H$_{23}$Cl$_3$N$_4$O$_3$Ti: C, 40.6; H, 4.9; N, 11.8. Found: C, 40.8; H, 4.7; N, 11.6.

(11) Selected examples: (a) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (c) Taube, R.; Krukowka, L.; *J. Organomet. Chem.* **1988**, *347*, C9. (d) Bochmann, M.; Jagger, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838. (e) Bochmann, M.; Jagger, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780.

(12) Preparation of **3**: a solution of [TiCl$_3$(bdmpza)] (**1**; 0.500 g, 1.24 mmol) in THF (50 mL) was stirred at 35 °C for 24 h. The solution was concentrated under vacuum and, after extraction with dicholoromethane (40 mL) and evaporation of the solvent, a orange solid (yield 89%) was isolated. Spectroscopic data for **3** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.36 (s, 1 H, CH), 6.45 (s, 1 H, H^4), 6.41 (s, 1 H, H$^{4'}$), 2.97 (s, 3 H, Me^3), 2.87 (s, 3 H, Me$^{3'}$), 2.87 (s, 3 H, Me^5), 2.86 (s, 3 H, Me$^{5'}$), 3.95 (m, 4H, THF), 2.10 (m, 4H, THF). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 67.6 (CH), 154.9, 153.7, 143.0, 142.9 (C$^{3\text{ or }3'\text{ or }5\text{ or }5'}$), 108.6, 108.3 (C$^{4\text{ or }4'}$), 15.4, 14.9 (Me$^{3,3'}$), 10.8, 10.7 (Me$^{5,5'}$), 163.2 (CO$_2^-$), 68.1, 26.2 (THF). IR (Nujol mull, cm^{-1}): 1650 ν_{as}(CO$_2^-$), 1459 ν_s(CO$_2^-$), 376 ν(Ti−Cl). Mass spectrum (FAB (*m*/*z* assignment, % intensity)): 437D [M], 100, 364D [M − THF], 40. Anal. Calcd for C$_{16}$H$_{23}$Cl$_3$N$_4$O$_3$Ti: C, 40.6; H, 4.9; N, 11.8. Found: C, 40.2; H, 4.5; N, 12.1.

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(14) (a) Mair, F. S.; Morris, J. H.; Gaines, D. F.; Powell, D. *J. Chem. Soc., Dalton Trans.* **1993**, 135. (b) Campello, M. P. C.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **1994**, *484*, 37. (c) Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A.; Woollam, S. F. *Organometallics* **1994**, *13*, 157. (d) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D. *Inorg. Chem.* **1996**, *35*, 537. (e) Peymann, T. Kück, K.; Gabel, D. *Inorg. Chem.* **1997**, *36*, 5138. (f) Batten, S. A.; Jeffery, J. C.; Rees, L. H.; Rudd, M. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2839.

(15) Crystal data for **2**: C$_{16}$H$_{23}$Cl$_3$N$_4$O$_3$Ti, monoclinic, $P2_1/c$, a = 7.987(1) Å, b = 16.209(1) Å, c = 16.996(1) Å; β = 100.47°; V = 2163.7(3) Å^3; Z = 4; D_{calcd} = 1.454 g cm^{-3}; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 0.789 mm^{-1}; T = 293 K; Nonius-MACH3 diffractometer, graphite monochromator; 5208 unique reflections; R = 0.0861; R_w = 0.1600.

(16) In solution we have confirmed the presence of these two enantiomers by addition of a chiral shift reagent, namely (*R*)-(−)-(9-anthryl)-2,2,2-trifluoroethanol, to a solution of **2**. This process gives rise to the appearance in the ^{1}H NMR spectrum of two signals for each proton that are due to the two diastereosiomers from the corresponding two enantiomers.

(17) *Polymerization procedure*: Ethylene polymerizations were carried out in a 1.0 dm^3 Büchi autoclave with magnetic stirring. Toluene was used as the solvent; the reaction time and the amount of catalyst introduced were chosen carefully in order to avoid mass transfer limitations. In a typical procedure, ethylene was first introduced into the reactor until saturation of toluene was achieved at the polymerization temperature. The appropriate amount of titanium complex precatalyst and MAO (Witco GmbH, 10% m/v) were first mixed and allowed to react for 15 min, and then the mixture was introduced into the reaction vessel.

Table 1. Ethylene Polymerization Results of [$TiCl_3$(bdmpza)] (1), [$TiCl_2$(bdmpza){$O(CH_2)_4Cl$}] (2), $TiCl_4$, and Ti-Based Complexes in Association with MAO

complex	run	MAO/Ti	*T* (°C)	yield (g)	activity (kg of PE ((mol of Ti) h bar)$^{-1}$)	$10^{-5}M_w$[c] (g mol^{-1})	M_w/M_n	ref
1	1	2000	25	10.8	636[a]	8.2	4.1	
1	2	3000	25	11.1	763[a]	11.0	3.0	
2	3	1000	25	1.76	103[a]	nd[d]	nd[d]	
2	4	2000	25	6.08	565[a]	nd[d]	nd[d]	
2	5	3000	25	7.22	592[a]	*e*	*e*	
2	6	2000	35	9.16	690[a]	12.5	4.5	
2	7	2000	45	6.90	400[a]	3.5	8.2	
$TiCl_4$	8	1000	25	0.16	11[b]			
$TiCl_4$	9	3000	25	0.17	12[b]			
Cp_2TiCl_2		3000	25		300			19
$CpTiCl_2\{NC_5H_4\text{-}(CPh_2O\text{-}2)\}$		1000	30		64			20
$Cp^*TiCl_2\{O\text{-}2.6\text{-}{}^iPr_2C_6H_3\}$		1000	60		300			21

[a] Experimental conditions: *P*(ethylene) = 3.4 bar; [Ti] = (2−3.3) × 10^{-5} M; *t* = 30 min; toluene as solvent. [b] Experimental conditions: *P*(ethylene) = 3.4 bar; [Ti] = 2.7 × 10^{-5} M; *t* = 30 min; toluene as solvent. [c] Determined by GPC.[17b] [d] nd = not determined. [e] Impossible to measure; equipment blocked.

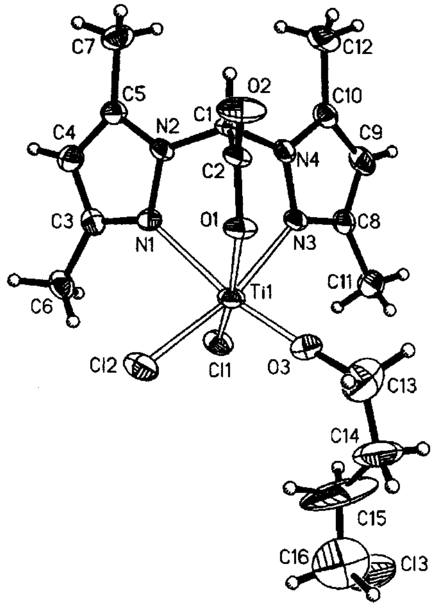

Figure 2. View of complex **2** (25% probability ellipsoids) with the atomic numbering scheme. Selected bond distances (Å) and angles (deg): Ti1−O1, 1.984(4); Ti1−O3, 1.731(5); Ti1−N1, 2.276(6); Ti1−N3, 2.204(6); Ti1−Cl1, 2.296(2); Ti1−Cl2, 2.294(2); O1−Ti1−Cl1, 165.5(1); N1−Ti1−N3, 79.8(2); N3−Ti1−O3, 92.5(2), O3−Ti1−Cl2, 97.8(2); O1−Ti1−N1, 80.4(2); O1−Ti1−N3, 81.6(2); O1−Ti1−O3, 92.3(2); O1−Ti1−Cl2, 92.3(1).

differences in the electronic effects. The data in Table 1 show that for complex **2** a maximum polymerization activity is attained at relatively low temperatures, i.e., 35 °C, and this result is in agreement with the typical behavior of titanocene complexes and the well-known instability of active Ti species at higher temperatures.[18]

As expected, the molecular weight of the produced PE decreases with temperature (see Table 1). However, the molecular weight distributions are much broader compared to those typical for single-site metallocene. Complex **1** seems to provide lower molecular weight polyethylenes than complex **2**.

To better understand the role played by the heteroscorpionate ligand upon activation with MAO, comparative ethylene polymerization tests have been performed in the presence of $TiCl_4$ activated by 1000−3000 equiv of MAO (see Table 1). The observed polymerization activity is about 50 times lower than that exhibited by complexes **1** and **2**, which makes clear the strong effect of the heteroscorpionate ligand on the catalytic activity.

Comparative data relating to the conventional titanocene complex Cp_2TiCl_2 and some mixed monocyclopentadienyl ligand species of the types $CpTiCl_2(L)$ and $Cp^*TiCl_2(L)$ are also displayed in Table 1. It can be seen that in the new titanium complexes **1** and **2** show an activity level similar to or higher than both that of the titanocene complex and the mixed monocyclopentadienyl ligand species.

In conclusion, we describe here a straightforward method for the preparation of a useful heteroscorpionate-containing titanium complex and show an unusual nucleophilic THF ring-opening process. The new complexes, which do not contain cyclopentadienyl units, in association with MAO exhibit remarkable activities (100−760 kg of PE/((mol of Ti) h bar) when compared to mixed cyclopentadienyl ligand complexes or even to conventional titanocene initiators. Further research aimed at developing this chemistry and studying the influence of ligand modification on the structure and activity of these new precatalysts is currently in progress.

Acknowledgment. We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior e Investigación Científica of Spain (Grant Nos. PB98-0159-C02-01 and PB97-0425) and from the Conselho de Reitores Universidades Portuguesas (Acções Integradas Luso-Espanholas LE-25/98).

Supporting Information Available: Tables giving details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles and drawings giving additional views of **2**; data are also available in electronic form in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] A marked decrease of activity has been described for the Cp_2TiCl_2/MAO system at temperatures higher than 50 °C, and this is thought to be due to an increase in the reduction of Ti(IV) to Ti(II). See: Tait, P. J. *Polym. Mater. Encycl.* **1996**, 4169.

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